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Generalized Langevin theory for many-body problems in chemical dynamics: Reactions in liquids

S. A. Adelman^{a)}

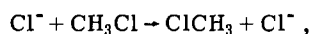
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A general theoretical framework for classical trajectory simulations of chemical reactions in liquids is presented. This framework is a development of the molecular timescale generalized Langevin equation (MTGLE) theory [S. A. Adelman, *Adv. Chem. Phys.* **44**, 143 (1980)] for condensed phase chemical reaction dynamics. This generalization permits one to treat solute configuration (r_0) dependent generalized damping forces in a computationally straightforward manner. Thus, for example, dynamical effects of common caging of reagents are realistically accounted for in the present theory. The theory is based on the following method. The nonequilibrium solvent density induced by *small* displacements $\Delta r_0(t)$ of the solute (chemical system) from a configuration point r_0 is computed by linear response theory. The time dependent reaction force that the solvent exerts on the solute is then computed from the nonequilibrium solvent density. This leads to a set of solute configuration dependent MTGLE parameters $\{\omega_{cp}^2(r_0), \omega_{cp+1}^2(r_0)\}$, $p = 0, 1, 2, \dots$, which account for dynamical effects of solvent-solute interaction. These parameters may be generated as a function of r_0 by performing molecular dynamics simulations of the solvent for a number of solute configurations r_0 . A generalized equivalent harmonic chain representation for solute dynamics is then developed. The force constants of the equivalent chain are the MTGLE parameters. Techniques for approximating the non-Markovian chain equations by Markovian model chain equations are presented. These Markovian equations are directly applicable to simulation of liquid state reactions.

I. INTRODUCTION

We develop in this paper a generalized Langevin equation of motion, Eq. (5.1) below, for realistic computer simulations of chemical reactions in liquids.

The physical concept upon which we build the theory is pictorialized in Fig. 1. A simple S_N2 reaction, for example,



in aqueous solution nicely illustrates the basic points.

First consider an isolated Cl^- anion moving through the water. In addition to its gross diffusive motion, the Cl^- also undergoes an intricate *molecular timescale* motion which we now qualitatively describe.

(i) The Cl^- anion oscillates in its hydration cage with a characteristic *Einstein frequency* ω_{e0} . If the cage were rigid, this oscillation would persist indefinitely like that of an isolated or Einstein harmonic oscillator. Thus, the designation Einstein frequency. The *structure* of the hydration sphere clearly determines the Einstein frequency. More precisely, the Einstein frequency depends on the *equilibrium* water density (spatial and orientational) in the neighborhood of the anion.

(ii) The hydration sphere is, of course, not rigid but instead "gives" in response to the Cl^- motion. This gives or relaxation damps out the Einstein oscillations since it permits energy dissipation into the bulk water. The magnitude of damping depends upon the strength of the ion-water interaction as measured by a coupling constant ω_{c1}^2 and also upon a solvent response function $\hat{\theta}_1(t)$. Both ω_{c1}^2 and $\hat{\theta}_1(t)$ depend on *dynamics* in the hydration sphere. More precisely, they depend on time correla-

tion functions which describe the fluctuations (spatial and orientational) in the local water density.

(iii) Superimposed on the chloride damped cage os-

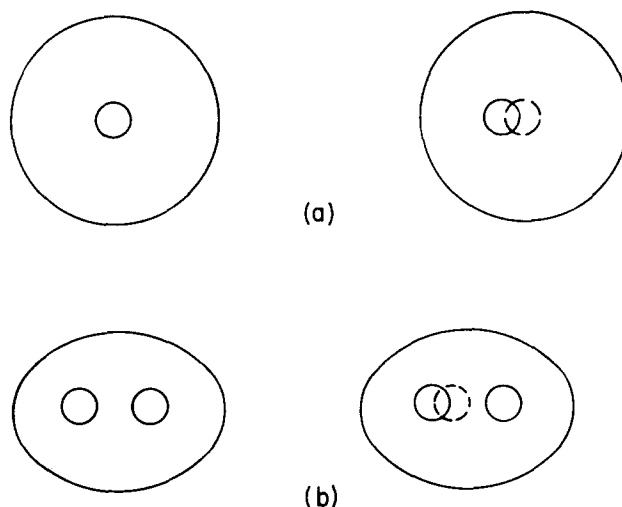


FIG. 1. (a) An atom of mass m is initially in equilibrium (left) with the spherically symmetric average local solvent density. The atom is then slightly displaced (right) by an amount Δr_0 . The ensemble average (see text) instantaneous restoring force on the atom F_i determines the Einstein frequency ω_{e0}^2 through $F_i = -m\omega_{e0}^2\Delta r_0$. Relaxation of the local solvent density to a new equilibrium about the displaced atom determines $\omega_{c1}^4\hat{\theta}_1(t)$. (b) A pair of identical interacting atoms of mass m separated by a distance R are in equilibrium (left) with the "ellipsoidal" local solvent density characteristic of common cage formation. One atom is then slightly displaced (right) by an amount Δr_0 . The ensemble average instantaneous restoring force on the displaced atom F_i determines the R -dependent diagonal element of the Einstein frequency matrix $\omega_{e0}^2(R)$ through $F_i = -m\omega_{e0}^2(R)\Delta r_0$. Relaxation of the ellipsoidal local solvent density to a new equilibrium value about the displaced atom determines $\omega_{c1}^4(R)\hat{\theta}_1(t; R)$.

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cillations is a stochastic motion driven by a random force $\omega_{c_1}^2 R_1(t)$. The random force arises from thermal fluctuations in the hydration sphere density. These fluctuations may be due to water molecule reorientations partial dehydrations, etc.

Now suppose that an encounter between Cl^- and CH_3Cl has occurred and that both species are now oscillating and colliding in a common cage. The water structure and dynamics in the "ellipsoidal" hydration layers which form the common cage differs from that in the spherical shell surrounding the isolated chloride ion. The structure and dynamics depend, in particular, on the spatial configuration r_0 [Eq. (3.2)] of the reagents.

Thus, $\omega_{e_0}^2$, $\omega_{c_1}^2$, etc., are modified by common caging to configuration dependent quantities $\omega_{e_0}^2(r_0)$, $\omega_{c_1}^2(r_0)$, $\dot{\theta}_1(t; r_0)$, and $R_1(t; r_0)$ during an encounter.

These modifications are important since $\omega_{e_0}^2(r_0)$, etc., influence the reaction dynamics in the following ways.

(i) The Einstein frequency $\omega_{e_0}(r_0)$ influences the number of collisions (reaction attempts) made during the lifetime of the common cage.

(ii) The coupling constant $\omega_{c_1}^2(r_0)$ and the solvent response function $\dot{\theta}_1(t; r_0)$ govern the efficiency of energy transfer between the reagents and the water.

(iii) The random force $\omega_{c_1}^2(r_0)R_1(t; r_0)$ is important for energizing the reagents, reorienting the CH_3Cl , etc.

Our brief discussion of S_N2 dynamics is presented to motivate the general theoretical problem we treat in this paper. This problem has two parts:

(i) We formally calculate the dependence of the basic quantities $\omega_{e_0}^2(r_0)$, $\omega_{c_1}^2(r_0)$, etc., on the solute configuration point r_0 . Our formal results may be practically implemented by performing molecular dynamics simulations of the solvent in the presence of the fixed solute for a number of solute configurations r_0 . These calculations generate parameter and response function surfaces analogous to gas phase Born-Oppenheimer potential energy surfaces.

(ii) We utilize our results for $\omega_{e_0}^2(r_0)$, etc., to construct a generalized equivalent harmonic chain representation¹ of the solute dynamics Eq. (5.1). This stochastic equation of motion we believe will prove important to the future development of liquid state reaction theory.

Our work here is a further development of the molecular timescale generalized Langevin equation (MTGLE) theory^{1,2} for condensed phase chemical reactions. The original MTGLE theory, while formally exact, yields a stochastic equation for the reagents which does not explicitly display the dependence on the configuration point r_0 . Thus, in practical applications of the original exact MTGLE theory one is forced to ignore the dependence on r_0 . This includes neglecting the common cage effect just discussed for S_N2 . Our purpose here is to provide an approximate MTGLE theory which remedies this problem.

Our treatment is based on the following method. We

calculate, via linear response theory,³ the change in the solvent density induced by small displacements $\Delta r_0(t)$ of the solute molecules from a given configuration r_0 . Generalized damping of the solute [i. e., $\omega_{c_1}^4(r_0)\dot{\theta}_1(t; r_0)$] is then computed from the time dependent reaction force the induced solvent density exerts on the solute. Since the induced density depends on r_0 , our procedure yields configuration dependent generalized damping forces. We stress that our linear response method does not require weak solvent-solute forces. Rather the main (but not only) approximation is that the generalized equivalent chain parameters are spatially slowly varying.

The plan of this paper is as follows. The physical interpretation of the formally exact MTGLE theory¹ is used in Sec. II to motivate the linear response treatment. The main results of the treatment are given in Sec. III. The actual calculation is, however, developed in Appendix A. The basic results of Sec. III are then used in Sec. IV to unfold the full hierarchy structure of the generalized MTGLE theory. Specific related results are derived in Appendices B and C. The most important consequence of the hierarchy structure is the generalized equivalent chain representation for the dynamics of the reagents. This is presented in Sec. V.

Sections II-V are sufficient to provide a basic understanding of the main ideas and results of this paper. For the reader wishing to delve more deeply we develop a generalized chain representation for response functions in Sec. VI. A novel and useful⁴ consequence of that representation, namely, that response functions may be generated as special chain trajectories, is also derived. Heatbath modeling methods based on the generalized chain are worked out in Sec. VII. Finally, in Appendix D we discuss certain subtle aspects of the MTGLE second fluctuation-dissipation theorem. These clarifications require a slight revision of certain results derived in Ref. 1.

II. MOTIVATION FOR THE LINEAR RESPONSE APPROXIMATION

To motivate the generalized (linear response) MTGLE theory developed here, we first briefly review the formally exact theory already available.¹ The exact MTGLE governing the dynamics of an atom, say, iodine, with coordinate $\mathbf{x}_0(t)$ moving in a liquid is

$$\ddot{\mathbf{x}}_0(t) = -\omega_{e_0}^2 \mathbf{x}_0(t) + \omega_{c_1}^4 \int_0^t \dot{\theta}_1(t-\tau) \mathbf{x}_0(\tau) d\tau + \omega_{c_1}^2 \mathbf{R}_{1x}(t). \quad (2.1)$$

The physical meaning of the Einstein frequency ω_{e_0} and other MTGLE quantities are discussed in the Introduction. We additionally mention that $\mathbf{R}_{1x}(t)$ may be interpreted as an abstract coordinate variable characterizing the solvent dynamics in the vicinity of the iodine. Also, $\mathbf{R}_{1x}(t)$ and $\dot{\theta}_1(t)$ are not independent. Rather, they are linked by the MTGLE second fluctuation-dissipation theorem, which is given by

$$\dot{\theta}_1(t) = \frac{m}{3k_B T} \langle \dot{\mathbf{R}}_{1x}(t) \cdot \dot{\mathbf{R}}_{1x}(0) \rangle, \quad (2.2)$$

where $\langle \rangle$ denotes a thermal average over solvent coor-

dinates. (The precise meaning of this thermal average is discussed in Appendix D.) Equation (2.2) allows one to determine the statistical information about the random force $\omega_{c1}^2 \mathbf{R}_{1x}(t)$, which is required for trajectory simulations, from the heatbath response function $\theta_1(t)$.

Now suppose a second iodine atom with coordinate $\mathbf{y}_0(t)$ collides with the first iodine atom. To simulate the recombination reaction, one could couple Eq. (2.1) to an analogous MTGLE for atom 2 via the atom-atom potential of mean force $W(R)$, where R is the interatomic distance. This would give the following pair of effective equations of motion for the recombination process (note m = mass of an iodine atom):

$$\ddot{\mathbf{x}}_0(t) = -m^{-1} \frac{\partial W(R)}{\partial \mathbf{x}_0} - \omega_{e0}^2 \mathbf{x}_0(t) + \omega_{c1}^4 \int_0^t \theta_1(t-\tau) \mathbf{x}_0(\tau) d\tau + \omega_{c1}^2 \mathbf{R}_{1x}(t), \quad (2.3a)$$

and

$$\ddot{\mathbf{y}}_0(t) = -m^{-1} \frac{\partial W(R)}{\partial \mathbf{y}_0} - \omega_{e0}^2 \mathbf{y}_0(t) + \omega_{c1}^4 \int_0^t \theta_1(t-\tau) \mathbf{y}_0(\tau) d\tau + \omega_{c1}^2 \mathbf{R}_{1y}(t). \quad (2.3b)$$

The coupled MTGLE system, Eqs. (2.3), is not directly useful for trajectory simulations. This is because the non-Markovian memory or integral kernel term must be computed at each integration step. These difficulties may be avoided by the *model heatbath method* described earlier^{1,4} for the formally exact MTGLE theory and developed in Sec. VII for the new generalized theory. The idea of the model heatbath method is that one simulates the *non-Markovian* equations (2.3) by a rapidly convergent and physically realistic sequence of *Markovian* equations.

The model heatbaths are collinear nearest neighbor harmonic chains composed of N fictitious atoms where $N=1, 2, 3, \dots$. An N -atom model heatbath reduces the many-body iodine recombination reaction to a $2(N+1)$ -atom effective gas phase collision problem. For the simplest case $N=1$, the effective gas-phase problem is the following *four-body* problem:

$$\ddot{\mathbf{x}}_0(t) = -m^{-1} \frac{\partial W(R)}{\partial \mathbf{x}_0} - \omega_{e0}^2 \mathbf{x}_0(t) + \omega_{c1}^2 \mathbf{x}_1(t), \quad (2.4a)$$

$$\ddot{\mathbf{x}}_1(t) = -\Omega_1^2 \mathbf{x}_1(t) + \omega_{c1}^2 \mathbf{x}_0(t) - \beta_2 \dot{\mathbf{x}}_1(t) + \mathbf{f}_x(t),$$

and

$$\ddot{\mathbf{y}}_0(t) = -m^{-1} \frac{\partial W(R)}{\partial \mathbf{y}_0} - \omega_{e0}^2 \mathbf{y}_0(t) + \omega_{c1}^2 \mathbf{y}_1(t), \quad (2.4b)$$

$$\ddot{\mathbf{y}}_1(t) = -\Omega_1^2 \mathbf{y}_1(t) + \omega_{c1}^2 \mathbf{y}_0(t) - \beta_2 \dot{\mathbf{y}}_1(t) + \mathbf{f}_y(t).$$

Note that $\mathbf{x}_0(t)$ and $\mathbf{y}_0(t)$, as before, are the coordinates of the real iodine atoms while $\mathbf{x}_1(t)$ and $\mathbf{y}_1(t)$ are the coordinates of the fictitious model heatbath atoms. The model heatbath equations involve parameters Ω_1^2 and β_2 which characterize the low frequency response of the solvent. Methods for optimally choosing these parameters have been described elsewhere.⁴ The quantity $\mathbf{f}_2(t) = \mathbf{f}_x(t)$ or $\mathbf{f}_y(t)$ is a standard δ -correlated white noise Gaussian stochastic source of the type assumed in

phenomenological Brownian motion theory.^{5,6} Thus, $\mathbf{f}_2(t)$ and β_2 are related by a fluctuation-dissipation theorem of the form

$$\langle \mathbf{f}_2(t) \cdot \mathbf{f}_2(0) \rangle = (6k_B T/m) \beta_2 \delta(t). \quad (2.5)$$

The most important points concerning Eqs. (2.4) are

(i) The simplest $N=1$ model heatbath reproduces all of the solvent effects included in Eqs. (2.3) in a qualitatively correct manner. In particular, it accounts for iodine caging and the chemically crucial *initial* energy transfer between the iodine atoms and the solvent. This is because the basic parameters ($\omega_{e0}^2, \omega_{c1}^2$) characterizing short-timescale solvent response are properly built into the $N=1$ model heatbath equations (2.4).

(ii) Non-Markovian kernels do not appear in Eqs. (2.4). Thus, the equations are readily integrable by standard Monte Carlo classical trajectory methods. Detailed methods for sampling the initial conditions $\mathbf{x}_0(0), \dot{\mathbf{x}}_0(0), \mathbf{x}_1(0), \dot{\mathbf{x}}_1(0)$ and $\mathbf{y}_0(0), \dot{\mathbf{y}}_0(0), \mathbf{y}_1(0), \dot{\mathbf{y}}_1(0)$ are described elsewhere.^{1a,7}

The $N=1$ model heatbath equations (2.4) quite accurately simulate the coupled MTGLE equations (2.3) and the accuracy may be readily improved by increasing N . The Equations (2.3), however, suffer from a qualitative flaw. The quantities $\omega_{e0}^2, \omega_{c1}^2, \theta_1(t)$ describe iodine dynamics only when the iodine atoms are infinitely far apart. Thus, common caging (see Introduction) and other dynamical effects of iodine interaction are missing from Eqs. (2.3) and (2.4). At a minimum the model heatbath parameters $\omega_{e0}^2, \omega_{c1}^2, \Omega_1^2$, and β_2 should depend on the interatomic distance R . We will see, Eqs. (5.11) and (7.12) below, that the actual situation is more complex.

We now motivate the generalized MTGLE theory which properly includes the R -dependent effects missing from Eqs. (2.3) and (2.4). Our motivation is based on the physical interpretation of the quantities appearing in the formally exact MTGLE, Eq. (2.1). We note the following points:

(i) Suppose we have an ensemble of solutions of the following type. Each solution has a single solute atom and that solute atom is located at the origin at $t=0$. Each solute atom is in equilibrium with the local solvent density. What we mean by this is that the force on each solute atom has only a random component; i.e., it arises only from $\omega_{c1}^2 \mathbf{R}_1(t)$. Thus, the ensemble averaged force on a solute atom is $\omega_{c1}^2 \langle \mathbf{R}_1(t) \rangle = 0$. Now suppose each solute atom is displaced slightly by an amount $\Delta \mathbf{r}_0$. Equation (2.1) shows that the ensemble average *instantaneous* restoring force (per unit mass) on a solute atom is *exactly* $-\omega_{e0}^2 \Delta \mathbf{r}_0$. The situation just discussed is illustrated in Fig. 1(a). Our discussion shows how ω_{e0}^2 may be computed from the equilibrium local density $\rho(r)$. Moreover, it shows how the concept of an Einstein frequency for a single solute atom may be generalized to yield a solute configuration dependent Einstein frequency matrix for a group of n interacting solute atoms. The essential point is that the equilibrium local density and, hence, the Einstein frequency depends on the spatial arrangement of the solute atoms. We illustrate this point in Fig. 1(b) for the ellipsoidal local sol-

vent density characteristic of two interacting solute atoms.

(ii) The initial Einstein restoring force relaxes to a final adiabatic restoring force $-\Omega_0^2 \Delta r_0$ due to adjustment of the local solvent density to the displacement Δr_0 . The quantity Ω_0 is the adiabatic frequency discussed elsewhere¹ and below. For a single solute atom in a liquid the solvent density is unconstrained, relaxation is perfect, and, thus, $\Omega_0 = 0$. For several interacting solute atoms, however (or for a single atom in a solid), Ω_0 is nonvanishing. Quite generally $\Omega_0 < \omega_{e0}$ since the initial tension due to a displacement relaxes to a smaller final tension.

(iii) Immediately after the small atomic displacement Δr_0 , the local solvent density begins to relax to its new equilibrium value. This density relaxation gives rise to a relaxing restoring force on the atom. The temporal development of the restoring force is described by a solvent response function given in Eq. (A20). This response function is determined by a linear response calculation in which Δr_0 is the smallest parameter (Appendix A). The key point is that this response function is *approximately* $\omega_{c1}^4 \hat{\theta}_1(t)$. This observation shows how one may make an approximate computation of $\omega_{c1}^4 \hat{\theta}_1(t)$ for the single solute atom case. The real value of the approximation, however, is that it may be extended to the case of n interacting solute atoms. For example, consider the case of two interacting solute atoms [Fig. 1(b)]. If one atom is slightly displaced then the initial ellipsoidal density relaxes to a new final value. The time-dependent ellipsoidal density gives rise to a relaxing solvent-solute force and a response function $\omega_{c1}^4(R) \hat{\theta}_1(t; R)$ which depends on the interatomic separation.

We mention, in passing, that our linear response approximation for $\omega_{c1}^4 \hat{\theta}_1(t)$ is exact for atomic displacements from the equilibrium configuration in harmonic systems.

(iv) We have shown elsewhere¹ that the MTGLE random force $\omega_{c1}^2 \mathbf{R}_1(t)$ has a simple interpretation within the exact equivalent harmonic chain representation^{1,4} of the atom dynamics. It is the force on the solute atom due to the *equivalent chain heatbath* given that the atom is clamped at equilibrium [i.e., $\mathbf{r}_{01}(t) = 0$ in Eq. (2.1)]. This interpretation suggests that the MTGLE random force may be approximated as the force exerted on the atom by the *real heatbath* given that the atom is clamped and in equilibrium with the local solvent density. Thus, according to this approximation, $\omega_{c1}^2 \mathbf{R}_1(t)$ is the force on a clamped solute atom due to fluctuations of the local density from its equilibrium value. This approximation may be extended to the n solute atom case in an obvious manner.

The above approximation for $\omega_{c1}^2 \mathbf{R}_1(t)$ is, in fact, required by the MTGLE second fluctuation-dissipation theorem, Eq. (2.2), if one invokes the approximation for $\omega_{c1}^4 \hat{\theta}_1(t)$ discussed in (iii). Thus, the approximation is exact for harmonic heatbaths.

We note that the above approximation for $\omega_{c1}^2 \mathbf{R}_1(t)$ is not equivalent to assuming the conventional Mori^{8,9} ran-

dom force $\mathbf{f}_m(t)$ is the solvent force on a clamped solute atom.

The above discussion motivates the linear response treatment presented in Appendix A. We next summarize the key results of that treatment.

III. LINEAR RESPONSE THEORY: RESULTS

We present here the basic results of the treatment of Appendix A. These results are sufficient to build up the full hierarchy structure of the generalized MTGLE theory (see Sec. IV). This structure in turn leads directly to the major result of this paper, the generalized equivalent chain representation, Eq. (5.1), for the dynamics of the reagents.

We begin by defining notation used in the remainder of the article.

A. Notation

We assume a solvent made up of N_s identical atoms of mass M . The solute is assumed to be composed of n identical atoms of mass m . The solute atoms may or may not be chemically bound to one another. Treatment of solutes composed of several atomic species and treatment of molecular and/or mixed solvents is straightforward. We avoid this, however, since it leads to technical and notational complexity which obscures more basic issues.

Let q_λ equal the coordinate of solvent atom λ ; \mathbf{r}_{0i} is the coordinate of solute atom i . We will employ a shorthand notation for these coordinates as well as for other matrix quantities which arise. We denote the solvent atom coordinates collectively by q , and the solute atom coordinates collectively by \mathbf{r}_0 . Explicitly,

$$q = \begin{pmatrix} q_1 \\ \vdots \\ q_{N_s} \end{pmatrix}, \quad (3.1)$$

$$\mathbf{r}_0 = \begin{pmatrix} \mathbf{r}_{01} \\ \vdots \\ \mathbf{r}_{0n} \end{pmatrix}. \quad (3.2)$$

The potential energy functions which couple the solvent and solute atoms are

$$U_{vv}(q) = \text{solvent-solvent potential}, \quad (3.3a)$$

$$U_{vu}(q, \mathbf{r}_0) = \text{solvent-solute potential}, \quad (3.3b)$$

$$U_{uu}(\mathbf{r}_0) = \text{solute-solute potential}. \quad (3.3c)$$

These potential functions may or may not be pairwise additive.

Let

$$\mathbf{F} \equiv \mathbf{F}(q, \mathbf{r}_0) = -\frac{\partial}{\partial \mathbf{r}_0} [U_{vu}(q, \mathbf{r}_0) + U_{uu}(\mathbf{r}_0)] \quad (3.4)$$

be the total instantaneous force on the solute when it is located at configuration point \mathbf{r}_0 . Let

$$\mathcal{F} \equiv \mathcal{F}(q, \mathbf{r}_0) = -\frac{\partial}{\partial \mathbf{r}_0} U_{vu}(q, \mathbf{r}_0) \quad (3.5)$$

be the total solvent force on the solute at r_0 . Note both F and \mathcal{F} are n -dimensional vectors; e. g., $\mathcal{F}_i = -(\partial/\partial r_{0i})U_{uu}(r_0)$.

Let iL_0 denote the Liouville operator governing the dynamics of the solvent given that the solute is clamped at r_0 [Eq. (A7)]. We will later require the time evolution of solvent dynamical variables A according to the clamped solute dynamics iL_0 . We thus define

$$A_0(t; r_0) = \exp(iL_0 t)A. \quad (3.6)$$

Finally, we use the following notation for equilibrium averages:

$$\langle \dots \rangle = \text{canonical average over both solvent and solute coordinates and momenta}, \quad (3.7)$$

$$\langle \dots \rangle_{r_0} = \text{canonical average over solvent coordinates and momenta conditional that the solute is clamped at } r_0. \quad (3.8)$$

B. Basic results

The basic results required to build the generalized MTGLE theory are the Einstein frequency $\omega_{e_0}(r_0)$, the solvent-solute coupling constant $\omega_{c_1}(r_0)$, and the solvent response function $\dot{b}_1(t; r_0)$. These quantities are $n \times n$ matrices and are functions of the solute configuration point r_0 . The information in $\dot{b}_1(t; r_0)$ is also carried by the abstract coordinate variable $R_1(t; r_0)$. This variable, like $R_1(t)$ in the exact MTGLE theory, describes the temporal development of solvent density fluctuations about the solute clamped at r_0 . The quantity $\omega_{c_1}(r_0)R_1(t; r_0)$ serves as a random force on the solute due to the density fluctuations. Note that both the random force and $R_1(t; r_0)$ are n -component vectors [cf. Eq. (3.2) for r_0]. The theory of Appendix A yields the following results for the basic MTGLE quantities (note T denotes a matrix transpose and recall the definitions of Sec. IIIA)

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

$$\omega_{c_1}^4(r_0) = \frac{1}{mk_B T} \langle \dot{\mathcal{F}}_0 \dot{\mathcal{F}}_0^T \rangle_{r_0}, \quad (3.10)$$

$$\omega_{c_1}^2(r_0)R_1(t; r_0) = m^{-1} \dot{\mathcal{F}}_0(t; r_0), \quad (3.11)$$

$$\dot{b}_1(t; r_0) = \frac{m}{k_B T} \langle \dot{R}_1(t; r_0) \dot{R}_1^T(0; r_0) \rangle_{r_0}. \quad (3.12)$$

Note that $\dot{\mathcal{F}}_0 \equiv iL_0 \mathcal{F}$ and $\mathcal{F}(t; r_0) = \mathcal{F}(t; r_0) - \langle \mathcal{F} \rangle_{r_0}$. Also note that Eq. (3.12) is the generalized form of the MTGLE second fluctuation-dissipation theorem [cf. Eq. (2.2)].

The basic results of Eqs. (3.9)–(3.12) permit one to construct the full MTGLE hierarchy from the solute-solute gas phase forces and the solvent density fluctuations about the solute clamped at r_0 . This latter information, as mentioned, may be obtained by the molecular dynamics simulation method. Notice the formal results of Eqs. (3.9)–(3.12) accord with the physical discussion of Sec. II.

To construct model heatbaths we also require the adi-

abatic frequency $\Omega_0(r_0)$. The following result for the adiabatic frequency is derived in Appendix B:

$$\Omega_0^2(r_0) = -m^{-1} \frac{\partial}{\partial r_0} \langle F \rangle_{r_0}. \quad (3.13)$$

One may generally show that (see Appendix B)

$$\Omega_0^2(r_0) \leq \omega_{e_0}^2(r_0) \quad (3.14)$$

in accord with our discussion in Sec. II.

C. Basic properties

The quantities $\omega_{e_0}^2(r_0)$, etc., just presented satisfy symmetry restrictions which are necessary in order to build up the full MTGLE theory. From the definitions Eqs. (3.9), (3.10), and (3.13) one sees that $\omega_{e_0}^2(r_0)$, etc., are symmetric matrices, i. e.,

$$\omega_{e_0}^2(r_0) = [\omega_{e_0}^2(r_0)]^T, \quad (3.15a)$$

$$\omega_{c_1}^2(r_0) = [\omega_{c_1}^2(r_0)]^T, \quad (3.15b)$$

$$\Omega_0^2(r_0) = [\Omega_0^2(r_0)]^T. \quad (3.15c)$$

Because of time reversal symmetry one has the relationship

$$\langle \dot{R}_1(-t; r_0) \dot{R}_1^T(0; r_0) \rangle_{r_0} = \langle \dot{R}_1(t; r_0) \dot{R}_1^T(0; r_0) \rangle_{r_0}. \quad (3.16)$$

Moreover, because of the stationary property of equilibrium time correlation functions, one has the additional equality

$$\langle \dot{R}_1(t + \tau; r_0) \dot{R}_1^T(\tau; r_0) \rangle_{r_0} = \langle \dot{R}_1(t; r_0) \dot{R}_1^T(0; r_0) \rangle_{r_0}. \quad (3.17a)$$

Setting $\tau = -t$ in Eq. (3.17a) yields

$$\langle \dot{R}_1(0; r_0) \dot{R}_1^T(-t; r_0) \rangle_{r_0} = \langle \dot{R}_1(t; r_0) \dot{R}_1^T(0; r_0) \rangle_{r_0}. \quad (3.17b)$$

Taking the matrix transpose of Eq. (3.17b) and comparing the result with Eq. (3.16) yields

$$\langle \dot{R}_1(t; r_0) \dot{R}_1^T(0; r_0) \rangle_{r_0} = \langle \dot{R}_1(t; r_0) \dot{R}_1^T(0; r_0) \rangle_{r_0}^T. \quad (3.18)$$

Comparing Eqs. (3.16) and (3.18) with Eq. (3.12) shows that $\dot{b}_1(t; r_0)$ is even in time and also a symmetric matrix. Moreover, comparison of Eqs. (3.10)–(3.12) shows $\dot{b}_1(0; r_0) = 1$. Thus, $\dot{b}_1(t; r_0)$ has the following basic properties

$$\begin{aligned} \dot{b}_1(-t; r_0) &= \dot{b}_1(t; r_0) = \dot{b}_1^T(t; r_0), \\ \dot{b}_1(0; r_0) &= 0, \quad \dot{b}_1(0; r_0) = 1. \end{aligned} \quad (3.19)$$

These properties will permit us to build the MTGLE hierarchy. We now turn to this problem.

IV. HEATBATH HIERARCHY

The present generalized MTGLE theory has a hierarchy structure analogous to that of the formally exact MTGLE theory. That is for each configuration point r_0 , there exists an infinite sequence of abstract heatbaths. The p th heatbath, $p = 1, 2, 3, \dots$, is characterized by a response function $\theta_p(t; r_0)$ (an $n \times n$ symmetric matrix) and an associated dynamical variable $R_p(t; r_0)$ (an n -component vector). The response functions satisfy a coupled hierarchy of effective equations of motion. The dynamical variables satisfy an analogous coupled hierarchy of MTGLE's. We first turn to the hierarchy for response functions.

A. Response function hierarchy

We begin by defining the spectral density, $\sigma_1(\omega; r_0)$, of the response function $\dot{\theta}_1(t; r_0)$ by the Fourier transform relationship

$$\sigma_1(\omega; r_0) = \frac{2}{\pi} \int_0^\infty \cos \omega t \dot{\theta}_1(t; r_0) dt. \quad (4.1a)$$

The inverse relationship is

$$\dot{\theta}_1(t; r_0) = \int_0^\infty \cos \omega t \sigma_1(\omega; r_0) d\omega. \quad (4.1b)$$

Because $\dot{\theta}_1(0; r_0) = 1$, Eq. (4.1b) shows that $\sigma_1(\omega; r_0)$ is unit normalized, i. e.,

$$\int_0^\infty \sigma_1(\omega; r_0) d\omega = 1. \quad (4.2)$$

We next define an Einstein frequency matrix $\omega_{e1}(r_0)$ for the first heatbath by

$$\omega_{e1}^2(r_0) = \int_0^\infty \omega^2 \sigma_1(\omega; r_0) d\omega. \quad (4.3)$$

We also define a coupling constant matrix, $\omega_{c2}^2(r_0)$, which links the first and second heatbaths by

$$\omega_{c2}^4(r_0) = \int_0^\infty [\omega^2 - \omega_{e1}^2(r_0)] \sigma_1(\omega; r_0) [\omega^2 - \omega_{e1}^2(r_0)] d\omega. \quad (4.4)$$

Both $\omega_{e1}(r_0)$ and $\omega_{c2}^2(r_0)$ are symmetric $n \times n$ matrices.

Because $\dot{\theta}_1(t; r_0)$ satisfies the basic relations, Eqs. (3.19), one may show¹⁰ that $\dot{\theta}_1(t; r_0)$ also satisfies the following exact effective equation of motion

$$\ddot{\theta}_1(t; r_0) = -\omega_{e1}^2(r_0) \theta_1(t; r_0) + \int_0^t d\tau \omega_{c2}^2(r_0) \times \theta_2(t - \tau; r_0) \omega_{c2}^2(r_0) \theta_1(\tau; r_0). \quad (4.5)$$

The matrix $\theta_2(t; r_0)$ is the response function of the heatbath's heatbath. It is defined by Eq. (4.5). From Eq. (4.5), one may show that $\theta_2(t; r_0)$ is an even function of time and that also $\theta_2(0; r_0) = 1$. One may additionally demonstrate that $\theta_2(t; r_0)$ is a symmetric matrix. This last result is readily proven from the Laplace space form of Eq. (4.5) which is¹¹

$$\begin{aligned} \hat{\theta}_1(z; r_0) &= [z^2 + \omega_{e1}^2(r_0) - \omega_{c2}^2(r_0) \hat{\theta}_2(z; r_0) \omega_{c2}^2(r_0)]^{-1} \\ &= [z^2 + \omega_{e1}^2(r_0)]^{-1} + [z^2 + \omega_{e1}^2(r_0)]^{-1} \\ &\quad \times [\omega_{c2}^2(r_0) \hat{\theta}_2(z; r_0) \omega_{c2}^2(r_0)] [z^2 + \omega_{e1}^2(r_0)]^{-1} + \dots \end{aligned} \quad (4.6)$$

One may show from the second form of Eq. (4.6) that $\hat{\theta}_2^T = \hat{\theta}_2$ and hence that $\theta_2(t; r_0)$ is symmetric.

The above results may be summarized by the statement that $\theta_2(t; r_0)$ has basic properties identical to those of $\dot{\theta}_1(t; r_0)$ [Eq. (3.19)]; i. e.,

$$\begin{aligned} \theta_2(-t; r_0) &= \theta_2(t; r_0) = \dot{\theta}_2^T(t; r_0), \\ \theta_2(0; r_0) &= 0, \quad \dot{\theta}_2(0; r_0) = 1. \end{aligned} \quad (4.7)$$

Using Eq. (4.7) one may show $\dot{\theta}_2(t; r_0)$ satisfies an equation of motion analogous to Eq. (4.5) involving a response function $\dot{\theta}_3(t; r_0)$. This, in turn, satisfies an analogous equation of motion, etc. Thus, Eq. (4.7) is sufficient to guarantee that the hierarchy propagates indefinitely.

One, thus, has that the general p th response function $\dot{\theta}_p(t; r_0)$ satisfies the following basic relations:

$$\begin{aligned} \dot{\theta}_p(-t; r_0) &= \dot{\theta}_p(t; r_0) = \dot{\theta}_p^T(t; r_0), \\ \dot{\theta}_p(0; r_0) &= 0, \quad \ddot{\theta}_p(0; r_0) = 1. \end{aligned} \quad (4.8)$$

The spectral density $\sigma_p(\omega; r_0)$ of $\dot{\theta}_p(t; r_0)$ is defined by the relationship

$$\sigma_p(\omega; r_0) = \frac{2}{\pi} \int_0^\infty \cos \omega t \dot{\theta}_p(t; r_0) dt, \quad (4.9a)$$

or equivalently by the inverse relation

$$\dot{\theta}_p(t; r_0) = \int_0^\infty \cos \omega t \sigma_p(\omega; r_0) d\omega. \quad (4.9b)$$

Equations (4.8) and (4.9b) imply that $\sigma_p(\omega; r_0)$ is unit normalized i. e.,

$$\int_0^\infty \sigma_p(\omega; r_0) d\omega = 1. \quad (4.10)$$

One may also define the Einstein frequency $\omega_{ep}^2(r_0)$ of the p th heatbath and the coupling constant $\omega_{c,p+1}^2(r_0)$ linking the p th and $(p+1)$ th heatbaths by the moment relations

$$\omega_{ep}^2(r_0) = \int_0^\infty \omega^2 \sigma_p(\omega; r_0) d\omega \quad (4.11a)$$

and

$$\omega_{c,p+1}^2(r_0) = \int_0^\infty [\omega^2 - \omega_{ep}^2(r_0)] \sigma_p(\omega; r_0) [\omega^2 - \omega_{ep}^2(r_0)] d\omega. \quad (4.11b)$$

From Eqs. (4.8), one may show $\theta_p(t; r_0)$ exactly satisfies the effective equation of motion

$$\begin{aligned} \ddot{\theta}_p(t; r_0) &= -\omega_{ep}^2(r_0) \theta_p(t; r_0) + \int_0^t d\tau \omega_{c,p+1}^2(r_0) \\ &\quad \times \theta_{p+1}(t - \tau; r_0) \omega_{c,p+1}^2(r_0) \theta_p(\tau; r_0). \end{aligned} \quad (4.12)$$

The Laplace space form of Eq. (4.12) is

$$\begin{aligned} \hat{\theta}_p(z; r_0) &= [z^2 + \omega_{ep}^2(r_0) - \omega_{c,p+1}^2(r_0) \\ &\quad \times \hat{\theta}_{p+1}(z; r_0) \omega_{c,p+1}^2(r_0)]^{-1}. \end{aligned} \quad (4.13)$$

Equations (4.8)–(4.13) define the generalized MTGLE hierarchy for response functions. The hierarchy is closed by the defining relations for $\dot{\theta}_1(t; r_0)$, Eqs. (3.11)–(3.12). These defining relations, along with the recursion scheme derived above, permit one to compute the MTGLE parameters $\{\omega_{ep}^2(r_0), \omega_{c,p+1}^2(r_0)\}$, $p \geq 1$, in terms of moments of $\sigma_1(\omega; r_0)$.¹² This latter quantity, in turn, may be determined via molecular dynamics simulations through the force–force correlation function $\langle \mathcal{F}_0(t; r_0) \times \mathcal{F}^T(0; r_0) \rangle_{r_0}$.

B. Dynamic variable hierarchy

We now develop the coupled hierarchy of MTGLE's for the abstract coordinate variables $R_p(t; r_0)$, $p = 1, 2, 3, \dots$. As a preliminary step, we work out the formal statistical properties of the variable $R_1(t; r_0)$. We begin with the MTGLE second fluctuation theorem, Eq. (3.12), and its integrated form

$$\theta_1(t; r_0) = \frac{m}{k_B T} \langle R_1(t; r_0) \dot{R}_1^T(0; r_0) \rangle_{r_0}$$

$$= -\frac{m}{k_B T} \langle \dot{R}_1(t; r_0) \dot{R}_1^T(0; r_0) \rangle_{r_0}. \quad (4.14)$$

We also define the adiabatic frequency of the ($p=1$) heatbath by¹³

$$\Omega_1^2(r_0) = \hat{\theta}_1(z=0; r_0). \quad (4.15)$$

Note that $\Omega_1(r_0)$ is a symmetric $n \times n$ matrix.

Evaluating Eq. (3.12) at $t=0$ and using $\dot{\theta}_1(0; r_0)=1$ yields

$$\frac{1}{2}m \langle \dot{R}_1(0; r_0) \dot{R}_1^T(0; r_0) \rangle_{r_0} = \frac{1}{2}k_B T. \quad (4.16a)$$

Evaluating Eq. (4.14) at $t=0$ and using $\dot{\theta}_1(0; r_0)=0$ yields a second relationship

$$\langle R_1(0; r_0) \dot{R}_1^T(0; r_0) \rangle_{r_0} = 0. \quad (4.16b)$$

Finally, comparing Eq. (4.15) with the time integral of Eq. (4.14) yields

$$\frac{1}{2}m \Omega_1(r_0) \langle R_1(0; r_0) \dot{R}_1^T(0; r_0) \rangle_{r_0} \Omega_1(r_0) = \frac{1}{2}k_B T. \quad (4.16c)$$

Notice that Eqs. (4.16a)–(4.16c) formally resemble

(a) the classical equipartition of kinetic energy,

(b) the classical statistical independence of position and velocity,

(c) the classical equipartition of potential energy for a harmonic oscillator with coordinate $R_1(t; r_0)$ and frequency $\Omega_1(r_0)$.

Thus, we have shown that the abstract variable $R_1(t; r_0) = \omega_{c_1}^{-2}(r_0) \mathcal{F}_0(t; r_0)$ [see Eq. (3.11)] has formal statistical properties identical to those of an ordinary harmonic oscillator coordinate variable.

We next develop an MTGLE for $R_1(t; r_0)$. Combining Eq. (4.14) with the equation of motion for $\theta_1(t; r_0)$, Eq. (4.5), yields

$$\begin{aligned} \langle \ddot{R}_1(t; r_0) \dot{R}_1^T(0; r_0) \rangle_{r_0} \\ = -\omega_{e_1}^2(r_0) \langle R_1(t; r_0) \dot{R}_1^T(0; r_0) \rangle_{r_0} + \int_0^t d\tau \omega_{c_1}^2(r_0) \\ \times \theta_2(t-\tau; r_0) \omega_{c_2}^2(r_0) \langle R_1(\tau; r_0) \dot{R}_1^T(0; r_0) \rangle_{r_0}. \end{aligned} \quad (4.17)$$

Equation (4.17) is equivalent to the following MTGLE:

$$\begin{aligned} \ddot{R}_1(t; r_0) = -\omega_{e_1}^2(r_0) R_1(t; r_0) + \int_0^t d\tau \omega_{c_2}^2(r_0) \theta_2(t-\tau; r_0) \\ \times \omega_{c_2}^2(r_0) R_1(\tau; r_0) + \omega_{c_2}^2(r_0) R_2(t; r_0), \end{aligned} \quad (4.18)$$

along with the orthogonality constraint

$$\langle R_2(t; r_0) \dot{R}_1^T(0; r_0) \rangle_{r_0} = 0. \quad (4.19)$$

This is because Eq. (4.17) may be readily derived from Eq. (4.18) using Eq. (4.19).

$R_2(t; r_0)$ satisfies a second statistical constraint in addition to Eq. (4.19). This is the fluctuation–dissipation theorem,

$$\dot{\theta}_2(t; r_0) = \frac{m}{k_B T} \langle \dot{R}_2(t; r_0) \dot{R}_2^T(0; r_0) \rangle_{r_0}. \quad (4.20)$$

Equation (4.20) is required in order that the formal kinetic energy associated with the coordinate $R_1(t; r_0)$ satisfies the equipartition theorem Eq. (4.16a). The proof

of Eq. (4.20) is similar to the proof of an analogous theorem presented elsewhere¹⁴ and therefore will be omitted here.

Using Eqs. (4.12) for $p=2$ and Eq. (4.20) one may show that $R_2(t; r_0)$ satisfies an MTGLE identical in form to Eq. (4.18) involving a random force $\omega_{c_3}^2(r_0) \times R_3(t; r_0)$. Moreover, from Eqs. (4.8) and (4.20), one may show $R_2(t; r_0)$ has formal statistical properties analogous to those of $R_1(t; r_0)$. A consequence is that $R_3(t; r_0)$ satisfies a fluctuation–dissipation theorem analogous to Eq. (4.20), etc. Thus the MTGLE hierarchy for the dynamical variables $R_p(t; r_0)$ propagates. One has for the p th abstract variable the following relations:

(i) the orthogonality constraint

$$\langle R_p(t; r_0) \dot{R}_{p-1}^T(0; r_0) \rangle_{r_0} = 0; \quad (4.21)$$

(ii) the MTGLE fluctuation–dissipation theorem

$$\dot{\theta}_p(t; r_0) = \frac{m}{k_B T} \langle \dot{R}_p(t; r_0) \dot{R}_p^T(0; r_0) \rangle_{r_0}; \quad (4.22)$$

(iii) the statistical properties¹⁵

$$\frac{1}{2}m \langle \dot{R}_p(0; r_0) \dot{R}_p^T(0; r_0) \rangle_{r_0} = \frac{1}{2}k_B T, \quad (4.23a)$$

$$\langle R_p(0; r_0) \dot{R}_p^T(0; r_0) \rangle_{r_0} = 0, \quad (4.23b)$$

$$\begin{aligned} \frac{1}{2}m \Omega_p(r_0) \\ \times \langle R_p(0; r_0) \dot{R}_p^T(0; r_0) \rangle_{r_0, R_1, \dots, R_{p-1}} \Omega_p(r_0) = \frac{1}{2}k_B T, \end{aligned} \quad (4.23c)$$

where

$$\Omega_p^2(r_0) = \hat{\theta}_p(z=0; r_0) \quad (4.24)$$

(iv) the MTGLE

$$\begin{aligned} \ddot{R}_p(t; r_0) \\ = -\omega_{e_p}^2(r_0) R_p(t; r_0) + \int_0^t d\tau \omega_{c_{p+1}}^2(r_0) \theta_p(t-\tau; r_0) \\ \times \omega_{c_{p+1}}^2(r_0) R_p(\tau; r_0) + \omega_{c_{p+1}}^2(r_0) R_{p+1}(t; r_0). \end{aligned} \quad (4.25)$$

This concludes our development of the MTGLE hierarchy for the abstract coordinate variables $R_p(t; r_0)$.

V. EQUIVALENT HARMONIC CHAIN REPRESENTATION FOR SOLUTE DYNAMICS

The principal result of this paper, the generalized chain representation of solute dynamics Eq. (5.1), is presented in Sec. V A. We specialize this result to the $n=1$ case in Sec. V B and to the $n=2$ case in Sec. V C.

A. The chain equations of motion

The generalized equivalent chain representation for the dynamics of the solute molecules is

$$\begin{aligned} \ddot{r}_0(t) &= -m^{-1} \langle F \rangle_{r_0} - \omega_{e_0}^2(r_0) r_0(t) + \omega_{c_1}^2(r_0) r_1(t) \\ \ddot{r}_1(t) &= -\omega_{e_1}^2(r_0) r_1(t) + \omega_{c_1}^2(r_0) r_0(t) + \omega_{c_2}^2(r_0) r_2(t) \\ &\vdots \\ \ddot{r}_N(t) &= -\omega_{e_N}^2(r_0) r_N(t) + \omega_{c_N}^2(r_0) r_{N-1}(t) \end{aligned}$$

$$+ \int_0^t d\tau \omega_{c_{N+1}}^2(r_0) \theta_{N+1}(t-\tau; r_0) \omega_{c_{N+1}}^2(r_0) r_N(\tau) \\ + \omega_{c_{N+1}}^2(r_0) R_{N+1}(t; r_0), \quad (5.1)$$

where $r_0 \equiv r_0(t)$. Equation (5.1) is to be supplemented by the fluctuation-dissipation theorem [Eq. (4.22)]

$$\dot{\theta}_{N+1}(t) = \frac{m}{k_B T} \langle \dot{R}_{N+1}(t; r_0) \dot{R}_{N+1}^T(0; r_0) \rangle_{r_0}. \quad (5.2)$$

The argument for Eq. (5.1) is presented in Appendix A. Equation (5.1) is based on two independent approximations. These are

(i) The chain parameters $\{\omega_{e_p}^2(r_0), \omega_{p+1}^2(r_0)\}$ are computed in the linear response approximation. For the $n=1$ case, this means that the solvent response to unconstrained solute motion is approximated to be the solvent response to small forced solute displacements.

(ii) The mean force $\langle F \rangle_{r_0}$ and the chain parameters $\{\omega_{e_p}^2(r_0), \omega_{p+1}^2(r_0)\}$ are assumed to vary slowly on a time-scale compared to a solvent molecule momentum relaxation time. This means that we assume that *either* the mean force and MTGLE parameters vary slowly with r_0 *or* that r_0 changes slowly. Unless small solute configuration changes yield large parameter changes, this approximation is physically reasonable. This is because gross configurational changes of the solute occur more slowly than momentum relaxation.

Both approximations may be investigated numerically. Assumption (i) may be rigorously tested for the case $n=1$ (see, e.g., Sec. VB). Assumption (ii) is exact for the $n=1$ case ($\langle \mathbf{F} \rangle_{r_0} = 0$ and $\omega_{e_0}^2$, etc., are independent of r_0) and thus is reasonable when the reagents are asymptotically separated. Assumption (ii), in addition, is reasonable for encounter dynamics since then large configurational changes in the solute molecules are inhibited because the molecules are confined to a common cage.

B. Single solute atom limit

In order to make a preliminary check of assumption (i), we next examine Eq. (5.1) for the case of a single solute atom ($n=1$) with coordinate $\mathbf{r}_0(t)$. We then compare the exact and linear response values of the basic MTGLE parameters $\omega_{e_0}^2$ and $\omega_{c_1}^2$. Equation (5.1) for the $n=1$ case reduces to

$$\ddot{\mathbf{r}}_0(t) = -\omega_{e_0}^2 \mathbf{r}_0(t) + \omega_{c_1}^2 \mathbf{r}_1(t) \\ \ddot{\mathbf{r}}_1(t) = -\omega_{e_1}^2 \mathbf{r}_1(t) + \omega_{c_1}^2 \mathbf{r}_0(t) + \omega_{c_2}^2 \mathbf{r}_2(t) \\ \vdots \\ \ddot{\mathbf{r}}_N(t) = -\omega_{e_N}^2 \mathbf{r}_N(t) + \omega_{c_N}^2 \mathbf{r}_{N-1}(t) \\ + \omega_{c_{N+1}}^4 \int_0^t \theta_{N+1}(t-\tau) \mathbf{r}_N(\tau) d\tau + \omega_{c_{N+1}}^2 \mathbf{R}_{N+1}(t). \quad (5.3)$$

Equation (5.3) is identical in form to the chain representation of the formally exact MTGLE theory. The exact and linear response parameters are, however, in general unequal. The basic parameters of the formally exact theory are¹⁶

$$\omega_{e_0}^2 = \frac{1}{3mk_B T} \langle \mathbf{F} \cdot \mathbf{F} \rangle, \quad (5.4a)$$

$$\omega_{c_1}^4 = \frac{1}{3mk_B T} \left\{ \langle \dot{\mathbf{F}} \cdot \dot{\mathbf{F}} \rangle - \frac{\langle \mathbf{F} \cdot \mathbf{F} \rangle^2}{3mk_B T} \right\}, \quad \text{exact}. \quad (5.4b)$$

Note $\dot{\mathbf{F}} = iL\mathbf{F}$, where iL is the full system (atom plus solvent) Liouville operator. The corresponding parameters of the linear response theory are [Eqs. (3.9) and (3.10)]

$$\omega_{e_0}^2 = -\frac{1}{3m} \left\langle \frac{\partial}{\partial \mathbf{r}_0} \cdot \mathbf{F} \right\rangle_{\mathbf{r}_0}, \quad (5.5a)$$

$$\omega_{c_1}^4 = \frac{1}{3mk_B T} \langle \dot{\mathbf{F}}_0 \cdot \dot{\mathbf{F}}_0 \rangle_{r_0}, \quad \text{linear response}. \quad (5.5b)$$

The Einstein frequency $\omega_{e_0}^2$ from the linear response theory is expected to be exact (Sec. II). This may be shown from the relations

$$\left\langle \frac{\partial}{\partial \mathbf{r}_0} \cdot \mathbf{F} \right\rangle_{\mathbf{r}_0} = \left\langle \frac{\partial}{\partial \mathbf{r}_0} \cdot \mathbf{F} \right\rangle = -\frac{1}{k_B T} \langle \mathbf{F} \cdot \mathbf{F} \rangle. \quad (5.6)$$

The first and second equalities in Eqs. (5.6) follow respectively from the isotropy of the liquid and the virial theorem. Equations (5.6) show that Eqs. (5.4a) and (5.5a) are identical.

The coupling constant from the exact theory Eq. (5.4b) may be reworked into the form

$$\omega_{c_1}^4 = \frac{k_B T}{M} \sum_{\lambda=1}^{N_s} \left\langle \frac{\partial \mathbf{F}}{\partial \mathbf{q}} : \frac{\partial \mathbf{F}}{\partial \mathbf{q}} \right\rangle \\ + \frac{1}{3m^2} \left\{ \left\langle \frac{\partial \mathbf{F}}{\partial \mathbf{r}_0} : \frac{\partial \mathbf{F}}{\partial \mathbf{r}_0} \right\rangle - \frac{1}{3} \left\langle \frac{\partial}{\partial \mathbf{r}_0} \cdot \mathbf{F} \right\rangle^2 \right\}, \quad \text{exact}. \quad (5.7a)$$

The linear response coupling constant Eq. (5.5b) may similarly be recast as

$$\omega_{c_1}^4 = \frac{k_B T}{M} \sum_{\lambda=1}^{N_s} \left\langle \frac{\partial \mathbf{F}}{\partial \mathbf{q}} : \frac{\partial \mathbf{F}}{\partial \mathbf{q}} \right\rangle, \quad \text{linear response}. \quad (5.7b)$$

Equations (5.7) show that the exact and linear response values of $\omega_{c_1}^4$ differ by the term in curly brackets in Eq. (5.7a). This term becomes zero if one makes the approximation of breaking the average

$$\left\langle \frac{\partial \mathbf{F}}{\partial \mathbf{r}_0} : \frac{\partial \mathbf{F}}{\partial \mathbf{r}_0} \right\rangle;$$

i.e., if one assumes

$$\left\langle \frac{\partial \mathbf{F}}{\partial \mathbf{r}_0} : \frac{\partial \mathbf{F}}{\partial \mathbf{r}_0} \right\rangle \cong \left\langle \frac{\partial \mathbf{F}}{\partial \mathbf{r}_0} \right\rangle \cdot \left\langle \frac{\partial \mathbf{F}}{\partial \mathbf{r}_0} \right\rangle = \frac{1}{3} \left\langle \frac{\partial}{\partial \mathbf{r}_0} \cdot \mathbf{F} \right\rangle^2.$$

Finally, we note that if the atom-solvent potential energy $U_{vu}(q, \mathbf{r}_0)$ is assumed to be pairwise additive, then $\omega_{e_0}^2$ and $\omega_{c_1}^4$ (in the linear response approximation) may be expressed in terms of the atom-solvent radial distribution function $g(r)$. The results are

$$\omega_{e_0}^2 = \frac{4}{3} \pi m^{-1} \rho \int_0^\infty x^2 g(x) \left[u''(x) + \frac{2}{x} u'(x) \right] dx \quad (5.8)$$

and

$$\omega_{c_1}^4 = \frac{4\pi\rho}{3mM} \int_0^\infty x^2 g(x) \left[\{u''(x)\}^2 + \left\{ \frac{2u'(x)}{x} \right\}^2 \right] dx, \quad (5.9)$$

where $u(r)$ is the atom-solvent potential and ρ is the bulk solvent density.

C. Two solute atoms

Assume two identical solute atoms. Let the coordinates of these atoms be

$$\mathbf{r}_0(t) = \begin{pmatrix} \mathbf{x}_0(t) \\ \mathbf{y}_0(t) \end{pmatrix}. \quad (5.10a)$$

Let the coordinates of the p th fictitious chain atoms be

$$\mathbf{r}_p(t) = \begin{pmatrix} \mathbf{x}_p(t) \\ \mathbf{y}_p(t) \end{pmatrix}. \quad (5.10b)$$

Assume the interatomic separation of the physical atoms is $R \equiv R(t)$. For this case Eq. (5.1) may be written explicitly as

$$\begin{aligned} \ddot{\mathbf{x}}_0(t) = & -m^{-1} \frac{\partial W[R]}{\partial \mathbf{x}_0} - [\omega_{e_0}^2(R)]_{11} \mathbf{x}_0(t) + [\omega_{e_1}^2(R)]_{11} \mathbf{x}_1(t) \\ & - [\omega_{e_0}^2(R)]_{12} \mathbf{y}_0(t) + [\omega_{e_1}^2(R)]_{12} \mathbf{y}_1(t), \\ \ddot{\mathbf{x}}_1(t) = & -[\omega_{e_1}^2(R)]_{11} \mathbf{x}_1(t) + \dots, \text{ etc.} \end{aligned} \quad (5.11a)$$

and

$$\begin{aligned} \ddot{\mathbf{y}}_0(t) = & -m^{-1} \frac{\partial W[R]}{\partial \mathbf{y}_0} - [\omega_{e_0}^2(R)]_{11} \mathbf{y}_0(t) + [\omega_{e_1}^2(R)]_{11} \mathbf{y}_1(t) \\ & - [\omega_{e_0}^2(R)]_{12} \mathbf{x}_0(t) + [\omega_{e_1}^2(R)]_{12} \mathbf{x}_1(t), \\ \ddot{\mathbf{y}}_1(t) = & -[\omega_{e_1}^2(R)]_{11} \mathbf{y}_1(t) + \dots, \text{ etc.} \end{aligned} \quad (5.11b)$$

Notice that the two particle chain equations cannot be "derived" simply by coupling the physical atoms via $W[R]$ and then making the $\omega_{e_0}^2$, etc. R dependent (see Sec. II). This simple picture emerges only as $R \rightarrow \infty$ since in this limit the off-diagonal elements of $\omega_{e_0}^2$, etc., vanish. For small R (common caging) the full vectorial nature of Eq. (5.1) (atom p of chain i coupled to atoms $p-1$ and $p+1$ of all other chains) must be taken into account.

VI. EQUIVALENT HARMONIC CHAIN REPRESENTATION FOR RESPONSE FUNCTIONS

We now present an equivalent harmonic chain representation for the response functions $\dot{\theta}_p(t; r_0)$. This result generalizes an analogous chain representation developed from the formally exact MTGLE theory.¹⁷ This earlier representation permits one to conveniently generate *isolated atom* response functions as numerical chain trajectories. Application of this chain trajectory method to modeling of typical solid and liquid state atom response functions has been presented elsewhere.⁴

The present generalized MTGLE chain representation permits one to analogously generate *interacting atom* response functions as numerical chain trajectories.

The generalized chain representation is developed in Appendix C. The chain equations of motion are

$$\begin{aligned} \ddot{\rho}_1(t) = & -\omega_{e_1}^2(r_0) \rho_1(t) + \omega_{e_2}^2(r_0) \rho_2(t) \\ \ddot{\rho}_2(t) = & -\omega_{e_2}^2(r_0) \rho_2(t) + \omega_{e_3}^2(r_0) \rho_3(t) \\ & \vdots \\ \ddot{\rho}_N(t) = & -\omega_{e_N}^2(r_0) \rho_N(t) + \omega_{e_{N+1}}^2(r_0) \rho_{N+1}(t) \end{aligned}$$

$$+ \int_0^t \omega_{e_{N+1}}^2(r_0) \theta_{N+1}(t - \tau; r_0) \omega_{e_{N+1}}^2(r_0) \rho_N(\tau) d\tau. \quad (6.1)$$

The chain equations (6.1) require three comments.

(i) While the chain representation for solute dynamics, Eq. (5.1), is approximate, Eq. (6.1) is an *exact* consequence of the basic properties of $\dot{\theta}_1(t; r_0)$, Eq. (3.19).

(ii) The "atom" coordinates

$$\rho_p(t) = \begin{pmatrix} \rho_{p1}(t) \\ \rho_{p2}(t) \\ \vdots \\ \rho_{pn}(t) \end{pmatrix}, \quad p = 1, 2, \dots, N \quad (6.2)$$

are defined recursively in Eq. (C5).

(iii) The number of chain "atoms" N may equal 1, 2, 3, Thus (cf. Sec. V), the chain representation, Eq. (6.1), is actually an infinite class of representations.

The elements of the response function matrices $\dot{\theta}_p(t; r_0)$, $p = 1, 2, \dots, N$, may be generated as particular trajectories of chain atom p . The ij th element of $\dot{\theta}_1(t; r_0)$ is the velocity of the i th component of atom 1 given that the j th component of atom 1 has an initial unit velocity but that the remainder of the chain is initially quiescent; i.e.,

$$[\dot{\theta}_1(t; r_0)]_{ij} = \dot{\rho}_{1i}(t), \quad (6.3a)$$

given the initial conditions

$$\begin{aligned} \dot{\rho}_{1k}(0) = & \delta_{kj}, \\ \rho_1(0) = & 0, \\ \rho_p(0) = \dot{\rho}_p(0) = & 0, \quad p \geq 2. \end{aligned} \quad (6.3b)$$

The elements of $\dot{\theta}_2(t; r_0)$ may similarly be determined from trajectories of atom 2 if one sets $\rho_1(t) = 0$; i.e., if atom 1 is clamped at equilibrium [and if the equation of motion for $\rho_1(t)$ is ignored]. We have specifically that

$$[\dot{\theta}_2(t; r_0)]_{ij} = \rho_{2i}(t) \quad (6.4a)$$

given the clamping condition

$$\rho_1(t) = 0 \quad (6.4b)$$

and the initial conditions

$$\begin{aligned} \dot{\rho}_{2k}(0) = & \delta_{kj}, \\ \rho_2(0) = & 0, \\ \rho_p(0) = \dot{\rho}_p(0) = & 0, \quad p \geq 3. \end{aligned} \quad (6.4c)$$

The general response function $\dot{\theta}_q(t; r_0)$ for $q \leq N$ may be similarly generated from trajectories of atom q for which atoms 1, 2, ..., $q-1$ are clamped at equilibrium. Explicitly,

$$[\dot{\theta}_q(t; r_0)]_{ij} = \rho_{qi}(t) \quad (6.5a)$$

given the clamping conditions

$$\rho_1(t) = \rho_2(t) = \dots = \rho_{q-1}(t) = 0 \quad (6.5b)$$

and the initial conditions

$$\begin{aligned}\dot{\rho}_{qk}(0) &= \delta_{kj}, \\ \rho_q(0) &= 0, \\ \rho_p(0) &= \dot{\rho}_p(0) = 0, \quad p \geq q+1.\end{aligned}\quad (6.5c)$$

This concludes our presentation of the chain formalism for response functions.

VII. HEATBATH MODELING

Our basic generalized chain representation for the solute dynamics, Eq. (5.1), becomes a practical equation of motion for computer simulations of reactions in liquids if the memory term is modeled by a Markovian (time local) frictional term. We develop the appropriate modeling techniques in this section. Our method closely parallels our earlier work¹ (cf. Sec. II) performed within the context of the exact MTGLE theory. The basic quantities which we require for the modeling are the adiabatic frequency $\Omega_p(r_0)$ and the friction coefficient $\beta_{p+1}(r_0)$ of the p th heatbath. These quantities ($n \times n$ symmetric matrices) depend on the low frequency response of the solvent.

A. Low frequency parameters

The adiabatic frequencies $\Omega_p(r_0)$, $p=0, 1, 2, \dots$, have been defined earlier [Eqs. (3.13) and (4.24)] as

$$\Omega_0^2(r_0) = m^{-1} \frac{\partial}{\partial r_0} \langle F \rangle_{r_0} \quad (7.1)$$

and

$$\Omega_p^2(r_0) = \hat{\theta}_p(z=0; r_0), \quad p=1, 2, 3, \dots \quad (7.2)$$

We have also derived the following relationship in Appendix B [Eq. (B.5b)]:

$$\omega_{e_0}^2(r_0) - \Omega_0^2(r_0) = \omega_{c_1}^2(r_0) \hat{\theta}_1(z=0; r_0) \omega_{c_1}^2(r_0). \quad (7.3a)$$

Using Eqs. (7.2) and (7.3a) one may derive the additional relationship

$$\Omega_1^2(r_0) = \omega_{c_1}^2(r_0) [\omega_{e_0}^2(r_0) - \Omega_0^2(r_0)]^{-1} \omega_{c_1}^2(r_0). \quad (7.4a)$$

Equations (4.13) and (7.2) further yield

$$\omega_{e_p}^2(r_0) - \Omega_p^2(r_0) = \omega_{c_{p+1}}^2(r_0) \hat{\theta}_{p+1}(z=0; r_0) \omega_{c_{p+1}}^2(r_0), \quad (7.3b)$$

where $p=1, 2, 3, \dots$. Equations (7.2) and (7.3b) then yield the general relation

$$\Omega_p^2(r_0) = \omega_{c_p}^2(r_0) [\omega_{e_{p-1}}^2(r_0) - \Omega_{p-1}^2(r_0)]^{-1} \omega_{c_p}^2(r_0). \quad (7.4b)$$

Equations (7.4) provide a series of recursion relations which permit one to determine $\Omega_p^2(r_0)$, $p=1, 2, 3, \dots$, from $\Omega_0^2(r_0)$ and the MTGLE parameters $\{\omega_{e_p}^2(r_0), \omega_{c_{p+1}}^2(r_0)\}$. These recursion relations permit one to compute $\Omega_p^2(r_0)$ from molecular dynamics data

One may develop a similar set of recursion relations for the friction coefficients $\beta_{p+1}(r_0)$. We begin by defining the friction kernels $\beta_{p+1}(t; r_0)$ by

$$\beta_{p+1}(t; r_0) = \int_0^\infty d\tau \omega_{c_{p+1}}^2(r_0) \theta_{p+1}(\tau; r_0) \omega_{c_{p+1}}^2(r_0). \quad (7.5)$$

The friction kernel $\beta_1(t; r_0)$ is directly calculable from

molecular dynamics data via the relation [Eq. (B7)]

$$\beta_1(t; r_0) = \frac{1}{mk_B T} \langle \tilde{\mathcal{F}}_0(t; r_0) \tilde{\mathcal{F}}^T \rangle_{r_0}. \quad (7.6)$$

The friction coefficients are defined by

$$\begin{aligned}\beta_{p+1}(r_0) &\equiv \hat{\beta}_{p+1}(z=0; r_0) \\ &= -\frac{d}{dz} [\omega_{c_{p+1}}^2(r_0) \hat{\theta}_{p+1}(z; r_0) \omega_{c_{p+1}}^2(r_0)]_{z=0}.\end{aligned}\quad (7.7)$$

Using the above relations it is straightforward to derive the following recursion scheme for the friction coefficients:

$$\beta_{p+1}(r_0) = \Omega_p^2(r_0) \omega_{c_p}^2(r_0) \beta_p(r_0) \omega_{c_p}^2(r_0) \Omega_p^2(r_0). \quad (7.8)$$

Equations (7.6) and (7.8) permit $\beta_{p+1}(r_0)$ to be determined from molecular dynamics simulations of the solvent dynamics for the solute clamped at r_0 .

B. Modeling of response functions

We first illustrate our modeling techniques for response functions. We rewrite the integral kernel term in Eq. (6.1) as

$$\begin{aligned}&\int_0^t \omega_{c_{N+1}}^2(r_0) \theta_{N+1}(t-\tau; r_0) \omega_{c_{N+1}}^2(r_0) \rho_N(\tau) d\tau \\ &= \omega_{e_N}^2(r_0) - \Omega_N^2(r_0) + \int_0^t \beta_{N+1}(t-\tau; r_0) \dot{\rho}_N(\tau) d\tau,\end{aligned}\quad (7.9)$$

where we have used $\rho_N(0)=0$ and Eqs. (7.3) and (7.5). We next make the Markovian approximation

$$\beta_{N+1}(t; r_0) \cong 2\hat{\beta}_{N+1}(z=0; r_0) \delta(t) = 2\beta_{N+1}(r_0) \delta(t). \quad (7.10)$$

Combining Eqs. (6.1), (7.9), and (7.10) yields the following truncated chain representation for the response functions:

$$\begin{aligned}\ddot{\rho}_1(t) &= -\omega_{e_1}^2(r_0) \rho_1(t) + \omega_{c_2}^2(r_0) \rho_2(t) \\ \ddot{\rho}_2(t) &= -\omega_{e_2}^2(r_0) \rho_2(t) + \omega_{c_2}^2(r_0) \rho_1(t) + \omega_{c_3}^2(r_0) \rho_3(t) \\ &\vdots \\ \ddot{\rho}_N(t) &= -\Omega_N^2(r_0) \rho_N(t) \\ &\quad + \omega_{c_N}^2(r_0) \rho_{N-1}(t) - \beta_{N+1}(r_0) \dot{\rho}_N(t).\end{aligned}\quad (7.11)$$

Approximate response functions $\hat{\rho}_q(t; r_0)$ may be generated as trajectories of the Markovian chain equations (7.11) which satisfy the clamping and initial conditions of Eqs. (6.5b) and (6.5c). By examining the convergence of these approximate response functions as N increases, one may check the Markovian truncation. This has already been done within the context of the exact MTGLE theory.⁴ We note that in practice the truncation parameters $\Omega_N^2(r_0)$, $\omega_{c_N}^2(r_0)$, $\beta_{N+1}(r_0)$ may be modified from their values prescribed by the theory to new values $\hat{\Omega}_N^2(r_0)$, $\hat{\omega}_{c_N}^2(r_0)$, and $\hat{\beta}_{N+1}(r_0)$ which speed up the convergence.⁴ This may be done since the chemically important short timescale response is unaffected by the values of the truncation parameters.

C. Markovian representation of solute dynamics

The Markovian truncation of Sec. VII B may also be applied to our generalized chain representation for the solute dynamics, Eq. (5.1). This yields the following Markovian equation of motion for the solute [recall $r_0 \equiv r_0(t)$]:

$$\begin{aligned}\ddot{r}_0(t) &= -m^{-1}\langle F \rangle_{r_0} - \omega_{e_0}^2(r_0)r_0(t) + \omega_{c_1}^2(r_0)r_1(t) \\ \ddot{r}_1(t) &= -\omega_{e_1}^2(r_0)r_1(t) + \omega_{c_1}^2(r_0)r_0(t) + \omega_{c_2}^2(r_0)r_2(t) \\ &\vdots \\ \ddot{r}_N(t) &= -\Omega_N^2(r_0)r_N(t) + \omega_{c_N}^2(r_0)r_{N-1}(t) \\ &\quad - \beta_{N+1}(r_0)\dot{r}_N(t) + f_{N+1}(t; r_0).\end{aligned}\quad (7.12)$$

The stochastic force $f_{N+1}(t; r_0)$ is taken to be a white noise Gaussian source⁵ which satisfies the fluctuation-dissipation theorem

$$\langle f_{N+1}(t; r_0) f_N^T(0; r_0) \rangle = \frac{2k_B T}{m} \beta_{N+1}(r_0) \delta(t). \quad (7.13)$$

Equation (7.12) with (7.13) provides a computationally manageable and physically realistic equation of motion for chemical reactions in liquids. A description of detailed methods for numerical solution of Eq. (7.12), along with prescriptions for selecting the initial conditions $r_p(0)$, $\dot{r}_p(0)$, will be presented in subsequent papers where we apply Eq. (7.12) to the realistic simulation of liquid state reactions.

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APPENDIX A: THE LINEAR RESPONSE TREATMENT

We here develop the linear response³ treatment upon which the results of Secs. III–VII are based. Our notation is that of Sec. III A.

We assume the solute atoms are undergoing *small* displacements $\Delta r_0(t)$ about a configuration point r_0 . Thus, the solute configuration point at time t , $r_0(t)$, is

$$r_0(t) = r_0 + \Delta r_0(t). \quad (A1)$$

The Hamiltonian of the solvent at time t , H_t , is thus

$$H_t = \sum_{\lambda=1}^{N_s} \frac{p_{\lambda}^2}{2M} + U_{vv}(q) + U_{vu}[q, r_0 + \Delta r_0(t)], \quad (A2)$$

where $\dot{p}_{\lambda} = M\dot{q}_{\lambda}$. To linear order in $\Delta r_0(t)$, one may write

$$H_t = H_0 + H_1(t), \quad (A3)$$

where

$$H_0 = \sum_{\lambda=1}^{N_s} \frac{p_{\lambda}^2}{2M} + U_{vv}(q) + U_{vu}(q, r_0) \quad (A4)$$

and

$$H_1(t) = -\mathcal{F}^T \Delta r_0(t). \quad (A5)$$

Note that H_0 is the solvent Hamiltonian when the solute is clamped at r_0 ; $H_1(t)$ is the perturbation Hamiltonian due to displacement of the solute atoms. The Liouville operator form of Eqs. (A3)–(A5) is

$$iL_t = iL_0 + iL_1(t), \quad (A6)$$

where

$$iL_0 = \sum_{\lambda=1}^{N_s} \frac{p_{\lambda}}{M} \cdot \frac{\partial}{\partial q_{\lambda}} - \frac{\partial}{\partial q_{\lambda}} [U_{vv}(q) + U_{vu}(q, r_0)] \cdot \frac{\partial}{\partial p_{\lambda}} \quad (A7)$$

and

$$iL_1(t) = \sum_{\lambda=1}^{N_s} \frac{\partial}{\partial q_{\lambda}} [\mathcal{F}^T \Delta r_0(t)] \cdot \frac{\partial}{\partial p_{\lambda}}. \quad (A8)$$

The solvent phase space distribution function $f[q, r_0; t] \equiv f(t)$ evolves from its initial value $f(r_0)$ according to the Liouville equation

$$\partial f(t)/\partial t = -iL_t f(t). \quad (A9)$$

For small $\Delta r_0(t)$, linear response theory³ yields the following solution of Eq. (A9):

$$f(t) = f_0(t; r_0) - \int_0^t d\tau \exp[-iL_0(t-\tau)] iL_1(\tau) f_0(\tau; r_0), \quad (A10)$$

where

$$f_0(t; r_0) = \exp(-iL_0 t) f_0(r_0). \quad (A11)$$

We next assume $f_0(r_0)$ is the Boltzmann distribution for the solvent coordinates conditional that the solute is clamped at r_0 ; i. e.,

$$f_0(r_0) = z_0^{-1}(r_0) \exp(-H_0/k_B T), \quad (A12)$$

where the partition function $z_0(r_0) = \text{Tr} \exp(-H_0/k_B T)$.

For the above choice of $f(r_0)$, Eq. (A11) shows that $f_0(t; r_0) = f(r_0)$. Thus, Eq. (A10) becomes

$$f(t) = f_0(r_0) - \int_0^t d\tau \exp[-iL_0(t-\tau)] iL_0(\tau) f_0(r_0). \quad (A13)$$

Equations (A4), (A7), (A8), and (A11), however, yield the following result,

$$\begin{aligned}iL_1(t) f_0(r_0) &= -\frac{1}{k_B T} f_0(r_0) iL_0 \mathcal{F}^T \Delta r_0(t) \\ &= -\frac{1}{k_B T} f_0(r_0) \dot{\mathcal{F}}_0^T \Delta r_0(t).\end{aligned}\quad (A14)$$

Combining Eqs. (A13) and (A14) then yields the following final result for $f(t)$:

$$f(t) = f_0(r_0) \left[1 + \frac{1}{k_B T} \int_0^t d\tau \dot{\mathcal{F}}_0^T(\tau - t; r_0) \Delta r_0(\tau) \right]. \quad (A15)$$

Using Eq. (A15), one may readily compute the average solvent density $\langle \rho(\mathbf{r}) \rangle_t = \text{Tr}[f(t)\rho(\mathbf{r})]$ induced by the solute as

$$\begin{aligned}\langle \rho(\mathbf{r}) \rangle_t &= \langle \rho(\mathbf{r}) \rangle_{r_0} \\ &\quad - \frac{1}{k_B T} \int_0^t d\tau \langle \dot{\rho}_0[\mathbf{r}, t-\tau; r_0] \mathcal{F}^T \rangle_{r_0} \Delta r_0(\tau),\end{aligned}\quad (A16)$$

where the instantaneous density $\rho(\mathbf{r})$ is

$$\rho(\mathbf{r}) = \sum_{\lambda=1}^{N_s} \delta(\mathbf{r} - \mathbf{r}_\lambda). \quad (\text{A17})$$

Using the above result for $\langle \rho(\mathbf{r}) \rangle_t$, one may compute the reaction force on the solute and, hence, the solute-solvent contribution to the quantities $\omega_{e_0}^2(r_0)$ and $\omega_{c_1}^2(r_0) \times \dot{\theta}_1(t; r_0)$. This procedure based on nonequilibrium densities provides a graphic picture of the physics underlying our treatment. The calculation, however, is actually more easily (and generally) performed by working directly with $f(t)$.

We write the total instantaneous force on the solute at time t as

$$F(t) \equiv F[q, r_0(t)] = F_0[r_0(t)] + \mathfrak{F}[q, r_0(t)], \quad (\text{A18})$$

where

$$F_0[r_0(t)] = -\frac{\partial}{\partial r_0} U_{uu}[r_0(t)] \quad (\text{A19})$$

is the gas phase solute-solute force.

To linear order in $\Delta r_0(t)$, the average force $\langle F \rangle_t$ is found from Eqs. (A15) and (A18) to be

$$\begin{aligned} \langle F \rangle_t = \langle F \rangle_{r_0} + \left\langle \frac{\partial F^T}{\partial r_0} \right\rangle_{r_0} \Delta r_0(t) \\ - \frac{1}{k_B T} \int_0^t \langle \dot{\mathfrak{F}}_0(t-\tau) \mathfrak{F}^T \rangle_{r_0} \Delta r_0(\tau) d\tau. \end{aligned} \quad (\text{A20})$$

The quantity $\langle F \rangle_{r_0}$ is the usual n -atom mean force determined from the n -atom potential of mean force $W(r_0)$ by

$$\langle F \rangle_{r_0} = -\frac{\partial}{\partial r_0} W(r_0). \quad (\text{A21})$$

The meaning of the other quantities in Eq. (A20) is made clear by considering the case of a single solute atom, coordinate $\mathbf{r}_0(t)$, moving in an isotropic liquid and then comparing the result with that expected from the exact MTGLE, Eq. (2.1). For the single solute atom case, $F(q, r_0) = \mathbf{F}(q, \mathbf{r}_0) = \mathfrak{F}(q)$, $\langle F \rangle_{r_0} = \langle \mathfrak{F} \rangle_{r_0} = 0$, etc. Thus, Eq. (A20) reduces to

$$\begin{aligned} \langle \mathfrak{F} \rangle_t = \frac{1}{3} \left\langle \frac{\partial}{\partial \mathbf{r}_0} \cdot \mathfrak{F} \right\rangle_{r_0} \Delta \mathbf{r}_0(t) \\ - \frac{1}{3k_B T} \int_0^t \langle \dot{\mathfrak{F}}_0(t-\tau) \cdot \mathfrak{F} \rangle_{r_0} \Delta \mathbf{r}_0(\tau) d\tau. \end{aligned} \quad (\text{A22})$$

We next average Eq. (2.1) over solvent density fluctuations and assume $\omega_{c_1}^2 \langle \mathbf{R}_{1x}(t) \rangle_{\text{SOLV}} = 0$. Moreover, we assume the solute atom is making small displacements $\Delta \mathbf{r}_0(t)$ about an equilibrium point $\mathbf{x}_0 = 0$. Thus, we identify $\langle \mathbf{x}_0(t) \rangle_{\text{SOLV}}$ with $\Delta \mathbf{r}_0(t)$ in Eq. (2.1). This identification gives

$$\begin{aligned} m \Delta \ddot{\mathbf{r}}_0(t) = \langle \mathfrak{F} \rangle_t = -m \omega_{e_0}^2 \Delta \mathbf{r}_0(t) \\ + m \omega_{c_1}^4 \int_0^t \theta_1(t-\tau) \Delta \mathbf{r}_0(\tau) d\tau. \end{aligned} \quad (\text{A23})$$

Comparing Eqs. (A22) and (A23) yields the identifications

$$\omega_{e_0}^2 = -\frac{1}{3m} \left\langle \frac{\partial}{\partial \mathbf{r}_0} \cdot \mathfrak{F} \right\rangle_{r_0}, \quad (\text{A24a})$$

$$\omega_{c_1}^4 = \frac{1}{3mk_B T} \langle \dot{\mathfrak{F}}_0 \cdot \mathfrak{F}_0 \rangle_{r_0}, \quad (\text{A24b})$$

$$\omega_{c_1}^2 \mathbf{R}_1(t) = m^{-1} \mathfrak{F}_0(t), \quad (\text{A24c})$$

$$\dot{\theta}_1(t) = \frac{m}{3k_B T} \langle \mathbf{R}_1(t) \cdot \mathbf{R}_1(0) \rangle. \quad (\text{A24d})$$

The results in Eqs. (A24b)–(A24d) are *not* exact. This is because the MTGLE, Eq. (2.1), rigorously describes heatbath forces on an atom undergoing random motion but not on an atom executing a prescribed trajectory.

Equations (A24) along with the discussion in Sec. II (also see Fig. 1) lead us immediately to results for $\omega_{e_0}^2(r_0)$, etc., for the n -solute atom case. The natural generalizations of Eqs. (A24) are the equalities given in Eqs. (3.9)–(3.12). Using these results Eq. (A20) may be written as

$$\begin{aligned} \langle F \rangle_t = \langle F \rangle_{r_0} - m \omega_{e_0}^2(r_0) \Delta r_0(t) \\ + m \int_0^t \omega_{c_1}^2(r_0) \theta_1(t-\tau; r_0) \omega_{c_1}^2(r_0) \Delta r_0(\tau) d\tau. \end{aligned} \quad (\text{A25})$$

The total force on the solute $F(t)$ is the average force $\langle F \rangle_t$ plus the random force $\dot{\mathfrak{F}}_0(t; r_0) = m \omega_{c_1}^2(r_0) \mathbf{R}_0(t; r_0)$. Thus,

$$\begin{aligned} F(t) = \langle F \rangle_{r_0} - m \omega_{e_0}^2(r_0) \Delta r_0(t) + m \int_0^t \omega_{c_1}^2(r_0) \theta_1(t-\tau; r_0) \\ \times \omega_{c_1}^2(r_0) \Delta r_0(\tau) d\tau + m \omega_{c_1}^2(r_0) \mathbf{R}_1(t; r_0). \end{aligned} \quad (\text{A26})$$

We next develop a rigorous equivalent harmonic chain representation of the force $F(t)$ acting on the solute. Defining the fictitious coordinate $\Delta r_1(t)$ by

$$\Delta r_1(t) = \mathbf{R}_1(t; r_0) + \int_0^t d\tau \theta_1(t-\tau; r_0) \omega_{c_1}^2(r_0) \Delta r_0(\tau), \quad (\text{A27})$$

Equation (A26) becomes

$$F(t) = \langle F \rangle_{r_0} - m \omega_{e_0}^2(r_0) \Delta r_0(t) + m \omega_{c_1}^2(r_0) \Delta r_1(t). \quad (\text{A28a})$$

Using the results of Sec. IV one may show $\Delta r_1(t)$ satisfies the following equation of motion:

$$\begin{aligned} \Delta \ddot{r}_1(t) = -\omega_{e_1}^2(r_0) \Delta r_1(t) + \omega_{c_1}^2(r_0) \Delta r_0(t) \\ + \int_0^t d\tau \omega_{c_2}^2(r_0) \theta_2(t-\tau; r_0) \omega_{c_2}^2(r_0) \Delta r_1(\tau) \\ + \omega_{c_2}^2(r_0) \mathbf{R}_2(t; r_0). \end{aligned} \quad (\text{A28b})$$

Equations (A28) constitute the $(N+1)$ -atom chain representation for the case $N=1$. The general representation is found by continuing the above procedure. It is

$$\begin{aligned} F(t) = \langle F \rangle_{r_0} - m \omega_{e_0}^2(r_0) \Delta r_0(t) + m \omega_{c_1}^2(r_0) \Delta r_1(t) \\ \Delta \ddot{r}_1(t) = -\omega_{e_1}^2(r_0) \Delta r_1(t) + \omega_{c_1}^2(r_0) \Delta r_0(t) + \omega_{c_2}^2(r_0) \Delta r_2(t) \\ \vdots \\ \Delta \ddot{r}_N(t) = -\omega_{e_N}^2(r_0) \Delta r_N(t) + \omega_{c_N}^2(r_0) \Delta r_{N-1}(t) \\ + \int_0^t d\tau \omega_{c_{N+1}}^2(r_0) \theta_{N+1}(t-\tau; r_0) \omega_{c_{N+1}}^2(r_0) \Delta r_N(\tau) + \end{aligned}$$

$$+ \omega_{c_{N+1}}^2(r_0) R_{N+1}(t; r_0). \quad (\text{A29})$$

The fictitious coordinates $\Delta r_p(t)$ are defined recursively in terms of $\Delta r_0(t)$ by

$$\Delta r_p(t) = R_p(t; r_0) + \int_0^t d\tau \theta_p(t - \tau; r_0) \omega_{c_p}^2(r_0) \Delta r_{p-1}(\tau). \quad (\text{A30})$$

For the case of a single solute atom, one may take the following identifications in Eq. (A29): $\mathbf{F}(t) = \mathbf{F}(t) \rightarrow m\ddot{\mathbf{r}}_0(t)$, $\Delta \mathbf{r}_p(t) = \mathbf{r}_p(t)$. This identification [which is essentially the inverse of the procedure used to obtain Eq. (A23)] yields the single solute atom chain equations quoted in Eq. (5.3). These chain equations are exactly equivalent to utilizing the linear response approximation for $\omega_{c_1}^4 \theta_1(t)$ [Eqs. (A24)] in the exact MTGLE, Eq. (2.1).

We next make the analogous identification for the general n -solute atom case. That is we replace $\mathbf{F}(t) \rightarrow m\ddot{\mathbf{r}}_0(t)$, $\Delta \mathbf{r}_p(t) = \mathbf{r}_p(t)$. This procedure yields the chain equations quoted in Eqs. (5.1). These generalized chain equations involve a second approximation in addition to the linear response approximation. The chain parameters must not change drastically on timescales comparable to the velocity relaxation time of the solvent.

APPENDIX B: THE ADIABATIC FREQUENCY MATRIX $\Omega(r_0)$

We here derive the result for the adiabatic frequency matrix $\Omega(r_0)$ quoted in Eq. (3.13). We begin with Eq. (A25) specialized to the case of a constant displacement $\Delta r_0(t) = \Delta r_0$. For this case

$$\langle F \rangle_t = \langle F \rangle_{r_0} - m\omega_{e_0}^2(r_0) \Delta r_0 + m \left[\int_0^t \omega_{c_1}^2(r_0) \theta_1(\tau; r_0) \omega_{c_1}^2(r_0) d\tau \right] \Delta r_0. \quad (\text{B1})$$

The initial tension due to a displacement $\langle F \rangle_{t=0} - \langle F \rangle_{r_0}$ is according to Eq. (B1)

$$\langle F \rangle_{t=0} - \langle F \rangle_{r_0} = -m\omega_{e_0}^2(r_0) \Delta r_0. \quad (\text{B2})$$

Notice the result of Eq. (B2) is in accord with the discussion of Sec. II and also Fig. 1.

According to our discussion in Sec. II, the fully relaxed tension $\langle F \rangle_{t=\infty} - \langle F \rangle_{r_0}$ should be related to the adiabatic frequency by

$$\langle F \rangle_{t=\infty} - \langle F \rangle_{r_0} = -m\Omega_0^2(r_0) \Delta r_0. \quad (\text{B3})$$

Equation (B3) may be taken as the definition of $\Omega_0(r_0)$. For a constant displacement Δr_0 , however,

$$\langle F \rangle_{t=\infty} = \langle F \rangle_{r_0 + \Delta r_0}. \quad (\text{B4})$$

Combining Eqs. (B3) and (B4) and taking the limit $\Delta r_0 \rightarrow 0$ yields Eq. (3.13).

An additional important result may be derived by comparing Eqs. (B1) and (B3). This is

$$\omega_{e_0}^2(r_0) - \Omega_0^2(r_0) = \omega_{c_1}^2(r_0) \left[\int_0^\infty \theta_1(\tau; r_0) d\tau \right] \omega_{c_1}^2(r_0). \quad (\text{B5a})$$

Equation (B5a) may be written in several useful alternative forms. These are

$$\omega_{e_0}^2(r_0) - \Omega_0^2(r_0) = \omega_{c_1}^2(r_0) \hat{\theta}_1(z=0; r_0) \omega_{c_1}^2(r_0) \quad (\text{B5b})$$

and

$$\omega_{e_0}^2(r_0) - \Omega_0^2(r_0) = \beta_1(0; r_0) = \frac{1}{mk_B T} \langle \tilde{\mathbf{F}} \tilde{\mathbf{F}}^T \rangle_{r_0}. \quad (\text{B5c})$$

The friction kernel $\beta_1(t; r_0)$ is defined by

$$\beta_1(t; r_0) = \int_t^\infty \omega_{c_1}^2(r_0) \theta_1(\tau; r_0) \omega_{c_1}^2(r_0) d\tau. \quad (\text{B6})$$

Using Eqs. (3.11), (3.12), and (B6) the friction kernel may be written as

$$\beta_1(t; r_0) = \frac{1}{mk_B T} \langle \tilde{\mathbf{F}}_0(t; r_0) \tilde{\mathbf{F}}^T \rangle_{r_0}. \quad (\text{B7})$$

Finally, Eq. (B7) implies the inequality quoted in Eq. (3.14).

APPENDIX C: THE CHAIN REPRESENTATION FOR RESPONSE FUNCTIONS

We now derive the chain representation for response functions Eq. (6.1). We define the n -component "atomic" coordinate $\rho_1(t)$ [cf. Eq. (6.2)] in terms of its initial value ρ_1 and the initial value of its time derivative by

$$\rho_1(t) = \dot{\theta}_1(t; r_0) \rho_1 + \theta_1(t; r_0) \dot{\rho}_1. \quad (\text{C1})$$

Comparing Eqs. (C1) and (4.5), one may show that $\rho_1(t)$ satisfies the following equation of motion:

$$\ddot{\rho}_1(t) = -\omega_{e_1}^2(r_0) \rho_1(t) + \int_0^t d\tau \omega_{c_2}^2(r_0) \theta_2(t - \tau; r_0) \omega_{c_2}^2(r_0) \rho_1(\tau). \quad (\text{C2})$$

We now define a second atomic coordinate $\rho_2(t)$ by

$$\rho_2(t) = \int_0^t d\tau \theta_2(t - \tau; r_0) \omega_{c_2}^2(r_0) \rho_1(\tau) d\tau. \quad (\text{C3})$$

Using Eq. (C3) we rewrite Eq. (C2) as

$$\ddot{\rho}_1(t) = -\omega_{e_1}^2(r_0) \rho_1(t) + \omega_{c_2}^2(r_0) \rho_2(t). \quad (\text{C4a})$$

From Eq. (C3) and Eq. (4.12) (specialized to the case $p=2$) one may readily show that $\rho_2(t)$ satisfies the effective equation of motion

$$\ddot{\rho}_2(t) = -\omega_{e_2}^2(r_0) \rho_2(t) + \omega_{c_3}^2(r_0) \rho_1(t) - \int_0^t \omega_{c_3}^2(r_0) \theta_3(t - \tau; r_0) \omega_{c_3}^2(r_0) \rho_2(\tau) d\tau. \quad (\text{C4b})$$

Equations (C4) constitute the chain equations for the case $N=2$. One may verify using Eqs. (C1) and (C3) that the chain trajectories which satisfy the initial conditions of Eq. (6.3b) yield $\dot{\theta}_1(t; r_0)$ according to Eq. (6.3a). The general chain representation, Eq. (6.1), may be derived by continuing the above procedure. The p th atomic coordinate is defined recursively in terms of $\rho_1(t)$ by [cf. Eq. (6.3)]

$$\rho_p(t) = \int_0^t d\tau \theta_p(t - \tau; r_0) \omega_{c_p}^2(r_0) \rho_{p-1}(\tau) d\tau. \quad (\text{C5})$$

APPENDIX D: FLUCTUATION-DISSIPATION THEOREMS

We here clarify certain aspects of the fluctuation-dissipation theorems which arise in the formally exact MTGLE theory. We begin by integrating Eq. (2.2) with respect to time to yield $[\mathbf{R}_{1x} - \mathbf{R}_1]$,

$$\theta_1(t) = \frac{m}{3k_B T} \langle \mathbf{R}_1(t) \cdot \dot{\mathbf{R}}_1(0) \rangle. \quad (\text{D1})$$

The precise meaning of the thermal average $\langle \dots \rangle$ was not made clear in Ref. 1. This average in Eq. (D1) may be correctly interpreted as *either*:

(i) an average over the initial coordinates and momenta of *all* equivalent chain atoms including the physical atom O. We denote this average by $\langle \dots \rangle$.

(ii) an average over coordinates and momenta of the *only* the heatbath atoms 1, 2, 3, ... in the equivalent chain with atom O clamped at equilibrium; i.e., $\mathbf{r}_0(t) = 0$. We denote this average by $\langle \dots \rangle_{\mathbf{r}_0}$.

Now suppose we wish to "exchange dots" in Eq. (D1) using the familiar relation

$$\langle A(t)\dot{B}(0) \rangle = -\langle \dot{A}(t)B(0) \rangle. \quad (\text{D2})$$

We may do this only if we use interpretation (ii). That is,

$$\theta_1(t) = \frac{m}{3k_B T} \langle \dot{\mathbf{R}}_1(t) \cdot \mathbf{R}_1(0) \rangle_{\mathbf{r}_0} \quad (\text{D3})$$

is a correct relationship; however,

$$\theta_1(t) \neq -\frac{m}{3k_B T} \langle \dot{\mathbf{R}}_1(t) \cdot \mathbf{R}_1(0) \rangle.$$

This is because

(i) the propagation of $\mathbf{R}_1(t)$ is governed by clamped atom dynamics, $\mathbf{r}_0(t) = 0$, in the equivalent chain representation (see Sec. II);

(ii) Eq. (D2) is guaranteed to be correct only if the *same* Hamiltonian governs statistics and dynamics.

Thus, all results which follow from Eq. (D3) must be interpreted as involving clamped thermal averages $\langle \dots \rangle_{\mathbf{r}_0}$.

Similar considerations hold for the general, $(p+1)$ th, MTGLE fluctuation-dissipation theorem. The analog of Eq. (D3) for this case is

$$\theta_p(t) = -\frac{m}{3k_B T} \langle \dot{\mathbf{R}}_1(t) \cdot \mathbf{R}_1(0) \rangle_{\mathbf{r}_0, \mathbf{r}_1, \dots, \mathbf{r}_{p-1}}. \quad (\text{D4})$$

Note $\langle \dots \rangle_{\mathbf{r}_0, \dots, \mathbf{r}_{p-1}}$ denotes a thermal average in the equivalent chain subject to the clamping conditions $\mathbf{r}_0(t) = \mathbf{r}_1(t) = \dots = \mathbf{r}_{p-1}(t) = 0$.

These considerations require a revision of Eqs. (3.28b) and (3.29) of Ref. 1(a) to read

$$\frac{1}{2} m \Omega_p^2 \langle R_p^2(0) \rangle_{\mathbf{r}_0, \mathbf{r}_1, \dots, \mathbf{r}_{p-1}} = \frac{3}{2} k_B T, \quad (\text{D5})$$

$$\langle \mathbf{f}_p(t) \cdot \mathbf{f}_p(0) \rangle_{\mathbf{r}_0, \mathbf{r}_1, \dots, \mathbf{r}_{p-1}} = \frac{3k_B T}{m} \beta_p(t), \quad (\text{D6})$$

where

$$\mathbf{f}_p(t) = \omega_{c_{p+1}}^2 \mathbf{R}_p(t). \quad (\text{D7})$$

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²The MTGLE theory first emerged as a generalization of methods developed for inelastic and reactive gas-solid collisions. See S. A. Adelman and J. D. Doll, J. Chem. Phys. **61**, 4242 (1974); **64**, 2374 (1976). S. A. Adelman and B. J. Garrison, J. Chem. Phys. **65**, 3751 (1976); J. D. Doll and D. R. Dion, J. Chem. Phys. **65**, 3762 (1976). S. A. Adelman and J. D. Doll, Acc. Chem. Res. **10**, 378 (1977). Also see M. Shugard, J. C. Tully, and A. Nitzan, J. Chem. Phys. **68**, 2354 (1977). A. C. Diebold, S. A. Adelman, and C. Y. Mou, J. Chem. Phys. **71**, 3236 (1979). The departure point for this work was an important early paper by R. Zwanzig, J. Chem. Phys. **32**, 1173 (1960).

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⁵See, for example, G. E. Uhlenbeck and L. S. Ornstein, Phys. Rev. **36**, 323 (1930); M. C. Wang and G. E. Uhlenbeck, Rev. Mod. Phys. **17**, 323 (1945); S. Chandrasekhar, Rev. Mod. Phys. **15**, 1 (1943); for a recent review, see R. F. Fox, Phys. Rev. C **48**, 179 (1978).

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⁷For first trajectory simulations based on the MTGLE theory, see C. L. Brooks III, M. Berkowitz, and S. A. Adelman, J. Chem. Phys. (to be published).

⁸H. Mori, Prog. Theor. Phys. **33**, 423 (1965); **34**, 399 (1965).

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¹⁰The proof parallels that of Eq. (2.36) of Ref. 1(a).

¹¹Here and below we indicate the Laplace transform of an arbitrary function $f(t)$ by $\hat{f}(z)$; i.e.,

$$\hat{f}(z) \equiv \int_0^\infty e^{-zt} f(t) dt.$$

¹²The development parallels that of Sec. V. C of Ref. 1(a).

¹³Compare Eq. (3.15) of Ref. 1(a).

¹⁴See Appendix A of Ref. 1(a).

¹⁵The average $\langle \rangle_{\mathbf{r}_0, \mathbf{r}_1, \dots, \mathbf{r}_{p-1}}$ refers to clamping of (vectorial) atoms 0, 1, ..., $p-1$, in the equivalent chain representation Eq. (5.1). Compare Eq. (D.4) of Appendix D.

¹⁶These results may be readily derived from Eqs. (2.1), (2.16), (2.12), and (2.32) of Ref. 1(a).

¹⁷See Eq. (2.11) of Ref. 4.