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# Theory of vibrational energy relaxation in liquids: Construction of the generalized Langevin equation for solute vibrational dynamics in monatomic solvents

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Algorithms which permit the explicit, albeit approximate, construction of a physically realistic generalized Langevin equation of motion for the energy relaxation dynamics of a specified solute normal mode coordinate  $y$  in a monatomic solvent are developed. These algorithms permit the construction, from equilibrium solute-solvent pair correlation functions, of the liquid state frequency  $\omega_l$  of the normal mode and of the Gaussian model approximation to the autocorrelation function  $\langle \tilde{\mathcal{F}}(t) \tilde{\mathcal{F}} \rangle_0$  of the fluctuating generalized force exerted by the solvent on the normal mode. From these quantities one may compute, from equilibrium solute-solvent pair correlation functions, the vibrational energy relaxation time  $T_1$  of the solute normal mode and also related quantities which permit one to assess the relative importance of direct [ $y$  coordinate  $\rightarrow$  solvent] and indirect [ $y$  coordinate  $\rightarrow$  solute translation-rotational coordinates  $\rightarrow$  solvent] energy flow pathways in solute vibrational energy relaxation. The basis of the construction of  $T_1$  is the formula  $T_1 = \beta^{-1}(\omega_l)$  where  $\beta(\omega) = \int_0^\infty \beta(t) \cos \omega t dt$  and where  $\beta(t) = [k_B T]^{-1} \langle \tilde{\mathcal{F}}(t) \tilde{\mathcal{F}} \rangle_0$  is the friction kernel of the solute normal mode. This formula is valid if  $T_1 \gg T_2 =$  vibrational phase relaxation time. The approximate formulas for  $T_1$  are worked out in detail for diatomic solutes. The approximations are tested for this diatomic solute case by comparing with molecular dynamics results.

## I. INTRODUCTION

This paper is the first in a series in which we will develop a new theoretical treatment of vibrational energy relaxation (VER)<sup>1</sup> in dense fluid solvents. This treatment of VER is based on our general approach<sup>2</sup> to the dynamics of chemical processes occurring in liquid solution.

We deal in this paper (paper I) with a theoretical treatment of the simplest problem, namely the VER of a single harmonic normal mode of a solute molecule immersed at infinite dilution in a *monatomic* solvent. The following paper (paper II)<sup>3</sup> presents numerical applications of the theoretical results derived here to the prototype case of diatomic solutes in monatomic solvents. The applications of paper II permit one to illustrate, in the context of a prototype problem, some of the basic physics which governs the rates and mechanisms of condensed phase energy transfer processes. The applications also permit a test of the theory against experimental<sup>4</sup> and computer simulation<sup>5,6</sup> results.

The main results of this paper are approximate analytic expressions which permit computation of solute normal mode VER rates in monatomic solvents. These expressions permit one to compute both the absolute magnitude of the VER time<sup>1</sup>  $T_1$  and also to estimate the relative contributions of direct [solute vibrational coordinate  $\leftrightarrow$  solvent] and indirect [solute vibrational coordinate  $\leftrightarrow$  solute translational-rotational coordinates  $\leftrightarrow$  solvent] energy flow pathways<sup>1</sup> to  $T_1$ .

These analytic expressions may be evaluated for specific systems from the pair potential energy functions  $u_i(r)$  and pair correlation (radial distribution) functions  $g_i(r)$  linking solute atom  $i = 1, 2, \dots$  and a solvent atom. Since the pair correlation functions  $g_i(r)$  may be readily computed, e.g., as

solutions to the Percus-Yevick integral equation,<sup>7,8</sup> the expressions for solute VER developed here may be conveniently evaluated for specific solute-monatomic solvent systems. This is done for the diatomic solute case in paper II.

The analytic expressions just discussed are based on a formula for the VER time  $T_1$ , given in Eq. (1.1) below, which was first obtained by Metiu and co-workers<sup>9</sup> in the context of a hydrodynamic treatment of VER in liquids. Our derivation of Eq. (1.1) is based on a stochastic solution<sup>10</sup> of the linearized form of a physically realistic generalized Langevin equation of motion, Eq. (2.1), derived elsewhere<sup>11</sup> which governs the dynamics of the specified solute normal mode.

The result for  $T_1$  is ( $k_B T =$  Boltzmann's constant times Kelvin temperature)

$$T_1 = \frac{2k_B T}{\pi \rho_{\mathcal{F}}(\omega_l)}. \quad (1.1a)$$

In Eq. (1.1a),  $\omega_l$  is the "rigid cage" liquid state frequency of the solute normal mode defined in Eq. (2.6), and  $\rho_{\mathcal{F}}(\omega)$  is the frequency spectrum of the autocorrelation function  $\langle \tilde{\mathcal{F}}(t) \tilde{\mathcal{F}} \rangle_0$  of the fluctuating generalized force  $\tilde{\mathcal{F}}_0(t)$  exerted by the solvent on the solute normal mode coordinate  $y$ . Explicitly  $\rho_{\mathcal{F}}(\omega)$  is given by

$$\rho_{\mathcal{F}}(\omega) = \frac{2}{\pi} \int_0^\infty \langle \tilde{\mathcal{F}}(t) \tilde{\mathcal{F}}(0) \rangle_0 \cos \omega t dt. \quad (1.2)$$

The derivation of Eq. (1.1a), discussed in more detail in Sec. II, requires that the VER time  $T_1$  of the solute normal mode be much greater than either its phase relaxation time<sup>1(c)</sup>  $T_2$  or its period  $\tau_v = 2\pi\omega_l^{-1}$ . From the practical standpoint Eq. (1.1a) is valid if  $T_1 \gg T_2$ .

Equation (1.1a) may be recast into an even simpler form, Eq. (1.1b) below. To do this, we define the friction kernel  $\beta(t)$  in the standard manner (second fluctuation-dissipation theorem<sup>2</sup>) as

$$\beta(t) = [k_B T]^{-1} \langle \mathcal{F}(t) \mathcal{F} \rangle_0. \quad (1.3)$$

The frequency-dependent friction coefficient of the normal mode  $\beta(\omega)$  is then defined by

$$\beta(\omega) = \int_0^\infty \beta(t) \cos \omega t \, dt. \quad (1.4)$$

Comparing Eqs. (1.1)–(1.4) yields the following alternative form for  $T_1$ :

$$T_1 = \beta^{-1}(\omega_l) \quad (1.1b)$$

which has a transparent physical meaning.

Most of the remainder of this paper is concerned with a theoretical analysis which provides a bridge between the formal result for  $T_1$  given in Eq. (1.1) and the practical expressions, mentioned above, which permit its numerical evaluation for specific solute–monatomic solvent systems. This theoretical analysis is based on mathematical methods<sup>2(a),11,12</sup> which may be applied to a broad class of liquid state chemical phenomena. (For related work of others see Refs. 13 and 14.) Thus the analysis presented below may be regarded as a paradigm which illustrates techniques for choosing molecular friction which are of considerable generality. For this reason, it is presented in some detail.

Specifically, the main concern of the present paper is the development of approximate algorithms which permit the explicit construction of the linearized equation of motion, Eq. (2.5), for solute normal mode dynamics. Since, as mentioned, Eq. (1.1) may be developed<sup>10</sup> from this equation of motion, the algorithms immediately yield the practical expressions for  $T_1$  and for its energy flow pathway dependence. The algorithms developed here, in particular, give convenient approximate expressions for the vibrational frequency  $\omega_l$  and for the autocorrelation function  $\langle \mathcal{F}(t) \mathcal{F} \rangle_0$ . These expressions then permit computation of  $T_1$  from Eqs. (1.1)–(1.4).

The plan of this paper is as follows. The basic concepts underlying the present approach are summarized in Sec. II. The results used in paper II, namely the analytical expressions for  $T_1$  and its energy flow pathway dependence specialized to the diatomic solute case are, for convenience, given in Sec. III. These expressions are actually derived later in the paper.

The approximate algorithms are based on a harmonic-oscillator rigid top model for solute dynamics, which is developed in Secs. IV and V. Using this model, a construction of  $\omega_l$  and of  $\langle \mathcal{F}(t) \mathcal{F} \rangle_0$ , within the Gaussian approximation, is made in Secs. VI–VIII and Appendix A. The diatomic results of Sec. III may be developed from this construction using additional results given in Appendices B and C. Finally the approximate algorithms are tested for the diatomic solute case against “exact” molecular dynamics results in Sec. IX. We close the paper in Sec. X with a brief summary and discussion.

## II. BASIC CONCEPTS

This section contains a summary of the physical concepts<sup>2(a),2(c)</sup> and mathematical procedures<sup>2(a),11</sup> upon which the present treatment of solute vibrational energy relaxation (VER) of a specified solute normal mode in monatomic solvents is based.

We first discuss the separation in time scales which exists between the solute and solvent motions which occur during liquid state chemical events. This time scale separation, and the closely related idea of weak solvent response<sup>2(c)</sup> to the solute motions, provides the physical basis of our approach to solute VER. We next introduce the equation of motion, Eq. (2.1), which governs the liquid state dynamics of the solute normal mode. This equation of motion provides the mathematical basis of the present treatment of VER in liquids. We then outline an approximate solution of Eq. (2.1) based on the physics of weak solvent response. This solution yields Eq. (2.10) for the velocity autocorrelation function of the normal mode which, in turn, implies Eq. (1.1) for its VER time  $T_1$ . We close this section with the development of a Gaussian model for  $T_1$ . This model provides the basis for the practical expressions for  $T_1$  and its energy flow pathway dependence discussed in the Introduction.

### A. The solute–solvent time scale separation

The solute–solvent time scale separation is the underlying physical factor which determines the qualitative character of the solvent effect on the solute motions which occur during liquid state chemical reactions. The basic idea is that liquid state chemical events are typically<sup>15</sup> characterized by a time scale separation of the type: fast or high frequency solute/slow or low frequency solvent. This time scale separation is *exactly opposite* in type to the time scale separation (slow “primary” variables/fast heatbath) which has been the traditional concern of the theory of irreversible processes.<sup>16–18</sup>

The time scale separation is a consequence of the fact that the solute motions which are important in chemical kinetics are very often highly accelerated and characterized by either of two criteria.

(i) Solute speeds which are fast compared to mean thermal solvent speeds. This occurs, for example, in typical “thermal” organic reactions which involve activation barriers in the 25–35 kcal/mol range.<sup>19</sup>

(ii) Solute vibrational frequencies which are sufficiently high that they have only weak resonance overlap with the translational–rotational branches<sup>12</sup> of the solvent frequency spectrum  $\rho_{\mathcal{F}}(\omega)$  in Eq. (1.2). [The precise criterion for weak resonance overlap is given in Eq. (2.11).]

A consequence of the time scale separation is the weak solvent response to the solute motions. That is, if the time scale separation holds the local solvent density field surrounding the solute atoms cannot even approximately adiabatically readjust in response to the motion of these atoms. Rather the response to the solute motions important in chemical kinetics is *weak* relative to its response to the more familiar<sup>20</sup> thermal solute motions. (More precisely stated,

the actual solvent response is weak relative to the hypothetical response which would result if the solute motions could be executed along the *same paths* but at thermal velocities or translational-rotational frequencies.)

Weak solvent response influences every aspect of the solute motions which occur in liquid state chemical events. As discussed in detail in Ref. 2(c), it is, in fact, the underlying factor which gives these motions their unique qualitative character.

Weak solvent response, for example, implies a special type of solute force law. Specifically, on the kinetically significant time scales, the (ensemble averaged) solute force may be written as a superposition of a conservative force characteristic of a nonresponding ("rigid cage") solvent and a relatively weak dissipative force arising from the weak solvent response. This unique type of force law leads to a special type of solute dynamics which can differ qualitatively<sup>2(c)</sup> from either the dynamics which is characteristic of gas-phase chemical processes or from thermal<sup>20</sup> solute dynamics. (An example is provided by the barrier recrossing effect<sup>2(b)</sup> recently observed in the molecular dynamics simulation of Bergsma *et al.*<sup>21</sup> of a model  $SN_2$  reaction.)

These points are illustrated for the special case of solute VER in Sec. II D.

We next discuss a realistic equation of motion for the solute normal mode coordinate  $y$  which brings out the physics of weak solvent response.

## B. The equation of motion

A generalized Langevin equation of motion governing the dynamics of a small set of chemically relevant "explicit" generalized coordinates of a solute system moving in a molecular solvent has been developed elsewhere.<sup>11(b)</sup> This equation of motion realistically accounts for the coupled influence of the solvent and the remaining "implicit" solute generalized coordinates on the explicit coordinates.

Specializing this equation of motion to the present case of a single explicit solute coordinate  $y$ , which is a harmonic normal mode,<sup>22</sup> and a monatomic solvent yields [ $\beta \equiv (k_B T)^{-1}$ ]

$$\ddot{y}(t) = \langle F \rangle_{0(t)} + \left\langle \frac{\partial \mathcal{F}}{\partial y} \right\rangle_0 y(t) + \beta \int_0^t \langle \tilde{\mathcal{F}}(t-\tau) \tilde{\mathcal{F}} \rangle_0 y(\tau) d\tau + \tilde{\mathcal{F}}_{0(t)}(t). \quad (2.1a)$$

The precise molecular definitions of all quantities appearing in Eq. (2.1a) will be developed later in the paper. For now we will restrict ourselves to the following points.

(i) All quantities appearing in Eq. (2.1a) are defined in accord with the prescriptions of the "partial clamping" model introduced elsewhere.<sup>11(a)</sup> Specifically, when constructing Eq. (2.1a), the solute normal mode coordinate  $y$  is to be *fixed* while the remaining degrees of freedom of the liquid solution, both solute and solvent, are allowed to move freely subject to this one constraint. Thus, for example, all solute-solvent forces appearing in Eq. (2.1a) may be constructed from the generalized force  $\mathcal{F}_0(t)$ . This is the force exerted by the solvent on the normal mode coordinate  $y$  given

en this coordinate is fixed at equilibrium while the solute molecule translates, rotates, and vibrates through the fluid subject only to this single constraint. As a second example, the symbol  $\langle \cdots \rangle_0$  denotes a canonical ensemble average over the solvent and implicit solute coordinates subject to the same constraint on the coordinate  $y$ .

The partial clamping model is based on two principle approximations<sup>11(b)</sup> which may be summarized as follows.

(a) The physical motion of the normal mode coordinate  $y$  is assumed to be sufficiently small amplitude that the solvent response to this motion may be treated to linear order in  $y$ . This linear response approximation, which is consistent with our assumption of a harmonic normal mode, determines the form of the systematic force appearing in Eq. (2.1a).

(b) The contribution to the temporal fluctuations of the local solvent density from its equilibrium value *induced* by the vibrations of the normal mode coordinate  $y$  is assumed to be negligible. This assumption, which determines the form of the fluctuating forces appearing in Eq. (2.1a), is realistic if the temporal density fluctuations are inherently small as is expected to be true at liquid state densities. Then, because the amplitude of the normal mode vibrational motions are small and because additionally, the solvent response to these motions is weak the neglected induced fluctuations are of the third order of smallness.

(ii) The fluctuating generalized force  $\tilde{\mathcal{F}}_{0(t)}(t)$  is defined as follows:

$$\tilde{\mathcal{F}}_{0(t)}(t) = \tilde{\mathcal{F}}_0(t) + \left[ \frac{\partial \tilde{\mathcal{F}}_0(t)}{\partial y} \right] y(t). \quad (2.2)$$

The fluctuating force component  $\tilde{\mathcal{F}}_0(t)$  mediates normal mode-solvent energy exchange processes while the component  $[\partial \tilde{\mathcal{F}}_0(t)/\partial y]$  mediates the corresponding phase randomization processes. These components are defined by

$$\tilde{\mathcal{F}}_0(t) = \mathcal{F}_0(t) - \langle \mathcal{F} \rangle_0 \quad (2.3)$$

and

$$\left[ \frac{\partial \tilde{\mathcal{F}}_0(t)}{\partial y} \right] = \left[ \frac{\partial \mathcal{F}_0(t)}{\partial y} \right] - \left\langle \frac{\partial \mathcal{F}}{\partial y} \right\rangle_0, \quad (2.4)$$

where  $\langle \mathcal{F} \rangle_0$  is the liquid state contribution to the mean force and where  $\langle \partial \mathcal{F} / \partial y \rangle_0$  governs the strength of the instantaneous cage restoring force to be discussed below. The prescriptions of the partial clamping model guarantee that  $\tilde{\mathcal{F}}_{0(t)}(t)$  properly mediates processes of both the direct (see the Introduction) and indirect type.

We will, henceforth, assume that the vibrational energy relaxation time  $T_1$  of the solute normal mode is much larger than its phase relaxation time  $T_2$ . We may then drop the phase randomization component of  $\tilde{\mathcal{F}}_{0(t)}(t)$  and set  $\tilde{\mathcal{F}}_{0(t)}(t) = \tilde{\mathcal{F}}_0(t)$ . Equation (2.1a) then reduces to the following form:

$$\ddot{y}(t) = \langle F \rangle_{0(t)} + \left\langle \frac{\partial \mathcal{F}}{\partial y} \right\rangle_0 y(t) + \beta \int_0^t \langle \tilde{\mathcal{F}}(t-\tau) \tilde{\mathcal{F}} \rangle_0 y(\tau) d\tau + \tilde{\mathcal{F}}_0(t). \quad (2.1b)$$

Equation (2.1b) is the basis of the work in the remainder of this paper.

(iii) The mean generalized force  $\langle F \rangle_0$  acting on the normal mode coordinate is to be evaluated assuming this coordinate is to be fixed at its *instantaneous* value  $y(t)$ . This is indicated by the designation  $\langle F \rangle_{0(t)}$  in Eq. (2.1). The remaining terms are to be evaluated with the normal mode coordinate fixed at its equilibrium value  $y = y_0 = 0$ .<sup>22</sup> This convention guarantees that Eq. (2.1b) is valid to linear order in  $y(t)$ .

We conclude this discussion of Eq. (2.1) by noting that it clearly brings out the physics discussed in Sec. II A. Specifically the term  $[\langle F \rangle_{0(t)} + \langle \partial \mathcal{F} / \partial y \rangle_0 y(t)]$  is the (ensemble averaged) conservative "rigid cage" force characteristic of an nonresponding solvent while the term  $\beta \int_0^t \langle \tilde{\mathcal{F}}(t-\tau) \tilde{\mathcal{F}} \rangle_0 y(\tau) d\tau$  is the dissipative "cage relaxation" force arising from the weak solvent response.

### C. Linearization of the mean force

For a harmonic solute normal mode, one may linearize the mean force term  $\langle F \rangle_{0(t)}$  appearing in Eq. (2.1b). This linearization (see Sec. VI) yields the following form for Eq. (2.1b):

$$\ddot{y}(t) = -\omega_l^2 y(t) + \beta \int_0^t \langle \tilde{\mathcal{F}}(t-\tau) \tilde{\mathcal{F}} \rangle_0 y(\tau) d\tau + \tilde{\mathcal{F}}_0(t). \quad (2.5)$$

The liquid state frequency  $\omega_l$  of the solute normal mode is given by

$$\omega_l^2 = \omega_g^2 + \omega_{cf}^2 + \omega_e^2, \quad (2.6)$$

where  $\omega_g$  is the gas-phase fundamental frequency of the normal mode, where  $\omega_{cf}$  is a centripetal force contribution defined in Eq. (6.9) below, and where  $\omega_e$  is a liquid state frequency shift defined by

$$\omega_e^2 = - \left\langle \frac{\partial \mathcal{F}}{\partial y} \right\rangle_0. \quad (2.7)$$

Note that  $\omega_l$  is the (ensemble average) frequency that the normal mode would have in a hypothetical nonresponding solvent. The frequency shift  $\omega_e$ , in particular, arises from the rigid cage restoring force which resists displacements of vibrational coordinate  $y$  from its equilibrium value.

### D. Weak solvent response and solute VER

The physical factors discussed in Sec. II A in many cases manifest themselves as complex effects on the solute dynamics. The present problem of VER in liquids, however, provides a simple prototype for which the solvent effect on the solute dynamics is straightforward to understand.

Briefly stated if the VER time  $T_1$  is much greater than the vibrational period  $\tau_v = 2\pi\omega_l^{-1}$  the conditions for weak solvent response hold. That is the local solvent density field cannot even approximately adiabatically follow the vibrational motion of the solute normal mode. Thus in zeroth order, the normal mode coordinate  $y$  executes undamped harmonic oscillations with the rigid cage frequency  $\omega_l$ . These oscillations "probe" the solvent at frequency  $\omega_l$ . The

weak solvent response to this probe leads, to first order, to weak dissipation with damping coefficient  $\frac{1}{2}\beta(\omega_l)$ . [Recall,  $\beta(\omega)$  is the frequency-dependent friction coefficient of the normal mode defined in Eqs. (1.3) and (1.4).] This weak dissipation gives rise to solute VER with time constant  $T_1 = \beta^{-1}(\omega_l)$ , Eq. (1.1b).

These physical concepts may be given a precise mathematical formulation by introducing the normalized velocity autocorrelation function (VAF)  $\dot{\chi}(t)$  of the normal mode. This is defined by<sup>22</sup>

$$\dot{\chi}(t) = [k_B T]^{-1} \langle \dot{y}(t) \dot{y} \rangle. \quad (2.8)$$

Comparing Eqs. (2.5) and (2.8) yields the following equation of motion for the VAF:

$$\ddot{\chi}(t) = -\omega_l^2 \chi(t) + \beta \int_0^t \langle \tilde{\mathcal{F}}(t-\tau) \tilde{\mathcal{F}} \rangle_0 \chi(\tau) d\tau. \quad (2.9)$$

The zeroth order solution of Eq. (2.9), which is found by dropping the integral kernel term in Eq. (2.9), is  $\chi(t) = \cos \omega_l t$ . This zeroth order solution describes undamped harmonic motion in the hypothetical nonresponding solvent. The zeroth order form for  $\dot{\chi}(t)$  may be made the basis of a perturbation solution<sup>10</sup> of Eq. (2.9) which includes the first order effects of dissipation. This perturbation treatment yields the following form for  $\dot{\chi}(t)$ :

$$\dot{\chi}(t) = \cos \omega_l t \exp[-\frac{1}{2}\beta(\omega_l)t]. \quad (2.10)$$

The solution of Eq. (2.9) given in Eq. (2.10) is valid<sup>10</sup> if the following criterion is satisfied:

$$\omega_l \gg \beta(\omega_l). \quad (2.11)$$

Comparison of Eqs. (1.1b) and (2.11) shows that Eq. (2.11) is equivalent to our criterion for weak solvent response  $T_1 \gg \tau_v$ .

Notice that if the condition for weak solvent response holds the velocity autocorrelation function  $\dot{\chi}(t)$  is a highly oscillatory function which is very weakly damped with an exponentially decaying envelope.<sup>23</sup> This form is qualitatively different from that of the VAFs which characterize thermal liquid state motions.<sup>20</sup> This difference illustrates the points made at the end of Sec. II A.

Weak solvent response determines the form of the rate constant for energy relaxation, i.e., the form of  $T_1$ , as well as the nature of the vibrational dynamics. This follows because Eq. (1.1) for  $T_1$  may be derived from Eq. (2.10) for  $\dot{\chi}(t)$ . The procedure involves construction of the temporal development of the average energy of the normal mode  $\langle E \rangle_t$  by stochastic solution of Eq. (2.5). Using Eq. (2.10), the form for  $\langle E \rangle_t$  may be simplified to an exponential thermalization law with thermalization time  $T_1$  given by Eq. (1.1). The procedure, which provides an alternative to the earlier derivation of Metiu *et al.*,<sup>9</sup> is described elsewhere.<sup>10</sup>

We next turn to the problem of the explicit construction of  $T_1$  from Eq. (1.1) for specific solute-solvent systems.

### E. Gaussian model for the VER time $T_1$

The formal prescriptions of the partial clamping model<sup>11(b)</sup> permit one to explicitly construct  $\omega_l$  and  $\langle \tilde{\mathcal{F}}(t) \tilde{\mathcal{F}} \rangle_0$  and hence  $T_1$  [from Eqs. (1.1)–(1.4)]. These

quantities may be exactly determined (Sec. IX) by molecular dynamics simulation. Alternatively an approximate but more convenient analytic construction may be made. We next turn to the basis of this approximate construction of  $T_1$ .

This basis is provided by the following Gaussian model for  $\langle \mathcal{F}(t)\mathcal{F} \rangle_0$ , namely,

$$\langle \mathcal{F}(t)\mathcal{F} \rangle_0 \cong \langle \mathcal{F}^2 \rangle_0 \exp\left[-\frac{1}{2} \frac{\langle \mathcal{F}^2 \rangle_0}{\langle \mathcal{F}^2 \rangle_0} t^2\right]. \quad (2.12)$$

The Gaussian model frequency spectrum  $\rho_{\mathcal{F}}(\omega)$  may be obtained by comparison of Eqs. (1.2) and (2.12). This yields

$$\rho_{\mathcal{F}}(\omega) \cong \frac{1}{\pi} \langle \mathcal{F}^2 \rangle_0 \left[ \frac{2\pi \langle \mathcal{F}^2 \rangle_0}{\langle \mathcal{F}^2 \rangle_0} \right]^{1/2} \times \exp\left[-\frac{1}{2} \frac{\langle \mathcal{F}^2 \rangle_0}{\langle \mathcal{F}^2 \rangle_0} \omega^2\right]. \quad (2.13)$$

The VER time  $T_1$  may now be readily constructed within the Gaussian model. Comparison of Eqs. (1.1) and (2.13) yields

$$T_1 \cong \left[ \frac{2k_B T}{\langle \mathcal{F}^2 \rangle_0} \right] \left[ \frac{\langle \mathcal{F}^2 \rangle_0}{2\pi \langle \mathcal{F}^2 \rangle_0} \right]^{1/2} \exp\left[ \frac{1}{2} \frac{\langle \mathcal{F}^2 \rangle_0}{\langle \mathcal{F}^2 \rangle_0} \omega_i^2 \right]. \quad (2.14)$$

The Gaussian model construction of  $T_1$  is completed by using the following decomposition of  $\langle \mathcal{F}^2 \rangle_0$ , developed in Sec. VIII B:

$$\langle \mathcal{F}^2 \rangle_0 = \langle \mathcal{F}^2 \rangle_{od} + \langle \mathcal{F}^2 \rangle_{oi}, \quad (2.15)$$

where  $\langle \mathcal{F}^2 \rangle_{od(i)}$  mediates, respectively, the direct (indirect) energy exchange processes discussed in the Introduction.

The Gaussian model for  $T_1$ , Eqs. (2.14) and (2.15), will be used exclusively in the remainder of this paper and the companion paper II. The Gaussian model provides a simplification in that it permits one to construct  $T_1$  and its energy flow pathway dependence from *equilibrium* properties of the liquid solution, namely  $\omega_i^2$ ,  $\langle \mathcal{F}^2 \rangle_0$ ,  $\langle \mathcal{F}^2 \rangle_{od}$ , and  $\langle \mathcal{F}^2 \rangle_{oi}$ . Using the Kirkwood superposition approximation these equilibrium properties may be expressed (see, e.g., Sec. III) as integrals over equilibrium solute-solvent pair correlation functions  $g_i(r)$ .

The justification for the use of the Gaussian model, aside from its practicality and the fact that it is the simplest model which provides a qualitatively realistic account of the solvent effect, is twofold:

(i) The Gaussian model for  $\langle \mathcal{F}(t)\mathcal{F} \rangle_0$  [Eq. (2.12)], which is exact to order  $t^2$ , has been numerically tested in Sec. IX against molecular dynamics constructions of  $\langle \mathcal{F}(t)\mathcal{F} \rangle_0$  for some of the diatomic solute systems studied in paper II. The Gaussian model has been found to be of satisfactory accuracy for these systems in the chemically important<sup>2</sup> short-time scale regime. Moreover, the Gaussian model correctly reproduces the trends in the breadth of  $\langle \mathcal{F}(t)\mathcal{F} \rangle_0$ , and hence  $\rho_{\mathcal{F}}(\omega)$ , as one moves from system to system. It is these trends in the breadth of  $\rho_{\mathcal{F}}(\omega)$  which govern the trends in the VER time (for  $\omega_i$  relatively fixed) as illustrated in paper II.

(ii) We have elsewhere<sup>24</sup> presented an argument which

indicates that the Gaussian model frequency spectrum, Eq. (2.13), is often accurate in the asymptotic ( $\omega \rightarrow \infty$ ) wings. When Eq. (2.11) holds, it is this asymptotic region of the frequency spectrum which determines  $T_1$  for monatomic solvents.

The analytic expressions for  $\omega_i^2$  and for  $\langle \mathcal{F}^2 \rangle_0$ ,  $\langle \mathcal{F}^2 \rangle_{od}$ ,  $\langle \mathcal{F}^2 \rangle_{oi}$  required to construct  $T_1$  and its energy flow pathway dependence are developed in Secs. IV–VIII. For convenience, the expressions specialized to the diatomic solute case are presented, prior to the derivation, in Sec. III.

### III. ANALYTIC EXPRESSIONS FOR DIATOMIC SOLUTES

The expressions for diatomic solutes presented in this section are developed in Appendix C as specializations of more general expressions valid for arbitrary solutes, derived in Secs. VI–VIII.

We will use the following notation in this section, which is a specialization of the more general notation defined in Sec. IV A. The solvent is assumed to consist of  $N_s$  atoms each of mass  $M_s$  confined to a volume  $V$ . The thermodynamic state of the solvent is determined by its number density  $\rho_0 = V^{-1}N_s$  and Kelvin temperature  $T$ . We will label the atomic coordinates and masses of the diatomic solute by, respectively,  $\mathbf{r}_1$  and  $\mathbf{r}_2$  and  $m_1$  and  $m_2$ . The total and reduced masses of the diatomic solute will be denoted by  $M = m_1 + m_2$  and  $\mu = M^{-1}m_1m_2$ . The internuclear separation of the solute molecule will be denoted by  $\rho$  and its equilibrium internuclear separation will be denoted by  $\rho_{eq}$ .

Most of the expressions presented below are integrals over the local equilibrium solvent density surrounding the diatomic solute molecule given that that molecule is fixed at its equilibrium internuclear separation  $\rho_{eq}$ . We will denote this local solvent density at point  $\mathbf{q}$  by  $\rho^{(3)}[\rho_{eq}; \mathbf{q}]$ . The expressions are integrals over the point  $\mathbf{q}$ . These integrals are most conveniently evaluated in a coordinate system whose  $z$  axis runs through the bond axis of the diatomic molecule and whose origin bisects that bond axis. Further simplification arises if one performs the integration over  $\mathbf{q}$  using the spherical polar coordinates  $\mathbf{q} = (q, \theta, \phi)$ . Then, since the integrands are independent of the angle  $\phi$ , the integration over  $\phi$  may be performed analytically. Thus *all* the integrals presented below are over the spherical polar coordinates  $q, \theta$  in the coordinate system just described. These integrals are straightforward to evaluate using standard numerical quadrature algorithms.

We begin with the expressions for the liquid state frequency  $\omega_l$  of the solute normal mode. This is given by [Eq. (2.6)]

$$\omega_l^2 = \omega_g^2 + \omega_{cf}^2 + \omega_e^2, \quad (3.1)$$

where  $\omega_g$  is the gas-phase fundamental frequency and where the centripetal force  $\omega_{cf}$  and instantaneous cage restoring force  $\omega_e$  contributions are given by ( $k_B$  = Boltzmann's constant)

$$\omega_{cf}^2 = \frac{6k_B T}{\mu \rho_{eq}^2} \quad (3.2)$$

and

$$\omega_e^2 = -M^{-1} \left[ \left( \frac{m_2}{m_1} \right) \left[ \left\langle \frac{\partial \mathcal{F}_{r_1}}{\partial \mathbf{r}_1} \right\rangle_{\rho_{eq}} \right]_{\parallel} + \left( \frac{m_1}{m_2} \right) \left[ \left\langle \frac{\partial \mathcal{F}_{r_2}}{\partial \mathbf{r}_2} \right\rangle_{\rho_{eq}} \right]_{\parallel} \right]. \quad (3.3)$$

The quantities  $\left[ \left\langle \frac{\partial \mathcal{F}_{r_i}}{\partial \mathbf{r}_i} \right\rangle_{\rho} \right]_{\parallel}$ ,  $i = 1$  and  $2$ , appearing in Eq. (3.3) are integrals over  $q$  and  $\theta$  of the type just discussed, namely,

$$\begin{aligned} & \left[ \left\langle \frac{\partial \mathcal{F}_{r_i}}{\partial \mathbf{r}_i} \right\rangle_{\rho} \right]_{\parallel} \\ &= 2\pi \int_0^\infty q^2 dq \int_0^\pi \sin \theta d\theta \\ & \times \left[ \frac{[q \cos \theta - (-)^i (\mu/m_i) \rho]^2}{y_i^2} \frac{d^2 u_i(y_i)}{dy_i^2} \right. \\ & \left. + \left[ 1 - \frac{[q \cos \theta - (-)^i (\mu/m_i) \rho]^2}{y_i^2} \right] \right. \\ & \left. \times y_i^{-1} \frac{du_i(y_i)}{dy_i} \right] \rho^{(3)}[\rho; \mathbf{q}], \end{aligned} \quad (3.4)$$

where  $y_i = q - r_i$ , and where  $u_i(y_i)$  is the pair potential energy function which governs the interaction of a solvent atom at point  $\mathbf{q}$  with solute atom  $i = 1$  or  $2$  located at point  $\mathbf{r}_i$ .

We next turn to the construction of the Gaussian model parameters  $\langle \tilde{\mathcal{F}}^2 \rangle_0$  and  $\langle \tilde{\mathcal{F}}^2 \rangle_{0i}$ . The mean square force  $\langle \tilde{\mathcal{F}}^2 \rangle_0$  is proportional to  $\omega_e^2$  and is, therefore, determined by Eqs. (3.3) and (3.4). The expression for  $\langle \tilde{\mathcal{F}}^2 \rangle_0$  is

$$\langle \tilde{\mathcal{F}}^2 \rangle_0 = k_B T \omega_e^2. \quad (3.5)$$

To evaluate  $\langle \tilde{\mathcal{F}}^2 \rangle_{0i}$ , recall that it may be decomposed into direct and indirect contributions, namely [Eq. (2.15)],

$$\langle \tilde{\mathcal{F}}^2 \rangle_{0i} = \langle \tilde{\mathcal{F}}^2 \rangle_{0d} + \langle \tilde{\mathcal{F}}^2 \rangle_{0i}. \quad (3.6)$$

The direct contribution is given by

$$\begin{aligned} \langle \tilde{\mathcal{F}}^2 \rangle_{0d} &= \left[ \frac{k_B T}{M_s M} \right] \left[ \left( \frac{m_2}{m_1} \right) N_s \left[ \left\langle \frac{\partial \mathcal{F}_{r_1}}{\partial \mathbf{q}_1} \cdot \frac{\partial \mathcal{F}_{r_1}}{\partial \mathbf{q}_1} \right\rangle_{\rho_{eq}} \right]_{\parallel} \right. \\ & \left. + \left( \frac{m_1}{m_2} \right) N_s \left[ \left\langle \frac{\partial \mathcal{F}_{r_2}}{\partial \mathbf{q}_1} \cdot \frac{\partial \mathcal{F}_{r_2}}{\partial \mathbf{q}_1} \right\rangle_{\rho_{eq}} \right]_{\parallel} \right], \end{aligned} \quad (3.7)$$

where the quantities  $N_s$  [ ]<sub>||</sub> are given by

$$\begin{aligned} N_s \left[ \left\langle \frac{\partial \mathcal{F}_{r_i}}{\partial \mathbf{q}_1} \cdot \frac{\partial \mathcal{F}_{r_i}}{\partial \mathbf{q}_1} \right\rangle_{\rho} \right]_{\parallel} \\ &= 2\pi \int_0^\infty q^2 dq \int_0^\pi \sin \theta d\theta \\ & \times \left[ \frac{[q \cos \theta - (-)^i (\mu/m_i) \rho]^2}{y_i^2} \left( \frac{d^2 u(y_i)}{dy_i^2} \right)^2 \right. \\ & \left. + \left[ 1 - \frac{[q \cos \theta - (-)^i (\mu/m_i) \rho]^2}{y_i^2} \right] y_i^{-2} \right. \\ & \left. \times \left( \frac{du_i(y_i)}{dy_i} \right)^2 \right] \rho^{(3)}[\rho; \mathbf{q}] \end{aligned} \quad (3.8)$$

for  $i = 1$  and  $2$ .

The indirect contribution to  $\langle \tilde{\mathcal{F}}^2 \rangle_0$  may be written as

$$\begin{aligned} \langle \tilde{\mathcal{F}}^2 \rangle_{0i} &= \frac{k_B T}{M} \left[ 2 \left\langle \left[ \frac{\partial \mathcal{F}}{\partial X} \right]^2 \right\rangle_{y_0 z_0} + \left\langle \left[ \frac{\partial \mathcal{F}}{\partial Z} \right]^2 \right\rangle_{y_0 z_0} \right] \\ & + \frac{2k_B T}{\mu \rho_{eq}^2} \left\langle \left[ \frac{\partial \mathcal{F}}{\partial \theta} \right]^2 \right\rangle_{y_0 z_0}. \end{aligned} \quad (3.9)$$

The term  $k_B T/M$  [ ] determines the efficiency of solute vibrational $\leftrightarrow$ solute translational $\leftrightarrow$ solvent energy exchange while the term proportional to  $\langle [\partial \mathcal{F}/\partial \theta]^2 \rangle_{y_0 z_0}$  determines the efficiency of solute vibrational $\leftrightarrow$ solute rotational $\leftrightarrow$ solvent energy exchange. These terms may be calculated from the following expressions:

$$\left\langle \left[ \frac{\partial \mathcal{F}}{\partial X} \right]^2 \right\rangle_{y_0 z_0} = M^{-1} \left[ \left( \frac{m_2}{m_1} \right) I_{1x} + \left( \frac{m_1}{m_2} \right) I_{2x} \right], \quad (3.10a)$$

$$\begin{aligned} \left\langle \left[ \frac{\partial \mathcal{F}}{\partial Z} \right]^2 \right\rangle_{y_0 z_0} &= M^{-1} \left[ \left( \frac{m_2}{m_1} \right) [I_{1z} + J_{1z}] \right. \\ & \left. + \left( \frac{m_1}{m_2} \right) [I_{2z} + J_{2z}] \right] \end{aligned} \quad (3.10b)$$

and

$$\begin{aligned} \left\langle \left[ \frac{\partial \mathcal{F}}{\partial \theta} \right]^2 \right\rangle_{y_0 z_0} &= \frac{\mu \rho_{eq}^2}{M^2} \left[ \left( \frac{m_2}{m_1} \right)^2 I_{1x} + \left( \frac{m_1}{m_2} \right)^2 I_{2x} \right] \\ & + \frac{1}{M} \left[ \left( \frac{m_2}{m_1} \right) K_{1\theta} + \left( \frac{m_1}{m_2} \right) K_{2\theta} \right] \\ & - 2 \left( \frac{\mu}{M} \right) \left[ \frac{m_2}{m_1^2} M_{1\theta} - \frac{m_1}{m_2^2} M_{2\theta} \right] \rho_{eq}. \end{aligned} \quad (3.11)$$

The integrals appearing in Eqs. (3.10) and (3.11) are, as discussed earlier, quadratures over the variables  $q$  and  $\theta$ . The explicit expressions are

$$\begin{aligned} I_{1x} &= \pi \left[ \int_0^\infty q^4 dq \int_0^\pi \sin^3 \theta d\theta \left[ q \cos \theta - (-)^i \frac{\mu}{m_i} \rho_{eq} \right]^2 \right. \\ & \left. \times y_i^{-4} U_i^2[y_i] \rho^{(3)}[\rho_{eq}; \mathbf{q}] \right], \end{aligned} \quad (3.12)$$

$$\begin{aligned} I_{1z} &= 2\pi \int_0^\infty q^2 dq \int_0^\pi \sin \theta d\theta \left[ y_i^{-2} \right. \\ & \times \left[ q \cos \theta - (-)^i \frac{\mu}{m_i} \rho_{eq} \right]^2 \\ & \left. \times U_i[y_i] + y_i^{-1} \frac{du_i[y_i]}{dy_i} \right]^2 \rho^{(3)}[\rho_{eq}; \mathbf{q}], \end{aligned} \quad (3.13)$$

$$\begin{aligned} J_{1z} &= \left[ 2\pi \int_0^\infty q^2 dq \int_0^\pi \sin \theta d\theta \right. \\ & \times \left[ y_i^{-2} \left[ q \cos \theta - (-)^i \frac{\mu}{m_i} \rho_{eq} \right]^2 \right. \\ & \left. \times U_i[y_i] + y_i^{-1} \frac{du_i[y_i]}{dy_i} \right] \rho^{(3)}[\rho_{eq}; \mathbf{q}] \left. \right]^2, \end{aligned} \quad (3.14)$$

$$\begin{aligned} K_{1\theta} &= \pi \int_0^\infty q^4 dq \int_0^\pi \sin^3 \theta d\theta y_i^{-2} \\ & \times \left[ \frac{du_i[y_i]}{dy_i} \right]^2 \rho^{(3)}[\rho_{eq}; \mathbf{q}], \end{aligned} \quad (3.15)$$



$$M_{i\theta} = -\pi \int_0^\infty q^4 dq \int_0^\pi \sin^3 \theta d\theta y_i^{-3} \\ \times \left[ q \cos \theta - (-)^i \frac{\mu}{m_i} \rho_{eq} \right] \\ \times U_i[y_i] \frac{du_i[y_i]}{dy_i} \rho^{(3)}[\rho_{eq}; \mathbf{q}], \quad (3.16)$$

where the quantity  $U_i[y_i]$  is defined by

$$U_i[y_i] \equiv \frac{d^2 u_i[y_i]}{dy_i^2} - y_i^{-1} \frac{du_i[y_i]}{dy_i}. \quad (3.17)$$

To evaluate the above integrals one requires a form for the local solvent density  $\rho^{(3)}[\rho_{eq}; \mathbf{q}]$  surrounding the solute atoms. While one may evaluate this density exactly, via molecular dynamics or Monte Carlo simulation, it is more convenient to determine it approximately using the Kirkwood superposition approximation (SA). The SA yields the following form for the density:

$$\rho^{(3)}[\rho; \mathbf{q}] \approx \rho_0 g_1[|\mathbf{r}_1 - \mathbf{q}|] g_2[|\mathbf{r}_2 - \mathbf{q}|], \quad \text{SA}, \quad (3.18)$$

where  $g_i(r)$  is the solute-solvent pair correlation function (radial distribution function) for solute atom  $i$ .

Equation (2.14) along with the equations presented in this section permit one to evaluate  $T_1$  numerically for specific diatomic solute-monatomic solvent systems from equilibrium solute-solvent pair correlation functions. Such numerical evaluation is performed in paper II for solutions of molecular iodine and molecular bromine in a number of monatomic solvents.

## IV. TWO-FICTITIOUS SOLUTIONS

We next turn to the problem of the Gaussian model construction of the generalized Langevin equation of motion for solute normal mode dynamics in monatomic solvents. This requires an analysis of the statistics and dynamics of two fictitious solutions described in this section. Before beginning this analysis, it is necessary to specify the liquid solution and in the process introduce the notation [describe in detail in Ref. 11(b)] used in the remainder of this paper.

### A. The liquid solution

We assume an  $n$ -atom solute system immersed at infinite dilution in an otherwise pure  $N_s$ -atom monatomic solvent at Kelvin temperature  $T$  and number density  $\rho_0 = V^{-1}N_s$ . The mass of a solvent atom will be denoted by  $M_s$ . The solute atom masses will be denoted by  $m_1, m_2, \dots, m_n$ . The total mass of the solute system will be denoted by  $M = m_1 + m_2 + \dots + m_n$ .

The solvent phase point will be specified by the  $6N_s$  Cartesian phase space coordinates  $p_q q$ . While we will sometimes specify the solute phase point by the  $6n$  Cartesian phase space coordinates  $p, r$ , it will usually be more convenient to specify this phase point by the  $6n$  generalized coordinates  $p, y$  and  $p_z z$ . The generalized coordinate  $y$  as mentioned earlier, is the coordinate of the explicit solute normal mode. The coordinates  $z$  are the remaining  $3n - 1$  implicit solute generalized coordinate. The quantities  $p_y$  and  $p_z$  are the corresponding conjugate generalized momenta.

It will prove convenient for our later work to partition the implicit solute coordinates  $z$  into a set of external coordinates  $z_e$  and into a set of internal coordinates  $z_i$ . The external coordinates  $z_e$  will be taken to be the  $6(5)$  molecular framework translational-rotational coordinates of the solute molecule. The internal coordinates  $z_i$  will be taken as the  $3n - 7(6)$  implicit vibrational coordinates of the solute molecule. The equilibrium values of the solute vibrational coordinates will be denoted by  $y_0 = 0$  and  $z_0 = 0$ .<sup>22</sup>

We next introduce the first of the two fictitious solutions.

### B. The fixed explicit coordinate solution

The generalized forces  $F$  and  $\mathcal{F}$  appearing in the equation of motion Eq. (2.1) are, according to the prescriptions of the partial clamping theory,<sup>11(b)</sup> the forces exerted on the solute normal mode coordinate  $y$  in a fictitious solution in which  $y$  is fixed while the remaining solution phase space coordinates  $Q \equiv p_q q p_z z$  are allowed to move freely subject to this single constraint. We will refer to this fictitious solution as the fixed explicit coordinate solution.

The Hamiltonian  $K_0[Q]$  of this fictitious solution is

$$K_0[Q] = K_V[p_q q] + K_U[p_z z] + K_{VU}[qyz], \quad (4.1)$$

where  $K_V$  = pure solvent Hamiltonian,  $K_{VU}$  = solute-solvent potential energy function, and where  $K_U$  = gas-phase solute Hamiltonian subject to the fixed explicit coordinate constraint. This gas-phase Hamiltonian is given by

$$K_U[p_z z] = \frac{1}{2} p_z^T [m_{zz}[yz]]^{-1} p_z + U[yz_i]. \quad (4.2)$$

Note that the gas-phase solute potential energy function  $U$  depends only on the internal coordinates  $yz_i$ . The mass matrix  $m_{zz}[yz]$  is defined in Ref. 11(b) and worked out for diatomic solutes in Appendix B.

Equilibrium statistics in this fictitious solution is generated by the canonical ensemble distribution function  $f_0[Q]$  defined by

$$f_0[Q] = Z_0^{-1}[y] \exp[-\beta K_0[Q]], \quad (4.3)$$

where  $Z_0[y] = \int \exp[-\beta K_0[Q]] dQ$ . Dynamics is generated by the Liouville operator  $iL_0$  defined by

$$iL_0 = \left[ \frac{\partial K_0[Q]}{\partial p_q^T} \cdot \frac{\partial}{\partial q} - \frac{\partial K_0[Q]}{\partial q^T} \cdot \frac{\partial}{\partial p_q} \right] \\ + \left[ \frac{\partial K_0[Q]}{\partial p_z^T} \cdot \frac{\partial}{\partial z} - \frac{\partial K_0[Q]}{\partial z^T} \cdot \frac{\partial}{\partial p_z} \right]. \quad (4.4)$$

We may now give a complete specification of the terms appearing in Eq. (2.1). The total generalized force exerted on the normal mode coordinate  $y$  is given by

$$F[Q] = - \frac{\partial K_0[Q]}{\partial y}. \quad (4.5)$$

The solvent contribution to this generalized force is

$$\mathcal{F}[qyz] = - \frac{\partial K_{VU}[qyz]}{\partial y}. \quad (4.6)$$

The symbol  $\langle \rangle_0$  denotes an average over the phase space distribution function  $f_0[Q]$ , e.g.,  $\langle F \rangle_0 = \int F[Q] f_0[Q] dQ$ . The time development of the terms in Eq. (2.1) is generated by  $iL_0$ , e.g.,  $\mathcal{F}_0(t) \equiv \exp[iL_0 t] \mathcal{F}[qyz]$ .



### C. The fixed solute solution

We next turn to the second fictitious solution. The solute in this solution is fixed at some configuration point  $yz$ . The solvent fluctuations characteristic of this fixed solute solution permit only direct [ $y$  coordinate  $\leftrightarrow$  solvent] processes to occur.

The Hamiltonian of this fixed solute solution is [cf. Eq. (4.1)]

$$K_0[p_q q] = K_v[p_q q] + K_{vU}[qyz]. \quad (4.7)$$

The phase space distribution function of this fictitious solution will be denoted by

$$f_0[p_q q] = Z_0^{-1}[yz_i] \exp[-\beta K_0[p_q q]], \quad (4.8)$$

where  $Z_0[yz_i] = \int \exp[-\beta K_0[p_q q]] dp_q dq$ . Ensemble averages over  $f_0[p_q q]$  will be denoted by  $\langle \rangle_{yz}$ , e.g.,  $\langle \mathcal{F} \rangle_{yz} \equiv \int f_0[p_q q] \mathcal{F}[qyz] dp_q dq$ .

### V. AN APPROXIMATE FORM FOR $f_0[Q]$

To construct Eq. (2.1), one requires ensemble averages  $\langle \rangle_0$  over the phase space distribution function  $f_0[Q]$  defined in Eq. (4.3). We next develop an approximate but physically realistic form for  $f_0[Q]$  which considerably simplifies the construction of these ensemble averages.

This form is based on: (i) a harmonic oscillator-rigid top model for the motion of the implicit solute coordinates  $z_i$ ; (ii) a suppression of the effects of fluctuations of the internal coordinates  $z_i$  on the motion of the normal mode coordinate  $y$ . This later approximation is equivalent to assuming that solute intramolecular vibrational energy redistribution does not importantly influence the dynamics of the normal mode coordinate  $y$ .

We begin with a rigorous factorization<sup>11(a)</sup> of the phase space distribution function  $f_0[Q]$ .

#### A. Factorized form of $f_0[Q]$

This rigorous factorization is

$$f_0[Q] = f_0[p_z z] f_0[p_q q]. \quad (5.1)$$

The phase space distribution function  $f_0[p_q q]$  [Eq. (4.8)] describes equilibrium solvent fluctuations in the presence of the fixed solute. The distribution function  $f_0[p_z z]$  reinstates the effects of implicit solute coordinate fluctuations. It is defined by

$$f_0[p_z z] = Z_0^{-1}[y] \exp[-\beta(\frac{1}{2} p_z^T [m_{zz}[yz]]^{-1} p_z + W[yz_i])], \quad (5.2)$$

where  $W[yz_i]$  is the solute potential of mean force defined by

$$W[yz_i] = U[yz_i] + w[yz_i] \quad (5.3)$$

with  $w[yz_i] = -k_B T \ln Z_0[yz_i]$  = solute cavity potential, where  $Z_0[yz_i]$  is defined after Eq. (4.8). From Eq. (5.1), it is straightforward to show that  $\int f_0[p_z z] dp_z dz = 1$ . Thus  $Z_0[y]$ , defined after Eq. (4.3) as a many-body configurational integral, may be reexpressed, using Eq. (5.2), as the

following  $(3n - 1)$ -dimensional configurational integral:

$$Z_0[y] = \int \exp[-\frac{1}{2} p_z^T [m_{zz}[yz]]^{-1} p_z + W[yz_i]] dp_z dz. \quad (5.4)$$

### B. Harmonic model for solute vibrational motion

We have assumed that the internal coordinates  $yz_i$  may be treated as harmonic normal modes. Consequently the potential of mean force  $W[yz_i]$  takes the following form<sup>22</sup>:

$$W[yz_i] = -\frac{1}{2} \Omega_i^2 y^2 - \frac{1}{2} \sum_{\alpha=1}^{3n-7(6)} \Omega_\alpha^2 z_{i\alpha}^2, \quad (5.5)$$

where  $\Omega_i$ , and  $\Omega_\alpha$ ,  $\alpha = 1, 2, \dots, 3n - 7(6)$ , are the potential energy contributions to the frequencies of the solute normal modes with small static liquid state corrections included. We will later discuss a much larger *dynamic* liquid state correction to the frequency of the normal  $y$ . This dynamic correction arises from the instantaneous cage restoring force  $\langle \partial \mathcal{F} / \partial y \rangle_0 y$  appearing in Eq. (2.1).

### C. Rigid top model for the solute rotational motion

The solute kinetic energy  $T_U = \frac{1}{2} p_z^T [m_{zz}[yz]]^{-1} p_z$  may be exactly decomposed into pure vibrational, pure translational-rotational, and vibrational-rotational coupling contributions. This decomposition may be conveniently formulated by partitioning the mass matrix  $m_{zz}[yz]$  in a corresponding manner as

$$m_{zz}[yz] = \begin{pmatrix} m_{zz_i}[yz] & m_{zz_e}[yz] \\ m_{zz_i}[yz] & m_{zz_e}[yz] \end{pmatrix}. \quad (5.6)$$

We next introduce two simplifications of the mass matrix which are equivalent to treating the rotational motion of the solute molecule within the rigid top model. These are

$$m_{zz_i}[yz] = m_{zz_e}[yz] \doteq 0, \quad (5.7a)$$

$$m_{zz_e}[yz] \doteq m_{zz_e}[y_0 z_0], \quad (5.7b)$$

where, recall,  $y_0$  and  $z_0$  are the equilibrium values of  $y$  and  $z_i$  and where we define  $z_0 \equiv z_e z_0$ . Given our notational convention<sup>22</sup> for the mass factors of harmonic normal modes, we also have  $m_{zz_i}[yz] = 1$ . Thus Eq. (5.6) takes the following approximate form:

$$m_{zz}[yz] \doteq \begin{pmatrix} 1 & 0 \\ 0 & m_{zz_e}[y_0 z_0] \end{pmatrix}. \quad (5.8)$$

### D. Approximate form for $f_0[Q]$

Given the harmonic oscillator-rigid top approximation it is straightforward to develop the following approximate form for  $f_0[Q]$  from Eqs. (5.1), (5.3), and (5.5),

$$f_0[Q] \doteq f_0^{(0T)}[p_z z] f_0[p_q q], \quad (5.9)$$

where

$$f_0^{(0T)}[p_z z] = [Z_0[y]]^{-1} \exp \left\{ -\beta \left( \frac{1}{2} p_z^T [m_{zz_e}[y_0 z_0]]^{-1} p_z + \frac{1}{2} \sum_{\alpha=1}^{3n-7(6)} [z_{i\alpha}^2 + \Omega_\alpha^2 z_{i\alpha}^2] \right) \right\}. \quad (5.10)$$

### E. Suppression of $z_i$ fluctuations

Further simplification arises from our assumption that the influence of  $z_i$  fluctuations on the dynamics of the normal mode coordinate  $y$  may be ignored. It permits, one to fix the internal coordinates  $z_i$  at their equilibrium values  $z_{i0} = 0$ . Thus, e.g., we will replace  $\mathcal{F}[qyz] \rightarrow \mathcal{F}[qyz_0]$ . Moreover Eqs. (5.9) and (5.10) simplify to

$$f_0[Q] \doteq f_0^{(T)}[p_{z_e} z_e] f_0[p_q q], \quad (5.11)$$

where

$$f_0^{(T)}[p_{z_e} z_e] = [Z_0[y]]^{-1} \times \exp\left\{-\beta\left(\frac{1}{2} p_{z_e}^T [m_{z_{z_e}}[y_0 z_0]]^{-1} p_{z_e}\right)\right\}. \quad (5.12)$$

Note  $Z_0[y]$  is evaluated at a consistent level of approximation from Eq. (5.4) to yield

$$Z_0[y] \doteq \left(\frac{2\pi}{\beta}\right)^{6(5)} \int [\det m_{z_{z_e}}[y_0 z_0]]^{1/2} dz_e. \quad (5.13)$$

Similarly the Liouville operator  $iL_0$  defined in Eq. (4.4) simplifies to

$$iL_0 = \left[ \frac{\partial K_0[Q]}{\partial p_q^T} \cdot \frac{\partial}{\partial q} - \frac{\partial K_0[Q]}{\partial q^T} \cdot \frac{\partial}{\partial p_q} \right] + \left[ \frac{\partial K_0[Q]}{\partial p_{z_e}^T} \cdot \frac{\partial}{\partial z_e} - \frac{\partial K_0[Q]}{\partial z_e^T} \cdot \frac{\partial}{\partial p_{z_e}} \right]. \quad (5.14)$$

## VI. THE MEAN FORCE $\langle F \rangle_0$

In the next two sections we develop approximate calculationally convenient expressions for the mean force  $\langle F \rangle_0$  and the mean force gradient  $\langle \partial \mathcal{F} / \partial y \rangle_0$  [see Eq. (2.1)] based on the model of Sec. V E.

### A. Decomposition of the mean force into kinetic and potential energy contributions

The mean force  $\langle F \rangle_0$  may be decomposed into kinetic energy, i.e., centripetal force, and potential energy contributions as follows:

$$\langle F \rangle_0 = \langle F_{cf} \rangle_0 + \langle F_v \rangle_0, \quad (6.1)$$

where the centripetal force contribution is

$$\langle F_{cf} \rangle_0 = \left\langle -\frac{\partial}{\partial y} \left[ \frac{1}{2} p_{z_e}^T [m_{z_{z_e}}[y z_0]]^{-1} p_{z_e} \right] \right\rangle_0 \quad (6.2)$$

and where the potential energy contribution is

$$\langle F_v \rangle_0 = \left\langle -\frac{\partial}{\partial y} (U + K_{vU}) \right\rangle_0, \quad (6.3)$$

where, recall,  $\langle \rangle_0$  denotes an ensemble average over  $f_0[Q]$ .

### B. Construction of the mean centripetal force

Using Eq. (5.11), Eq. (6.2) may be reduced to the following form:

$$\langle F_{cf} \rangle_0 = \int f_0^{(T)}[p_{z_e} z_e] \times \left[ -\frac{\partial}{\partial y} \left[ \frac{1}{2} p_{z_e}^T [m_{z_{z_e}}[y z_0]]^{-1} p_{z_e} \right] \right] dp_{z_e} dz_e. \quad (6.4)$$

Using Eqs. (5.12) and (5.13) the integral in Eq. (6.4) may be evaluated exactly to give

$$\langle F_{cf} \rangle_0 = \frac{1}{2} k_B T \left[ \int [\det m_{z_{z_e}}[y_0 z_0]]^{1/2} dz_e \right]^{-1} \times \left[ -\frac{\partial}{\partial y} \int [\det m_{z_{z_e}}[y_0 z_0]]^{1/2} \times \text{tr} [m_{z_{z_e}}[y_0 z_0] m_{z_{z_e}}^{-1}[y z_0]] dz_e \right], \quad (6.5)$$

where  $\text{tr}$  denotes a matrix trace.

### C. Construction of $\langle F_v \rangle_0$

Comparing Eqs. (5.11) and (6.3) yields the following form for the potential energy contribution to  $\langle F \rangle_0$ :

$$\langle F_v \rangle_0 = \int f_0^{(T)}[p_{z_e} z_e] \langle F_v \rangle_{y z_0} dp_{z_e} dz_e, \quad (6.6)$$

where, recall,  $\langle \rangle_{y z_0}$  denotes an ensemble average over  $f[p_q q]$ . For isotropic liquids, however,  $\langle F_v \rangle_{y z_0}$ , the mean force exerted on the fixed solute, is independent of the solute translational-rotational coordinates  $z_e$ , i.e.,  $\langle F_v \rangle_{y z_0} = \langle F_v \rangle_{y z_{0i}}$ . Thus Eq. (5.6) simplifies to

$$\langle F_v \rangle_0 = \langle F_v \rangle_{y z_{0i}} = -\frac{\partial W[y z_{0i}]}{\partial y}. \quad (6.7)$$

### D. The liquid state frequency $\Omega_l$

Within the harmonic approximation for the dynamics of the normal mode coordinate  $y$ , the full form of the mean force  $\langle F \rangle_0$  is not required. Rather one requires only the frequency  $\Omega_l$  defined by

$$\Omega_l^2 = -\left[ \frac{\partial \langle F \rangle_0}{\partial y} \right]_{y=y_0}. \quad (6.8a)$$

Using Eqs. (5.5), (6.1), and (6.7) the frequency  $\Omega_l$  may be decomposed as follows:

$$\Omega_l^2 = \Omega_l^2 + \omega_{cf}^2 = \omega_g^2 + \omega_{cf}^2 + \Omega_0^2, \quad (6.8b)$$

where  $\omega_g$  is the gas phase frequency,  $\omega_{cf}$  is the centripetal force correction given by

$$\omega_{cf}^2 = -\left[ \frac{\partial \langle F_{cf} \rangle_0}{\partial y} \right]_{y=y_0}, \quad (6.9)$$

and where  $\Omega_0$  is the contribution to  $\Omega_l$  due to the solute cavity potential. This contribution is given by

$$\Omega_0^2 = -\left[ \frac{\partial \langle \mathcal{F} \rangle_{y z_0}}{\partial y} \right] = -\left[ \frac{\partial \langle \mathcal{F} \rangle_0}{\partial y} \right]_{y=y_0}, \quad (6.10)$$

where the last equality holds within the model of Sec. V E.

### E. The frequencies $\Omega_l$ and $\omega_l$

The gradient of the mean force  $[\partial \langle \mathcal{F} \rangle_0 / \partial y]$ , appearing in Eq. (6.10), determines the magnitude of the mean restoring force that the solvent would exert on coordinate  $y$  if the local solvent density field could perfectly follow the motion of that coordinate.

The mean force gradient  $\langle \partial \mathcal{F} / \partial y \rangle_0$ , in contrast, determines the magnitude of the restoring force in the opposite limit that the local density field cannot relax in response to the motion of the vibrational coordinate. On physical

grounds<sup>2</sup> it follows that [see Sec. IX for a numerical test of Eq. (6.11)]

$$\left\langle \frac{\partial \mathcal{F}}{\partial y} \right\rangle_0 \gg \frac{\partial \langle \mathcal{F} \rangle_0}{\partial y}. \quad (6.11)$$

Typically the local solvent density field follows the solute vibrational motion highly imperfectly. Consequently, as discussed in Sec. II D, the appropriate zeroth order frequency is  $\omega_l$  rather than  $\Omega_l$  where [Eqs. (2.6) and (2.7)]  $\omega_l^2 = \omega_g^2 + \omega_{cf}^2 + \omega_e^2$  with  $\omega_e^2 = -\langle \partial \mathcal{F} / \partial y \rangle_0$ . Thus we next turn to the problem of constructing  $\langle \partial \mathcal{F} / \partial y \rangle_0$ . Recall (Sec. II B) this quantity is required only for  $y = y_0 = 0$ .

## VII. THE INSTANTANEOUS CAGE RESTORING FORCE

We construct  $\langle \partial \mathcal{F} / \partial y \rangle_0$  within the model of Sec. V E. Within this model one may develop the following result for  $\langle \partial \mathcal{F} / \partial y \rangle_0$  evaluated for  $y = y_0 = 0$ :

$$\left\langle \frac{\partial \mathcal{F}}{\partial y} \right\rangle_0 = \left\langle \frac{\partial \mathcal{F}}{\partial y} \right\rangle_{y_0 z_0}, \quad (7.1)$$

where we have used the fact [cf. Eq. (6.7)] that  $\langle \partial \mathcal{F} / \partial y \rangle_{yz}$  is independent of the external coordinates  $z_e$ . To make further progress, we next expand  $\langle \partial \mathcal{F} / \partial y \rangle_0$  in terms of the force gradients of the individual solute atoms.

### A. Expansion of $\partial \mathcal{F} / \partial y$ in terms of atomic force gradients

This expansion is based on the following relationship developed in Appendix A:

$$\frac{\partial}{\partial y} = \sum_{i=1}^n \mu^i(z_e) \cdot \frac{\partial}{\partial \mathbf{r}_i}, \quad (7.2)$$

where  $\mathbf{r} = (x_i, y_i, z_i)$  are the Cartesian coordinates of solute atom  $i$  and where  $\mu^i(z_e)$  is a transformation coefficient defined in Appendix A. Notice this transformation coefficient depends only on the external coordinates  $z_e$ . This is proven in Appendix A.

Comparing Eqs. (4.6) and (7.2) yields the following expansion of the generalized force  $\mathcal{F}$ :

$$\mathcal{F} = \sum_{i=1}^n \mu^i(z_e) \cdot \mathcal{F}_{r_i}, \quad (7.3)$$

where

$$\mathcal{F}_{r_i} = - \frac{\partial K_{vu}[qyz]}{\partial \mathbf{r}_i} \quad (7.4)$$

is the force exerted by the solvent on solute molecule  $i$ . The analogous expansion of the generalized force gradient follows by comparing Eqs. (7.2)–(7.4). It is

$$\frac{\partial \mathcal{F}}{\partial y} = \sum_{i=1}^n \sum_{j=1}^n \mu^i(z_e) \mu^j(z_e) : \frac{\partial \mathcal{F}_{r_i}}{\partial \mathbf{r}_j}. \quad (7.5)$$

### B. Pairwise additive forces

In the remainder of this paper, we will assume pairwise additive solute–solvent forces. That is we assume

$$K_{vu}[qyz] = \sum_{i=1}^n \sum_{\lambda=1}^{N_i} u_i[\mathbf{q}_\lambda \mathbf{r}_i], \quad (7.6)$$

where  $u_i$  is the solute–solvent pair potential for solute atom  $i$ . For pairwise additive forces Eq. (7.5) simplifies to

$$\frac{\partial \mathcal{F}}{\partial y} = \sum_{i=1}^n \mu^i(z_e) \mu^i(z_e) : \frac{\partial \mathcal{F}_{r_i}}{\partial \mathbf{r}_i}. \quad (7.7)$$

### C. Final expression for $\langle \partial \mathcal{F} / \partial y \rangle_0$

Comparing Eqs. (7.1) and (7.7) yields the following expansion of  $\langle \partial \mathcal{F} / \partial y \rangle_0$ :

$$\left\langle \frac{\partial \mathcal{F}}{\partial y} \right\rangle_0 = \sum_{i=1}^n \mu^i(z_e) \mu^i(z_e) : \left\langle \frac{\partial \mathcal{F}_{r_i}}{\partial \mathbf{r}_i} \right\rangle_{y_0 z_0}. \quad (7.8)$$

We next consider the local equilibrium solvent density surrounding the solute atoms conditional that these atoms are fixed at configuration point  $\mathbf{r} \equiv (\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n) = yz$ . This density is defined by

$$\rho^{(n+1)}[\mathbf{r}; \mathbf{q}] = N_s \int d\mathbf{p}_q d\mathbf{q}_2 \cdots d\mathbf{q}_N f_0[\mathbf{p}_q \mathbf{q}] \quad (7.9)$$

Comparing Eqs. (7.8) and (7.9) yields the following form for  $\langle \partial \mathcal{F} / \partial y \rangle_0$  valid for pairwise additive forces:

$$\begin{aligned} \left\langle \frac{\partial \mathcal{F}}{\partial y} \right\rangle_0 &= \sum_{i=1}^n \mu^i(z_e) \mu^i(z_e) : \\ &\times \left[ \int \left[ - \frac{\partial^2 u_i[\mathbf{q} \mathbf{r}_i]}{\partial \mathbf{r}_i \partial \mathbf{r}_i} \right]_{\mathbf{r}_i = \mathbf{r}_0} \rho^{(n+1)}[\mathbf{r}_0; \mathbf{q}] d\mathbf{q} \right], \end{aligned} \quad (7.10)$$

where  $\mathbf{r}_0 = y_0 z_0$  and where  $\mathbf{r}_0$  = equilibrium position of solute atom  $i$ .

Equation (7.10) may be recast in a more useful form by noting  $u_i[\mathbf{q} \mathbf{r}_i]$  depends only on the magnitude  $y_i$  of the vector  $\mathbf{y}_i = \mathbf{q} - \mathbf{r}_i$ . Because of this fact

$$\frac{\partial^2 u_i[\mathbf{q} \mathbf{r}_i]}{\partial \mathbf{r}_i \partial \mathbf{r}_i} = \mathbf{e}_{y_i} \mathbf{e}_{y_i} \frac{d^2 u_i(y_i)}{dy_i^2} + [1 - \mathbf{e}_{y_i} \mathbf{e}_{y_i}] y_i^{-1} \frac{du_i[y_i]}{dy_i}, \quad (7.11)$$

where  $1$  is the unit tensor and where  $\mathbf{e}_{y_i} = y_i^{-1} \mathbf{y}_i$ . Comparing Eqs. (7.10) and (7.11) yields the following form for  $\langle \partial \mathcal{F} / \partial y \rangle_0$ :

$$\begin{aligned} \left\langle \frac{\partial \mathcal{F}}{\partial y} \right\rangle_0 &= - \sum_{i=1}^n \mu^i(z_e) \mu^i(z_e) : \left[ \int \left[ \mathbf{e}_{y_i} \mathbf{e}_{y_i} \frac{d^2 u_i(y_i)}{dy_i^2} \right. \right. \\ &\quad \left. \left. + \frac{[1 - \mathbf{e}_{y_i} \mathbf{e}_{y_i}]}{y_i} \frac{du_i[y_i]}{dy_i} \right]_{\mathbf{r}_i = \mathbf{r}_0} \rho^{(n+1)}[\mathbf{r}_0; \mathbf{q}] d\mathbf{q} \right], \end{aligned} \quad (7.12)$$

where  $\mathbf{r}_i = \mathbf{r}_0$  denotes evaluation for the molecule fixed at vibrational equilibrium.

Comparison of Eqs. (2.7) and (7.12) yields the following result for  $\omega_e^2$ :

$$\begin{aligned} \omega_e^2 &= \sum_{i=1}^n \mu^i(z_e) \mu^i(z_e) : \\ &\times \left[ \int \left[ \mathbf{e}_{y_i} \mathbf{e}_{y_i} \frac{d^2 u_i(y_i)}{dy_i^2} + \frac{[1 - \mathbf{e}_{y_i} \mathbf{e}_{y_i}]}{y_i} \frac{du_i[y_i]}{dy_i} \right]_{\mathbf{r}_i = \mathbf{r}_0} \right. \\ &\quad \left. \times \rho^{(n+1)}[\mathbf{r}_0; \mathbf{q}] d\mathbf{q} \right]. \end{aligned} \quad (7.13)$$

### VIII. THE AUTOCORRELATION FUNCTION OF THE FLUCTUATING FORCE $\langle \dot{\mathcal{F}}(t)\dot{\mathcal{F}} \rangle_0$

We next turn to the construction of the autocorrelation function of the fluctuating force at  $y = y_0 = 0$ . Using Eq. (5.1),  $\langle \dot{\mathcal{F}}(t)\dot{\mathcal{F}} \rangle_0$  may be exactly written as

$$\begin{aligned} \langle \dot{\mathcal{F}}(t)\dot{\mathcal{F}} \rangle_0 &= \int f_0[p_z z] dp_z dz \\ &\times \int f_0[p_q q] [\exp[iL_0 t] \dot{\mathcal{F}}[qyz]] \dot{\mathcal{F}}[qyz] dp_q dq, \end{aligned} \quad (8.1)$$

where  $\dot{\mathcal{F}}[qyz] = \mathcal{F}[qyz] - \langle \mathcal{F} \rangle_0$ .

As discussed in Sec. II E, we will restrict ourselves in this paper to construction of the Gaussian model for  $\langle \dot{\mathcal{F}}(t)\dot{\mathcal{F}} \rangle_0$ . Thus, in this section, we will concern ourselves with the quantities  $\langle \dot{\mathcal{F}}^2 \rangle_0$ ,  $\langle \dot{\mathcal{F}}^2 \rangle_{od}$ , and  $\langle \dot{\mathcal{F}}^2 \rangle_{oi}$  needed to determine  $\langle \dot{\mathcal{F}}(t)\dot{\mathcal{F}} \rangle_0$  from Eqs. (2.12) and (2.15). We begin with a determination of  $\langle \dot{\mathcal{F}}^2 \rangle_0$ .

#### A. Construction of $\langle \dot{\mathcal{F}}^2 \rangle_0$

Our construction of  $\langle \dot{\mathcal{F}}^2 \rangle_0$ , which is approximate but convenient, is based on the following exact identity<sup>2(a)</sup>:

$$\frac{\partial \langle \mathcal{F} \rangle_0}{\partial y} = \left\langle \frac{\partial \mathcal{F}}{\partial y} \right\rangle_0 + \frac{\langle \dot{\mathcal{F}}^2 \rangle_0}{k_B T}. \quad (8.2)$$

Using the strong inequality given in Eq. (6.11), Eq. (8.2) takes the following approximate form:

$$\langle \dot{\mathcal{F}}^2 \rangle_0 = -k_B T \left\langle \frac{\partial \mathcal{F}}{\partial y} \right\rangle_0 = k_B T \omega_e^2, \quad (8.3)$$

where the final equality follows from Eq. (2.7). Thus

$$\langle \dot{\mathcal{F}}^2 \rangle_{oi} = \frac{k_B T \int [\det m_{z,z_e}[y_{z_0}]]^{1/2} \text{tr} [m_{z,z_e}^{-1}[y_{z_0}] \langle (\partial \mathcal{F} / \partial z_e) (\partial \mathcal{F} / \partial z_e^T) \rangle_{y_{z_0}}] dz_e}{\int [\det m_{z,z_e}[y_{z_0}]]^{1/2} dz_e}. \quad (8.7)$$

The integral in Eq. (8.7) is over the center of mass translational and overall rotational coordinates  $z_e$  of the solute molecule and is to be performed in a *space-fixed* coordinate system. One may show that Eq. (8.7) may be simplified to yield

$$\langle \dot{\mathcal{F}}^2 \rangle_{oi} = k_B T \text{tr} \left[ m_{z,z_e}^{-1}[y_{z_0}] \left\langle \frac{\partial \mathcal{F}}{\partial z_e} \frac{\partial \mathcal{F}}{\partial z_e^T} \right\rangle_{y_{z_0}} \right], \quad (8.8)$$

where the right-hand side of Eq. (8.8) is to be evaluated in a solute molecule *body-fixed* coordinate system.

#### C. Construction of $\langle \dot{\mathcal{F}}^2 \rangle_{od}$

We next develop an expression for  $\langle \dot{\mathcal{F}}^2 \rangle_{od}$  as an integral over the local solvent density  $\rho^{(n+1)}[r, \mathbf{q}]$ , defined in Eq. (7.9), from Eq. (8.6). Expanding the generalized force gradients  $\partial \mathcal{F} / \partial \mathbf{q}_i$  in terms of atomic forces gradients  $\partial \mathcal{F}_{r_i} / \partial \mathbf{q}_i$  using Eqs. (4.6) and (7.2), neglecting off-diagonal terms (see Sec. IX) of the form  $\langle (\partial \mathcal{F}_{r_i} / \partial \mathbf{q}_i) (\partial \mathcal{F}_{r_j} / \partial \mathbf{q}_j) \rangle_{y_{z_0}}$  ( $i \neq j$ ) and then performing

$\langle \dot{\mathcal{F}}^2 \rangle_0$  may be computed from Eqs. (7.13) and (8.3).

We next turn to the decomposition of  $\langle \dot{\mathcal{F}}^2 \rangle_0$  into direct and indirect components.

#### B. Decomposition of $\langle \dot{\mathcal{F}}^2 \rangle_0$

Within the model of Sec. V E,  $\langle \dot{\mathcal{F}}^2 \rangle_0$  is given by

$$\begin{aligned} \langle \dot{\mathcal{F}}^2 \rangle_0 &= \int f_0^{(T)}(p_z, z_e) \\ &\times \int f_0[p_q q] \dot{\mathcal{F}}[Q] \dot{\mathcal{F}}[Q] dp_q dq, \end{aligned} \quad (8.4)$$

where  $\dot{\mathcal{F}}[Q] \equiv iL_0 \mathcal{F}[qyz]$  with  $iL_0$  defined by Eq. (5.14). The explicit form of  $\dot{\mathcal{F}}[Q]$  is

$$\dot{\mathcal{F}}[Q] = \frac{p_q^T}{M_s} \cdot \frac{\partial \mathcal{F}}{\partial q} + p_{z_e}^T \cdot [m_{z,z_e}[y_{z_0}]]^{-1} \cdot \frac{\partial \mathcal{F}}{\partial z_e}. \quad (8.5)$$

The first term in Eq. (8.5) arises from solute motion about the fixed solute while the second term arises from the motion of the external coordinates. If only the first term were present the theory would account for only direct energy exchange processes. The second term reinstates the effects of indirect processes.

A calculation based on Eqs. (8.4) and (8.5) yields the decomposition of  $\langle \dot{\mathcal{F}}^2 \rangle_0$  into direct  $\langle \dot{\mathcal{F}}^2 \rangle_{od}$  and indirect  $\langle \dot{\mathcal{F}}^2 \rangle_{oi}$  contributions given in Eq. (2.15) with these contributions given explicitly by

$$\langle \dot{\mathcal{F}}^2 \rangle_{od} = \frac{N_s k_B T}{M_s} \left\langle \frac{\partial \mathcal{F}}{\partial \mathbf{q}_1} \cdot \frac{\partial \mathcal{F}}{\partial \mathbf{q}_1} \right\rangle_{y_{z_0}} \quad (8.6)$$

and

an analysis similar to the one which leads from Eqs. (7.1)–(7.12) yields the required result for  $\langle \dot{\mathcal{F}}^2 \rangle_{od}$  which is

$$\begin{aligned} \langle \dot{\mathcal{F}}^2 \rangle_{od} &= \frac{k_B T}{M_s} \sum_{i=1}^n \mu^i(z_e) \mu^i(z_e) \\ &\times \left[ \int \left[ \mathbf{e}_{y_i} \mathbf{e}_{y_i} \left[ \frac{d^2 u_i(y_i)}{dy_i^2} \right]^2 + \frac{[1 - \mathbf{e}_{y_i} \mathbf{e}_{y_i}]}{y_i^2} \right. \right. \\ &\times \left. \left. \left[ \frac{du_i[y_i]}{dy_i} \right]^2 \right] \rho^{(n+1)}[r_0; \mathbf{q}] d\mathbf{q} \right]. \end{aligned} \quad (8.9)$$

A general analysis of  $\langle \dot{\mathcal{F}}^2 \rangle_{oi}$  analogous to the analysis just sketched for  $\langle \dot{\mathcal{F}}^2 \rangle_{od}$  is straightforward but will be omitted here for reasons of brevity. A restricted analysis of  $\langle \dot{\mathcal{F}}^2 \rangle_{oi}$  valid only for diatomic solutes will be given in Appendix C. In Appendix C, we will, in addition, specialize the general results derived in Secs. VI–VIII to the diatomic solute case to yield the results presented in Sec. III.

## IX. NUMERICAL TESTS OF THE APPROXIMATIONS

We next present numerical tests of the approximate analysis just presented. The approximations tested in this section are:

(i) The Gaussian model, Eq. (2.12), for the fluctuating force autocorrelation function  $\langle \mathcal{F}(t)\mathcal{F} \rangle_0$ .

(ii) Neglect of the contributions to  $\langle \mathcal{F}(t)\mathcal{F} \rangle_0$  which are *off-diagonal* (see Fig. 1) in the solute atom indices. This neglect was implicit in the development of Eq. (8.9) for  $\langle \mathcal{F}^2 \rangle_{od}$  and also in the development of the expressions for  $\langle \mathcal{F}^2 \rangle_{oi}$  presented in Appendix C.

(iii) Use of the harmonic oscillator-rigid top model developed in Sec. V and the Kirkwood superposition approximation (SA), Eq. (3.18), to evaluate  $\omega_e^2$  and the Gaussian model parameters  $\langle \mathcal{F}^2 \rangle_o$ ,  $\langle \mathcal{F}^2 \rangle_{od}$ , and  $\langle \mathcal{F}^2 \rangle_{oi}$ .

(iv) The strong inequality (6.11). This inequality is the basis of the approximate relationship, Eq. (8.3), used to evaluate  $\langle \mathcal{F}^2 \rangle_o$ .

The numerical tests are made by performing molecular

dynamics (MD) simulations of the motions of the diatomic solute and the solvent according to the prescriptions (Sec. II B) of the partial clamping model.<sup>11</sup> That is MD simulations<sup>25</sup> are made of the motion of the solvent atoms and the solute translational-rotational degrees of freedom subject to the constraint that the bond length of the solute molecule is fixed at its equilibrium value  $\rho_{eq}$ .

The results of such MD simulations of the fluctuating force autocorrelation function  $\langle \mathcal{F}(t)\mathcal{F} \rangle_0$ , defined in Eq. (8.1), are plotted in Fig. 1 for several of the Lennard-Jones solutions of molecular iodine and molecular bromine studied in paper II. Lennard-Jones potential energy function parameters for these solutions are listed in Table I of paper II.

The plots of Fig. 1 provide both a qualitative test of the Gaussian model [point (i)] and a quantitative test of the neglect of off-diagonal contributions to  $\langle \mathcal{F}(t)\mathcal{F} \rangle_0$  [point (ii)]. From Fig. 1, it is evident that the off-diagonal contribution to  $\langle \mathcal{F}(t)\mathcal{F} \rangle_0$  is  $< 10\%$  of the diagonal contribution. Moreover the shapes of the dominant diagonal contributions are at least qualitatively Gaussian.

The plots of Fig. 2 provide a comparison of the MD results for the normalized autocorrelation functions  $\langle \mathcal{F}(t)\mathcal{F} \rangle_0 / \langle \mathcal{F}^2 \rangle_0$  with the corresponding Gaussian model results. The Gaussian model results are found to agree with the MD results to within statistical errors in the simulations in the important<sup>2</sup> short-time scale regime. Some deviation is found at longer times but this is not expected to significantly effect the frequency spectra  $\rho_{\mathcal{F}}(\omega)$  in the high frequency wings important for vibrational energy relaxation (see Sec. II E). This agreement between the Gaussian model and MD results for  $\langle \mathcal{F}(t)\mathcal{F} \rangle_0$  test both the Gaussian approximation [point (i)] and our approximate implementation of this approximation [point (iii)]. There is one caveat which must be mentioned. While the approximations [point (iii)] to  $\langle \mathcal{F}^2 \rangle_o$  and  $\langle \mathcal{F}^2 \rangle_{oi}$  lead to very little error in *nor-*

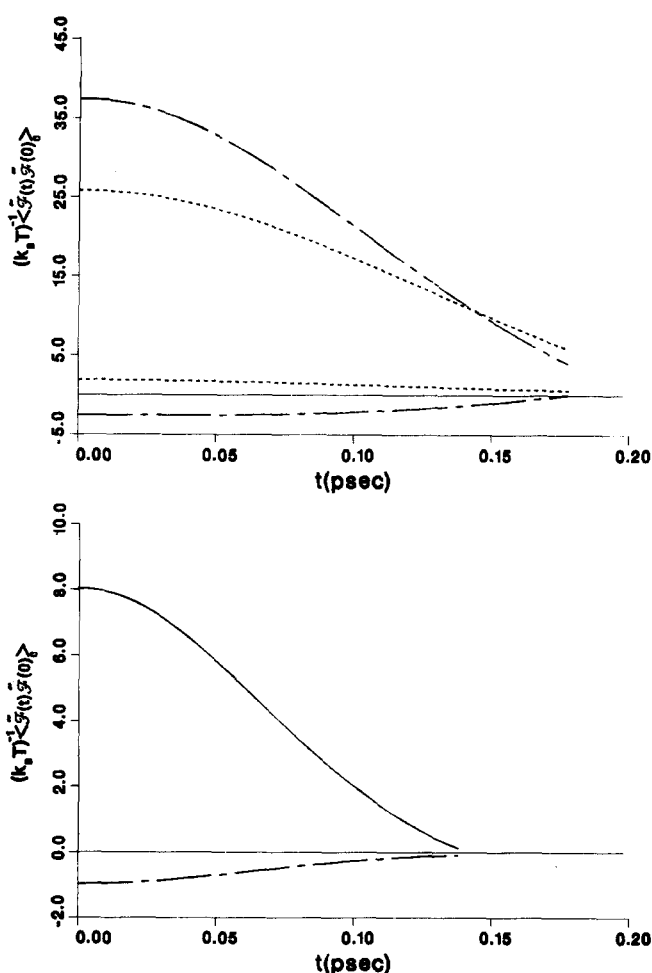


FIG. 1. (a) Molecular dynamics (MD) calculations of diagonal and off-diagonal contributions to  $\langle \mathcal{F}(t)\mathcal{F} \rangle_0 / k_B T$  for the model solutions  $I_2/Xe$  (—) at thermodynamic state  $T = 298$  K and  $\rho_0 = 0.014 \text{ \AA}^{-3}$  and  $I_2/CCl_4$  (---) at  $T = 298$  K and  $\rho_0 = 0.63 \times 10^{-2} \text{ \AA}^{-3}$ . Off-diagonal/diagonal  $< 10\%$ . (b) Same except for  $Br_2/Ar$  solution at  $T = 298$  K and  $\rho_0 = 0.96 \times 10^{-2} \text{ \AA}^{-3}$  (—; diagonal contribution, ---; off-diagonal contribution).

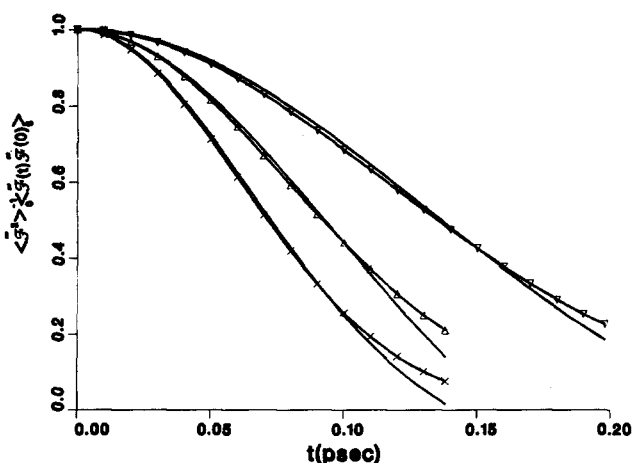


FIG. 2. Comparison of MD and Gaussian model normalized autocorrelation functions  $\langle \mathcal{F}(t)\mathcal{F} \rangle_0 / \langle \mathcal{F}^2 \rangle_0$  for  $I_2/CCl_4$  at  $T = 298$  K and  $\rho_0 = 0.63 \times 10^{-2}$  (top curves,  $\nabla$ ) and  $I_2/Xe$  at  $T = 298$  K and  $\rho_0 = 0.14 \times 10^{-1}$  (middle curves,  $\Delta$ ) and  $Br_2/Ar$  at  $T = 298$  K and  $\rho_0 = 0.96 \times 10^{-2}$  (bottom curves,  $\times$ ) MD curves fall below Gaussian model curves for all cases as  $t \rightarrow \infty$ .

TABLE I. Test of the inequality of Eq. (6.11) for several of the model solutions of paper II.  $\langle \partial \mathcal{F} / \partial y \rangle_0$  and  $\partial \langle \mathcal{F} \rangle_0 / \partial y$ , in  $\text{ps}^{-2}$ ,  $\partial \langle \mathcal{F} \rangle_0 / \partial y$  is calculated from solution pair correlation functions as in Ref. 2(a). The packing fraction (PF) is defined in terms of the solvent density  $\rho_0$  as  $\text{PF} = \frac{4}{3} \pi \rho_0 \sigma_{VV}^3$ , where  $\sigma_{VV}$  = solvent atom Lennard-Jones diameter.

System	$T$ (K)	Packing fraction	$-\langle \partial \mathcal{F} / \partial y \rangle_0$	$-\partial \langle \mathcal{F} \rangle_0 / \partial y$
$\text{Br}_2/\text{Ar}$	300	0.200	7.59	0.78
$\text{I}_2/\text{Xe}$	290	0.500	21.6	-0.15
$\text{I}_2/\text{Xe}$	298	0.010	0.43	0.07
$\text{I}_2/\text{Xe}$	280	0.302	8.45	1.22
$\text{I}_2/\text{C}_2\text{H}_6$	298	0.396	8.47	0.70
$\text{I}_2/\text{C}_2\text{H}_6$	314	0.229	4.19	0.62
$\text{I}_2/\text{CCl}_4$	305	0.483	7.80	0.46

### malized autocorrelation function

$$\langle \tilde{\mathcal{F}}(t) \tilde{\mathcal{F}}(0) \rangle_0 / \langle \tilde{\mathcal{F}}^2 \rangle_0 = \exp \left[ -\frac{1}{2} \frac{\langle \tilde{\mathcal{F}}^2 \rangle_0}{\langle \tilde{\mathcal{F}}^2 \rangle_0} t^2 \right],$$

which depends on the ratio  $\langle \tilde{\mathcal{F}}^2 \rangle_0 / \langle \tilde{\mathcal{F}}^2 \rangle_0$ , these approximations lead to a more substantial error (sometimes as large as 30%) in the actual values of  $\langle \tilde{\mathcal{F}}^2 \rangle_0$  and  $\langle \tilde{\mathcal{F}}^2 \rangle_0$ . This error, which we believe arises largely from the superposition approximation, leads to systematic errors in the preexponential contribution to  $T_1$ . Since the trends in the temperature, density, solute, and solvent dependence of  $T_1$  are dominated by the exponential, rather than the preexponential factor, we do not believe that the source of error just mentioned will affect the value of our theory to predict qualitative trends.

Finally a test of the inequality of Eq. (6.11) [point (iv)] is given in Table I for seven of the model solutions of paper I. It is found that

$$\frac{\partial \langle \mathcal{F} \rangle_0}{\partial y} / \left( \frac{\partial \mathcal{F}}{\partial y} \right)_0 < 15\%$$

for all the solutions studied.

## X. SUMMARY

This paper has dealt with the development of approximate algorithms which permit the explicit construction, for specific solute-solvent systems, of a physically realistic generalized Langevin equation of motion, Eq. (2.5), which generates the dynamics of a specified harmonic normal mode of a solute molecule moving in a monatomic solvent.

This construction permits numerical evaluation for specific solute-solvent systems of the vibrational energy relaxation time  $T_1$  and its energy flow pathway dependence from the Gaussian model formulas [Eqs. (2.14) and (2.15)].

The principle approximations employed in developing the results of this paper are:

(i) The effects of solvent induced intramolecular vibrational energy redistribution among the solute normal modes is ignored. (This, of course, introduces no error for the diatomic solute systems studied in paper II.)

(ii) The inequality (6.11) is used in order to obtain Eq. (8.3) for  $\langle \tilde{\mathcal{F}}^2 \rangle_0$ .

(iii) The motion of the solute molecule is treated within the harmonic oscillator-rigid top approximation.

(iv) The Kirkwood superposition approximation has been invoked for the local solvent one-particle density  $\rho^{(n+1)}[r_0; \mathbf{q}]$ , defined in Eq. (7.9), and a closely related approximation, Eq. (C19), has been made for the local solvent two-particle density. The superposition approximation permits one to determine  $T_1$  in terms of easily computable solute-solvent pair correlation (i.e., radial distribution) functions.

Approximations (ii)-(iv) have been tested in Sec. IX for the diatomic solute case against "exact" molecular dynamics results (Table I and Figs. 1 and 2) and have found to be of satisfactory accuracy. One additional point must be mentioned concerning the approximations. It is well known<sup>26</sup> that the superposition approximation can lead to substantial errors. As discussed in Sec. IX, we do not believe that these errors will effect the ability of the present theory to reproduce the qualitative trends in the variation of  $T_1$  with temperature, density, etc.

## APPENDIX A: THE TRANSFORMATION COEFFICIENTS $\mu^{ia}(r)$

We next define the transformation coefficients  $\mu^{ia}(r)$  where  $r = (\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n) = yz$ . These link the solute generalized coordinate  $\alpha$  with the Cartesian coordinates of solute atom  $i$ . We also prove that  $\mu^{il}(r)$ , the transformation coefficient linking the normal mode coordinate  $y$  and solute atom  $i$ , depends only on the external coordinates  $z_e$ .

We begin by grouping the  $3n$  solute Cartesian coordinates as follows:

$$r = \begin{pmatrix} r_1 \\ r_2 \\ \vdots \\ r_{3n} \end{pmatrix} = \begin{pmatrix} \mathbf{r}_1 \\ \mathbf{r}_2 \\ \vdots \\ \mathbf{r}_n \end{pmatrix}, \quad (\text{A1})$$

where  $r_{3(i-1)+1}, r_{3(i-1)+2}, r_{3(i-1)+3}$  are, respectively, the  $x, y, z$  coordinates of solute atom  $i$ .

The corresponding Cartesian differential operators will be denoted by

$$\frac{\partial}{\partial r} = \begin{pmatrix} \frac{\partial}{\partial r_1} \\ \vdots \\ \frac{\partial}{\partial r_{3n}} \end{pmatrix} = \begin{pmatrix} \frac{\partial}{\partial \mathbf{r}_1} \\ \vdots \\ \frac{\partial}{\partial \mathbf{r}_n} \end{pmatrix}. \quad (\text{A2})$$

We will similarly group the  $3n$  solute generalized coordinates  $x \equiv (yz) = (yz_e z_i)$ . That is, we define

$$x = \begin{pmatrix} x_1 \\ x_2 \\ \vdots \\ x_{3n} \end{pmatrix} \text{ and } \frac{\partial}{\partial x} = \begin{pmatrix} \frac{\partial}{\partial x_1} \\ \frac{\partial}{\partial x_2} \\ \vdots \\ \frac{\partial}{\partial x_{3n}} \end{pmatrix}, \quad (\text{A3})$$

where

$$x_1 = y, \quad \begin{pmatrix} x_2 \\ x_3 \\ \vdots \\ x_{7(6)} \end{pmatrix} = z_e \quad \text{and} \quad \begin{pmatrix} x_{8(7)} \\ x_{9(8)} \\ \vdots \\ x_{3n} \end{pmatrix} = z_i. \quad (\text{A4})$$

It is then straightforward to show that

$$\frac{\partial}{\partial x_\alpha} = \sum_{i=1}^{3n} \mu^{i\alpha}(r) \frac{\partial}{\partial r_i}, \quad (\text{A5})$$

where

$$\mu^{i\alpha}(r) = \left[ \frac{\partial r_i}{\partial x_\alpha} \right]_{x \neq x_\alpha}. \quad (\text{A6})$$

The required vector transformation coefficients  $\mu^{i\alpha}(r)$  are defined in terms of the scalar transformation coefficients  $\mu^{i\alpha}(r)$  by

$$\mu^{i\alpha}(r) = \begin{pmatrix} \mu^{[3(i-1)+1]\alpha}(r) \\ \mu^{[3(i-1)+2]\alpha}(r) \\ \mu^{[3(i-1)+3]\alpha}(r) \end{pmatrix} \quad (\text{A7})$$

or equivalently by

$$\mu^{i\alpha}(r) = \left( \frac{\partial r_i}{\partial x_\alpha} \right)_{x \neq x_\alpha}. \quad (\text{A8})$$

We next prove  $\mu^{i1}(r)$  is independent of the internal coordinates  $z_i$ , that is,

$$\mu^{i1}(r) = \mu^{i1}(z_e). \quad (\text{A9})$$

We begin by noting that so far we have implicitly assumed that the coordinates of solute atom  $i$ ,  $r_i$ , are specified relative to some *space-fixed* Cartesian coordinate system. We next introduce a body-fixed coordinate system whose origin is located at the center of mass  $\mathbf{R}$  of the solute molecule. We denote the coordinates of solute atom  $i$  in this body-fixed system by  $\mathbf{S}_i$  where

$$\mathbf{S}_i = \mathbf{r}_i - \mathbf{R}. \quad (\text{A10})$$

Next fix the internal coordinates  $y z_i$  at their equilibrium values  $y_0 = 0, z_{i0} = 0$ . We will denote the corresponding value of  $\mathbf{S}_i$  by  $\mathbf{S}_{ieq}$ . Clearly  $\mathbf{S}_{ieq}$  depends only on the external coordinates  $z_e$  (actually only on the rotational coordinates). Thus  $\mathbf{S}_{ieq} = \mathbf{S}_{ieq}[z_e]$ . Next let the vibrational coordinates fluctuate at fixed  $z_e$  from their equilibrium values to new values  $y$  and  $z$ . The corresponding fluctuation of  $\mathbf{S}_i$  will be denoted by

$$\delta \mathbf{S}_i[yz] = \mathbf{S}_i - \mathbf{S}_{ieq}[z_e]. \quad (\text{A11})$$

Comparing Eqs. (A10) and (A11) yields the following expression for the coordinate vector  $\mathbf{r}_i$ ,

$$\mathbf{r}_i = \mathbf{R} + \delta \mathbf{S}_i[yz] + \mathbf{S}_{ieq}[z_e]. \quad (\text{A12})$$

However, since the internal coordinates  $y z_i$  are harmonic normal modes one may replace  $\delta \mathbf{S}_i[yz]$  by its linear order expansion in the displacements  $y z_i$  from equilibrium. That is one may rewrite Eq. (A12) as

$$\mathbf{r}_i = \mathbf{R} + \mathbf{S}_{ieq}[z_e] + \left[ \frac{\partial \delta \mathbf{S}_i[yz]}{\partial y} \right]_{y_0 z_0} y + \sum_{\alpha=8(7)}^{3n} \left[ \frac{\partial \delta \mathbf{S}_i[yz]}{\partial z_{i\alpha}} \right]_{y_0 z_0} z_{i\alpha}. \quad (\text{A13})$$

Comparison of Eqs. (A8) and (A13) immediately proves Eq. (A9).

It is additionally clear that the corresponding transformation coefficients  $\mu^{i\alpha}(r)$ ,  $\alpha = 8(7), \dots, 3n$  of the other internal coordinates  $z_i$  also depend only on the external coordinates  $z_e$  (actually only on the rotational coordinates).

## APPENDIX B: MASS MATRIX AND TRANSFORMATION COEFFICIENTS OF A DIATOMIC SOLUTE

In this Appendix we develop formulas for the mass matrix  $m[yz]$  and transformation coefficients  $\mu^{i\alpha}(r)$  for the diatomic solute. We will use the notation introduced at the beginning of Sec. III.

The formulas for the mass matrix and transformation coefficients are developed for a generalized coordinate system  $x = yz$  which is based on the center of mass  $\mathbf{R} = (m_1 \mathbf{r}_1 + m_2 \mathbf{r}_2)/(m_1 + m_2)$  and relative  $\mathbf{p} = \mathbf{r}_2 - \mathbf{r}_1$  coordinates of the solute molecule. We will, in particular, describe  $\mathbf{R}$  in terms of its Cartesian components  $X, Y, Z$  and  $\mathbf{p}$  in terms of its spherical polar components  $\rho, \theta, \phi$ . Then the explicit coordinate  $y$  will be defined, using the notation of Eqs. (A3) and (A4) as

$$y = x_1 = \mu^{1/2}[\rho - \rho_{eq}]. \quad (\text{B1})$$

(This definition guarantees that  $y_0 = 0$  and that the mass factor associated with  $y$  is unity in accord with the notational conventions<sup>22</sup> used in the main body of this paper.) The explicit coordinates  $z$  will be taken as

$$z = z_e = \begin{pmatrix} x_2 \\ x_3 \\ x_4 \\ x_5 \\ x_6 \end{pmatrix} = \begin{pmatrix} X \\ Y \\ Z \\ \theta \\ \phi \end{pmatrix}. \quad (\text{B2})$$

The solute kinetic energy  $T_U$  may be readily constructed in terms of these generalized coordinates as

$$T_U = \frac{1}{2} M [\dot{X}^2 + \dot{Y}^2 + \dot{Z}^2] + \frac{1}{2} [\dot{y}^2 + \mu(\rho_{eq} + \mu^{-1/2}y)^2 (\dot{\theta}^2 + \sin^2 \theta \dot{\phi}^2)]. \quad (\text{B3})$$

Since  $T_U = \frac{1}{2} \dot{p}_x^T [m[yz]]^{-1} \dot{p}_x = \frac{1}{2} \dot{x}^T m[yz] \dot{x}$ , Eq. (B3) yields the following exact form for the mass matrix:

$$m_{yy}[yz] = 1, \quad (\text{B4a})$$

$$m_{yz}[yz] = m_{zy}[yz] = 0, \quad (\text{B4b})$$

$$m_{zz}[yz] = m_{zz^*}[yz]$$

$$= \begin{pmatrix} M & & & & \\ & M & & & \\ & & M & & \\ & & & \mu[\rho_{eq} + \mu^{-1/2}y]^2 & \\ & & & & \mu[\rho_{eq} + \mu^{-1/2}y]^2 \sin^2 \theta \end{pmatrix}. \quad (\text{B4c})$$



In particular  $m_{z,z_e}[y_0 z_0]$  is given by

$$m_{z,z_e}[y_0 z_0] = \begin{pmatrix} M & & & & & \\ & M & & & & \\ & & M & & & \\ & & & \mu \rho_{eq}^2 & & \\ & & & & \mu \rho_{eq}^2 \sin^2 \theta & \\ & & & & & \mu \rho_{eq}^2 \sin^2 \theta \end{pmatrix}. \quad (\text{B5})$$

The transformation coefficients  $\mu^{ia}(r)$  may be constructed using the following relationships between the solute Cartesian coordinates  $\mathbf{r}_1 = (r_1, r_2, r_3)$  and  $\mathbf{r}_2 = (r_4, r_5, r_6)$  and the generalized coordinates  $(X, Y, Z)$  and  $(\rho, \theta, \phi)$ :

$$\begin{aligned} r_1 &= X - \frac{m_2}{M} \rho \sin \theta \cos \phi, \\ r_2 &= Y - \frac{m_2}{M} \rho \sin \theta \sin \phi, \\ r_3 &= Z - \frac{m_2}{M} \rho \cos \theta, \end{aligned} \quad (\text{B6a})$$

$$\begin{aligned} r_4 &= X + \frac{m_1}{M} \rho \sin \theta \cos \phi, \\ r_5 &= Y + \frac{m_1}{M} \rho \sin \theta \sin \phi, \\ r_6 &= Z + \frac{m_1}{M} \rho \cos \theta. \end{aligned} \quad (\text{B6b})$$

The transformation coefficients may be constructed from Eqs. (A1), (A6), (B1), (B2), and (B6). This yields

$$\mu^{11}(z_e) = - \left[ \frac{m_2}{m_1 M} \right]^{1/2} \sin \theta \cos \phi = - \left[ \frac{m_2}{m_1} \right] \mu^{41}(z_e), \quad (\text{B7a})$$

$$\mu^{21}(z_e) = - \left[ \frac{m_2}{m_1 M} \right]^{1/2} \sin \theta \sin \phi = - \left[ \frac{m_2}{m_1} \right] \mu^{51}(z_e), \quad (\text{B7b})$$

$$\mu^{31}(z_e) = - \left[ \frac{m_2}{m_1 M} \right]^{1/2} \cos \theta = - \left[ \frac{m_2}{m_1} \right] \mu^{61}(z_e), \quad (\text{B7c})$$

$$\mu^{12}(r) = \mu^{42}(r) = 1, \quad (\text{B8a})$$

$$\mu^{23}(r) = \mu^{53}(r) = 1, \quad (\text{B8b})$$

$$\mu^{34}(r) = \mu^{64}(r) = 1, \quad (\text{B8c})$$

$$\mu^{22}(r) = \mu^{52}(r) = \mu^{32}(r) = \mu^{62}(r) = 0, \quad (\text{B9a})$$

$$\mu^{13}(r) = \mu^{43}(r) = \mu^{33}(r) = \mu^{63}(r) = 0, \quad (\text{B9b})$$

$$\mu^{14}(r) = \mu^{44}(r) = \mu^{24}(r) = \mu^{54}(r) = 0, \quad (\text{B9c})$$

$$\mu^{15}(r) = - \left[ \frac{m_2}{M} \right] \rho \cos \theta \cos \phi = - \left[ \frac{m_2}{m_1} \right] \mu^{45}(r), \quad (\text{B10a})$$

$$\mu^{25}(r) = - \left[ \frac{m_2}{M} \right] \rho \cos \theta \sin \phi = - \left[ \frac{m_2}{m_1} \right] \mu^{55}(r), \quad (\text{B10b})$$

$$\mu^{35}(r) = \left[ \frac{m_2}{M} \right] \rho \sin \theta = - \left[ \frac{m_2}{m_1} \right] \mu^{65}(r), \quad (\text{B10c})$$

$$\mu^{16}(r) = \frac{m_2}{M} \rho \sin \theta \sin \phi = - \left[ \frac{m_2}{m_1} \right] \mu^{46}(r), \quad (\text{B11a})$$

$$\mu^{56}(r) = - \frac{m_2}{M} \rho \sin \theta \cos \phi = - \left[ \frac{m_2}{m_1} \right] \mu^{56}(r), \quad (\text{B11b})$$

$$\mu^{36}(r) = \mu^{66}(r) = 0. \quad (\text{B11c})$$

Notice that the transformation coefficients  $\mu^{a1}$ , Eq. (B7), for the internal coordinate  $y$  depend only on the external coordinates  $z_e$  (in fact, only on the rotational coordinates  $\theta, \phi$ ) in accord with the general proof given in Appendix A.

### APPENDIX C: DERIVATION OF THE RESULTS OF SEC. III

In this Appendix, we specialize the results developed in Secs. VI–VIII to diatomic solutes. We also work out (see discussion at the end of Sec. VIII) the explicit form for  $\langle \mathcal{F}^2 \rangle_{0i}$  for the special case of diatomic solutes. The analysis of this Appendix provides the derivation of the results, Eqs. (3.2)–(3.17), quoted without proof in Sec. III.

The formulas developed here apply for the choice of explicit and implicit coordinates  $y$  and  $z_e$  defined in Eqs. (B1) and (B2). The analysis will be performed in the body-fixed coordinate system described in Sec. III. This choice of coordinate system leads to substantial simplification. For example, in this coordinate system the spherical polar angles  $\theta$  and  $\phi$  [see Eq. (B2)] take the values  $\theta = \phi = 0$  and as a result the transformation coefficients given in Eqs. (B7)–(B11) greatly simplify. Such simplifications will be utilized without further comment in this Appendix.

#### 1. Construction of $\omega_{cf}^2$

We begin with an evaluation of the centripetal force contribution  $\omega_{cf}$  to the solute normal mode vibrational frequency  $\omega_l$ . We first specialize the expression for the mean centripetal force  $\langle F_{cf} \rangle_0$ , given in Eq. (6.5), to diatomic solutes. Using Eq. (B4c) for the mass matrix  $m_{z,z_e}[y_0 z_0]$ , it follows immediately that

$$\begin{aligned} \text{tr} [m_{z,z_e}[y_0 z_0] m_{z,z_e}^{-1}[y_0 z_0]] \\ = 3 + 2\rho_{eq}^2 [\rho_{eq} + \mu^{-1/2} y]^{-2}. \end{aligned}$$

Using the above equation in Eq. (6.5) yields the following form for  $\langle F_{cf} \rangle_0$ :

$$\begin{aligned} \langle F_{cf} \rangle_0 = \frac{1}{2} k_B T \left[ - \frac{\partial}{\partial y} [3 + 2\rho_{eq}^2 \right. \\ \left. \times [\rho_{eq} + \mu^{-1/2} y]^{-2}] \right]. \end{aligned} \quad (\text{C1})$$

Comparison of Eqs. (C1) and (6.9) yields the result for  $\omega_{cf}^2$  quoted in Eq. (3.2).

#### 2. Construction of $\omega_e^2$

We next construct the contribution  $\omega_e$ , arising from the instantaneous cage restoring force  $\langle \partial \mathcal{F} / \partial y \rangle_0 y$ , to  $\omega_l$ . We begin with Eq. (2.7),  $\omega_e^2 = - \langle \partial \mathcal{F} / \partial y \rangle_0$ . Comparing this result with Eq. (7.8) specialized to the case of diatomic solutes yields

$$\omega_e^2 = - \sum_{i=1}^2 \mu^{i1}(z_e) \mu^{i1}(z_e) : \left\langle \frac{\partial \mathcal{F}_{r_i}}{\partial r_i} \right\rangle_{\rho_{eq}}, \quad (\text{C2})$$

where we have used the fact that the quantity  $\langle \partial \mathcal{F} / \partial r_i \rangle_{yz}$  depends only on the internuclear separation  $\rho$  for diatomic solutes.

Comparing Eqs. (7.8), (7.12), and (C2) yields the following result for  $\langle \partial \mathcal{F}_{r_i} / \partial \mathbf{r}_i \rangle_\rho$ :

$$\left\langle \frac{\partial \mathcal{F}_{r_i}}{\partial \mathbf{r}_i} \right\rangle_\rho = - \int d\mathbf{q} \left[ \mathbf{e}_{y_i} \mathbf{e}_{y_i} \frac{d^2 u_i(y_i)}{dy_i^2} + \frac{[1 - \mathbf{e}_{y_i} \mathbf{e}_{y_i}]}{y_i} \frac{du_i(y_i)}{dy_i} \right] \rho^{(3)}[\rho; \mathbf{q}]. \quad (\text{C3})$$

Moreover, in the body-fixed coordinate system of Sec. III, it is straightforward to show that  $\langle \partial \mathcal{F}_{r_i} / \partial \mathbf{r}_i \rangle_\rho$  has the following Cartesian tensor form:

$$\left\langle \frac{\partial \mathcal{F}_{r_i}}{\partial \mathbf{r}_i} \right\rangle_\rho = \left[ \left\langle \frac{\partial \mathcal{F}_{r_i}}{\partial \mathbf{r}_i} \right\rangle_\rho \right]_{\parallel} \mathbf{e}_z \mathbf{e}_z + \left[ \left\langle \frac{\partial \mathcal{F}_{r_i}}{\partial \mathbf{r}_i} \right\rangle_\rho \right]_{\perp} [\mathbf{e}_x \mathbf{e}_x + \mathbf{e}_y \mathbf{e}_y], \quad (\text{C4})$$

where from Eq. (C3) it follows that

$$\left[ \left\langle \frac{\partial \mathcal{F}_{r_i}}{\partial \mathbf{r}_i} \right\rangle_\rho \right]_{\parallel} = \int \rho^{(3)}[\rho; \mathbf{q}] \left[ (\mathbf{e}_z \cdot \mathbf{e}_{y_i})^2 \frac{d^2 u_i(y_i)}{dy_i^2} + [1 - (\mathbf{e}_z \cdot \mathbf{e}_{y_i})^2] y_i^{-1} \frac{du_i(y_i)}{dy_i} \right] d\mathbf{q} \quad (\text{C5a})$$

and

$$\left[ \left\langle \frac{\partial \mathcal{F}_{r_i}}{\partial \mathbf{r}_i} \right\rangle_\rho \right]_{\perp} = \int \rho^{(3)}[\rho; \mathbf{q}] \left[ (\mathbf{e}_x \cdot \mathbf{e}_{y_i})^2 \frac{d^2 u_i(y_i)}{dy_i^2} + [1 - (\mathbf{e}_x \cdot \mathbf{e}_{y_i})^2] y_i^{-1} \frac{du_i(y_i)}{dy_i} \right] d\mathbf{q}. \quad (\text{C5b})$$

Note  $\mathbf{e}_x, \mathbf{e}_y$ , and  $\mathbf{e}_z$  are the unit vectors of the body-fixed system.

Combining Eqs. (C2) and (C4) and evaluating the transformation coefficients  $\mu^i(z_e)$ , given in Eq. (B7), in the body-fixed frame then yields Eq. (3.3) for  $\omega_e^2$ . Thus we have proven Eq. (3.3) and, additionally shown that  $\omega_e^2$  depends only on  $[\langle \partial \mathcal{F}_{r_i} / \partial \mathbf{r}_i \rangle_\rho]_{\parallel}$ . Finally evaluating Eq. (C5a) in the body-fixed frame using the spherical polar representation  $\mathbf{q} = (q, \theta, \phi)$  immediately yields Eq. (3.4). Thus, Eqs. (3.3) and (3.4) for  $\omega_e^2$  have been established.

We next turn to the Gaussian model evaluation of  $\langle \mathcal{F}(t) \mathcal{F} \rangle_0$  for diatomic solutes and hence the proof of Eqs. (3.5)–(3.17). This evaluation requires the development of expressions for  $\langle \mathcal{F}^2 \rangle_0$ ,  $\langle \mathcal{F}^2 \rangle_{0d}$ , and  $\langle \mathcal{F}^2 \rangle_{0i}$ . Equation (3.5) for  $\langle \mathcal{F}^2 \rangle_0$  follows immediately from Eq. (8.3). Moreover the verification of Eqs. (3.7) and (3.8) for  $\langle \mathcal{F}^2 \rangle_{0d}$  follows from Eq. (8.9) via a calculation which parallels the proof just presented for Eqs. (3.3) and (3.4). Thus we will confine ourselves here to the derivation of Eqs. (3.9)–(3.17) for  $\langle \mathcal{F}^2 \rangle_{0i}$ .

### 3. Construction of $\langle \mathcal{F}^2 \rangle_{0i}$

Our starting point is Eq. (8.8). The mass matrix  $m_{z,ze}[yz]$  is diagonal for diatomic solutes [Eq. (B4c)], thus Eq. (8.8) simplifies to

$$\langle \mathcal{F}^2 \rangle_{0i} = k_B T \sum_{\alpha=2}^6 [m_{z,ze}^{-1}[y_0 z_0]]_{\alpha\alpha} \left\langle \frac{\partial \mathcal{F}}{\partial z_{e\alpha}} \frac{\partial \mathcal{F}}{\partial z_{e\alpha}} \right\rangle_{y_0 z_0} \quad (\text{C6})$$

Using Eqs. (B2) and (B5), Eq. (C6) may be rewritten as  $\langle \mathcal{F}^2 \rangle_{0i}$

$$= \frac{k_B T}{M} \left[ \left\langle \left[ \frac{\partial \mathcal{F}}{\partial X} \right]^2 \right\rangle_{y_0 z_0} + \left\langle \left[ \frac{\partial \mathcal{F}}{\partial Y} \right]^2 \right\rangle_{y_0 z_0} + \left\langle \left[ \frac{\partial \mathcal{F}}{\partial Z} \right]^2 \right\rangle_{y_0 z_0} + \frac{k_B T}{\mu \rho_{eq}^2} \left[ \left\langle \left[ \frac{\partial \mathcal{F}}{\partial \theta} \right]^2 \right\rangle_{y_0 z_0} + \sin^{-2} \theta \left\langle \left[ \frac{\partial \mathcal{F}}{\partial \phi} \right]^2 \right\rangle_{y_0 z_0} \right]. \quad (\text{C7})$$

A method of construction of the individual terms in Eq. (C7) will be described below. Using this method one may show

$$\left\langle \left[ \frac{\partial \mathcal{F}}{\partial Y} \right]^2 \right\rangle_{y_0 z_0} = \left\langle \left[ \frac{\partial \mathcal{F}}{\partial X} \right]^2 \right\rangle_{y_0 z_0} \quad (\text{C8})$$

and

$$\left\langle \left[ \frac{\partial \mathcal{F}}{\partial \phi} \right]^2 \right\rangle_{y_0 z_0} = \sin^2 \theta \left\langle \left[ \frac{\partial \mathcal{F}}{\partial \theta} \right]^2 \right\rangle_{y_0 z_0} \quad (\text{C9})$$

Equation (3.9) may be proven by comparison of Eqs. (C7)–(C9).

We next turn to the construction of the individual terms in Eq. (3.9). We will illustrate the general procedure for the term proportional to  $\langle [\partial \mathcal{F} / \partial X]^2 \rangle_{y_0 z_0}$ . We begin with the expansion

$$\frac{\partial \mathcal{F}}{\partial z_{e\alpha}} = \sum_{i=1}^2 \left[ \frac{\partial \mu^i(z_e)}{\partial z_{e\alpha}} \cdot \mathcal{F}_{r_i} + \mu^i(z_e) \cdot \frac{\partial \mathcal{F}_{r_i}}{\partial z_{e\alpha}} \right] \quad (\text{C10a})$$

which follows from Eq. (7.3). Using Eq. (A5) and the fact that

$$\frac{\partial \mathcal{F}_{r_i}}{\partial \mathbf{r}_j} = \delta_{ij} \frac{\partial \mathcal{F}_{r_i}}{\partial \mathbf{r}_i}$$

for pairwise additive forces, Eq. (C10a) may be rewritten as

$$\frac{\partial \mathcal{F}}{\partial z_{e\alpha}} = \sum_{i=1}^2 \left[ \frac{\partial \mu^i(z_e)}{\partial z_{e\alpha}} \cdot \mathcal{F}_{r_i} + \mu^i(z_e) \cdot \frac{\partial \mathcal{F}_{r_i}}{\partial \mathbf{r}_i} \cdot \mu^i(z_e) \right]. \quad (\text{C10b})$$

Evaluating in Eq. (C10b) for  $z_{e\alpha} = X$  yields

$$\frac{\partial \mathcal{F}}{\partial X} = \sum_{i=1}^2 \left[ \frac{\partial \mu^i(z_e)}{\partial X} \cdot \mathcal{F}_{r_i} + \mu^i(r) \cdot \frac{\partial \mathcal{F}_{r_i}}{\partial \mathbf{r}_i} \cdot \mu^i(z_e) \right]. \quad (\text{C11})$$

Using Eqs. (B7)–(B9) and specializing to the present choice of coordinate system [ $\theta = \phi = 0$ ], Eq. (C11) may be rewritten as

$$\frac{\partial \mathcal{F}}{\partial X} = \sum_{i=1}^2 A_i \mathbf{e}_x \cdot \frac{\partial \mathcal{F}_{r_i}}{\partial \mathbf{r}_i} \cdot \mathbf{e}_z, \quad (\text{C12})$$

where

$$A_1 = - \left[ \frac{m_2}{m_1 M} \right]^{1/2} \quad \text{and} \quad A_2 = + \left[ \frac{m_1}{m_2 M} \right]^{1/2}. \quad (\text{C13})$$

From Eq. (C12), it follows that

$$\left\langle \left[ \frac{\partial \mathcal{F}}{\partial X} \right]^2 \right\rangle_{y_0 z_0} = \sum_{i=1}^2 A_i^2 \left\langle \left[ \mathbf{e}_x \frac{\partial \mathcal{F}_{r_i}}{\partial \mathbf{r}_i} \cdot \mathbf{e}_z \right]^2 \right\rangle_{y_0 z_0}. \quad (\text{C14})$$

In deriving Eq. (C14) we have neglected off-diagonal ( $i \neq j$ ) contributions to  $\langle [\partial \mathcal{F} / \partial X]^2 \rangle_{y_0 z_0}$ . This neglect has been justified by detailed calculations presented in Sec. IX. Following the procedure used to derive Eq. (7.10) from Eq. (7.8), Eq. (C14) may be rewritten as

$$\begin{aligned} \left\langle \left[ \frac{\partial \mathcal{F}}{\partial X} \right]^2 \right\rangle_{y_0 z_0} &= M^{-1} \left[ \left( \frac{m_2}{m_1} \right) [I_{1x} + J_{1x}] \right. \\ &\quad \left. + \left( \frac{m_1}{m_2} \right) [I_{2x} + J_{2x}] \right], \end{aligned} \quad (\text{C15})$$

where

$$I_{ix} = \int \left[ \mathbf{e}_x \frac{\partial^2 u_i[\mathbf{q}\mathbf{r}_i]}{\partial \mathbf{r}_i \partial \mathbf{r}_i} \cdot \mathbf{e}_z \right]^2 \rho^{(3)}[\rho_{\text{eq}}; \mathbf{q}] d\mathbf{q} \quad (\text{C16})$$

and where

$$\begin{aligned} J_{ix} &= \int \left[ \mathbf{e}_x \frac{\partial^2 u_i[\mathbf{q}\mathbf{r}_i]}{\partial \mathbf{r}_i \partial \mathbf{r}_i} \cdot \mathbf{e}_z \right] \\ &\quad \times \left[ \mathbf{e}_x \frac{\partial^2 u_i[\mathbf{q}'\mathbf{r}_i]}{\partial \mathbf{r}_i \partial \mathbf{r}_i} \cdot \mathbf{e}_z \right] \rho^{(4)}[\rho_{\text{eq}}; \mathbf{q}\mathbf{q}'] d\mathbf{q} d\mathbf{q}'. \end{aligned} \quad (\text{C17})$$

Note that  $\rho^{(4)}[\rho; \mathbf{q}_1 \mathbf{q}_2]$  is defined by [cf. Eq. (7.9)]

$$\rho^{(4)}[\rho; \mathbf{q}_1 \mathbf{q}_2] = N_s^2 \int d\mathbf{p}_q d\mathbf{q}_3 \cdots d\mathbf{q}_N f_0[p_q q]. \quad (\text{C18})$$

We will next make the following approximation for  $\rho^{(4)}[\rho; \mathbf{q}\mathbf{q}']$ ,

$$\rho^{(4)}[\rho; \mathbf{q}\mathbf{q}'] \doteq \rho^{(3)}[\rho; \mathbf{q}] \rho^{(3)}[\rho; \mathbf{q}']. \quad (\text{C19})$$

Given Eq. (C19),  $J_{ix}$  may be approximately expressed as

$$J_{ix} \doteq \left[ \int \left[ \mathbf{e}_x \frac{\partial^2 u_i[\mathbf{q}\mathbf{r}_i]}{\partial \mathbf{r}_i \partial \mathbf{r}_i} \cdot \mathbf{e}_z \right] \rho^{(3)}[\rho_{\text{eq}}; \mathbf{q}] d\mathbf{q} \right]^2. \quad (\text{C20})$$

Using Eq. (7.11), one has that

$$\mathbf{e}_x \cdot \left[ \frac{\partial^2 u_i[\mathbf{q}\mathbf{r}_i]}{\partial \mathbf{r}_i \partial \mathbf{r}_i} \right] \cdot \mathbf{e}_z = [\mathbf{e}_x \cdot \mathbf{e}_{y_i}] [\mathbf{e}_z \cdot \mathbf{e}_{y_i}] U_i[y_i], \quad (\text{C21})$$

where  $U[y_i]$  is defined in Eq. (3.17). Finally in the body-fixed coordinate system

$$\mathbf{e}_{y_i} \equiv y_i^{-1} \left[ \mathbf{q} - (-)^i \frac{\mu}{m_i} \rho \mathbf{e}_z \right]. \quad (\text{C22})$$

Thus

$$\mathbf{e}_x \cdot \mathbf{e}_{y_i} = y_i^{-1} q \sin \theta \cos \phi \quad (\text{C23})$$

and

$$\mathbf{e}_z \cdot \mathbf{e}_{y_i} = y_i^{-1} \left[ q \cos \theta - (-)^i \frac{\mu}{m_i} \rho \right], \quad (\text{C24})$$

where  $\theta$  and  $\phi$  are the spherical polar angles of  $\mathbf{q}$ .

Combining the above equations yields  $J_{ix} = 0$  and also Eq. (3.12) for  $I_{ix}$ . Thus it is evident from Eq. (C15) that we have proven Eqs. (3.10a) and (3.12). The results presented in Sec. III for the remaining contributions to  $\langle \dot{\mathcal{F}}^2 \rangle_{0i}$  may be

proven in a similar manner. Consequently, we will omit the details of the derivations here.

Thus the proof of the results of Sec. III is completed.

<sup>1</sup>For recent reviews of condensed phase vibrational relaxation see, for example, (a) A. Lauberau and W. Kaiser, *Rev. Mod. Phys.* **50**, 608 (1978); (b) D. W. Oxtoby, *Adv. Chem. Phys.* **47**, 487 (1981); (c) D. W. Oxtoby, *Annu. Rev. Phys. Chem.* **32**, 77 (1981); (d) J. Chesnoy and G. M. Gale, *Ann. Rev. Fr.* **9**, 893 (1984).

<sup>2</sup>(a) For a rigorous development of our theory of liquid solution chemical reaction dynamics based on the principles of nonequilibrium statistical mechanics see S. A. Adelman, *Adv. Chem. Phys.* **53**, 61 (1983). (b) For a brief description of the physical concepts see S. A. Adelman, *J. Stat. Phys.* **42**, 37 (1986); (c) For a more detailed nonmathematical description see S. A. Adelman, *Rev. Chem. Intermed.* **8**, 321 (1987).

<sup>3</sup>R. H. Stote and S. A. Adelman, *J. Chem. Phys.* **88**, 4415 (1988).

<sup>4</sup>M. E. Paige, D. J. Russell, and C. B. Harris, *J. Chem. Phys.* **85**, 3669 (1986).

<sup>5</sup>S. Nordholm, D. L. Jolly, and B. C. Freasier, *Chem. Phys. Lett.* **25**, 361 (1977).

<sup>6</sup>C. L. Brooks III, M. W. Balk, and S. A. Adelman, *J. Chem. Phys.* **79**, 784 (1983); M. W. Balk, C. L. Brooks III, and S. A. Adelman, *ibid.* **79**, 804 (1983).

<sup>7</sup>For a development of integral equation theory see *Classical Fluids*, edited by H. L. Frisch and J. L. Lebowitz (Benjamin, New York, 1964).

<sup>8</sup>The numerical algorithm which we use to solve the Percus-Yevick equation is given in M. W. Balk, *Mol. Phys.* **46**, 577 (1982).

<sup>9</sup>H. Metiu, D. W. Oxtoby, and K. F. Freed, *Phys. Rev. A* **15**, 361 (1977). Also see Eq. (5.7) of Ref. 1(b).

<sup>10</sup>S. A. Adelman (unpublished calculations).

<sup>11</sup>(a) S. A. Adelman, *Int. J. Quantum Chem. Symp.* **21**, 1991 (1987); (b) J. Chem. Phys. **81**, 2776 (1984).

<sup>12</sup>S. A. Adelman and M. W. Balk, *J. Chem. Phys.* **82**, 4641 (1985); **84**, 1752 (1986).

<sup>13</sup>The work of Ref. 11 was motivated in part by developments in gas-phase chemical reaction theory due to Marcus and Miller. See, for example, R. A. Marcus, *J. Chem. Phys.* **49**, 2617 (1968); W. H. Miller, *ibid.* **72**, 99 (1980).

<sup>14</sup>For related developments in the context of liquid state reaction theory see, for example, R. F. Grote and J. T. Hynes, *J. Chem. Phys.* **74**, 4465 (1981); **77**, 3736 (1982); J. L. Skinner and P. G. Wolynes, *ibid.* **69**, 2143 (1978); **72**, 4193 (1980); R. O. Rosenberg, B. J. Berne, and D. Chandler, *Chem. Phys. Lett.* **75**, 162 (1980); B. J. Berne, J. L. Skinner, and P. G. Wolynes, *J. Chem. Phys.* **73**, 4314 (1980); B. Carmeli and A. Nitzan, *Phys. Rev. Lett.* **49**, 423 (1982); B. Carmeli and A. Nitzan, *J. Chem. Phys.* **80**, 3596 (1984); B. Bagchi and D. W. Oxtoby, *ibid.* **78**, 2735 (1983); B. Bagchi and D. W. Oxtoby, *ibid.* **78**, 2735 (1983); R. F. Grote and J. T. Hynes, *ibid.* **74**, 4465 (1981); J. T. Hynes, *Annu. Rev. Phys. Chem.* **36**, 573 (1984); *J. Stat. Phys.* **42**, 149 (1986).

<sup>15</sup>This statement may have to be qualified for cases for which there is strong resonance overlap between the chemically important solute frequencies and the solvent vibrational frequencies. Also as barrier heights (both in the forward and reverse directions), solute frequencies, cage strength (as measured by  $\langle \partial \mathcal{F} / \partial y \rangle_0$ ), and relevant solvent relaxation times decrease liquid state chemical dynamics shades smoothly into thermal solute dynamics.

<sup>16</sup>L. Onsager and S. Machlup, *Phys. Rev.* **91**, 1505 (1953); S. Machlup and L. Onsager, *ibid.* **91**, 1512 (1953).

<sup>17</sup>R. Kubo, *J. Phys. Soc. Jpn.* **12**, 570 (1957); *Rep. Prog. Theor. Phys.* **29**, 235 (1966).

<sup>18</sup>H. Mori, *Prog. Theor. Phys.* **33**, 423 (1965); **34**, 399 (1965).

<sup>19</sup>See for example, N. Turro, *Modern Molecular Photochemistry* (Benjamin/Cummings, Menlo Park, 1978). T. H. Lowry and K. S. Richardson, *Mechanism and Theory in Organic Chemistry* (Harper and Row, New York, 1981).

<sup>20</sup>See for example, F. H. Stillinger and A. Rahman, *J. Chem. Phys.* **57**, 1281 (1972); M. A. Wilson, A. Pohorille, and L. R. Pratt, *ibid.* **83**, 5832 (1985).

<sup>21</sup>J. P. Bergsma, B. J. Gertner, K. R. Wilson, and J. T. Hynes, *J. Chem. Phys.* **86**, 1356 (1987).

<sup>22</sup>We define the harmonic normal mode coordinate  $y$  so that its equilibrium value  $y = y_0 = 0$  and so that its mass factor is unity. This is the convention used in *Molecular Vibrations, The Theory of Infrared and Raman Spectra*, edited by E. B. Wilson Jr., J. C. Decius, and P. C. Cross (Dover, New

York, 1955).

<sup>23</sup>Equation (2.10) is, in fact, the velocity autocorrelation function of a Langevin oscillator of frequency  $\omega_l$  and friction coefficient  $\beta(\omega_l)$  in the limit of extreme underdamping. See, for example, S. Chandrasekhar, *Rev. Mod. Phys.* **15**, 1 (1943).

<sup>24</sup>S. A. Adelman (unpublished calculations).

<sup>25</sup>In enforcing the constraint of the partial clamping model in molecular

dynamics simulations we employ the SHAKE algorithm. See, for example, J. P. Ryckaert, G. Ciccotti, and H. J. C. Berendsen, *J. Comput. Phys.* **23**, 327 (1977). In our MD simulations, we used 64 particles in the primary simulation box.

<sup>26</sup>The limitations of the superposition approximation are discussed in *Theory of Simple Liquids*, edited by J. P. Hansen and J. R. McDonald (Academic, New York, 1976).