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Vibrational–translational–rotational energy transfer**

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Theory of vibrational energy relaxation in liquids: Vibrational-translational-rotational energy transfer

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The concepts underlying a theoretical treatment of the vibrational energy relaxation (VER) time T_1 of a solute normal mode in a molecular solvent are summarized, and results for T_1 , valid for VER processes mediated by vibrational-translational-rotational energy transfer, obtained from this treatment are presented. These results are based on the formula $T_1 = \beta_{\text{TR}}^{-1}(\omega_l)$, where $\beta_{\text{TR}}(\omega)$ is the translational-rotational branch of the friction kernel of the normal mode and where ω_l is its liquid phase frequency. $\beta_{\text{TR}}(\omega)$ is evaluated as the cosine transform of the autocorrelation function $\langle \mathcal{F}(t) \mathcal{F} \rangle_0$ of the fluctuating generalized force exerted by the solvent on the solute normal mode coordinate conditional that this coordinate is fixed at its equilibrium value and that all solvent molecules are constrained to have their equilibrium geometries. The Gaussian model is utilized to evaluate $\langle \mathcal{F}(t) \mathcal{F} \rangle_0$ and molecular level expressions for ω_l and for the Gaussian model parameters are presented for the infinitely dilute diatomic solution. The expressions involve site density integrals over the coordinates of a single solvent atomic site and over the coordinates of a pair of solvent atomic sites located on the same molecule. The results permit the evaluation of T_1 in terms of the atomic masses and gas phase bondlengths of the solute and the solvent molecules, the solute gas phase vibrational frequency, the solute-solvent site-site interaction potentials, and specified equilibrium site-site pair correlation functions of the liquid solution.

I. INTRODUCTION

Vibrational energy relaxation (VER) in liquids,¹⁻⁸ in part because of its fundamental significance for solution chemical dynamics,^{7,8(a)} is a process which continues to be of interest.^{7(b),8(b)} Elsewhere we have presented a molecular theory of liquid phase VER, based on our general approach to problems of chemical dynamics in liquids,⁹⁻¹⁸ valid for the special case of solute relaxation in a monatomic solvent.¹⁵ This monatomic solvent theory was recently extended to molecular solvents.¹⁸ This extended theory permits one to deal realistically with the problems arising from nonspherical solvent molecule geometries and from the possibility of energy transfer to the rotational and vibrational degrees of freedom of the solvent. The main results of the new theory are expressions for the vibrational-translational-rotational (VTR) and vibrational-vibrational (VV) contributions to the relaxation time T_1 . These expressions permit evaluation of both contributions to T_1 from molecular properties, interaction potentials, and equilibrium site-site pair correlation functions. The expressions thus yield a first-principles evaluation of the VER rate constant which permits its numerical study^{15(c)} as a function of system and thermodynamic state.

In the present paper and its companion, Ref. 17, we summarize these results for T_1 , giving the expressions for the VTR contribution here and for the VV contribution in Ref. 17. The expressions which we present are restricted to

infinitely dilute diatomic solutions. The methods used to derive these expressions, however, are applicable to more complex molecular fluids.

These methods of derivation will be described in more detail later. For the present we note that our work is based on the formulation of liquid phase VER outlined in Ref. 15(a). Within this formulation, VER arises from dissipation processes due to the high frequency friction exerted by the solvent on the relaxing solute normal mode. Specifically, one obtains a relationship, Eq. (1.1) (Ref. 19), which determines the vibrational lifetime T_1 from the high frequency friction $\beta(\omega_l)$. Our molecular expressions for T_1 are obtained from Eq. (1.1) by explicitly evaluating $\beta(\omega_l)$. This evaluation is made using a new statistical mechanical methodology^{9,15,18} for determining friction at the molecular level, i.e., from a first-principles analysis of the dynamics of the liquid.

Before proceeding further we discuss, in three points, the significance of the present work and place it in context in the literature.

(1) The present theory, whether implemented analytically or by molecular dynamics simulation,^{8(b),15(a)} provides the first practicable method for the rigorous *ab initio* evaluation of VER rates in liquids.

Specifically, while other rigorous and tractable treatments of VER exist,²⁰ these unlike our theory are restricted to the ideal gas regime. Additionally, while the familiar²⁻⁶ isolated binary collision (IBC) model^{1(b),21} also provides a

practicable treatment of *liquid phase* VER it, unlike our theory, does not yield a first-principles evaluation of T_1 , but rather requires as input the experimental²² gas phase rate constant.

(2) The new molecular level procedures^{9,15,18} mentioned earlier yield a significantly more realistic evaluation of friction than that provided by the continuum dynamics treatments²³ available prior to our work.

These continuum dynamics treatments include hydrodynamic^{23(a)} and dielectric friction^{23(b)} models designed to simulate frictional effects arising, respectively, from solvent translational and solvent rotational motions. Our new molecular friction procedures^{9,15,18} provide an improved evaluation of these transitional-rotational contributions. They, for example, yield expressions for these contributions which depend upon quantities which reflect the microscopic solute-solvent interactions (see Sec. II) rather than upon properties like viscosity and dielectric constant²³ which characterize the macroscopic solvent response. Our procedures also provide an evaluation of the frictional effects arising from solvent vibrational motions. This vibrational friction, which is formulated in Refs. 13 and 14, is beyond the scope of the available continuum treatments. It underlies the VV contribution to T_1 .

We additionally note that our improved procedures for friction^{9,15,18} are necessary for the realistic treatment of rate processes in liquids. This is indicated, for example, by the results of the IBC model^{1(b)} which show the equilibrium solvent structure microscopically near the solute, a factor ignored by the continuum friction treatments,²³ is a critical determinant of the density dependence of T_1 .

(3) The principles underlying the present work are quite general and thus may be applied to yield rate constant expressions, analogous to our molecular level formulas for T_1 , for a wide class of liquid phase kinetic phenomena.

Specifically, the rates of many liquid solution processes are directly controlled by the motion of only a small number of generalized coordinates of the solute molecule, which we will refer to as the "explicit" coordinates. For example, for liquid phase VER, the coordinate of the relaxing solute normal mode is the single explicit coordinate. Conductivity at infinite dilution in a polar solvent^{23(b)} and aqueous S_N2 activated barrier crossing^{16,24} provide two other typical examples. For these processes, the center of mass coordinates of the conducting ion, e.g., SO_4^{2-} , and the solute reaction coordinate²⁵ are, respectively, the explicit coordinates.

Our molecular friction procedures,^{9,15,18} however, are general techniques for evaluating the influence of the solvent on the motion of a (nearly²⁶) arbitrary set of solute generalized coordinates and thus may be applied to yield rate expressions for many processes.

The results presented here and in Ref. 17 are based on the following expression for the VER time T_1 [Refs. 15(a) and (19)]

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

In Eq. (1.1), $\beta(\omega)$ is the friction kernel of the relaxing

solute normal mode, which we evaluate here using Eq. (1.2), and ω_l is the liquid phase frequency of this mode specified in Eq. (2.9). The physical basis of Eq. (1.1) will be described shortly and the assumptions required for its derivation are discussed in Sec. III.

We next turn to the problem of evaluating $\beta(\omega)$. In the present work, we perform this evaluation within our partial clamping model. This model is described in detail in Ref. 14; for the present, we note that it requires the assumption (Sec. III) that the displacements of the relaxing solute mode be restricted to small amplitudes. This restriction permits determination of $\beta(\omega)$ from the linear response of the solvent to these mode displacements,¹⁴ the linear approximation being justified by their assumed small amplitude. This determination yields a result, Eq. (1.2), for $\beta(\omega)$ of the familiar linear response theory²⁷ type. Namely, $\beta(\omega)$ depends on the structure and dynamics of the liquid solution in the *absence* of the displacements, i.e., for the solute mode coordinate fixed at equilibrium. Specifically, one obtains

$$\beta(\omega) = (k_B T)^{-1} \int_0^\infty \langle \tilde{\mathcal{F}}(t) \tilde{\mathcal{F}} \rangle_{0v} \cos \omega t \, dt. \quad (1.2)$$

In Eq. (1.2), $\langle \tilde{\mathcal{F}}(t) \tilde{\mathcal{F}} \rangle_{0v}$ is the autocorrelation function of the fluctuating generalized force $\tilde{\mathcal{F}}[Q] \equiv \mathcal{F}[Q] - \langle \mathcal{F} \rangle_{0v}$ exerted by the solvent on the coordinate of the solute mode conditional that this coordinate is fixed. This prescription for $\beta(\omega)$ may be readily implemented. For example, $\beta(\omega)$ may be evaluated^{8(b),15(a)} from Eq. (1.2) in a constrained molecular dynamics simulation^{8(b),15(a)} in which the coordinate of the relaxing solute mode is kept at its equilibrium value while the remaining degrees of freedom of the solution (both solute and solvent) are allowed to move more freely subject to this single restriction.

We finally note that the fictitious constrained dynamics of the partial clamping model¹⁴ is the analog within the present theory (see Ref. 9) of the fictitious projected dynamics of the Mori²⁸ formalism. It is the relative ease of implementation of constrained dynamics (especially for complex systems) which gives Eq. (1.2) its practical advantage over the Mori²⁸ prescription for the friction kernel.

We next note that $\langle \tilde{\mathcal{F}}(t) \tilde{\mathcal{F}} \rangle_{0v}$ appearing in Eq. (1.2) refers to a *vibrating* solvent. Thus, in the present analytical evaluation of $\langle \tilde{\mathcal{F}}(t) \tilde{\mathcal{F}} \rangle_{0v}$ we must deal with the statistical mechanics of vibrating solvents. This introduces new complications since standard analytical procedures for dealing with liquids composed of vibrating molecules are not available. For *isolated* molecules however, the harmonic oscillator-rigid rotor model provides a useful zeroth order solution to the problem of rotational-vibrational motion. We have in Ref. 13(a) (also see Sec. III), however, presented a generalization of this model to the liquid phase. This generalization reduces the evaluation of time correlation functions of vibrating solvents to the evaluation of rigid solvent ensemble averages. This reduction permits use of available methods²⁹ for rigid molecular liquids to evaluate $\langle \tilde{\mathcal{F}}(t) \tilde{\mathcal{F}} \rangle_{0v}$.

Applying the procedures of Ref. 13(a), yields the fol-

lowing result for $\langle \mathcal{F}(t)\mathcal{F} \rangle_{0v}$ restricted to diatomic solvents

$$\langle \mathcal{F}(t)\mathcal{F} \rangle_{0v} = \langle \mathcal{F}(t)\mathcal{F} \rangle_0 + N_s M_D(t) \cos \omega_D t F(\Omega_D). \quad (1.3)$$

In Eq. (1.3), $\langle \rangle_0$ denotes a rigid solvent equilibrium phase space average conditional that the partial clamping constraint described above is satisfied. Thus, e.g., $\langle \mathcal{F}(t)\mathcal{F} \rangle_0$ is the rigid solvent analogue of $\langle \mathcal{F}(t)\mathcal{F} \rangle_{0v}$. Moreover, N_s is the number of solvent molecules, ω_D and Ω_D are solvent molecule vibrational frequencies discussed in the context of VV energy transfer in Ref. 17, and $F(\Omega) = \frac{1}{2} \hbar \Omega^{-1} \coth(\hbar \Omega / 2k_B T)$ is the mean square mass-weighted displacement of a harmonic oscillator of frequency Ω . Finally $M_D(t)$ is the rigid solvent vibrational force gradient autocorrelation function. It is defined as $M_D(t) = \langle \mathcal{F}_1^{(v)}(t)\mathcal{F}_1^{(v)} \rangle_0$, where $\mathcal{F}_1^{(v)} = (\partial \mathcal{F}[Q]/\partial v_1)$ is the derivative of the generalized force $\mathcal{F}[Q]$ [defined after Eq. 1.2)] with respect to the normal mode coordinate v_1 of a solvent molecule.

Equation (1.3) expresses $\langle \mathcal{F}(t)\mathcal{F} \rangle_{0v}$ as a superposition of a rigid-rotor term $\langle \mathcal{F}(t)\mathcal{F} \rangle_0$, which gives rise to the translational-rotational friction, and a harmonic correction term $\sim M_D(t)$, which gives rise to the vibrational friction. These two types of friction manifest themselves as distinct branches of $\beta(\omega)$, as is evident from Eq. (1.6).

We next develop Eq. (1.6) for $\beta(\omega)$. This development is based on the following simplification. For a relaxing solute normal mode of sufficiently high frequency ω_l , T_1 may usually³⁰ be evaluated from Eq. (1.1) using an approximate form for $\beta(\omega)$ which realistically describes only the asymptotic wings of its branches. These wings of $\beta(\omega)$, however, depend only on the *short-time* parts of $\langle \mathcal{F}(t)\mathcal{F} \rangle_0$ and $M_D(t)$ since the slowly decaying "tails" of these autocorrelation functions (which are difficult to evaluate accurately) contribute negligibly to the wings. The simplest approximations to the short-time parts are, however, provided by the following Gaussian models

$$\langle \mathcal{F}(t)\mathcal{F} \rangle_0 = \langle \mathcal{F}^2 \rangle_0 \exp(-\frac{1}{2} \langle \omega^2 \rangle_{\text{TR}} t^2) \quad (1.4a)$$

and

$$M_D(t) = \langle [\mathcal{F}_1^{(v)}]^2 \rangle_0 \exp(-\frac{1}{2} \langle \omega^2 \rangle_v t^2), \quad (1.4b)$$

where

$$\langle \omega^2 \rangle_{\text{TR}} = \frac{\langle \mathcal{F}^2 \rangle_0}{\langle \mathcal{F}^2 \rangle_0}$$

and

$$\langle \omega^2 \rangle_v = \frac{\langle \dot{\mathcal{F}}_1^{(v)} \dot{\mathcal{F}}_1^{(v)} \rangle_0}{\langle \mathcal{F}_1^{(v)} \mathcal{F}_1^{(v)} \rangle_0}. \quad (1.5)$$

Use of the Gaussian models for evaluation of the wings of $\beta(\omega)$ has a partial theoretical foundation³¹ and also has support (Sec. III) for Lennard-Jones liquids from molecular dynamics simulations. Comparing Eqs. (1.2)–(1.4) then yields the following asymptotic result for $\beta(\omega)$;

$$\begin{aligned} \beta(\omega) = & \frac{\langle \mathcal{F}^2 \rangle_0}{2k_B T} \left(\frac{2\pi}{\langle \omega^2 \rangle_{\text{TR}}} \right)^{1/2} \exp\left(-\frac{1}{2} \frac{\omega^2}{\langle \omega^2 \rangle_{\text{TR}}}\right) \\ & + \frac{F(\Omega_D) N_s \langle \mathcal{F}_1^{(v)} \mathcal{F}_1^{(v)} \rangle_0}{4k_B T} \left(\frac{2\pi}{\langle \omega^2 \rangle_v} \right)^{1/2} \\ & \times \exp\left(-\frac{1}{2} \frac{(\omega - \omega_D)^2}{\langle \omega^2 \rangle_v}\right). \end{aligned} \quad (1.6)$$

Notice within the approximation of Eq. (1.6), $\beta(\omega)$ involves only equilibrium quantities, e.g., $\langle \mathcal{F}^2 \rangle_0$. Thus the Gaussian models eliminate the need for a dynamical calculation to determine $\beta(\omega)$.

The vibrational lifetime T_1 may be evaluated from Eqs. (1.1), (1.5), (1.6), and (2.9) yielding a result which depends on purely equilibrium quantities. This evaluation shows that vibrational relaxation mediated by VTR energy transfer arises from the low frequency translational-rotational branch of $\beta(\omega)$ (Gaussian width $\langle \omega^2 \rangle_{\text{TR}}$) while relaxation mediated by VV energy transfer arises from the high frequency vibrational branch of $\beta(\omega)$ (Gaussian width $\langle \omega^2 \rangle_v$ centered at the solvent molecule vibrational frequency ω_D). From Eqs. (1.1) and (1.6), it is evident that the VER rate and its energy flow pathway dependence are governed by the magnitudes and Gaussian widths of these branches and their degree of resonance overlap with the solute vibrational frequency ω_l .

In this paper we will restrict ourselves to systems for which VV energy transfer is either absent or negligible. For such systems, e.g., pure liquids, we may ignore the vibrational branch of $\beta(\omega)$. Comparing Eqs. (1.1), (1.5), and (1.6) then yields the following result for T_1 valid for VER mediated solely by VTR energy transfer

$$T_1 = \left(\frac{2k_B T}{\langle \mathcal{F}^2 \rangle_0} \right) \left(\frac{\langle \mathcal{F}^2 \rangle_0}{2\pi \langle \mathcal{F}^2 \rangle_0} \right)^{1/2} \exp\left(\frac{1}{2} \frac{\langle \mathcal{F}^2 \rangle_0}{\langle \mathcal{F}^2 \rangle_0} \omega_l^2\right). \quad (1.7)$$

To evaluate T_1 from Eq. (1.7) we require explicit expressions for ω_l^2 , $\langle \mathcal{F}^2 \rangle_0$, and $\langle \mathcal{F}^2 \rangle_0$. In Sec. II and the Appendix we summarize the required expressions and in Sec. III we conclude the paper with a brief discussion which emphasizes the assumptions underlying their derivation. Before proceeding further, however, we first discuss the physical basis of Eq. (1.1), describe some possible applications of our results, and outline their method of derivation.

The physical basis of Eq. (1.1) follows from the principles of our theory⁹⁻¹⁸ of the solvent effect on solute reaction dynamics. This theory explains the solvent effect in terms of thermodynamic restoring forces, which play an enhanced role in reactions.

This enhancement derives from the asymmetric nature of the interactions in the solution, the asymmetry arising because *only* the solute molecules experience the special forces which result from typical³² (e.g., 1 eV activation barrier) gas phase potential energy surfaces. Because of these special forces, the nature of the solute motions which occur in reactions is such that the solvent following of these motions is highly imperfect relative to its following of thermal solute motions. That is, the solvent cannot even

approximately maintain equilibrium with the solute molecules as these molecules change their positions. Rather at any instant, the arrangement of solvent molecules around the solute is likely to be nonrepresentative of the canonical ensemble distribution of arrangements. Thus forces, acting on *both* the solute and the solvent molecules, which attempt to convert these nonrepresentative solute-solvent configurations into configurations more representative of thermodynamic equilibrium play a critical role. These restoring forces dominate the solvent dynamics and determine the solvent effect on the solute dynamics. The reaction dynamics is governed by the total force acting on the solute, which is the sum of the solute restoring force (which at any time depends on the solvent arrangement at that time and hence on the forces which have acted on the solvent) and the force arising from the solute gas phase potential energy surface.

These principles also apply to many nonreactive liquid solution phenomena. For VER, for example, imperfect following holds if^{15(a)} $\omega_l \gg \beta(\omega_l)$. This criterion is typically satisfied for nonresonant energy transfer, i.e., [see Eq. (1.6)] $\omega \gg [\langle \omega^2 \rangle_{\text{TR}}]^{1/2}$ and $|\omega_l - \omega_D| \gg [\langle \omega^2 \rangle_V]^{1/2}$, while for resonant VV processes, i.e., $\omega_l \sim \omega_D$, it requires that the magnitude of the vibrational branch of $\beta(\omega)$ be sufficiently small. This small magnitude can occur, for example, if $\langle \mathcal{F}_l^{(v)} \mathcal{F}_l^{(v)} \rangle_0$ is small, implying weak coupling between the resonant solute and solvent normal modes.

When imperfect following holds for VER, it manifests itself as motion of the relaxing solute normal mode in an environment which responds only weakly to this motion. This picture permits development of a simple classical model for VER (which ignores vibrational dephasing). When analyzed quantitatively,^{15(a)} this model yields Eq. (1.1) for T_1 . It may be summarized qualitatively as follows. In zeroth order, the relaxing solute normal mode executes *undamped* harmonic vibrations of frequency ω_l in a hypothetical nonresponding solution which moves as if the normal mode coordinate was fixed at its equilibrium value. In first order, these zeroth order motions "probe" the solution at frequency ω_l inducing a weak response, which increases with the magnitude of the solution's frequency spectrum at ω_l , $\sim \beta(\omega_l)$, and an associated energy transfer which gives rise to VER with T_1 given by Eq. (1.1).

We next discuss the origin of the results for ω_l given later, emphasizing the basis of Eq. (1.8) for its *liquid phase* component ω_e . This origin follows from the definition of ω_l as the (ensemble average) frequency of the relaxing solute mode in the nonresponding solution, which is equivalent to the constrained solution discussed earlier. The frequency ω_e , for example, may be evaluated from $\mathcal{F}(y) \equiv \langle \mathcal{F}[Q;y] \rangle_0$, where $\mathcal{F}[Q;y]$ is the liquid phase generalized force acting on the relaxing mode coordinate, when it has the value y , and where $\langle \rangle_0$ denotes a constrained solution canonical ensemble average. $\mathcal{F}(y)$ is a thermodynamic restoring force which acts to return the normal mode coordinate to its equilibrium value y_0 . This follows since $\mathcal{F}[Q;y]$ is the force on the mode coordinate when it is displaced to a value y , while $\langle \rangle_0$, in contrast, is

an average over a distribution of solution phase space coordinates Q which is the equilibrium distribution only if the mode coordinate is kept at y_0 . The frequency ω_e determines $\mathcal{F}(y)$ to the lowest nontrivial (linear)¹⁸ order in $y - y_0$. It is defined as

$$\omega_e^2 \equiv - \left(\frac{\partial \mathcal{F}(y)}{\partial y} \right)_{y=y_0} = - \left\langle \left(\frac{\partial \mathcal{F}[Q;y]}{\partial y} \right)_{y=y_0} \right\rangle_0,$$

or, equivalently

$$\omega_e^2 = - \left\langle \frac{\partial \mathcal{F}}{\partial y} \right\rangle_0, \quad (1.8)$$

where $\partial \mathcal{F} / \partial y \equiv (\partial \mathcal{F}[Q;y] / \partial y)_{y=y_0}$. The frequency ω_l may be analogously evaluated from the *total* generalized force $\mathcal{F}[Q;y]$ via the relation $\omega_l^2 = - \langle (\partial \mathcal{F}[Q;y] / \partial y)_{y=y_0} \rangle_0$. This yields Eq. (2.9), where ω_g and ω_{cf} , whose forms are given in Eqs. (2.10) and (2.11), arise^{15(a)} from the intramolecular and centripetal force components of the *gas phase* contribution to $\mathcal{F}[Q;y]$.

Applications of our theoretical results to the interpretation of VTR and VV rates for *both*^{15(c)} gas²² and liquid phase²⁻⁷ experimental systems will be reported elsewhere. For the present, we note that our results provide the following.

(1) The basis for a molecular level interpretation of the temperature dependence of the rate constant in the low temperature (non-Landau-Teller³³) regime important for liquid phase studies.

(2) A molecular basis for correlations between rates in the gas and liquid phases, including criteria^{15(c)} for the emergence of an IBC-like factorization of the rate constant and improved formulas^{15(c)} for its isothermal density dependence.

(3) Molecular level criteria [based on Eq. (2.15) and on Eq. (2.7) of Ref. 17] for determining relative efficiencies of energy flow pathways. For example, in gas phase exothermic VV processes these criteria will permit one to assess the relative efficiencies of the donor and acceptor molecules as recipients of the vibrational exothermicity.

(4) A molecular level description of isotope effects in terms of the interplay between isotopic shifts in ω_l (and ω_D) and corresponding shifts in the magnitudes and Gaussian widths of $\beta(\omega)$. This interplay can lead to (see, e.g., Fig. 1 of Lukasik and Ducuing^{22(b)}) critical temperatures where the rate isochors for different isotopes cross.

To close this section, we illustrate our methods of derivation of the results of Sec. II by outlining the development of Eqs. (2.12) and (2.13) for ω_e^2 from Eq. (1.8), for an infinitely dilute diatomic solution. We then briefly indicate how this simplest evaluation may be extended. (The full derivation of our results is lengthy and will be reported elsewhere.) In all evaluations, the molecules are kept rigid at their equilibrium separation (in accord with our earlier discussions); constraints denoted by a subscript 0. Thus, e.g., $\langle \rangle_0$ denotes a canonical ensemble average over the phase point of the rigid solution (this is equivalent to our earlier definition of $\langle \rangle_0$).

In our evaluations, we specify this rigid solution phase point in generalized (rather than Cartesian) coordinates, since this permits a natural description of VER. For example, VTR processes involve energy transfer from (see the following) the generalized coordinate y to the generalized coordinate w . Specifically, we describe the diatomic solute molecule by its center of mass translational and bond-axis rotational coordinates $z \equiv (X, Y, Z, \theta, \phi)$, along with the conjugate momenta p_z , and by its normal mode coordinate y , along with p_y . Analogously, each of the N_s solvent molecules is specified by its translational-rotational phase space coordinates $w_\lambda \equiv (X_\lambda, Y_\lambda, Z_\lambda, \theta_\lambda, \phi_\lambda)$ and p_{w_λ} and by its vibrational phase space coordinates v_λ and p_{v_λ} , $\lambda = 1, 2, \dots, N_s$. Additionally we define the full solvent phase space coordinates w, p_w, v , and p_v by $w \equiv (w_1, w_2, \dots, w_{N_s})$, etc.

We next turn to the determination of ω_e^2 from Eq. (1.8). This requires evaluation of $\langle \partial \mathcal{F} / \partial y \rangle_0$, which is an equilibrium average over the rigid solution phase point (z, p_z, w, p_w) . For isotropic liquids, this average may be simplified to yield

$$\left\langle \frac{\partial \mathcal{F}}{\partial y} \right\rangle_0 = \left\langle \frac{\partial \mathcal{F}}{\partial y} \right\rangle_{y_0 z}, \quad (1.9)$$

where $\langle \rangle_{y_0 z}$ denotes a canonical ensemble average over only the rigid solvent phase point (w, p_w) conditional that the solute is fixed in the liquid with configuration point $y_0 z$. Equation (1.9) follows by first averaging $\partial \mathcal{F} / \partial y$ over w, p_w with the solute fixed to obtain $\langle \partial \mathcal{F} / \partial y \rangle_{y_0 z}$ and then by averaging $\langle \partial \mathcal{F} / \partial y \rangle_{y_0 z}$ over z, p_z to obtain $\langle \partial \mathcal{F} / \partial y \rangle_0$. However, for isotropic liquids $\langle \partial \mathcal{F} / \partial y \rangle_{y_0 z}$ is independent of z (the location and orientation of the solute in the liquid) yielding Eq. (1.9).

We next define the generalized force \mathcal{F} by

$$\mathcal{F} = - \frac{\partial K_{vu}[yzvw]}{\partial y}, \quad (1.10)$$

where K_{vu} is the solute-solvent potential. We assume a site-site form²⁹ for K_{vu} , namely ($n = n_s = 2$ for diatomic solutions)

$$K_{vu} = \sum_{i=1}^n \sum_{\lambda=1}^{N_s} \sum_{k=1}^{n_s} u_{ik}[\mathbf{r}_i, \mathbf{q}_{\lambda k}], \quad (1.11)$$

where $u_{ik}[\mathbf{r}_i, \mathbf{q}_{\lambda k}]$ is the site-site potential linking solute atom i at point \mathbf{r}_i to atom k on solvent molecule λ at point $\mathbf{q}_{\lambda k}$.

To proceed further, we utilize the following expansion of $\partial / \partial y$ which holds^{15(a)} because $y = y(\mathbf{r}_1, \mathbf{r}_2)$ (point transformation²⁶)

$$\frac{\partial}{\partial y} = \sum_{i=1}^n \mu^i(yz) \cdot \frac{\partial}{\partial \mathbf{r}_i} = \sum_{i=1}^n \mu^i(z) \cdot \frac{\partial}{\partial \mathbf{r}_i}, \quad (1.12)$$

where $\mu^i(yz) \equiv \partial \mathbf{r}_i / \partial y$ and where the final equality is proven elsewhere.^{15(a)}

Comparison of Eqs. (1.10)–(1.12) then yields the expansion

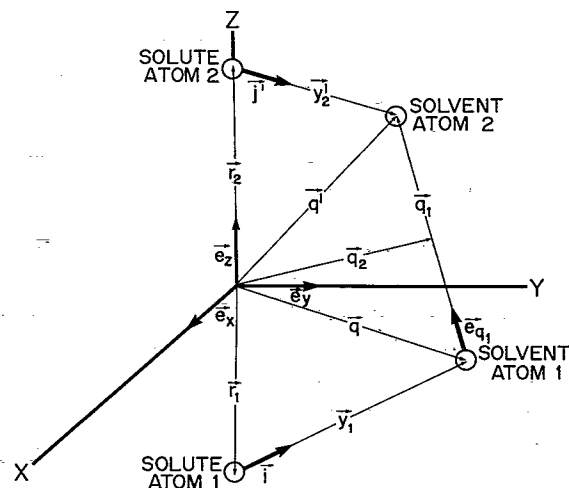


FIG. 1. Solute molecule body-fixed Cartesian axis system along with vector quantities discussed in Sec. II. Origin and z axis of the body-fixed system coincide, respectively, with the center of the mass and bond axis of the diatomic solute molecule.

$$\mathcal{F} = - \sum_{i=1}^n \sum_{\lambda=1}^{N_s} \sum_{k=1}^{n_s} \mu^i(z) \cdot \frac{\partial u_{ik}[\mathbf{r}_i, \mathbf{q}_{\lambda k}]}{\partial \mathbf{r}_i}. \quad (1.13)$$

Similarly comparing Eq. (1.8) with the previous equations yields, for ω_e^2 ,

$$\omega_e^2 = \sum_{i=1}^n \sum_{\lambda=1}^{N_s} \sum_{k=1}^{n_s} \mu^i(z) \mu^i(z) : \left\langle \frac{\partial^2 u_{ik}[\mathbf{r}_i, \mathbf{q}_{\lambda k}]}{\partial \mathbf{r}_i^2} \right\rangle_{y_0 z}. \quad (1.14)$$

Equation (1.14) may be straightforwardly re-expressed in terms of site density integrals as

$$\omega_e^2 = \sum_{i=1}^n \sum_{k=1}^{n_s} \mu^i(z) \mu^i(z) : \int \rho_k^{(n+1)}[b_g; \mathbf{q}] \frac{\partial^2 u_{ik}[\mathbf{r}_i, \mathbf{q}]}{\partial \mathbf{r}_i^2} d\mathbf{q}, \quad (1.15)$$

where

$$\rho_k^{(n+1)}[b_g; \mathbf{q}] \equiv \sum_{\lambda=1}^{N_s} \langle \delta(\mathbf{q} - \mathbf{q}_{\lambda k}) \rangle_{y_0 z} \quad (1.16)$$

is the ensemble averaged density of solvent sites of type k at point \mathbf{q} conditional that the solute is fixed (with its equilibrium separation b_g).

The site density integrals in Eq. (1.15) are most easily evaluated in the solute body-fixed frame, depicted in Fig. 1, requiring the following body-fixed representation of $\mu^i(z)$ (which is derived^{15(a),18} from the transformation relations between generalized and Cartesian coordinates \mathbf{r}_i):

$$\mu^i(z) = (-)^i \frac{\mu^{1/2}}{m_i} \mathbf{e}_z, \quad i=1 \text{ or } 2. \quad (1.17)$$

In Eq. (1.17), \mathbf{e}_z is the body-fixed unit vector depicted in Fig. 1 and μ and m_i are, respectively, the solute reduced mass and the mass of solute atom i . To complete the derivation, we further assume central field site-site potentials, i.e., $u_{ik}[\mathbf{r}_i, \mathbf{q}] = u_{ik}[y_i]$ where $y_i = |\mathbf{y}_i|$ with $\mathbf{y}_i = \mathbf{q} - \mathbf{r}_i$. Comparison of Eqs. (1.15) and (1.17) shows that we require

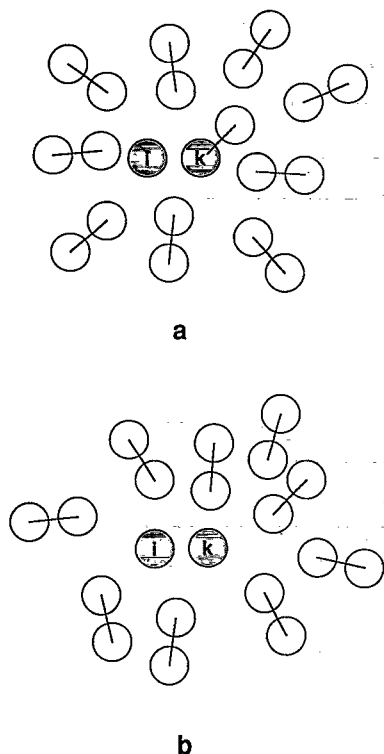


FIG. 2. (a) Equilibrium site-site pair correlation function g_{ik} links atomic solute site i and solvent site k located on a molecule. (b) Equilibrium site-site pair correlation function \bar{g}_{ik} links atomic solute site i and atomic solvent site k .

$$\mathbf{e}_z \mathbf{e}_z : \frac{\partial^2 u_{ik}[\mathbf{r}_i, \mathbf{q}]}{\partial \mathbf{r}_i^2} = \mathbf{e}_z \cdot \frac{\partial}{\partial \mathbf{y}_i} \left(\mathbf{e}_z \cdot \frac{\partial u_{ik}[\mathbf{y}_i]}{\partial \mathbf{y}_i} \right).$$

An evaluation yields

$$\mathbf{e}_z \mathbf{e}_z : \frac{\partial^2 u_{ik}[\mathbf{r}_i, \mathbf{q}]}{\partial \mathbf{r}_i^2} = (\mathbf{e}_z \cdot \mathbf{i})^2 U_{ik}[\mathbf{y}_i] + y_i^{-1} \frac{du_{ik}[\mathbf{y}_i]}{dy_i}, \quad (1.18)$$

where $\mathbf{i} \equiv y_i^{-1} \mathbf{y}_i$ and where $U_{ik}[\mathbf{y}_i]$ is defined in Eq. (2.3). Comparison of Eqs. (1.15), (1.17), and (1.18) then yields the required results for ω_e^2 ; Eqs. (2.12) and (2.13) with Eq. (2.1a).

The Kirkwood superposition approximation [Eq. (2.4)] is next used to express $\rho_k^{(n+1)}[b_g; \mathbf{q}]$ as a product of equilibrium solute-solvent site-site pair correlation functions. There is, however, ambiguity in the choice of these pair correlation functions. Four choices are possible; two of these are depicted in Fig. 2. The correct choice is $g_{ik}[\mathbf{y}_i]$ [Fig. 2(a)], which links a free solute atomic site i with a solvent atomic site k bound to a molecule. This follows since¹⁸ $\rho_k^{(n+1)}[b_g; \mathbf{q}] \propto$ the probability that site k is at point \mathbf{q} , averaged over all other solvent sites including the site $l \neq k$ located on the same molecule as k , but not averaged over the solute sites since they are fixed. Only $g_{ik}[\mathbf{y}_i]$ is in accord with this definition since it is defined as an ensemble average over sites other than i and k which excludes the solute site $j \neq i$ but includes the intramolecular solvent site $l \neq k$ in the averaging process.

The derivations of our remaining results follow the general outline just described for ω_e^2 and, therefore, will only be briefly discussed. The results for $\langle \mathcal{F}^2 \rangle_0$ [Eqs. (2.14), (2.22), (2.23), and (2.24a)], for example, follow from Eq. (1.13), the derivation yielding $\langle \mathcal{F}^2 \rangle_0$ in terms of integrals over ensemble averaged densities of sites k and l located on the same solvent molecule given that the solute is fixed. For $k=l$, the required site density is $\rho_k^{(n+1)}[b_g; \mathbf{q}]$ discussed earlier. For $k \neq l$, the site density is $\rho_{lk,1l}^{(n+1)}[b_g; \mathbf{q}, \mathbf{q}'] \propto$ the joint probability that sites k and l are, respectively, at points \mathbf{q} and \mathbf{q}' averaged over all other solvent sites but not over the solute sites. Given this definition, the superposition approximation for $\rho_{lk,1l}^{(n+1)}[b_g; \mathbf{q}, \mathbf{q}']$ requires the free atom site-site pair correlation function $\bar{g}_{ik}[\mathbf{y}_i]$ [Fig. 2(b)] since it properly excludes the solute site $j \neq i$ and the intramolecular solvent site $l \neq k$ in the ensemble average over sites other than i and k .

In the derivation of the results (Sec. II C) for $\langle \mathcal{F}^2 \rangle_0$, we begin with $\mathcal{F} = iL_0 \mathcal{F}$ where L_0 is the Liouville operator of the rigid solution. \mathcal{F} may be decomposed as

$$\mathcal{F} = \mathcal{F}_{d,t} + \mathcal{F}_{d,r} + \mathcal{F}_{i,t} + \mathcal{F}_{i,r}, \quad (1.19)$$

where $\mathcal{F}_{d,t(r)}$ and $\mathcal{F}_{i,t(r)}$ arise, respectively, from the solvent (d) and solute (i) translational (rotational) contributions to L_0 . The explicit form of $\mathcal{F}_{d,t}$, for example, is

$$\mathcal{F}_{d,t} = \sum_{\alpha} \frac{p_{z_{\alpha}}}{M} \frac{\partial \mathcal{F}}{\partial z_{\alpha}}, \quad (1.20)$$

where, in Eq. (1.20), z_{α} and $p_{z_{\alpha}}$ are the solute center of mass translational phase space coordinates and where M is the mass of the solute molecule. Defining $\langle \mathcal{F}^2 \rangle_{0d,t} = \langle \mathcal{F}_{d,t}^2 \rangle_0$, etc., and using Eq. (1.19) to evaluate $\langle \mathcal{F}^2 \rangle_0$ yields (because cross terms vanish since, e.g., $\langle p_{z_{\alpha}} p_{w_{\beta}} \rangle_0 = 0$) Eq. (2.15). We will illustrate the evaluation of the individual terms in Eq. (2.15) by outlining the derivation of the results [Eqs. (2.16a) and (2.22)–(2.24b)] for $\langle \mathcal{F}^2 \rangle_{0d,r}$. From Eq. (1.20) it follows that

$$\langle \mathcal{F}^2 \rangle_{0d,t} = \frac{k_B T}{M} \sum_{\alpha} \left\langle \frac{\partial \mathcal{F}}{\partial z_{\alpha}} \frac{\partial \mathcal{F}}{\partial z_{\alpha}} \right\rangle_0 \quad (1.21)$$

which holds since $\langle p_{z_{\alpha}} p_{z_{\beta}} \rangle_0 = M k_B T \delta_{\alpha\beta}$. The expressions for $\langle \mathcal{F}^2 \rangle_{0d,t}$ follow from Eq. (1.21) using Eq. (1.13), an expansion for $\partial/\partial z_{\alpha}$ analogous to Eq. (1.12), a reduction analogous to Eq. (1.9), and the result^{15(a)} $\partial \mu_{11}(z)/\partial z_{\alpha} = 0$ for the translational coordinates z_{α} .

II. DIATOMIC SOLUTION RESULTS

We next summarize the expressions for ω_l^2 , $\langle \mathcal{F}^2 \rangle_0$, and $\langle \mathcal{F}^2 \rangle_0$. The expressions given in this section apply to a diatomic solute present at infinite dilution in an otherwise pure diatomic solvent (see Fig. 1) at Kelvin temperature T and number density ρ_0 . In these expressions n and n_s are, respectively, the number of solute atoms and the number of solvent atoms per molecule. Thus $n = n_s = 2$.

A. Preliminaries

We first briefly describe the quantities appearing in the expressions.

1. Solute and solvent masses

The diatomic solution formulas involve the solute atomic, total, and reduced masses and the solute moment of inertia. These are given, respectively, by m_1 and m_2 , $M = m_1 + m_2$, $\mu = M^{-1} m_1 m_2$, and $I = \mu b_g^2$, where b_g is the gas phase solute equilibrium internuclear separation. They also involve a function T^{ij} of the solute atomic masses defined by

$$T^{ij} = (-)^{i+j} \frac{1}{3} \left(\frac{m_1 m_2}{m_i m_j} \right), \quad (2.1a)$$

where $i, j = 1$ or 2 . The formulas additionally involve the total mass $M_s = M_1 + M_2$ of a solvent molecule and a function of solvent atomic masses T_s^{kl} defined by

$$T_s^{kl} = (-)^{k+l} \frac{1}{3} \left(\frac{M_1 M_2}{M_k M_l} \right), \quad (2.1b)$$

where $k, l = 1$ or 2 .

2. Atomic sites and atomic coordinates

Solute atomic sites and atomic coordinates will be denoted, respectively, by i or j and \mathbf{r}_i (site i) and \mathbf{r}_j (site j). Solvent atomic sites and coordinates will correspondingly be denoted by k and l and \mathbf{q} (site k) and \mathbf{q}' (site l).

The vector displacements between solute and solvent atomic sites will be denoted by $\mathbf{y}_i = \mathbf{q} - \mathbf{r}_i$, $\mathbf{y}_j = \mathbf{q} - \mathbf{r}_j$, and $\mathbf{y}_{j'} = \mathbf{q}' - \mathbf{r}_j$. We will also require the corresponding scalar distances $y_i = |\mathbf{q} - \mathbf{r}_i|$, $y_j = |\mathbf{q} - \mathbf{r}_j|$, and $y_{j'} = |\mathbf{q}' - \mathbf{r}_j|$ and the associated unit vectors $\mathbf{i} = y_i^{-1} \mathbf{y}_i$, $\mathbf{j} = y_j^{-1} \mathbf{y}_j$, and $\mathbf{j}' = [y_{j'}]^{-1} \mathbf{y}_{j'}$.

3. Vector integrals

The diatomic solution formulas involve single vector integrals over the coordinates \mathbf{q} of a single solvent atomic site and double vector integrals over the coordinates \mathbf{q} and \mathbf{q}' of a pair of solvent atomic sites located on the same molecule. These integrals are performed with the solute molecule fixed in the liquid at its equilibrium internuclear separation b_g . Moreover, when performing the vector integrals, the solvent molecules are constrained to have their gas phase equilibrium internuclear separation b_{gs} . Consequently, the integrations over \mathbf{q} and \mathbf{q}' are performed subject to the constraint

$$q_1 \equiv |\mathbf{q}' - \mathbf{q}| = b_{gs}. \quad (2.2)$$

4. Site-site potentials

To evaluate the vector integrals, one requires the solute-solvent site-site potential energy functions $u_{ik}[y_i]$ and $u_{jl}[y_{j'}]$ and the auxiliary functions $U_{ik}[y_i]$ and $U_{jl}[y_{j'}]$ defined in terms of the site-site potentials by

$$U_{ik}[y_i] = \frac{d^2 u_{ik}[y_i]}{dy_i^2} - y_i^{-1} \frac{du_{ik}[y_i]}{dy_i}$$

and

$$U_{jl}[y_{j'}] = \frac{d^2 u_{jl}[y_{j'}]}{dy_{j'}^2} - [y_{j'}]^{-1} \frac{du_{jl}[y_{j'}]}{dy_{j'}}. \quad (2.3)$$

5. Ensemble averaged site densities

To evaluate the single vector integrals, we require the ensemble averaged densities $\rho_k^{(n+1)}[b_g; \mathbf{q}]$ and $\rho_l^{(n+1)}[b_g; \mathbf{q}']$ of a single solvent site, k or l , conditional that the solute molecule is fixed in the liquid at its equilibrium internuclear separation b_g . We utilize the following Kirkwood superposition approximations (SA) for these site densities

$$\rho_k^{(n+1)}[b_g; \mathbf{q}] \doteq \rho_0 \prod_{i=1}^n g_{ik}[y_i]$$

and

$$\rho_l^{(n+1)}[b_g; \mathbf{q}'] \doteq \rho_0 \prod_{j=1}^n g_{jl}[y_{j'}]. \quad (2.4)$$

To evaluate the double vector integrals we require analogous ensemble averaged site densities $\bar{\rho}_k^{(n+1)}[b_g; \mathbf{q}]$ and $\bar{\rho}_l^{(n+1)}[b_g; \mathbf{q}']$ which are given within the SA by

$$\bar{\rho}_k^{(n+1)}[b_g; \mathbf{q}] \doteq \rho_0 \prod_{i=1}^n \bar{g}_{ik}[y_i]$$

and

$$\bar{\rho}_l^{(n+1)}[b_g; \mathbf{q}'] \doteq \rho_0 \prod_{j=1}^n \bar{g}_{jl}[y_{j'}]. \quad (2.5)$$

6. Site-site equilibrium pair correlation functions

In Eqs. (2.4) and (2.5), g_{ik} and \bar{g}_{ik} are the *distinct* solute-solvent site-site equilibrium pair correlation functions discussed in Sec. I. As depicted in Fig. 2, (i) g_{ik} links an *atomic* solute site of type i with site k on a solvent molecule; (ii) \bar{g}_{ik} links an atomic solute site of type i with an atomic solvent site of type k . Both site-site correlation functions are defined assuming the sites [and the associated molecule for a site on a molecule] are immersed in an otherwise pure diatomic solvent at Kelvin temperature T and number density ρ_0 . Moreover, when evaluating the pair correlation functions, the rigid solvent model is assumed with the internuclear separation of a solvent molecule set at b_{gs} .

7. The coordinates \mathbf{q}_1 and \mathbf{q}_2

In order to conveniently enforce the rigid solvent molecule constraint $q_1 = b_{gs}$, Eq. (2.2), we transform to the coordinates \mathbf{q}_1 and \mathbf{q}_2 when evaluating the double vector integrals. These are defined in terms of the solvent site coordinates \mathbf{q} and \mathbf{q}' by

$$\mathbf{q}_1 \equiv \mathbf{q}' - \mathbf{q}$$

and

$$\mathbf{q}_2 \equiv \frac{1}{2}(\mathbf{q} + \mathbf{q}'). \quad (2.6)$$

We also define the solvent molecule bond-axis unit vector \mathbf{e}_{q_1} by

$$\mathbf{e}_{q_1} = \mathbf{e}_{q_1}(\mathbf{q}, \mathbf{q}') = b_{gs}^{-1}(\mathbf{q}' - \mathbf{q}) = b_{gs}^{-1} \mathbf{q}_1. \quad (2.7)$$

8. The body-fixed frame

The vector integrals will be evaluated in the solute molecule body-fixed frame (Fig. 1) mentioned in Sec. I. The origin and z axis of this frame coincide with the center of mass and bond axis of the diatomic solute molecule. The Cartesian unit vectors of the body-fixed frame are \mathbf{e}_x , \mathbf{e}_y , and \mathbf{e}_z .

All vector and tensor quantities introduced in this section will be represented in the body-fixed frame. For example, the solute atomic coordinates \mathbf{r}_i and \mathbf{r}_j will be represented by

$$\mathbf{r}_i = r_i \mathbf{e}_z$$

and

$$\mathbf{r}_j = r_j \mathbf{e}_z$$

where

$$r_{i(j)} = (-)^{i(j)} \frac{\mu}{m_{i(j)}} b_g. \quad (2.8)$$

9. Spherical polar representation for the single vector integrals

The single vector integrals are evaluated as quadratures over the spherical polar coordinates (q, θ, ϕ) of \mathbf{q} referred to the body-fixed frame. The quantities required to construct the integrands of these integrals are given as functions of q , θ , and ϕ in Appendix A.

10. Spherical polar representations for the double vector integrals

The double vector integrals are evaluated as quadratures over the body-fixed spherical polar coordinates (q_1, θ_1, ϕ_1) and (q_2, θ_2, ϕ_2) of \mathbf{q}_1 and \mathbf{q}_2 subject to the constraint $q_1 = b_{gs}$. The quantities required to construct the integrands of the double vector integrals are given as functions of (q_1, θ_1, ϕ_1) and (q_2, θ_2, ϕ_2) in Appendix A.

Given these definitions, we next summarize the diatomic solution results for ω_l , $\langle \tilde{\mathcal{F}}^2 \rangle_0$, and $\langle \tilde{\mathcal{F}}^2 \rangle_0$.

B. Diatomic solution results for ω_l^2

The solute liquid phase frequency ω_l is given by

$$\omega_l^2 = \omega_g^2 + \omega_{cf}^2 + \omega_e^2, \quad (2.9)$$

where ω_g , ω_{cf} , and ω_e are, respectively, the intramolecular potential, centripetal force, and thermodynamic restoring force (see Sec. I) contributions to ω_l .

1. Results for ω_g^2 and ω_{cf}^2

The expressions for ω_g and ω_{cf} are

$$\begin{aligned} \omega_g^2 &= \text{square of the fundamental} \\ &\quad \text{gas phase frequency} \\ &\quad \text{of the diatomic solute} \end{aligned} \quad (2.10)$$

and

$$\omega_{cf}^2 = \frac{6k_B T}{I}. \quad (2.11)$$

2. Result for ω_e^2

The result for ω_e^2 is

$$\omega_e^2 = 3M^{-1} \sum_{i=1}^n \sum_{k=1}^{n_s} T^{ij} \mathbf{e}_z \cdot \mathbf{K}_{ik} \cdot \mathbf{e}_z, \quad (2.12)$$

where $\mathbf{e}_z \cdot \mathbf{K}_{ik} \cdot \mathbf{e}_z$ is a single vector integral given by

$$\begin{aligned} \mathbf{e}_z \cdot \mathbf{K}_{ik} \cdot \mathbf{e}_z &= \int_0^{2\pi} d\phi \int_0^\infty q^2 dq \int_0^\pi \sin \theta d\theta \rho_k^{(n+1)}[b_g; \mathbf{q}] \\ &\quad \times \left([\mathbf{e}_z \cdot \mathbf{i}]^2 U_{ik}[y_i] + y_i^{-1} \frac{du_{ik}[y_i]}{dy_i} \right)_{b_g}. \end{aligned} \quad (2.13)$$

In Eq. (2.13), the symbol b_g indicates that the solute molecule is fixed at its equilibrium internuclear separation in the body-fixed frame, as shown in Fig. 1. Moreover, $\rho_k^{(n+1)}[b_g; \mathbf{q}]$ is evaluated from Eq. (2.4), $U_{ik}[y_i]$ is evaluated from Eq. (2.3), and y_i and $\mathbf{e}_z \cdot \mathbf{i}$ are evaluated as functions of q , θ , and ϕ from Eqs. (A1) and (A2). Equations (2.9)–(2.13) provide the required results for ω_l .

C. Diatomic solution results for $\langle \tilde{\mathcal{F}}^2 \rangle_0$ and $\langle \tilde{\mathcal{F}}^2 \rangle_0$

We next give the diatomic solution results for the Gaussian model parameters $\langle \tilde{\mathcal{F}}^2 \rangle_0$ and $\langle \tilde{\mathcal{F}}^2 \rangle_0$. These will involve the single and double vector integrals discussed earlier. For example, in the formula for $\langle \tilde{\mathcal{F}}^2 \rangle_0$, Eq. (2.14), the single vector integral is $\mathbf{e}_z \mathbf{e}_z : I_{ijkl}$ and the double vector integral is $\mathbf{e}_z \mathbf{e}_z : I_{ijkl}$ ($k \neq l$).

1. Result for $\langle \tilde{\mathcal{F}}^2 \rangle_0$

The result for $\langle \tilde{\mathcal{F}}^2 \rangle_0$ is

$$\langle \tilde{\mathcal{F}}^2 \rangle_0 = 3M^{-1} \sum_{i,j=1}^n \sum_{k,l=1}^{n_s} T^{ij} \mathbf{e}_z \mathbf{e}_z : I_{ijkl}. \quad (2.14)$$

2. Decomposition of $\langle \tilde{\mathcal{F}}^2 \rangle_0$

$\langle \tilde{\mathcal{F}}^2 \rangle_0$ may be decomposed as

$$\langle \tilde{\mathcal{F}}^2 \rangle_0 = \langle \tilde{\mathcal{F}}^2 \rangle_{0d,t} + \langle \tilde{\mathcal{F}}^2 \rangle_{0d,r} + \langle \tilde{\mathcal{F}}^2 \rangle_{0i,t} + \langle \tilde{\mathcal{F}}^2 \rangle_{0i,r}. \quad (2.15)$$

The separate terms in Eq. (2.15) are associated with the distinct solute energy flow pathways [see Sec. I, especially Eq. (1.19)] which can occur in VTR vibrational energy relaxation processes. Specifically, the terms $\langle \tilde{\mathcal{F}}^2 \rangle_{0d,t}$ and $\langle \tilde{\mathcal{F}}^2 \rangle_{0d,r}$ are associated with direct (solute V to solvent) vibrational energy transfer to, respectively, the solvent T and R degrees of freedom while the terms $\langle \tilde{\mathcal{F}}^2 \rangle_{0i,t}$ and $\langle \tilde{\mathcal{F}}^2 \rangle_{0i,r}$ are associated with indirect (solute V to solute T or solute R to solvent) energy transfer.

3. Expressions for components of $\langle \tilde{\mathcal{F}}^2 \rangle_0$

The results for the components of $\langle \tilde{\mathcal{F}}^2 \rangle_0$ are

$$\langle \tilde{\mathcal{F}}^2 \rangle_{0d,t} = \frac{3k_B T}{MM_s} \sum_{i,j=1}^n \sum_{k,l=1}^{n_s} T^{ij} \mathbf{e}_z \mathbf{e}_z : \mathbf{K}_{ijkl}, \quad (2.16a)$$

$$\langle \hat{\mathcal{F}}^2 \rangle_{0,r} = \frac{9k_B T}{MM_s} \sum_{i,j=1}^n \sum_{k,l=1}^{n_s} T^{ij} T^{kl} (\mathbf{e}_z \mathbf{e}_z \cdot \mathbf{K}_{ijkl} - \mathbf{e}_z \mathbf{e}_z \mathbf{e}_{q_1} \mathbf{e}_{q_1} \cdot \mathbf{K}_{ijkl}), \quad (2.16b)$$

$$\langle \hat{\mathcal{F}}^2 \rangle_{0,i} = \frac{3k_B T}{M^2} \sum_{i,j=1}^n \sum_{k,l=1}^{n_s} T^{ij} [\mathbf{e}_z \mathbf{e}_z \cdot \mathbf{K}_{ijkl} + (\mathbf{e}_z \cdot \mathbf{K}_{ik} \cdot \mathbf{e}_z)(\mathbf{e}_z \cdot \mathbf{K}_{jl} \cdot \mathbf{e}_z)], \quad (2.16c)$$

and

$$\langle \hat{\mathcal{F}}^2 \rangle_{0,r} = \frac{6k_B T}{M^2} \sum_{i,j=1}^n \sum_{k,l=1}^{n_s} T^{ij} \times \left(\frac{M}{I} \mathbf{e}_x \mathbf{e}_x \cdot \mathbf{I}_{ijkl} (-)^j \frac{2M}{m_j b_g} \mathbf{e}_x \mathbf{e}_x \cdot \mathbf{J}_{ijkl} + 3T^{ij} \mathbf{e}_x \mathbf{e}_x \mathbf{e}_z \cdot \mathbf{K}_{ijkl} \right). \quad (2.16d)$$

We next give results for the integrals appearing in Eqs. (2.14) and (2.16).

4. The integrals $\mathbf{e}_z \cdot \mathbf{K}_{ik} \cdot \mathbf{e}_z$ and $\mathbf{e}_z \cdot \mathbf{K}_{jl} \cdot \mathbf{e}_z$

We begin with the single vector integrals $\mathbf{e}_z \cdot \mathbf{K}_{ik} \cdot \mathbf{e}_z$ and $\mathbf{e}_z \cdot \mathbf{K}_{jl} \cdot \mathbf{e}_z$ appearing in Eq. (2.16c). The integral $\mathbf{e}_z \cdot \mathbf{K}_{ik} \cdot \mathbf{e}_z$ is given in Eq. (2.13). The integral $\mathbf{e}_z \cdot \mathbf{K}_{jl} \cdot \mathbf{e}_z$ is correspondingly given by

$$\mathbf{e}_z \cdot \mathbf{K}_{jl} \cdot \mathbf{e}_z = \int_0^{2\pi} d\phi \int_0^\infty q^2 dq \int_0^\pi \sin \theta d\theta \rho_l^{(n+1)} [b_g; \mathbf{q}] \times \left([\mathbf{e}_z \cdot \mathbf{j}]^2 U_{jl} [y_j] + y_j^{-1} \frac{du_{jl} [y_j]}{dy_j} \right)_{b_g} \quad (2.17)$$

5. The integral $\mathbf{e}_z \mathbf{e}_z \mathbf{e}_{q_1} \mathbf{e}_{q_1} \cdot \mathbf{K}_{ijkl}$

We next summarize our results for the double vector integral $\mathbf{e}_z \mathbf{e}_z \mathbf{e}_{q_1} \mathbf{e}_{q_1} \cdot \mathbf{K}_{ijkl}$ appearing in Eq. (2.16b). This integral may be decomposed as

$$\mathbf{e}_z \mathbf{e}_z \mathbf{e}_{q_1} \mathbf{e}_{q_1} \cdot \mathbf{K}_{ijkl} = \delta_{kl} \mathbf{e}_z \mathbf{e}_z \mathbf{e}_{q_1} \mathbf{e}_{q_1} \cdot \mathbf{K}_{ijkk} + [1 - \delta_{kl}] \mathbf{e}_z \mathbf{e}_z \mathbf{e}_{q_1} \mathbf{e}_{q_1} \cdot \mathbf{K}_{ijkl}. \quad (2.18)$$

The integrals in Eq. (2.18) are given, respectively, by

$$\begin{aligned} \mathbf{e}_z \mathbf{e}_z \mathbf{e}_{q_1} \mathbf{e}_{q_1} \cdot \mathbf{K}_{ijkk} &= (4\pi \rho_0)^{-1} \int_0^{2\pi} d\phi_2 \int_0^\pi \sin \theta_2 d\theta_2 \int_0^\infty q_2^2 dq_2 \\ &\times \int_0^{2\pi} d\phi_1 \int_0^\pi \sin \theta_1 d\theta_1 (\bar{\rho}_k^{(n+1)} [b_g; \mathbf{q}] \bar{\rho}_l^{(n+1)} \\ &\times [b_g; \mathbf{q}'] A_{ijkk} [b_g; \mathbf{q}\mathbf{q}']) \end{aligned} \quad (2.19a)$$

and ($k \neq l$)

$$\begin{aligned} \mathbf{e}_z \mathbf{e}_z \mathbf{e}_{q_1} \mathbf{e}_{q_1} \cdot \mathbf{K}_{ijkl} &= (4\pi \rho_0)^{-1} \int_0^{2\pi} d\phi_2 \int_0^\pi \sin \theta_2 d\theta_2 \int_0^\infty q_2^2 dq_2 \\ &\times \int_0^{2\pi} d\phi_1 \int_0^\pi \sin \theta_1 d\theta_1 (\bar{\rho}_k^{(n+1)} [b_g; \mathbf{q}] \bar{\rho}_l^{(n+1)} \\ &\times [b_g; \mathbf{q}'] A_{ijkl} [b_g; \mathbf{q}\mathbf{q}']). \end{aligned} \quad (2.19b)$$

The index \bar{k} in Eq. (2.19a) is defined as

$$\bar{k} = 1 \text{ if } k = 2 \text{ and } \bar{k} = 2 \text{ if } k = 1. \quad (2.20)$$

The function $A_{ijkk} [b_g; \mathbf{q}\mathbf{q}']$ in Eq. (2.19a) is given by

$$\begin{aligned} A_{ijkk} [b_g; \mathbf{q}\mathbf{q}'] &= \left([\mathbf{e}_z \cdot \mathbf{i}] [\mathbf{e}_{q_1} \cdot \mathbf{i}] U_{ik} [y_i] + [\mathbf{e}_z \cdot \mathbf{e}_{q_1}] y_i^{-1} \frac{du_{ik} [y_i]}{dy_i} \right) \\ &\times \left([\mathbf{e}_z \cdot \mathbf{j}] [\mathbf{e}_{q_1} \cdot \mathbf{j}] U_{jk} [y_j] + [\mathbf{e}_z \cdot \mathbf{e}_{q_1}] y_j^{-1} \frac{du_{jk} [y_j]}{dy_j} \right), \end{aligned} \quad (2.21a)$$

while $A_{ijkl} [b_g; \mathbf{q}\mathbf{q}']$ in Eq. (2.19b) is given by

$$\begin{aligned} A_{ijkl} [b_g; \mathbf{q}\mathbf{q}'] &= \left([\mathbf{e}_z \cdot \mathbf{i}] [\mathbf{e}_{q_1} \cdot \mathbf{i}] U_{ik} [y_i] + [\mathbf{e}_z \cdot \mathbf{e}_{q_1}] y_i^{-1} \right. \\ &\times \frac{du_{ik} [y_i]}{dy_i} \left. \right) \left([\mathbf{e}_z \cdot \mathbf{j}'] [\mathbf{e}_{q_1} \cdot \mathbf{j}'] U_{jl} [y_{j'}] \right. \\ &\left. + [\mathbf{e}_z \cdot \mathbf{e}_{q_1}] [y_{j'}]^{-1} \frac{du_{jl} [y_{j'}]}{dy_{j'}} \right). \end{aligned} \quad (2.21b)$$

6. The remaining integrals

The remaining integrals in Eqs. (2.14) and (2.16) all have an identical generic form and, therefore, will be collectively denoted by A_{ijkl} . For example, they may all be decomposed as

$$A_{ijkl} = \delta_{kl} A_{ijkk} + (1 - \delta_{kl}) A_{ijkl}, \quad (2.22)$$

where A_{ijkk} is a single vector integral over the spherical polar coordinates (q, θ, ϕ) and where ($k \neq l$) A_{ijkl} is a double vector integral over the spherical polar coordinates (θ_1, ϕ_1) and (q_2, θ_2, ϕ_2). Explicitly, one has

$$\begin{aligned} A_{ijkk} &= \int_0^{2\pi} d\phi \int_0^\infty q^2 dq \int_0^\pi \sin \theta d\theta \rho_k^{(n+1)} [b_g; \mathbf{q}] \\ &\times A_{ijkk} [b_g; \mathbf{q}\mathbf{q}'] \end{aligned} \quad (2.23a)$$

and ($k \neq l$)

$$\begin{aligned} A_{ijkl} &= (4\pi \rho_0)^{-1} \int_0^{2\pi} d\phi_2 \int_0^\pi \sin \theta_2 d\theta_2 \int_0^\infty q_2^2 dq_2 \\ &\times \int_0^{2\pi} d\phi_1 \int_0^\pi \sin \theta_1 d\theta_1 (\bar{\rho}_k^{(n+1)} [b_g; \mathbf{q}] \bar{\rho}_l^{(n+1)} \\ &\times [b_g; \mathbf{q}'] A_{ijkl} [b_g; \mathbf{q}\mathbf{q}']). \end{aligned} \quad (2.23b)$$

The integrals differ from one another only through the functions $A_{ijkk} [b_g; \mathbf{q}\mathbf{q}']$, required to evaluate the single vector integrals, and $A_{ijkl} [b_g; \mathbf{q}\mathbf{q}']$, required to evaluate the

double vector integrals. Moreover, the functions $A_{ijkl}[b_g; \mathbf{q}\mathbf{q}']$ may be obtained from the corresponding functions $A_{ijkl}[b_g; \mathbf{q}\mathbf{q}']$ by the transpositions [cf. Eqs. (2.21)] $\mathbf{j}' \rightarrow \mathbf{j}$, $y_{j'} \rightarrow y_j$, and $u_{jl}[y_{j'}] \rightarrow u_{jk}[y_j]$. Thus to specify the integrals, it is necessary only to specify the associated functions $A_{ijkl}[b_g; \mathbf{q}\mathbf{q}']$. These have the following forms:

$$\mathbf{e}_z \mathbf{e}_z : I_{ijkl}$$

$$A_{ijkl}[b_g; \mathbf{q}\mathbf{q}'] = [\mathbf{e}_z \cdot \mathbf{i}][\mathbf{e}_z \cdot \mathbf{j}'] \left(\frac{du_{ik}[y_i]}{dy_i} \frac{du_{jl}[y_{j'}]}{dy_{j'}} \right), \quad (2.24a)$$

$$\mathbf{e}_z \mathbf{e}_z : K_{ijkl}$$

$$\begin{aligned} A_{ijkl}[b_g; \mathbf{q}\mathbf{q}'] = & [\mathbf{e}_z \cdot \mathbf{i}][\mathbf{e}_z \cdot \mathbf{j}'] [\mathbf{i} \cdot \mathbf{j}'] U_{ik}[y_i] U_{jl}[y_{j'}] \\ & + [\mathbf{e}_z \cdot \mathbf{j}']^2 y_i^{-1} \frac{du_{ik}[y_i]}{dy_i} U_{jl}[y_{j'}] \\ & + [\mathbf{e}_z \cdot \mathbf{i}]^2 [y_{j'}]^{-1} \frac{du_{jl}[y_{j'}]}{dy_{j'}} U_{ik}[y_i] \\ & + [y_{j'}]^{-1} \left[\frac{du_{ik}[y_i]}{dy_i} \right] \left[\frac{du_{jl}[y_{j'}]}{dy_{j'}} \right], \quad (2.24b) \end{aligned}$$

$$\mathbf{e}_x \mathbf{e}_x : I_{ijkl}$$

$$A_{ijkl}[b_g; \mathbf{q}\mathbf{q}'] = [\mathbf{e}_x \cdot \mathbf{i}][\mathbf{e}_x \cdot \mathbf{j}'] \left(\frac{du_{ik}[y_i]}{dy_i} \right) \left(\frac{du_{jl}[y_{j'}]}{dy_{j'}} \right), \quad (2.24c)$$

$$\mathbf{e}_x \mathbf{e}_x \mathbf{e}_z : J_{ijkl}$$

$$A_{ijkl}[b_g; \mathbf{q}\mathbf{q}'] = -[\mathbf{e}_x \cdot \mathbf{i}][\mathbf{e}_x \cdot \mathbf{j}'] [\mathbf{e}_z \cdot \mathbf{j}'] U_{jl}[y_{j'}] \frac{du_{ik}[y_i]}{dy_i}, \quad (2.24d)$$

$$\mathbf{e}_x \mathbf{e}_x \mathbf{e}_z : K_{ijkl}$$

$$\begin{aligned} A_{ijkl}[b_g; \mathbf{q}\mathbf{q}'] = & [\mathbf{e}_x \cdot \mathbf{i}][\mathbf{e}_z \cdot \mathbf{i}][\mathbf{e}_x \cdot \mathbf{j}'] \\ & \times [\mathbf{e}_z \cdot \mathbf{j}'] U_{ik}[y_i] U_{jl}[y_{j'}]. \quad (2.24e) \end{aligned}$$

The formulas in Appendix A permit one to evaluate the quantities appearing in Eqs. (2.21) and (2.24) as functions of (q, θ, ϕ) (single vector integrals) and $(b_g, \theta_1, \phi_1, q_2, \theta_2, \phi_2)$ (double vector integrals).

D. Summary

Formulas for the liquid state frequency ω_l and for the Gaussian model parameters $\langle \mathcal{F}^2 \rangle_0$ and $\langle \mathcal{F}^2 \rangle_0$ for diatomic solutions are given in Secs. II B and II C. These formulas permit one to compute solute VER times T_1 from Eq. (1.7).

These formulas involve integrals over the coordinates \mathbf{q} of a single solvent atom and integrals over the coordinates \mathbf{q} and \mathbf{q}' of a pair of atoms on the same solvent molecule. Using results given in Sec. II A and Appendix A, these integrals may be evaluated numerically to obtain explicit results for ω_l^2 , for $\langle \mathcal{F}(t) \mathcal{F} \rangle_0$, and for T_1 .

The formulas require the following as input. (i) The atomic masses and equilibrium internuclear separations of the solute and solvent molecules. (ii) The gas phase vibra-

tional frequency ω_g of the solute molecule. (iii) The solute-solvent site-site potentials and site-site equilibrium pair correlation functions.

Finally, we note that the previous formulas may be applied to diatomic solutes in *monatomic* solvents by setting $n=2$, $n_s=1$, and $\langle \mathcal{F}^2 \rangle_{0d,r}=0$. An application of these monatomic solvent formulas has been given elsewhere.^{15(c)}

III. DISCUSSION

The treatment of liquid phase VER developed here and in Ref. 17 is based on a rigorous analysis requiring only a limited number of assumptions. We close the paper with a discussion of the main assumptions (some minor approximations are also invoked, see Ref. 34).

We assume that the small amplitude excursion approximation is valid for the vibrational motions of the solute and the solvent molecules. This assumption permits utilization of the harmonic oscillator approximation for all vibrational degrees of freedom of the solution and the partial clamping equation of motion¹⁴ for the relaxing solute normal mode.

Gas phase scattering calculations by Simpson^{6(a)} and others^{6(b)} indicate that VER under cryogenic conditions is often dominated by subthermal collisions, rather than by high energy collisions as is postulated in the traditional justification² of the IBC model. The small amplitude excursion approximation is quite reasonable when subthermal collisions dominate VER.

In deriving Eq. (1.1) for T_1 we assume (i) the effects of solvent fluctuations may be ignored (Thus our expression for T_1 involves only the ensemble averaged solute frequency ω_l); (ii) the weak response limit $\omega_l \gg \beta(\omega_l)$ holds.

Assumption (i) is valid if the time scale for fluctuations is short relative to the timescale for VER. For VTR energy transfer this is true if $T_1 \gg [\langle \mathcal{F}^2 \rangle_0^{-1} \langle \mathcal{F}^2 \rangle_0]^{1/2}$. Assumption (ii) was discussed in Sec. I.

The simplifications which yield Eq. (1.3) require the validity of the model for the statistical mechanics of vibrating solvents discussed in Sec. I. This model, as mentioned, is a generalization to the liquid phase of the harmonic oscillator-rigid rotor approximation. The main new (i.e., liquid phase) assumption required to justify this model is that the solvent vibrational force field is dominated by the intramolecular potential energy functions.

We utilize the Gaussian model for $\langle \mathcal{F}(t) \mathcal{F} \rangle_0$.

Molecular dynamics tests by us^{9,15(a)} and others^{35,36} have shown for a number of Lennard-Jones systems that the Gaussian model gives an accurate description of the short-time part of $\langle \mathcal{F}(t) \mathcal{F} \rangle_0$ important for VER; see, e.g., Fig. 1 of Ref. 35.

We utilize the Kirkwood superposition approximations, along with integral equation evaluations of the equilibrium pair correlation functions, to obtain useful approximations for the solvent site densities. Tests due to us⁹ and others³⁵ indicate that the SA and integral equation evaluations, in the present context, yield results of semiquantitative (i.e., few percent) accuracy; see, e.g., Table I of Ref. 35.

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APPENDIX A: SPHERICAL POLAR COORDINATE EXPRESSIONS FOR QUANTITIES APPEARING IN THE VECTOR INTEGRALS

We give in this Appendix body-fixed (Fig. 1) spherical polar coordinate expressions for the quantities appearing in the vector integrals defined in Sec. II. We begin with the single vector integrals.

1. The single vector integrals

To evaluate these integrals, we require expressions for the solute-solvent interatomic separations $y_i = |\mathbf{q} - \mathbf{r}_i|$, $y_j = |\mathbf{q} - \mathbf{r}_j|$, the body-fixed Cartesian components of the unit vectors $\mathbf{i} = y_i^{-1}[\mathbf{q} - \mathbf{r}_i]$ and $\mathbf{j} = y_j^{-1}[\mathbf{q} - \mathbf{r}_j]$, and the scalar product $\mathbf{i} \cdot \mathbf{j}$ all as functions of $(q, \theta, \phi) = \mathbf{q}$. Using Eq. (2.8) one has

$$y_{i(j)} = (q^2 + r_{i(j)}^2 - 2qr_{i(j)} \cos \theta)^{1/2}, \quad (\text{A1})$$

$$\mathbf{e}_x \cdot \mathbf{i}(j) = y_{i(j)}^{-1} q \sin \theta \cos \phi,$$

$$\mathbf{e}_y \cdot \mathbf{i}(j) = y_{i(j)}^{-1} q \sin \theta \sin \phi, \quad (\text{A2})$$

$$\mathbf{e}_z \cdot \mathbf{i}(j) = y_{i(j)}^{-1} (q \cos \theta - r_{i(j)}).$$

Moreover

$$\mathbf{i} \cdot \mathbf{j} = [\mathbf{e}_x \cdot \mathbf{i}][\mathbf{e}_x \cdot \mathbf{j}] + [\mathbf{e}_y \cdot \mathbf{i}][\mathbf{e}_y \cdot \mathbf{j}] + [\mathbf{e}_z \cdot \mathbf{i}][\mathbf{e}_z \cdot \mathbf{j}]. \quad (\text{A3})$$

2. The double vector integral $\mathbf{e}_z \mathbf{e}_{q_1} \mathbf{e}_{q_1} \mathbf{e}_{q_2} : K_{ijkl}$

To evaluate the double vector integral $\mathbf{e}_z \mathbf{e}_{q_1} \mathbf{e}_{q_1} \mathbf{e}_{q_2} : K_{ijkl}$ defined in Eqs. (2.19a) and (2.21a) we require expressions for the solute-solvent interatomic separations y_i and y_j , for the body-fixed Cartesian components of the unit vectors \mathbf{i} , \mathbf{j} , and \mathbf{e}_{q_1} , and for the scalar products $\mathbf{e}_{q_1} \cdot \mathbf{i}$ and $\mathbf{e}_{q_1} \cdot \mathbf{j}$ all as functions of the spherical polar coordinates (q_1, θ_1, ϕ_1) and (q_2, θ_2, ϕ_2) of \mathbf{q}_1 and \mathbf{q}_2 . Using Eqs. (2.6)–(2.8) one has

$$y_{i(j)} = [(q_2^2 + \frac{1}{4}q_1^2 + r_{i(j)}^2) - 2r_{i(j)}(q_2 \cos \theta_2 - \frac{1}{2}q_1 \cos \theta_1) - \mathbf{q}_1 \cdot \mathbf{q}_2]^{1/2}, \quad (\text{A4})$$

where

$$\mathbf{q}_1 \cdot \mathbf{q}_2 = q_1 q_2 [\cos \theta_1 \cos \theta_2 + \sin \theta_1 \sin \theta_2 \cos(\phi_2 - \phi_1)]. \quad (\text{A5})$$

Moreover,

$$\mathbf{e}_x \cdot \mathbf{i}(j) = y_{i(j)}^{-1} (q_2 \sin \theta_2 \cos \phi_2 - \frac{1}{2}q_1 \sin \theta_1 \cos \phi_1), \quad (\text{A6a})$$

$$\mathbf{e}_y \cdot \mathbf{i}(j) = y_{i(j)}^{-1} (q_2 \sin \theta_2 \sin \phi_2 - \frac{1}{2}q_1 \sin \theta_1 \sin \phi_1), \quad (\text{A6b})$$

$$\mathbf{e}_z \cdot \mathbf{i}(j) = y_{i(j)}^{-1} (q_2 \cos \theta_2 - \frac{1}{2}q_1 \cos \theta_1 - r_{i(j)}), \quad (\text{A6c})$$

$$\mathbf{e}_x \cdot \mathbf{e}_{q_1} = b_{gs}^{-1} q_1 \sin \theta_1 \cos \phi_1, \quad (\text{A7a})$$

$$\mathbf{e}_y \cdot \mathbf{e}_{q_1} = b_{gs}^{-1} q_1 \sin \theta_1 \sin \phi_1, \quad (\text{A7b})$$

$$\mathbf{e}_z \cdot \mathbf{e}_{q_1} = b_{gs}^{-1} q_1 \cos \theta_1, \quad (\text{A7c})$$

and

$$\begin{aligned} \mathbf{e}_{q_1} \cdot \mathbf{i}(j) &= [\mathbf{e}_x \cdot \mathbf{e}_{q_1}][\mathbf{e}_x \cdot \mathbf{i}(j)] + [\mathbf{e}_y \cdot \mathbf{e}_{q_1}][\mathbf{e}_y \cdot \mathbf{i}(j)] \\ &\quad + [\mathbf{e}_z \cdot \mathbf{e}_{q_1}][\mathbf{e}_z \cdot \mathbf{i}(j)]. \end{aligned} \quad (\text{A8})$$

3. The remaining double vector integrals

To evaluate the remaining double vector integrals we require the results of Eqs. (A4)–(A8) and additional expressions for the interatomic separation $y_{j'} = |\mathbf{q}' - \mathbf{r}_j|$, for the body-fixed Cartesian components of the unit vector $\mathbf{j}' = [y_{j'}]^{-1}[\mathbf{q}' - \mathbf{r}_j]$, and for the scalar products $\mathbf{e}_{q_1} \cdot \mathbf{j}'$ and $\mathbf{i} \cdot \mathbf{j}'$ all as functions of (q_1, θ_1, ϕ_1) and (q_2, θ_2, ϕ_2) . The required expressions are

$$\begin{aligned} y_{j'} &= [(q_2^2 + \frac{1}{4}q_1^2 + r_j^2) - 2r_j(q_2 \cos \theta_2 + \frac{1}{2}q_1 \cos \theta_1) \\ &\quad + \mathbf{q}_1 \cdot \mathbf{q}_2]^{1/2} \end{aligned} \quad (\text{A9})$$

and

$$\mathbf{e}_x \cdot \mathbf{j}' = [y_{j'}]^{-1} (q_2 \sin \theta_2 \cos \phi_2 + \frac{1}{2}q_1 \sin \theta_1 \cos \phi_1), \quad (\text{A10a})$$

$$\mathbf{e}_y \cdot \mathbf{j}' = [y_{j'}]^{-1} (q_2 \sin \theta_2 \sin \phi_2 + \frac{1}{2}q_1 \sin \theta_1 \sin \phi_1), \quad (\text{A10b})$$

$$\mathbf{e}_z \cdot \mathbf{j}' = [y_{j'}]^{-1} (q_2 \cos \theta_2 + \frac{1}{2}q_1 \cos \theta_1 - r_j). \quad (\text{A10c})$$

Finally $\mathbf{i} \cdot \mathbf{j}'$ and $\mathbf{e}_{q_1} \cdot \mathbf{j}'$ are given, respectively, by Eqs. (A3) and (A8) with \mathbf{j} replaced by \mathbf{j}' .

Finally note that Eqs. (A1)–(A10) are evaluated with the solute and solvent molecules constrained to have their equilibrium internuclear separations b_g and b_{gs} . These constraints are enforced by using Eqs. (2.2) and (2.8) to evaluate, respectively, q_1 and $r_{i(j)}$.

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