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

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A theoretical treatment of the vibrational-vibrational (VV) contribution to the vibrational energy relaxation time T_1 of a solute normal mode in a molecular solvent, which extends a previous treatment [S. A. Adelman, R. H. Stote, and R. Muralidhar, *J. Chem. Phys.* **99**, 1320 (1993), henceforth called Paper I] of the vibrational-translational-rotational (VTR) contribution to T_1 , is outlined and expressions for this VV contribution, valid for the infinitely dilute diatomic solution, are presented. The treatment is based on the formula $T_1 = \beta^{-1}(\omega_l)$, where $\beta(\omega)$ is the friction kernel of the relaxing solute mode and where ω_l is its liquid phase frequency. $\beta(\omega)$ is evaluated as the cosine transform of the autocorrelation function $\langle \mathcal{F}(t)\mathcal{F} \rangle_{0v}$ of the fluctuating generalized force exerted by the vibrating solvent on the solute normal mode coordinate conditional that this coordinate is fixed at its equilibrium value. $\langle \mathcal{F}(t)\mathcal{F} \rangle_{0v}$ is expressed as a superposition of the rigid solvent autocorrelation function $\langle \mathcal{F}(t)\mathcal{F} \rangle_0$ and a correction which accounts for solvent vibrational motion. For diatomic solvents one has $\langle \mathcal{F}(t)\mathcal{F} \rangle_{0v} = \langle \mathcal{F}(t)\mathcal{F} \rangle_0 + N_S M_D(t) \cos \omega_D t F(\Omega_D)$, where N_S = number of solvent molecules, $M_D(t)$ is the vibrational force gradient autocorrelation function, ω_D and Ω_D are solvent molecule liquid phase frequencies, and $F(\Omega) = 1/2\hbar\Omega^{-1} \coth[\hbar\Omega/2k_B T]$. The Gaussian model is assumed for $\langle \mathcal{F}(t)\mathcal{F} \rangle_0$ and $M_D(t)$ yielding $\beta(\omega)$ as a superposition of a Gaussian centered at $\omega=0$ which mediates VTR processes and a Gaussian centered at $\omega=\omega_D$ which mediates VV processes. Vector integral expressions for $M_D(t)$, ω_D , and Ω_D are presented which are similar to the expressions for ω_l and $\langle \mathcal{F}(t)\mathcal{F} \rangle_0$ given in Paper I. These expressions permit the evaluation of the VV contribution to T_1 from the atomic masses, bondlengths, vibrational frequencies, and site-site interaction potentials of the solute and solvent molecules and from specified rigid solvent equilibrium site-site pair correlation functions of the liquid solution.

I. INTRODUCTION

In Ref. 1, henceforth called Paper I, we outlined a molecular theory² of liquid phase vibrational energy relaxation (VER), based on our general approach to problems of chemical dynamics in liquids,³⁻¹⁰ and presented formulas, based on the theory, for the relaxation time T_1 valid for vibrational-translational-rotational (VTR) processes. (Paper I includes many references to the related literature which, for brevity, are omitted here.) In this paper, we continue our discussion emphasizing vibrational-vibrational (VV) processes and, in particular, give formulas for the VV contribution to T_1 which extend the infinitely dilute diatomic solution Gaussian model results of Paper I. These formulas permit the evaluation of this VV contribution from molecular properties, interaction potentials, and equilibrium site-site pair correlation functions.

To make this extension, one must deal with the problem of evaluating the molecular vibrational friction discussed in Paper I. This type of friction was introduced in Refs. 7 and 8(b) and has also been discussed by Whitnell *et al.*¹¹ and Zawadzki and Hynes.¹²

Our work here, as in Paper I, is based on the following formula^{9,13} for T_1 :

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

where $\beta(\omega)$ is the friction kernel of the relaxing solute mode and where ω_l is its liquid phase frequency. We evaluate ω_l using Eq. (2.9) of Paper I and we evaluate $\beta(\omega)$ using [Eq. (1.6) of Paper I]

$$\begin{aligned} \beta(\omega) = & \frac{\langle \mathcal{F}^2 \rangle_0}{2k_B T} \left(\frac{2\pi}{\langle \omega^2 \rangle_{\text{TR}}} \right)^{1/2} \exp \left(-\frac{1}{2} \frac{\omega^2}{\langle \omega^2 \rangle_{\text{TR}}} \right) \\ & + \frac{F(\Omega_D) N_S \langle \mathcal{F}_1^{(v)} \mathcal{F}_1^{(v)} \rangle_0}{4k_B T} \left(\frac{2\pi}{\langle \omega^2 \rangle_v} \right)^{1/2} \\ & \times \exp \left(-\frac{1}{2} \frac{(\omega - \omega_D)^2}{\langle \omega^2 \rangle_v} \right), \end{aligned} \quad (1.2)$$

where

$$F(\Omega) = \frac{1}{2} \hbar \Omega^{-1} \coth \left(\frac{\hbar \Omega}{2k_B T} \right).$$

We deal here with the VV contribution to T_1 and, hence, with the evaluation of the vibrational branch of $\beta(\omega)$ [$\sim F(\Omega_D)$] in Eq. (1.2). We will thus be concerned with the determination of the solvent molecule liquid phase

vibrational frequencies ω_D and Ω_D , with the mean square vibrational force gradient $\langle \mathcal{F}_1^{(v)} \mathcal{F}_1^{(v)} \rangle_0$, and with

$$\langle \omega^2 \rangle_v = \frac{\langle \mathcal{F}_1^{(v)} \mathcal{F}_1^{(v)} \rangle_0}{\langle \mathcal{F}_1^{(v)} \mathcal{F}_1^{(v)} \rangle_0}, \quad (1.3)$$

where as in Paper I, $\langle \rangle_0$ denotes a rigid solution equilibrium phase space average.

The frequencies ω_D and Ω_D refer to the *pure solvent*,² they govern [see Eq. (1.3) of Paper I] the dynamics of a solvent molecule and its equilibrium mean square displacement, respectively. Thus ω_D is a *nonequilibrium* frequency analogous to ω_l . It is given by Eq. (2.18) which is analogous to Eq. (2.9) of Paper I. In contrast, Ω_D is the *equilibrium* frequency of a typical solvent molecule 1. It is the frequency molecule 1 would have if the remainder of the solvent could maintain equilibrium with it during vibrations of its normal mode coordinate. Following arguments given elsewhere,^{2,3} $\omega_D^2 - \Omega_D^2 \propto$ the mean square fluctuating force exerted by the solvent on the mode coordinate of molecule 1. Evaluating this mean square force [via a relationship analogous to Eq. (2.14) of Paper I] yields Eqs. (2.23)–(2.24) for Ω_D^2 from Eq. (2.18) for ω_D^2 .

To complete the determination of the vibrational branch of $\beta(\omega)$ from Eqs. (1.2) and (1.3), we require expressions for $\langle \mathcal{F}_1^{(v)} \mathcal{F}_1^{(v)} \rangle_0$ and $\langle \mathcal{F}_1^{(v)} \mathcal{F}_1^{(v)} \rangle_0$. These expressions may be derived by following procedures which are very similar to those discussed in Sec. I of Paper I. The present outline of their derivation will, therefore, be brief and will, moreover, use (without extensive redefinition) the notation and terminology of Paper I. As in Paper I, all molecules are kept rigid at their equilibrium separations in our evaluations.

We begin with the definition of the vibrational force gradient

$$\mathcal{F}_1^{(v)} = \frac{\partial \mathcal{F}}{\partial v_1}, \quad (1.4)$$

where v_1 is the normal mode coordinate of solvent molecule 1 and where \mathcal{F} is the generalized force exerted by the solvent on the coordinate y of the relaxing solute normal mode. \mathcal{F} is given by [Eq. (1.13) of Paper I]

$$\mathcal{F} = - \sum_{i=1}^n \sum_{\lambda=1}^{N_s} \sum_{k=1}^{n_s} \mu^{il}(z) \cdot \frac{\partial u_{ik}[\mathbf{r}_i, \mathbf{q}_{\lambda k}]}{\partial \mathbf{r}_i}, \quad (1.5)$$

where $n=n_s=2$ for diatomic solutions, where N_s is the number of solvent molecules, and 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 , $\lambda=1, 2, \dots, N_s$, at point $\mathbf{q}_{\lambda k}$. To evaluate $\mathcal{F}_1^{(v)}$ from Eqs. (1.4) and (1.5), we use an expansion for $\partial/\partial v_1$ analogous to the expansion for $\partial/\partial y$ given in Eq. (1.12) of Paper I, namely

$$\frac{\partial}{\partial v_1} = - \sum_{k=1}^{n_s} \mu^{k1}(w_1) \cdot \frac{\partial}{\partial \mathbf{q}_{1k}}, \quad (1.6)$$

where w_1 are the translational-rotational coordinates of solvent molecule 1. Comparing Eqs. (1.4)–(1.6) yields

$$\mathcal{F}_1^{(v)} = \sum_{i=1}^n \sum_{k=1}^{n_s} \mu^{il}(z) \mu^{k1}(w_1) : \frac{\partial^2 u_{ik}[\mathbf{r}_i, \mathbf{q}_{1k}]}{\partial \mathbf{r}_i^2}, \quad (1.7)$$

where we have used

$$\frac{\partial u_{ik}}{\partial \mathbf{q}_{1k}} = - \frac{\partial u_{ik}}{\partial \mathbf{r}_i},$$

which follows because we assume central field site-site potentials u_{ik} .

We next outline the derivation of the results for $\langle \mathcal{F}_1^{(v)} \mathcal{F}_1^{(v)} \rangle$ given in Sec. II. We begin with the simplification

$$\langle \mathcal{F}_1^{(v)} \mathcal{F}_1^{(v)} \rangle_0 = \langle \mathcal{F}_1^{(v)} \mathcal{F}_1^{(v)} \rangle_{y_0z}, \quad (1.8)$$

where $\langle \rangle_{y_0z}$ denotes a rigid solvent phase space average conditional that the solute is fixed in the liquid at an equilibrium configuration y_0z . Equation (1.8) follows from arguments analogous to those which lead to Eq. (1.9) of Paper I.

Comparing Eqs. (1.7) and (1.8) yields

$$\begin{aligned} \langle \mathcal{F}_1^{(v)} \mathcal{F}_1^{(v)} \rangle_0 &= \sum_{i,j=1}^n \sum_{k,l=1}^{n_s} \mu^{il}(z) \\ &\times \left\langle \mu^{k1}(w_1) : \frac{\partial^2 u_{ik}}{\partial \mathbf{r}_i^2} \frac{\partial^2 u_{jl}}{\partial \mathbf{r}_j^2} : \mu^{jl}(w_1) \right\rangle_{y_0z} \\ &\times \mu^{jl}(z). \end{aligned}$$

Finally, for one-component solvents, the ensemble average $\langle \rangle_{y_0z}$ in the previous equation is independent of the identity of the solvent molecule. It thus follows that

$$\begin{aligned} N_s \langle \mathcal{F}_1^{(v)} \mathcal{F}_1^{(v)} \rangle_0 &= \sum_{\lambda=1}^{N_s} \sum_{i,j=1}^n \sum_{k,l=1}^{n_s} \mu^{il}(z) \\ &\times \left\langle \mu^{k1}(w_\lambda) : \frac{\partial^2 u_{ik}}{\partial \mathbf{r}_i^2} \frac{\partial^2 u_{jl}}{\partial \mathbf{r}_j^2} : \mu^{jl}(w_\lambda) \right\rangle_{y_0z} \\ &\times \mu^{jl}(z). \end{aligned} \quad (1.9)$$

To proceed further, we specialize to the solute molecule body-fixed frame depicted in Fig. 1 of Paper I. In this frame we have [Eq. (1.17) of Paper I]

$$\mu^{il}(z) = (-)^i \frac{\mu^{1/2}}{m_i} \mathbf{e}_z, \quad i=1 \text{ or } 2. \quad (1.10a)$$

Note \mathbf{e}_z , the body-fixed z -axis unit vector, may be reinterpreted as the bond-axis unit vector of the solute molecule (see Fig. 1 of Paper I).

The result obtained² for $\mu^{k1}(w_\lambda)$ is analogous to Eq. (1.10a) for $\mu^{il}(z)$, namely

$$\mu^{k1}(w_\lambda) = (-)^k \frac{\mu_s^{1/2}}{M_k} \mathbf{e}_{q_\lambda}, \quad k=1 \text{ or } 2, \quad (1.10b)$$

where \mathbf{e}_{q_λ} is the bond-axis unit vector of solvent molecule λ (see Fig. 1 of Paper I) and where μ_s and M_k are, respectively, the reduced mass and the mass of the k th atom of a solvent molecule.

Using Eqs. (1.10), Eq. (1.9) may be rewritten as

$$N_s \langle \mathcal{F}_1^{(v)} \mathcal{F}_1^{(v)} \rangle_0 = \frac{9}{MM_s} \sum_{\lambda=1}^{N_s} \sum_{i,j=1}^n \sum_{k,l=1}^{n_s} T^{ij} T_s^{kl} \mathbf{e}_z \times \left\langle \mathbf{e}_{q_\lambda} : \frac{\partial^2 u_{ik}}{\partial \mathbf{r}_i^2} \frac{\partial^2 u_{jl}}{\partial \mathbf{r}_j^2} : \mathbf{e}_{q_\lambda} \right\rangle_{y_0 z} \mathbf{e}_z, \quad (1.11)$$

where M and M_s are, respectively, the total masses of the solute molecule and a solvent molecule and where T^{ij} and T_s^{kl} are defined in Eq. (2.1) of Paper I.

Following steps similar to (but more involved than) those which lead from Eq. (1.14) to Eq. (1.15) of Paper I, Eq. (1.11) may be expressed as

$$N_s \langle \mathcal{F}_1^{(v)} \mathcal{F}_1^{(v)} \rangle_0 = \frac{9}{MM_s} \sum_{i,j=1}^n \sum_{k,l=1}^{n_s} T^{ij} T_s^{kl} \times \int d\mathbf{q} d\mathbf{q}' \rho_{1k,1l}[\mathbf{q}, \mathbf{q}'; b_g] \mathbf{e}_z \mathbf{e}_{q_1} : \left(\frac{\partial^2 u_{ik}(y_i)}{\partial \mathbf{r}_i^2} \frac{\partial^2 u_{jl}(\bar{y}_j)}{\partial \mathbf{r}_j^2} \right) : \mathbf{e}_{q_1} \mathbf{e}_z, \quad (1.12)$$

where $\mathbf{e}_{q_1} = \mathbf{e}_{q_1}(\mathbf{q}, \mathbf{q}')$ is defined in Eq. (2.7) of Paper I. In Eq. (1.11) the following holds true.

The ensemble averaged solvent site density $\rho_{1k,1l}[\mathbf{q}, \mathbf{q}'; b_g]$ (discussed in Paper I) is proportional to the joint probability that sites k and l on the same molecule are, respectively, at points \mathbf{q} and \mathbf{q}' given that the solute is fixed in the liquid with its equilibrium internuclear separation b_g .

The index $\bar{l} = \bar{k}$, where \bar{k} is given by Eq. (2.14), if $l = k$ while $\bar{l} = l$ if $l \neq k$.

The interatomic distance $y_i = |\mathbf{y}_i| = |\mathbf{q} - \mathbf{r}_i|$ while the interatomic distance $\bar{y}_j = |\bar{\mathbf{y}}_j|$, with $\bar{\mathbf{y}}_j$ given by Eq. (2.4).

We next note that following steps analogous to those which lead to Eq. (1.18) of Paper I yields

$$\mathbf{e}_z \mathbf{e}_{q_1} : \frac{\partial^2 u_{ik}(y_i)}{\partial \mathbf{r}_i^2} = B_{zq_1}^{ik}[\mathbf{y}_i] \quad (1.13a)$$

and

$$\mathbf{e}_z \mathbf{e}_{q_1} : \frac{\partial^2 u_{jl}(\bar{y}_j)}{\partial \mathbf{r}_j^2} = B_{zq_1}^{jl}[\bar{\mathbf{y}}_j], \quad (1.13b)$$

where the functions on the right-hand side of Eqs. (1.13) are defined in Eqs. (2.2).

To complete the derivation of the results for $N_s \langle \mathcal{F}_1^{(v)} \mathcal{F}_1^{(v)} \rangle_0$ from Eqs. (1.12) and (1.13), we use the superposition approximation for $\rho_{1k,1l}[\mathbf{q}, \mathbf{q}'; b_g]$ discussed in Sec. I of Paper I and, moreover, recast the integrals in Eq. (1.12) in terms of \mathbf{q}_1 and \mathbf{q}_2 defined in Eq. (2.6) of Paper I. This then yields Eqs. (2.6), Eqs. (2.13), and Eq. (2.15a) for $N_s \langle \mathcal{F}_1^{(v)} \mathcal{F}_1^{(v)} \rangle_0$.

The results for $\langle \mathcal{F}_1^{(v)} \mathcal{F}_1^{(v)} \rangle_0$ are developed similarly, additionally requiring steps analogous to those given in Eqs. (1.19)–(1.21) of Paper I.

II. DIATOMIC SOLUTION RESULTS

In this section we summarize the results for $\langle \mathcal{F}_1^{(v)} \mathcal{F}_1^{(v)} \rangle_0$ and $\langle \mathcal{F}_1^{(v)} \mathcal{F}_1^{(v)} \rangle_0$ (Sec. II A) and for ω_D^2 and Ω_D^2 (Sec. II B). We use terminology and notation which is very similar to that used in Sec. II of Paper I. As in Paper I, we restrict ourselves to a diatomic solute present at infinite dilution in an otherwise pure diatomic solvent at Kelvin temperature T and number density ρ_0 . Thus, in the formulas presented below n and n_s , respectively, the number of solute atoms and the number of solvent atoms per molecule, have the values $n = n_s = 2$.

A. Diatomic solution results for $\langle \mathcal{F}_1^{(v)} \mathcal{F}_1^{(v)} \rangle_0$ and $\langle \mathcal{F}_1^{(v)} \mathcal{F}_1^{(v)} \rangle_0$

1. Quantities appearing in the expressions

Most of the quantities appearing in the formulas have been defined in Sec. II of Paper I and will be used without further definition in this section. We additionally require the reduced mass and moment of inertia of a solvent molecule, respectively, $\mu_s = M_s^{-1} M_1 M_2$ and $I_s = \mu_s b_{gs}^2$, where b_{gs} is the gas phase equilibrium internuclear separation of a solvent molecule and the auxiliary functions $W_{ik}[y_i]$ and $W_{jl}[\bar{y}_j]$ defined by

$$W_{ik}[y_i] = 3y_i^{-1} U_{ik}[y_i] - \frac{d^3 u_{ik}[y_i]}{dy_i^3} \quad (2.1)$$

and

$$W_{jl}[\bar{y}_j] = 3[\bar{y}_j]^{-1} U_{jl}[\bar{y}_j] - \frac{d^3 u_{jl}[\bar{y}_j]}{d\bar{y}_j^3}.$$

2. The vector integrals

The diatomic solution results for $\langle \mathcal{F}_1^{(v)} \mathcal{F}_1^{(v)} \rangle_0$ involve single and double vector integrals which are analogous to those discussed in Sec. II of Paper I. As in Paper I, the vector integrals are evaluated in the solute body-fixed frame (Fig. 1 of Paper I) as quadratures over the body-fixed spherical polar coordinates $(q, \theta, \phi) = \mathbf{q}$, $(q_1, \theta_1, \phi_1) = \mathbf{q}_1$, and $(q_2, \theta_2, \phi_2) = \mathbf{q}_2$ conditional that all molecules in the solution are constrained to have their gas phase equilibrium internuclear separations.

3. The B functions

The integrands of the vector integrals involve the following symmetric functions of the unit vectors \mathbf{e}_α , \mathbf{e}_β , \mathbf{e}_γ :

$$B_{\alpha\beta}^{ik}[\mathbf{y}_i] = [\mathbf{e}_\alpha \cdot \mathbf{i}] [\mathbf{e}_\beta \cdot \mathbf{i}] U_{ik}[y_i] + [\mathbf{e}_\alpha \cdot \mathbf{e}_\beta] y_i^{-1} \frac{du_{ik}[y_i]}{dy_i}, \quad (2.2a)$$

$$B_{\alpha\beta}^{jl}[\bar{\mathbf{y}}_j] = [\mathbf{e}_\alpha \cdot \bar{\mathbf{j}}] [\mathbf{e}_\beta \cdot \bar{\mathbf{j}}] U_{jl}[\bar{y}_j] + [\mathbf{e}_\alpha \cdot \mathbf{e}_\beta] \bar{y}_j^{-1} \frac{du_{jl}[\bar{y}_j]}{d\bar{y}_j}, \quad (2.2b)$$

and

$$B_{\alpha\beta\gamma}^{ik}[\mathbf{y}_i] = [\mathbf{e}_\alpha \cdot \mathbf{i}][\mathbf{e}_\beta \cdot \mathbf{i}][\mathbf{e}_\gamma \cdot \mathbf{i}]W_{ik}[\mathbf{y}_i] \\ - [[\mathbf{e}_\alpha \cdot \mathbf{i}][\mathbf{e}_\beta \cdot \mathbf{e}_\gamma] + [\mathbf{e}_\beta \cdot \mathbf{i}][\mathbf{e}_\alpha \cdot \mathbf{e}_\gamma] \\ + [\mathbf{e}_\gamma \cdot \mathbf{i}][\mathbf{e}_\alpha \cdot \mathbf{e}_\beta]]\mathbf{y}_i^{-1}U_{ik}[\mathbf{y}_i], \quad (2.3a)$$

$$B_{\alpha\beta\gamma}^{jl}[\bar{\mathbf{y}}_j] = [\mathbf{e}_\alpha \cdot \bar{\mathbf{j}}][\mathbf{e}_\beta \cdot \bar{\mathbf{j}}][\mathbf{e}_\gamma \cdot \bar{\mathbf{j}}]W_{jl}[\bar{\mathbf{y}}_j] \\ - [[\mathbf{e}_\alpha \cdot \bar{\mathbf{j}}][\mathbf{e}_\beta \cdot \mathbf{e}_\gamma] + [\mathbf{e}_\beta \cdot \bar{\mathbf{j}}][\mathbf{e}_\alpha \cdot \mathbf{e}_\gamma] \\ + [\mathbf{e}_\gamma \cdot \bar{\mathbf{j}}][\mathbf{e}_\alpha \cdot \mathbf{e}_\beta]]\bar{\mathbf{y}}_j^{-1}U_{jl}[\bar{\mathbf{y}}_j], \quad (2.3b)$$

where $\bar{\mathbf{y}}_j = |\bar{\mathbf{y}}_j|$ and $\bar{\mathbf{j}} = \bar{\mathbf{y}}_j^{-1}\bar{\mathbf{y}}_j$ with

$$\bar{\mathbf{y}}_j = \bar{\mathbf{q}} - \mathbf{r}_j$$

and

$$\bar{\mathbf{q}} = \begin{cases} \mathbf{q} & \text{if } l=k \\ \mathbf{q}' & \text{if } l \neq k \end{cases} \quad (2.4)$$

Thus if $l=k$, $\bar{\mathbf{y}}_j = \mathbf{y}_j$ while if $l \neq k$, $\bar{\mathbf{y}}_j = \mathbf{y}_{j'}$.

In our expressions for the integrands, \mathbf{e}_α , \mathbf{e}_β , \mathbf{e}_γ will be either the unit vectors \mathbf{e}_x , \mathbf{e}_y , \mathbf{e}_z of the solute body-fixed frame or the solvent molecule bond-axis unit vector \mathbf{e}_{q_1} defined by

$$\mathbf{e}_{q_1} = b_{gs}^{-1}\mathbf{q}_1. \quad (2.5)$$

As examples of these definitions, $B_{xzq_1}^{jl}[\bar{\mathbf{y}}_j]$ for $l=k$ is given by

$$B_{xzq_1}^{jk}[\mathbf{y}_j] = [\mathbf{e}_x \cdot \mathbf{j}][\mathbf{e}_z \cdot \mathbf{j}][\mathbf{e}_{q_1} \cdot \mathbf{j}]W_{jk}[\mathbf{y}_j] - [[\mathbf{e}_x \cdot \mathbf{j}] \\ \times [\mathbf{e}_z \cdot \mathbf{e}_{q_1}] + [\mathbf{e}_z \cdot \mathbf{j}][\mathbf{e}_x \cdot \mathbf{e}_{q_1}]]\mathbf{y}_j^{-1}U_{jk}[\mathbf{y}_j]$$

while $B_{xzq_1}^{jl}$ for $l \neq k$ is given by

$$B_{xzq_1}^{jl}[\mathbf{y}_{j'}] = [\mathbf{e}_x \cdot \mathbf{j}'][\mathbf{e}_z \cdot \mathbf{j}'][\mathbf{e}_{q_1} \cdot \mathbf{j}']W_{jl}[\mathbf{y}_{j'}] \\ - [[\mathbf{e}_x \cdot \mathbf{j}'][\mathbf{e}_z \cdot \mathbf{e}_{q_1}] \\ + [\mathbf{e}_z \cdot \mathbf{j}'][\mathbf{e}_x \cdot \mathbf{e}_{q_1}]]\mathbf{y}_{j'}^{-1}U_{jl}[\mathbf{y}_{j'}].$$

We next turn to the results for $\langle \mathcal{F}_1^{(v)} \mathcal{F}_1^{(v)} \rangle_0$ and $\langle \mathcal{F}_1^{(v)} \mathcal{F}_1^{(v)} \rangle_0$. These are expressed as superpositions of the vector integrals discussed earlier.

4. Result for $\langle \mathcal{F}_1^{(v)} \mathcal{F}_1^{(v)} \rangle_0$

The result for $\langle \mathcal{F}_1^{(v)} \mathcal{F}_1^{(v)} \rangle_0$ is

$$N_s \langle \mathcal{F}_1^{(v)} \mathcal{F}_1^{(v)} \rangle_0 = \frac{9}{MM_s} \sum_{i,j=1}^n \sum_{k,l=1}^{n_s} T^{ij} T_s^{kl} \mathbf{e}_{q_1} \mathbf{e}_{q_1} \mathbf{e}_z \mathbf{e}_z :: K_{ijkl}. \quad (2.6)$$

5. Decomposition of $\langle \mathcal{F}_1^{(v)} \mathcal{F}_1^{(v)} \rangle_0$

$\langle \mathcal{F}_1^{(v)} \mathcal{F}_1^{(v)} \rangle_0$ has a decomposition which is analogous to the decomposition of $\langle \mathcal{F}^2 \rangle_0$ given in Eq. (2.15) of Paper I, namely

$$N_s \langle \mathcal{F}_1^{(v)} \mathcal{F}_1^{(v)} \rangle_0 = N_s (\langle \mathcal{F}_1^{(v)} \mathcal{F}_1^{(v)} \rangle_{0d,t} + \langle \mathcal{F}_1^{(v)} \mathcal{F}_1^{(v)} \rangle_{0d,r} \\ + \langle \mathcal{F}_1^{(v)} \mathcal{F}_1^{(v)} \rangle_{0i,t} \\ + \langle \mathcal{F}_1^{(v)} \mathcal{F}_1^{(v)} \rangle_{0i,r}). \quad (2.7)$$

6. Expressions for the components of $\langle \mathcal{F}_1^{(v)} \mathcal{F}_1^{(v)} \rangle_0$

The results for the components of $\langle \mathcal{F}_1^{(v)} \mathcal{F}_1^{(v)} \rangle_0$ are

$$N_s \langle \mathcal{F}_1^{(v)} \mathcal{F}_1^{(v)} \rangle_{0d,t} = \frac{9k_B T}{M_s^2 M} \sum_{i,j=1}^n \sum_{k,l=1}^{n_s} T^{ij} T_s^{kl} \mathbf{e}_{q_1} \mathbf{e}_{q_1} \mathbf{e}_z \mathbf{e}_z :: M_{ijkl}, \quad (2.8a)$$

$$N_s \langle \mathcal{F}_1^{(v)} \mathcal{F}_1^{(v)} \rangle_{0d,r} = \frac{9k_B T}{M_s^2 M} \sum_{i,j=1}^n \sum_{k,l=1}^{n_s} T^{ij} T_s^{kl} \left(\frac{M_s}{I_s} (\mathbf{e}_z \mathbf{e}_z :: K_{ijkl} - \mathbf{e}_{q_1} \mathbf{e}_{q_1} \mathbf{e}_z \mathbf{e}_z :: K_{ijkl}) (-)^{k+l} \frac{2M_s}{M b_{gs}} (\mathbf{e}_{q_1} \mathbf{e}_z \mathbf{e}_z :: L_{ijkl} \right. \\ \left. - \mathbf{e}_{q_1} \mathbf{e}_{q_1} \mathbf{e}_z \mathbf{e}_z :: L_{ijkl}) + 3T_s^{kl} (\mathbf{e}_{q_1} \mathbf{e}_{q_1} \mathbf{e}_z \mathbf{e}_z :: M_{ijkl} - \mathbf{e}_{q_1} \mathbf{e}_{q_1} \mathbf{e}_{q_1} \mathbf{e}_z \mathbf{e}_z :: M_{ijkl}) \right), \quad (2.8b)$$

$$N_s \langle \mathcal{F}_1^{(v)} \mathcal{F}_1^{(v)} \rangle_{0i,t} = \frac{9k_B T}{M^2 M_s} \sum_{i,j=1}^n \sum_{k,l=1}^{n_s} T^{ij} T_s^{kl} \mathbf{e}_{q_1} \mathbf{e}_{q_1} \mathbf{e}_z \mathbf{e}_z :: M_{ijkl}, \quad (2.8c)$$

and

$$N_s \langle \mathcal{F}_1^{(v)} \mathcal{F}_1^{(v)} \rangle_{0i,r} \\ = \frac{18k_B T}{M^2 M_s} \sum_{i,j=1}^n \sum_{k,l=1}^{n_s} T^{ij} T_s^{kl} \left(\frac{M}{I} \mathbf{e}_{q_1} \mathbf{e}_{q_1} \mathbf{e}_x \mathbf{e}_x :: K_{ijkl} (-)^j \right. \\ \times \frac{2M}{m_j b_g} \mathbf{e}_{q_1} \mathbf{e}_{q_1} \mathbf{e}_z \mathbf{e}_x \mathbf{e}_x :: L_{ijkl} \\ \left. + 3T^{ij} \mathbf{e}_{q_1} \mathbf{e}_{q_1} \mathbf{e}_z \mathbf{e}_x \mathbf{e}_x :: M_{ijkl} \right). \quad (2.8d)$$

We next give expressions for the integrals appearing in Eqs. (2.6) and (2.8).

7. The integral $\mathbf{e}_z \mathbf{e}_z :: K_{ijkl}$

We begin with the integral $\mathbf{e}_z \mathbf{e}_z :: K_{ijkl}$ appearing in Eq. (2.8b). An expression for this integral was given in Eqs. (2.23) and (2.24b) of Paper I. In this paper we give an alternative equivalent expression in terms of the functions defined in Eqs. (2.2).

We decompose $\mathbf{e}_z \mathbf{e}_z :: K_{ijkl}$ as

$$\mathbf{e}_z \mathbf{e}_z \tilde{\mathbf{l}}::K_{ijkl} = \delta_{kl} \mathbf{e}_z \mathbf{e}_z \tilde{\mathbf{l}}::K_{ijkk} + (1 - \delta_{kl}) \mathbf{e}_z \mathbf{e}_z \tilde{\mathbf{l}}::K_{ijkl}, \quad (2.9)$$

where $\mathbf{e}_z \mathbf{e}_z \tilde{\mathbf{l}}::K_{ijkk}$ is the single vector integral defined by

$$\mathbf{e}_z \mathbf{e}_z \tilde{\mathbf{l}}::K_{ijkk} = \int_0^{2\pi} d\phi \int_0^\infty q^2 dq \int_0^\pi \sin \theta d\theta \rho_k^{(n+1)} [b_g; \mathbf{q}] \times A_{ijkk} [b_g; \mathbf{q}\mathbf{q}] \quad (2.10a)$$

and where $\mathbf{e}_z \mathbf{e}_z \tilde{\mathbf{l}}::K_{ijkl}$ ($k \neq l$) is the double vector integral defined by

$$\begin{aligned} \mathbf{e}_z \mathbf{e}_z \tilde{\mathbf{l}}::K_{ijkl} &= (4\pi\rho_0)^{-1} \int_0^{2\pi} d\phi_2 \int_0^\pi \sin \theta_2 d\theta_2 \int_0^\infty q_2^2 dq_2 \\ &\times \int_0^{2\pi} d\phi_1 \int_0^\pi \sin \theta_1 d\theta_1 (\bar{\rho}_k^{(n+1)}) \\ &\times [b_g; \mathbf{q}] \bar{\rho}_l^{(n+1)} [b_g; \mathbf{q}'] A_{ijkl} [b_g; \mathbf{q}\mathbf{q}']. \end{aligned} \quad (2.10b)$$

The function $A_{ijkl} [b_g; \mathbf{q}, \bar{\mathbf{q}}]$ appearing in Eqs. (2.10) is given by

$$A_{ijkl} [b_g; \mathbf{q}, \bar{\mathbf{q}}] = 2B_{xz}^{ik} [\mathbf{y}_i] B_{xz}^{jl} [\bar{\mathbf{y}}_j] + B_{zz}^{ik} [\mathbf{y}_i] B_{zz}^{jl} [\bar{\mathbf{y}}_j], \quad (2.11)$$

where $\bar{\mathbf{q}}$ and $\bar{\mathbf{y}}_j$ are defined in Eqs. (2.4).

8. The remaining integrals

The remaining integrals in Eqs. (2.6) and (2.8) all have an identical generic form and, therefore, will be collectively denoted by A_{ijkl} . For example, they may all be decomposed as

$$A_{ijkl} = \delta_{kl} A_{ijkk} + (1 - \delta_{kl}) A_{ijkl}, \quad (2.12)$$

where A_{ijkk} and A_{ijkl} are double vector integrals given, respectively, by

$$\begin{aligned} A_{ijkk} &= (4\pi\rho_0)^{-1} \int_0^{2\pi} d\phi_2 \int_0^\pi \sin \theta_2 d\theta_2 \int_0^\infty q_2^2 dq_2 \\ &\times \int_0^{2\pi} d\phi_1 \int_0^\pi \sin \theta_1 d\theta_1 (\bar{\rho}_k^{(n+1)}) [b_g; \mathbf{q}] \bar{\rho}_k^{(n+1)} \\ &\times [b_g; \mathbf{q}'] A_{ijkk} [b_g; \mathbf{q}\mathbf{q}] \end{aligned} \quad (2.13a)$$

and ($k \neq l$)

$$\begin{aligned} A_{ijkl} &= (4\pi\rho_0)^{-1} \int_0^{2\pi} d\phi_2 \int_0^\pi \sin \theta_2 d\theta_2 \int_0^\infty q_2^2 dq_2 \int_0^{2\pi} d\phi_1 \\ &\times \int_0^\pi \sin \theta_1 d\theta_1 (\bar{\rho}_k^{(n+1)}) [b_g; \mathbf{q}] \bar{\rho}_l^{(n+1)} \\ &\times [b_g; \mathbf{q}'] A_{ijkl} [b_g; \mathbf{q}\mathbf{q}'], \end{aligned} \quad (2.13b)$$

where the index \bar{k} in Eq. (2.13a) is defined as

$$\bar{k} = 1 \quad \text{if } k = 2$$

and

$$\bar{k} = 2 \quad \text{if } k = 1. \quad (2.14)$$

The integrals differ from one another only through the functions $A_{ijkl} [b_g; \mathbf{q}, \bar{\mathbf{q}}]$. The explicit results for these functions are

$$\mathbf{e}_{q_1} \mathbf{e}_{q_1} \mathbf{e}_z \mathbf{e}_z::K_{ijkl} \quad A_{ijkl} [b_g; \mathbf{q}, \bar{\mathbf{q}}] = B_{zq_1}^{ik} [\mathbf{y}_i] B_{zq_1}^{jl} [\bar{\mathbf{y}}_j], \quad (2.15a)$$

$$\mathbf{e}_{q_1} \mathbf{e}_{q_1} \mathbf{e}_x \mathbf{e}_x::K_{ijkl} \quad A_{ijkl} [b_g; \mathbf{q}, \bar{\mathbf{q}}] = B_{xq_1}^{ik} [\mathbf{y}_i] B_{xq_1}^{jl} [\bar{\mathbf{y}}_j], \quad (2.15b)$$

$$\mathbf{e}_{q_1} \mathbf{e}_{q_1} \mathbf{e}_q \mathbf{e}_z::L_{ijkl} \quad A_{ijkl} [b_g; \mathbf{q}, \bar{\mathbf{q}}] = B_{zq_1}^{ik} [\mathbf{y}_i] B_{zq_1 q_1}^{jl} [\bar{\mathbf{y}}_j], \quad (2.15c)$$

$$\mathbf{e}_{q_1} \mathbf{e}_{q_1} \mathbf{e}_z \mathbf{e}_x::L_{ijkl} \quad A_{ijkl} [b_g; \mathbf{q}, \bar{\mathbf{q}}] = B_{xq_1}^{ik} [\mathbf{y}_i] B_{xzq_1}^{jl} [\bar{\mathbf{y}}_j], \quad (2.15d)$$

$$\mathbf{e}_{q_1} \mathbf{e}_{q_1} \mathbf{e}_{q_1} \mathbf{e}_z \mathbf{e}_z::M_{ijkl} \quad A_{ijkl} [b_g; \mathbf{q}, \bar{\mathbf{q}}] = B_{zq_1 q_1}^{ik} [\mathbf{y}_i] B_{zq_1 q_1}^{jl} [\bar{\mathbf{y}}_j], \quad (2.15e)$$

$$\mathbf{e}_{q_1} \mathbf{e}_{q_1} \mathbf{e}_z \mathbf{e}_x \mathbf{e}_x::M_{ijkl} \quad A_{ijkl} [b_g; \mathbf{q}, \bar{\mathbf{q}}] = B_{xzq_1}^{ik} [\mathbf{y}_i] B_{xzq_1}^{jl} [\bar{\mathbf{y}}_j], \quad (2.15f)$$

$$\begin{aligned} \mathbf{e}_{q_1} \mathbf{e}_z \mathbf{e}_z \tilde{\mathbf{l}}::L_{ijkl} \quad A_{ijkl} [b_g; \mathbf{q}, \bar{\mathbf{q}}] &= 2B_{xz}^{ik} [\mathbf{y}_i] B_{xzq_1}^{jl} [\bar{\mathbf{y}}_j] + B_{zz}^{ik} [\mathbf{y}_i] B_{zzq_1}^{jl} [\bar{\mathbf{y}}_j], \end{aligned} \quad (2.15g)$$

$$\begin{aligned} \mathbf{e}_{q_1} \mathbf{e}_{q_1} \mathbf{e}_z \mathbf{e}_z \tilde{\mathbf{l}}::M_{ijkl} \quad A_{ijkl} [b_g; \mathbf{q}, \bar{\mathbf{q}}] &= 2B_{xzq_1}^{ik} [\mathbf{y}_i] B_{xzq_1}^{jl} [\bar{\mathbf{y}}_j] \\ &+ B_{zzq_1}^{ik} [\mathbf{y}_i] B_{zzq_1}^{jl} [\bar{\mathbf{y}}_j]. \end{aligned} \quad (2.15h)$$

10. Evaluation of the integrands

To complete the evaluation of the integrals, we must construct their integrands in terms of (q, θ, ϕ) for the single vector integral $\mathbf{e}_z \mathbf{e}_z \tilde{\mathbf{l}}::K_{ijkk}$ and in terms of $(b_{gs}, \theta_1, \phi_1)$ and (q_2, θ_2, ϕ_2) for the double vector integrals. This construction may be accomplished using the results of Appendix A of Paper I.

B. Diatomic solvent results for ω_D and Ω_D

We conclude this section by summarizing the diatomic solvent results for the liquid phase frequencies ω_D and Ω_D . Within the present formulation¹ these are the frequencies of a molecule in a *pure* diatomic solvent. Many of the quantities appearing in the expressions have already been defined. We next define the remaining required quantities.

1. Quantities appearing in the expressions

The expressions resemble certain results given in Paper I. For example, the expressions involve vector integrals which are analogous to those appearing in Eqs. (2.12) and (2.14) of Paper I. In Paper I, however, the integrals are performed with the solute molecule fixed in the liquid and in the solute body-fixed frame while here solvent molecule 1 is fixed and the integrals are performed in an analogous frame located on that molecule. The unit vectors of this body-fixed frame will be denoted by \mathbf{e}_{x_1} , \mathbf{e}_{y_1} , \mathbf{e}_{z_1} . The in-

tegrals required here may be obtained from those of Paper I if one utilizes the following notational transpositions. (i) Solute atomic sites and coordinates $i, j, \mathbf{r}_i, \mathbf{r}_j \rightarrow$ atomic sites and coordinates of solvent molecule 1, $k, l, \mathbf{q}_{1k}, \mathbf{q}_{1l}$. (ii) Solvent atomic sites and coordinates $k', l', \mathbf{q}, \mathbf{q}' \rightarrow$ solvent atomic sites and coordinates $k', l', \mathbf{q}, \mathbf{q}'$. (iii) $\mathbf{y}_i, y_i, \mathbf{i}$, etc. $\rightarrow \mathbf{y}_k = \mathbf{q} - \mathbf{q}_{1k}, \mathbf{y}_l = \mathbf{q} - \mathbf{q}_{1l}, \mathbf{y}_{l'} = \mathbf{q}' - \mathbf{q}_{1l}, y_k = |\mathbf{y}_k|, y_l = |\mathbf{y}_l|, y_{l'} = |\mathbf{y}_{l'}|, \mathbf{k} = \mathbf{y}_k^{-1} \mathbf{y}_k, \mathbf{l} = \mathbf{y}_l^{-1} \mathbf{y}_l, \mathbf{l}' = \mathbf{y}_{l'}^{-1} \mathbf{y}_{l'}$. (iv) Solute-solvent site-site potentials \rightarrow solvent-solvent site-site potentials $v_{kk'}[y_k], v_{ll'}[y_{l'}]$. Moreover, we define, in analogy to Eq. (2.3) of Paper I,

$$V_{kk'}[y_k] = \frac{d^2 v_{kk'}[y_k]}{dy_k^2} - y_k^{-1} \frac{dv_{kk'}[y_k]}{dy_k} \quad (2.16)$$

and

$$V_{ll'}[y_{l'}] = \frac{d^2 v_{ll'}[y_{l'}]}{dy_{l'}^2} - [y_{l'}]^{-1} \frac{dv_{ll'}[y_{l'}]}{dy_{l'}}.$$

(v) Solute-solvent site densities \rightarrow solvent-solvent site densities given in analogy to Eqs. (2.4) and (2.5) of Paper I by

$$\rho_{k'}^{(n_s+1)}[b_{gs}; \mathbf{q}] \doteq \rho_0 \prod_{k=1}^{n_s} g_{kk'}[y_k] \quad (2.17a)$$

and

$$\rho_{l'}^{(n_s+1)}[b_{gs}; \mathbf{q}'] \doteq \rho_0 \prod_{l=1}^{n_s} g_{ll'}[y_{l'}]$$

and

$$\bar{\rho}_{k'}^{(n_s+1)}[b_{gs}; \mathbf{q}] \doteq \rho_0 \prod_{k=1}^{n_s} \bar{g}_{kk'}[y_k] \quad (2.17b)$$

and

$$\bar{\rho}_{l'}^{(n_s+1)}[b_{gs}; \mathbf{q}'] \doteq \rho_0 \prod_{l=1}^{n_s} \bar{g}_{ll'}[y_{l'}],$$

where $g_{kk'}$ and $\bar{g}_{kk'}$ are solvent-solvent site-site pair correlation functions defined in analogy to the solute-solvent correlation functions g_{ik} and \bar{g}_{ik} . Given these definitions, we next summarize the results for ω_D and Ω_D .

2. Result for ω_D^2

The result for ω_D is analogous to the result for the solute liquid phase frequency ω_l given in Eqs. (2.9)–(2.13) of Paper I. Namely, ω_D is given by

$$\omega_D^2 = \omega_{gs}^2 + \omega_{cf,s}^2 + \omega_{D^b}^2 \quad (2.18)$$

$$\omega_{gs}^2 = \text{square of the fundamental gas phase frequency of the diatomic solvent molecule,} \quad (2.19)$$

$$\omega_{cf,s}^2 = \frac{6k_B T}{I_s}, \quad (2.20)$$

$$\omega_{D^b}^2 = 3M_s^{-1} \sum_{k=1}^{n_s} \sum_{k'=1}^{n_s} T_s^{kk'} \mathbf{e}_{z_1} \cdot \mathbf{K}_{kk'} \cdot \mathbf{e}_{z_1}, \quad (2.21)$$

where $\mathbf{e}_z \cdot \mathbf{K}_{kk'} \cdot \mathbf{e}_{z_1}$ is given by

$$\begin{aligned} & \mathbf{e}_{z_1} \cdot \mathbf{K}_{kk'} \cdot \mathbf{e}_{z_1} \\ &= \int_0^{2\pi} d\phi \int_0^\infty q^2 dq \int_0^\pi \sin \theta d\theta \rho_{k'}^{(n_s+1)}[b_{gs}; \mathbf{q}] \\ & \times \left([\mathbf{e}_{z_1} \cdot \mathbf{k}]^2 V_{kk'}[y_k] + y_k^{-1} \frac{dv_{kk'}[y_k]}{dy_k} \right)_{b_{gs}}. \end{aligned} \quad (2.22)$$

3. Result for Ω_D^2

The result for Ω_D^2 is

$$\Omega_D^2 = \omega_{gs}^2 + \omega_{cf,s}^2 + \Omega_{D^b}^2 \quad (2.23)$$

where

$$\Omega_{D^b}^2 = \omega_{D^b}^2 - 3(k_B T M_s)^{-1} \sum_{k,l=1}^{n_s} \sum_{k',l'=1}^{n_s} T_s^{kl} \mathbf{e}_{z_1} \cdot \mathbf{I}_{klk'l'} \cdot \mathbf{e}_{z_1} \quad (2.24)$$

The definition of the integral $\mathbf{e}_{z_1} \mathbf{e}_{z_1} : \mathbf{I}_{klk'l'}$ is analogous to the definition of the integral $\mathbf{e}_z \mathbf{e}_z : \mathbf{I}_{ijkl}$ given in Eqs. (2.22)–(2.24a) of Paper I. Namely

$$\mathbf{e}_{z_1} \mathbf{e}_{z_1} : \mathbf{I}_{klk'l'} = \delta_{k'l'} \mathbf{e}_{z_1} \mathbf{e}_{z_1} : \mathbf{I}_{klk'k'} + (1 - \delta_{k'l'}) \mathbf{e}_{z_1} \mathbf{e}_{z_1} : \mathbf{I}_{klk'l'}, \quad (2.25)$$

where

$$\begin{aligned} \mathbf{e}_{z_1} \mathbf{e}_{z_1} : \mathbf{I}_{klk'k'} &= \int_0^{2\pi} d\phi \int_0^\infty q^2 dq \int_0^\pi \sin \theta d\theta \rho_{k'}^{(n_s+1)} \\ & \times [b_{gs}; \mathbf{q}] A_{klk'k'}[b_{gs}; \mathbf{q}\mathbf{q}], \end{aligned} \quad (2.26a)$$

and ($k' \neq l'$)

$$\begin{aligned} \mathbf{e}_{z_1} \mathbf{e}_{z_1} : \mathbf{I}_{klk'l'} &= (4\pi\rho_0)^{-1} \int_0^{2\pi} d\phi_2 \int_0^\pi \sin \theta_2 d\theta_2 \int_0^\infty q_2^2 dq_2 \\ & \times \int_0^{2\pi} d\phi_1 \int_0^\pi \sin \theta_1 d\theta_1 (\bar{\rho}_{k'}^{(n_s+1)}[b_{gs}; \mathbf{q}] \\ & \times \bar{\rho}_{l'}^{(n_s+1)}[b_{gs}; \mathbf{q}'] A_{klk'l'}[b_{gs}; \mathbf{q}\mathbf{q}']) \end{aligned} \quad (2.26b)$$

with

$$A_{klk'k'}[b_{gs}; \mathbf{q}\mathbf{q}] = [\mathbf{e}_{z_1} \cdot \mathbf{k}] [\mathbf{e}_{z_1} \cdot \mathbf{l}] \left(\frac{dv_{kk'}[y_k]}{dy_k} \frac{dv_{ll'}[y_{l'}]}{dy_{l'}} \right) \quad (2.27a)$$

and

$$A_{klk'l'}[b_{gs}; \mathbf{q}\mathbf{q}'] = [\mathbf{e}_{z_1} \cdot \mathbf{k}] [\mathbf{e}_{z_1} \cdot \mathbf{l}'] \left(\frac{dv_{kk'}[y_k]}{dy_k} \frac{dv_{ll'}[y_{l'}]}{dy_{l'}} \right). \quad (2.27b)$$

The expressions for ω_D^2 and Ω_D^2 are evaluated within the rigid solvent model with all molecules at their equilibrium internuclear separation b_{gs} . Expressions which permit evaluation of the integrands in terms of the spherical polar coordinates are given in Appendix A.

C. Summary

Vector integral formulas for the solvent molecule liquid phase frequencies ω_D and Ω_D and for the vibrational force gradient Gaussian model parameters $\langle \mathcal{F}_1^{(v)} \mathcal{F}_1^{(v)} \rangle_0$

and $\langle \hat{\mathcal{F}}_1^{(v)} \hat{\mathcal{F}}_1^{(v)} \rangle_0$ are given in Secs. II A and II B. These formulas enable one to compute VV contributions to T_1 and, therefore, when used in conjunction with the VTR results of Paper I, permit determination of T_1 from Eqs. (1.1), (1.2) and (1.3). The formulas require the following as input. (i) The atomic masses, equilibrium internuclear separations, and gas phase vibrational frequencies of the solute and solvent molecules. (ii) The solute-solvent and solvent-solvent site-site potentials and site-site equilibrium pair correlation functions.

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

We give, in this Appendix, spherical polar coordinate expressions for the quantities appearing in the pure solvent vector integrals. These expressions hold in the body-fixed coordinate system located on solvent molecule 1 with unit vectors \mathbf{e}_{x_1} , \mathbf{e}_{y_1} , \mathbf{e}_{z_1} . This coordinate system is defined in analogy to the diatomic solute body-fixed system depicted in Fig. 1 of Paper I, namely its origin and z axis coincide, respectively, with the center of mass and bond axis of the diatomic solvent molecule 1. The results of this Appendix may be obtained from results given in Paper I using the notational transpositions discussed in Sec. II B 1. For example, the atomic coordinates $\mathbf{q}_{1k(l)}$ of solvent molecule 1, when represented in the body-fixed frame, are given in analogy to Eq. (2.8) of Paper I by

$$\mathbf{q}_{1k} = q_{1k} \mathbf{e}_{z_1} \quad \text{and} \quad \mathbf{q}_{1l} = q_{1l} \mathbf{e}_{z_1},$$

where

$$q_{1k(l)} = (-)^{k(l)} \frac{\mu_s}{M_{k(l)}} b_{gs}. \quad (\text{A1})$$

1. The single vector integrals

To evaluate the single vector integrals defined in Eqs. (2.22) and (2.26a) with Eq. (2.27a), we require expressions for the solvent-solvent interatomic separations $y_{k(l)}$ and for $\mathbf{e}_{z_1} \cdot \mathbf{k}(l)$ as functions of q , θ , ϕ . We have, in analogy to Eqs. (A1) and (A2) of Paper I,

$$y_{k(l)} = (q^2 + q_{1k(l)}^2 - 2qq_{1k(l)} \cos \theta)^{1/2} \quad (\text{A2a})$$

and

$$\mathbf{e}_{z_1} \cdot \mathbf{k}(l) = y_{k(l)}^{-1} (q \cos \theta - q_{1k(l)}). \quad (\text{A2b})$$

2. The double vector integral

To evaluate the double vector integral defined in Eqs. (2.26b) with (2.27b), we require expressions for the inter-

atomic separations $y_{k(l')}$ and for $\mathbf{e}_{z_1} \cdot \mathbf{k}(l')$ as functions of (q_1, θ_1, ϕ_1) and (q_2, θ_2, ϕ_2) . The required expressions are obtained in analogy to Eqs. (A4), (A5), (A6c), (A9), and (A10c) of Paper I as

$$y_k = [(q_2^2 + \frac{1}{4}q_1^2 + q_{1k}^2) - 2q_{1k}(q_2 \cos \theta_2 - \frac{1}{2}q_1 \cos \theta_1) - \mathbf{q}_1 \cdot \mathbf{q}_2]^{1/2}, \quad (\text{A3})$$

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

where

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

Also

$$\mathbf{e}_{z_1} \cdot \mathbf{k} = y_k^{-1} (q_2 \cos \theta_2 - \frac{1}{2}q_1 \cos \theta_1 - q_{1k}) \quad (\text{A6})$$

and

$$\mathbf{e}_{z_1} \cdot \mathbf{l}' = [y_{l'}]^{-1} (q_2 \cos \theta_2 + \frac{1}{2}q_1 \cos \theta_1 - q_{1l'}). \quad (\text{A7})$$

Equations (A1)–(A7) are evaluated with all solvent molecules constrained to have their equilibrium internuclear separations b_{gs} . This constraint is enforced by setting

$$q_1 = b_{gs} \quad (\text{A8})$$

in Eqs. (A3)–(A7) and by using Eq. (A1) to evaluate $q_{1k(l)}$.

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