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The harmonic mean field model for molecular solvents: A liquid state analog of the harmonic oscillator-rigid top approximation

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A liquid state analog of the gas phase harmonic oscillator-rigid top model is developed. This analog, which we call the harmonic mean field model, permits one to compute the equilibrium and dynamic properties of real, i.e., vibrating, molecular solvents from the structure and dynamics of the corresponding rigid solvents. The harmonic mean field model is based on: (i) A mean field harmonic model for the solvent vibrational (V) force field. (ii) A rigid solvent model treatment of translational–rotational (TR) fluctuations. (iii) Complete neglect of explicit coupling between V and TR fluctuations. (Implicit coupling is included in the vibrational force field.) The model is developed for statics via a sequence of physically motivated approximations to the exact canonical ensemble phase space distribution function of the solvent, $f_{CA}[S]$. This yields a model distribution function $f_{CA}^{(0)}[S]$ $= f_{CA}^{(0)}[p_v y] f_{CA}[p_w w; v_0]$, where $f_{CA}^{(0)}[p_v y]$ is an effective harmonic vibrational phase space distribution function which describes mean field harmonic V fluctuations and where $f_{CA}^{(0)}[p_w w; v_0]$ is the rigid solvent canonical ensemble distribution function. The nonequilibrium version of the model is defined as the solvent dynamics generated by a model Liouville operator $L^{(0)}$. This is defined via the model equilibrium Liouville equation $L^{(0)} f_{CA}^{(0)}[S] = 0$. Explicit results for equilibrium averages and time correlation functions of molecular solvents are obtained. The frequency spectra of the time correlation functions contain a low frequency "acoustic" branch arising from solvent TR motions and high frequency "optical" branches arising from collective solvent V motions. A detailed analysis of the frequency spectra of autocorrelation functions of diatomic solvents is presented.

I. INTRODUCTION

The harmonic oscillator-rigid rotor, or more generally rigid top model, provides a zeroth order description of isolated molecule dynamics. This description is the basis of familiar textbook treatments of gas phase microwave and infrared spectroscopy,[1] of gas phase translational-rotational energy transfer processes,[2] and of ideal gas statistical thermodynamics.[3]

This paper deals with the development of a liquid state analogue of the harmonic oscillator-rigid top model. For reasons which will become apparent below, we will refer to this analog as the harmonic mean field model. The new model provides an analytically simple treatment of static and dynamic fluctuations in molecular solvents while still preserving a reasonable measure of physical realism.

The present paper is part of a series[4] which will generalize our approach to chemical reaction dynamics in liquids[5] so that it is conveniently applicable to chemical processes in molecular solvents.[6]

The main point is that in molecular solvents the frequency spectrum of time correlation functions which control the efficiency of reagent-solvent energy exchange have vibrational bands as well as a rigid molecule branch.[7]

When the reagent frequencies relevant to a process of interest overlap the vibrational bands of the spectrum, then efficient energy exchange between the reagent motions and solvent vibrations can occur. Studies of simple liquid state photolysis processes[8-10] have indicated this type of energy exchange can qualitatively influence the course of solution reaction dynamics.

The effect of reagent energy exchange with solvent vibrations may be conveniently treated within the harmonic mean field model for solvent dynamics.

The outline of this paper is as follows. The harmonic mean field model is based on a rigorous statistical mechanical analysis of equilibrium translational-rotational (TR) and vibrational (V) solvent fluctuations. This analysis has been worked out elsewhere.[4] The analysis is reviewed and further developed in Sec. II. The static harmonic mean field model is defined in Sec. III. This static model is applied to construct equilibrium averages in Sec. IV. This construction permits one to compute equilibrium averages in real, i.e., vibrating, solvents from the structure of rigid solvents.

The harmonic mean field model is generalized to dynamics in Sec. V. This nonequilibrium version of the model is employed to construct time correlation functions for molecular solvents in Sec. VI. The frequency spectra of these time correlation functions have a rigid solvent translational-rotational branch and "optical" branches arising from the *collective* solvent vibrational (V) motions.

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An advantage of the model is that the vibrational contributions to the time correlation functions contain the full effects of many-body VV coupling but may be calculated from effective isolated solvent molecule dynamical matrices ω_D^2 and ω_{OD}^2. These matrices are of small dimension, namely $r \times r$ where r is the number of normal modes of an isolated solvent molecule. The matrices ω_D^2 and ω_{OD}^2 may be constructed from the structure of the solvent within the rigid solvent model. Thus the time correlation functions of the true, i.e., vibrating, solvent may be calculated from the properties of the rigid solvent model within the harmonic mean field approximation.

Section VII presents a qualitative discussion of the nature of the frequency spectra of molecular solvent autocorrelation functions. Finally we close the paper with a summary of its main results in Sec. VIII.

II. EQUILIBRIUM FLUCTUATIONS

This paper deals with a treatment of equilibrium averages and time correlation functions in molecular solvents which will be basic to the theory of chemical processes in such solvents to be presented elsewhere.[11]

As a background, we first summarize and further develop the analysis of equilibrium fluctuations in molecular solvents presented earlier.[4] We begin with a specification of the solvent.

A. Specification of the solvent

We assume a one-component polyatomic solvent composed of N_s molecules confined to a volume V. Each solvent molecule is composed of n_s atoms. The thermodynamic state of the solvent is characterized by its Kelvin temperature T and by its number density $\rho = V^{-1}N_s$.

The Cartesian coordinates and momenta of the kth atom of solvent molecule λ will be denoted by, respectively $\mathbf{q}_{\lambda k}$ and $\mathbf{p}_{q\lambda k} = M_k \mathbf{q}_{\lambda k}$ where M_k is the mass of the kth atom.

We employ in this paper a short-hand matrix notation, specified in detail in a footnote,[12] for the solvent phase space coordinates and atomic masses. The Cartesian phase space coordinates of solvent molecule λ, e.g., will be denoted by the $3n_s$-dimensional column vectors q_λ and $p_{q\lambda}$. The full set of Cartesian phase space coordinates of the solvent will be denoted by the $3n_sN_s$-dimensional column vectors q and p_q. The n_s atomic masses of solvent molecule λ will be collectively denoted by the $(3n_s \times 3n_s)$-dimensional diagonal mass matrix $M[q_\lambda]$.

B. High and low frequency coordinates

Solvent translational-rotational (TR) and vibrational (V) fluctuations are more conveniently analyzed in generalized rather than Cartesian coordinates. We, therefore, transform from the $3n_s$ Cartesian coordinates of solvent molecule λ to a set of $3n_s$ canonical[13] generalized coordinates.

We next partition these generalized coordinates into a set of r high frequency coordinates and $s = 3n_s - r$ low frequency coordinates. These will be denoted in column vector notation by, respectively, v_λ and w_λ. The conjugate momenta will be correspondingly denoted by the column vectors $p_{v\lambda}$ and $p_{w\lambda}$.

Usually the high frequency set v_λ will comprise the $3n_s$-6 [or $3n_s$-5] normal mode vibrational (V) coordinates of solvent molecule λ and the low frequency set w_λ will be the six (or five) coordinates which describe its center of mass translational and molecular framework rotational (TR) motion. Thus, for convenience, we will subsequently call the high frequency set the V coordinates and the low frequency set the TR coordinates.

Finally, in accord with our notation for the Cartesian coordinates, the full set of solvent V and TR phase space coordinates will be collectively denoted by the rN_s-dimensional column vectors p_v and v and the sN_s-dimensional column vectors p_w and w.[12]

The generalized and Cartesian coordinates for the cases of physical interest are related by a point canonical transformation.[13]

A consequence is that the conjugate momenta $p_{v\lambda}$ and $p_{w\lambda}$ are related to the generalized velocities $\dot{v}_\lambda$ and $\dot{w}_\lambda$ by[4]

$$\begin{pmatrix} p_{v\lambda} \\ p_{w\lambda} \end{pmatrix} = M[v_\lambda w_\lambda] \begin{pmatrix} \dot{v}_\lambda \\ \dot{w}_\lambda \end{pmatrix}, \tag{2.1}$$

where $M[v_\lambda w_\lambda]$ is the $(3n_s \times 3n_s)$-dimensional solvent mass matrix written in generalized coordinates. This is determined from the Cartesian coordinate mass matrix $M[q_\lambda]$ via the transformation relations of Eqs. (2.3) below.

It will prove convenient below to partition $M[v_\lambda w_\lambda]$ into pure V, pure TR, and V-TR coupling subblocks, i.e.,

$$M[v_\lambda w_\lambda] = \begin{pmatrix} M_{vv}[v_\lambda w_\lambda] & M_{vw}[v_\lambda w_\lambda] \\ M_{wv}[v_\lambda w_\lambda] & M_{ww}[v_\lambda w_\lambda] \end{pmatrix}. \tag{2.2a}$$

These subblocks are defined in matrix notation by

$$M_{vv}[v_\lambda w_\lambda] = \left[\frac{\partial q_\lambda}{\partial v_\lambda}\right]^T M[q_\lambda] \left[\frac{\partial q_\lambda}{\partial v_\lambda}\right], \tag{2.3a}$$

$$M_{vw}[v_\lambda w_\lambda] = M_{wv}^T[v_\lambda w_\lambda] = \left[\frac{\partial q_\lambda}{\partial v_\lambda}\right]^T M[q_\lambda] \left[\frac{\partial q_\lambda}{\partial w_\lambda}\right], \tag{2.3b}$$

$$M_{ww}[v_\lambda w_\lambda] = \left[\frac{\partial q_\lambda}{\partial w_\lambda}\right]^T M[q_\lambda] \left[\frac{\partial q_\lambda}{\partial w_\lambda}\right]. \tag{2.3c}$$

We close this section by introducing a short-hand notation for the full set of solvent phase space coordinates and for the solvent phase space volume element. Namely we define

$$S = (p_v v, p_w w),$$

$$dS = dp_v\, dv\, dp_w\, dw. \tag{2.4}$$

C. Approximate mass matrix

The subsequent analysis is greatly simplified if one assumes that the solvent mass matrix takes the following

approximate form when expressed in generalized coordinates

$$M[v_\lambda w_\lambda] \cong \begin{pmatrix} M_{vv} & 0 \\ 0 & M_{ww}[v_\lambda w_\lambda] \end{pmatrix}. \tag{2.2b}$$

The assumption that $M_{vv}[v_\lambda w_\lambda] = M_{vv}$ = constant is exact if v_λ and w_λ actually are the V and TR coordinates of solvent molecule λ. The assumption that $M_{vw}[v_\lambda w_\lambda]$ and $M_{wv}[v_\lambda w_\lambda]$ vanish holds if, in addition, V-TR Coriolis coupling is neglected.[1]

D. Mass-weighted vibrational displacements

We next introduce mass-weighted displacements of the vibrational coordinates from their *liquid state* equilibrium values. We will collectively denote these equilibrium values by $v_{0\lambda}$ for solvent molecule λ and by v_0 for the full solvent. They are defined in Sec. II J. There we show that, as expected, $v_{0\lambda}$ is identical for all solvent molecules, i.e.,

$$v_{01} = v_{02} = \cdots = v_{0N_s}. \tag{2.5}$$

The mass-weighted displacements for solvent molecule λ will be denoted by y_λ. Their conjugate momenta will be denoted by p_{y_λ}. The corresponding quantities for the full solvent will be denoted by y and p_y.

These are defined respectively by

$$y_\lambda = M_{vv}^{1/2}[v_\lambda - v_{0\lambda}], \tag{2.6a}$$

$$p_{y_\lambda} = M_{vv}^{-1/2} p_{v_\lambda} = \dot{y}_\lambda \tag{2.6b}$$

and

$$y = M^{1/2}[v - v_0], \tag{2.7a}$$

$$p_y = M^{-1/2} P_v = \dot{y}, \tag{2.7b}$$

where M is the $(3rN_s \times 3rN_s)$-dimensional vibrational mass matrix of the full solvent defined by

$$M = \begin{pmatrix} M_{vv} & & & \bigcirc \\ & M_{vv} & & \\ & & \ddots & \\ \bigcirc & & & M_{vv} \end{pmatrix}. \tag{2.8}$$

E. Solvent Hamiltonian

We next write down the solvent Hamiltonian expressed in generalized coordinates. We will require both the Hamiltonian of the physical vibrating solvent and the Hamiltonian of a fictitious solvent for which the vibrational coordinates are fixed at an arbitrary set of values v.

The physical Hamiltonian will be denoted by $K[S]$ [where recall $S = (p_v v, p_w w)$]. The fictitious Hamiltonian will be denoted by $K[p_w w; v]$.

The fictitious Hamiltonian may be expressed in terms of the solvent intramolecular potential energy functions $K_V[u_\lambda w_\lambda]$ and in terms of the intermolecular potential energy function of the full solvent $K_{VV}[vw]$, as

$$K[p_w w; v] = \frac{1}{2} \sum_{\lambda=1}^{N_s} \{ p_{w_\lambda}^T M_{ww}^{-1}[v_\lambda w_\lambda] p_{w_\lambda}$$

$$+ K_V[v_\lambda w_\lambda] \} + K_{VV}[vw]. \tag{2.9}$$

Given our neglect of Coriolis coupling [Eq. (2.2b)], the physical Hamiltonian may be constructed from the fictitious Hamiltonian via the relationship

$$K[S] = \frac{1}{2} p_v^T M^{-1} p_v + K[p_w w; v]$$

$$= \frac{1}{2} p_y^T p_y + K[p_w w; v]. \tag{2.10}$$

We will define the rigid solvent model as the fictitious solvent for which all vibrational coordinates are fixed at their equilibrium values v_0. Then the rigid solvent Hamiltonian is $K[p_w w; v_0]$ given by

$$K[p_w w; v_0]$$

$$= \sum_{\lambda=1}^{N_s} \left\{ \frac{1}{2} p_{w_\lambda}^T M_{ww}^{-1}[v_{0\lambda} w_\lambda] p_{w_\lambda} + K_V[v_{0\lambda} w_\lambda] \right\}$$

$$+ K_{VV}[v_0 w], \quad \text{rigid solvent Hamiltonian.} \tag{2.11}$$

F. Canonical ensemble distribution function

We will denote the canonical ensemble distribution function of the solvent by $f_{CA}[S]$. This is defined by [$\beta \equiv (k_B T)^{-1}$]:

$$f_{CA}[S] = Z^{-1} \exp[-\beta K[S]], \tag{2.12}$$

where

$$Z = \int \exp[-\beta K[S]] dS \tag{2.13}$$

is the solvent partition function.

One may show[4] from Eqs. (2.10) and (2.12) that $f_{CA}[S]$ may be exactly factorized into a distribution function $f_{CA}[p_w w; v]$ which governs equilibrium TR fluctuations and a distribution function $f_{CA}[p_y y]$ which governs *mean field* V fluctuations. Explicitly,

$$f_{CA}[S] = f_{CA}[p_y y] f_{CA}[p_w w; v]. \tag{2.14}$$

The TR phase space distribution function is given by

$$f_{CA}[p_w w; v] = [Z[v]]^{-1} \exp[-\beta K[p_w w; v]]), \tag{2.15}$$

where

$$Z[v] = \int \exp[-\beta K[p_w w; v]] dp_w \, dw \tag{2.16}$$

is the partition function of the solvent with the V coordinates fixed.

The vibrational phase space distribution function is given by

$$f_{CA}[p_y y] = Z^{-1} \exp\left[-\beta \left(\frac{1}{2} p_y^T p_y + W[v] \right) \right], \tag{2.17}$$

where $W[v]$ is defined by

$$-\beta W[v] = \ln Z[v]. \tag{2.18}$$

From Eq. (2.17) it is clear that $W[v]$ is an effective vibrational potential for the solvent, $W[v]$ will turn out to be the vibrational potential of mean force [see Eq. (2.27)].

It follows from Eqs. (2.12)–(2.16) that $f_{CA}[p_y y]$ is unit normalized, i.e.,

$$\int f_{CA}[p_y y] dp_y \, dy = 1. \tag{2.19}$$

An immediate consequence of Eqs. (2.17) and (2.19) is that

$$Z = \int \exp\left[-\beta\left(\frac{1}{2} p_y^T p_y + W(v)\right)\right] dp_y \, dy. \tag{2.20}$$

Thus the solvent partition function may be expressed as either a full [Eq. (2.13)] or a vibrational [Eq. (2.20)] phase space integral.

G. Symmetry property of the vibrational potential of mean force

The true solvent vibrational force field depends on the instantaneous spatial and orientational arrangement of the solvent molecules, i.e., on the TR coordinates w.

The potential of mean force $W[v]$ governs the vibrational force field which results after averaging over TR fluctuations. This is why we have referred to $f_{CA}[p_y y]$ as a *mean field* vibrational phase space distribution function.

After TR fluctuations have been averaged out, the vibrational force fields acting on all solvent molecules are identical. A consequence is that $W[v]$ is symmetric with respect to the interchange of the full set of vibrational coordinates on any pair of solvent molecules λ and λ'. That is

$$W[v] = W[v_1 v_2 \cdots v_\lambda \cdots v_{\lambda'} \cdots v_{N_s}]$$

$$= W[v_1 v_2 \cdots v_{\lambda'} \cdots v_\lambda \cdots v_{N_s}]. \tag{2.21}$$

A mathematical proof of Eq. (2.21) is given in Appendix A.

H. Dynamical variables and ensemble averages

We will often employ the following short-hand notation for arbitrary solvent dynamical variables $A[S] = A[p_v v, p_w w]$:

$$A \equiv A[S], \tag{2.22a}$$

$$A[v] \equiv A\,[p_v = 0v, p_w w]. \tag{2.22b}$$

We will also employ a corresponding notation for canonical ensemble averages

$$\langle A \rangle = \int f_{CA}[S] A[S] dS, \tag{2.23a}$$

$$\langle A \rangle_v = \int f_{CA}[p_w w; v] A\,[p_v = 0v, p_w w] dp_w \, dw. \tag{2.23b}$$

A and $\langle A \rangle$ are, respectively, the instantaneous and average values of $A[S]$ in the physical solvent. $A[v]$ and $\langle A \rangle_v$ are the corresponding instantaneous and average values of $A[S]$ in the fictitious solvent with the vibrational coordinates fixed at v.

Thus $A[v_0]$ and $\langle A \rangle_{v_0}$ are the instantaneous and average values of $A[S]$ for the rigid solvent model.

I. Vibrational forces

The instantaneous generalized forces acting on the vibrational coordinates of solvent molecule λ will be denoted by the r-dimensional column vector $\mathcal{F}_{v_\lambda}$. These vibrational forces are defined by

$$\mathcal{F}_{v_\lambda} = -\frac{\partial K[S]}{\partial v_\lambda}. \tag{2.24}$$

Comparing Eqs. (2.10) and (2.24) it follows [in the notation of Sec. II H] that

$$F_{v_\lambda} = F_{v_\lambda}[v] = -\frac{\partial K[p_w w; v]}{\partial v_\lambda}. \tag{2.25}$$

The mean vibrational force $\langle F_{v_\lambda} \rangle_v$ is defined by [cf. Eq. (2.23b)]

$$\langle F_{v_\lambda} \rangle_v = \int f_{CA}[p_w w; v] F_{v_\lambda}[v] dp_w \, dw. \tag{2.26}$$

$\langle F_{v_\lambda} \rangle_v$ may alternatively be constructed from $W[v]$ via the relationship[4]

$$\langle F_{v_\lambda} \rangle_v = -\frac{\partial W[v]}{\partial v_\lambda}. \tag{2.27}$$

Equation (2.27) shows that $W[v]$ is indeed the vibrational potential of mean force.

In accord with the notational convention used earlier, we will denote the full set of solvent instantaneous and mean vibrational forces by, respectively, the rN_s-dimensional column vectors $F_v = F_v[v]$ and $\langle F_v \rangle_v$.

J. Equilibrium values of the vibrational coordinates in the liquid

We have introduced the liquid state equilibrium values of the vibrational coordinates v_0 in Sec. II D.

We next define these precisely as the values for which the mean vibrational force $\langle F_v \rangle_v$ vanishes, that is we define v_0 by

$$\langle F_v \rangle_{v_0} = -\left[\frac{\partial W[v]}{\partial v}\right]_{v=v_0} = 0. \tag{2.28}$$

One expects that the equilibrium vibrational coordinates of all solvent molecules are identical. That is $v_{01} = v_{02} = \cdots v_{0N_s}$. This may be proven from Eq. (2.28) and the rigorous symmetry property Eq. (2.21).

K. Dynamical matrix of the solvent

Our subsequent work is based on a harmonic approximation to the vibrational force field. This harmonic model may be developed by expanding the vibrational potential of mean force $W[v]$ about $v = v_0$ to quadratic order in the vibrational displacements y.

We write this expansion as

$$W[v] \cong W[v_0] + \frac{1}{2} y^T \omega^2 y, \tag{2.29}$$

where ω^2 is an $(rN_s \times rN_s)$-dimensional dynamical matrix which governs the mean field solvent vibrational force field. It is defined by

$$\omega^2 = M^{-1/2}\left[\frac{\partial^2 W[v]}{\partial v \partial v^T}\right]_{v=v_0} M^{-1/2}. \tag{2.30}$$

The following alternative result for ω^2 may be developed from Eq. (2.30)[4]:

$$\omega^2 = -M^{-1/2}\left[\left\langle\frac{\partial F_v^T}{\partial v}\right\rangle_{v_0} + \beta\langle F_v F_v^T\rangle_{v_0}\right]M^{-1/2}. \tag{2.31}$$

Further insight may be obtained by partitioning ω^2 into N_s^2 subblocks each of dimension $r \times r$. A consequence of Eq. (2.21), proven in Appendix A, is that all diagonal subblocks are identical and will be denoted by ω_D^2 and all off-diagonal subblocks are identical and will be denoted by ω_{OD}^2. That is ω^2 has the matrix structure

$$\omega^2 = \begin{bmatrix} \omega_D^2 & \omega_{OD}^2 & \omega_{OD}^2 & \cdots \\ \omega_{OD}^2 & \omega_D^2 & \omega_{OD}^2 & \cdots \\ \omega_{OD}^2 & \omega_{OD}^2 & \omega_D^2 & \cdots \\ \vdots & & & \end{bmatrix}. \tag{2.32a}$$

Equation (2.32a) may be expressed more succinctly as

$$[\omega^2]_{\lambda\lambda'} = \omega_D^2 \delta_{\lambda\lambda'} + \omega_{OD}^2[1 - \delta_{\lambda\lambda'}]. \tag{2.32b}$$

We next discuss the physical meaning of ω_D^2 and ω_{OD}^2. The submatrix ω_D^2 governs the liquid state intramolecular force field. If we denote the dynamical matrix of an isolated solvent molecule by ω_g^2, then ω_D^2 is essentially ω_g^2 shifted by the effects of intermolecular forces [see Eq. (2.35a) below].

The off-diagonal submatrix ω_{OD}^2 governs intermolecular vibrational coupling within the harmonic mean field model. This coupling broadens the normal mode frequency spectrum of an isolated solvent molecule, which consists in the harmonic approximation of $r\delta$ functions, into a liquid state band spectrum.

L. Approximate evaluation of the dynamical matrix

We next present an approximate evaluation of the dynamical matrix. This evaluation, like much of our subsequent development, is based on the assumption that the intramolecular contributions to the vibrational force $F_{v\lambda}$ are much larger than the intermolecular contributions.

Given this assumption, as discussed in Appendix B, it follows that Eq. (2.31) approximately reduces to

$$\omega^2 \cong -M^{-1/2}\left\langle\frac{\partial F_v^T}{\partial v}\right\rangle_{v_0} M^{-1/2}. \tag{2.33}$$

We additionally assume that the intermolecular solvent forces are pairwise additive, i.e., that

$$K_{VV}[vw] = \sum_{\lambda=1}^{N_s}\sum_{\lambda'>\lambda}^{N_s} k_{VV}[v_\lambda w_\lambda, v_{\lambda'}w_{\lambda'}]. \tag{2.34}$$

Given Eqs. (2.33) and (2.34) [and two other milder approximations] we develop in Appendix B the following results for ω_D^2 and ω_{OD}^2:

$$\omega_D^2 = \omega_g^2 + N_s\int f_{CA}[p_w w; v_0]M_{vv}^{-1/2}$$
$$\times\left[\frac{\partial^2 k_{VV}[v_{01}w_{11}, v_{02}w_2]}{\partial v_{01}\partial v_{02}^T}\right]M_{vv}^{-1/2}dp_w\,dw, \tag{2.35a}$$

$$\omega_{OD}^2 = \int f_{CA}[p_w w; v_0]M_{vv}^{-1/2}$$
$$\times\left[\frac{\partial^2 k_{VV}[v_{01}w_{11}, v_{02}w_2]}{\partial v_{01}\partial v_{02}^T}\right]M_{vv}^{-1/2}dp_w\,dw. \tag{2.35b}$$

Equations (2.35) may be further reduced to integrals over the pair distribution function of the rigid solvent model. We denote this pair distribution function by $g[w_1 w_2; v_0]$. By analogy to the definition of the pair distribution function for monatomic solvents, $g[w_1 w_2; v_0]$ is defined by

$$g[w_1 w_2; v_0]$$
$$= \mathcal{V}^2[\det[M_{ww}[v_{01}w_1]]\det[M_{ww}[v_{02}w_2]]]^{-1/2}$$
$$\times\int f_{CA}[p_w w; v_0]dp_w\,dw_3\,dw_4\cdots dw_{N_s}, \tag{2.36}$$

where

$$\mathcal{V} = \int[\det M[v_{01}w_1]]^{1/2}dw_1 \tag{2.37}$$

is the volume of TR space.

Given these definitions, Eqs. (2.35) may be reduced to [recall $\rho = V^{-1}N_s$]:

$$\omega_D^2 = \omega_g^2 + \rho\left[\frac{V}{\mathcal{V}}\right]\int M_{vv}^{-1/2}\left[\frac{\partial^2 k_{VV}[v_{01}w_1, v_{02}w_2]}{\partial v_{01}\partial v_{02}^T}\right]$$
$$\times M_{vv}^{-1/2}g[w_1 w_2; v_0]d\bar{w}_2 \tag{2.38a}$$

and

$$\omega_{OD}^2 = N_s^{-1}\rho\left[\frac{V}{\mathcal{V}}\right]\int M_{vv}^{-1/2}\left[\frac{\partial^2 k_{VV}[v_{01}w_1, v_{02}w_2]}{\partial v_{01}\partial v_{02}^T}\right]$$
$$\times M_{vv}^{-1/2}g[w_1 w_2; v_0]d\bar{w}_2, \tag{2.38b}$$

where we define

$$d\bar{w}_2 = [\det M_{ww}[v_{01}w_1]]^{1/2}dw_2. \tag{2.39}$$

We will later frequently take the thermodynamic [i.e., $N_s \to \infty$] limit of expressions involving ω_D^2 and ω_{OD}^2. In taking this limit we will use the fact that ω_D^2 is of order N_s^0 and ω_{OD}^2 is of order N_s^{-1} [see Eq. (2.38)], i.e.,

$$\omega_D^2 = O(N_s^0),$$
$$\omega_{OD}^2 = O(N_s^{-1}). \tag{2.40}$$

M. Equilibrium geometry shifts

To evaluate the above expressions for ω_D^2 and ω_{OD}^2, as well as the results for the equilibrium and dynamical properties of the solvent developed below, we require the

liquid state values of the equilibrium vibrational coordinates $v_{0\lambda}$. These, in general, are not known.

We next present an approximate expression, Eq. (2.42) below, which permits us to determine $v_{0\lambda}$ from the gas phase equilibrium coordinates. We denote these by $v_{g\lambda}$. This expression, which is derived in Appendix B and which is based on the same set of approximations as those used to derive Eqs. (2.38), provides the basis for a simple theory of condensed phase equilibrium geometry shifts. We hope to further develop this theory elsewhere.

We define the mass-weighted vibrational equilibrium coordinate shift Δ by

$$\Delta = M_{vv}^{1/2}[v_{0\lambda} - v_{g\lambda}]. \tag{2.41}$$

We show in Appendix B that Δ is given by

$$\Delta = -\omega_g^{-2}\rho\left[\frac{V}{\mathcal{V}}\right]\int M_{vv}^{-1/2}\left[\frac{\partial k_{VV}[v_{01}w_1, v_{02}w_2]}{\partial v_{01}}\right]$$

$$\times g[w_1 w_2; v_0]d\bar{w}_2. \tag{2.42}$$

Equations (2.41) and (2.42) may be solved iteratively to obtain $v_{0\lambda}$ from $v_{g\lambda}$.

III. STATIC HARMONIC MEAN FIELD MODEL

Our subsequent analysis is based on a model which provides a liquid state analog of the harmonic oscillator-rigid top approximation for isolated molecule dynamics.

We develop the equilibrium version of this model in this section and the nonequilibrium version in Sec. V. We will refer to these, respectively, as the static and dynamic harmonic mean field models.

Both static and dynamic models are based on: (a) a mean field harmonic treatment of solvent V fluctuations; (b) a rigid solvent model treatment of TR fluctuations; and (c) complete neglect of V-TR coupling.

The static harmonic mean field model is developed from the factorized form of $f_{CA}[S]$, Eq. (2.14) by the introduction of two approximations. These are:

(i) We replace $W[v]$ appearing in Eq. (2.17) for $f_{CA}[p_y y]$ by its harmonic approximation Eq. (2.29).

(ii) We replace $f_{CA}[p_w w; v]$ by $f_{CA}[p_w w; v_0]$, the rigid solvent model equilibrium phase space distribution function.

Approximation (i) is self-explanatory. Approximation (ii) may be interpreted in two equivalent ways.

First it is equivalent to approximating the TR structure of the solvent by that of the rigid solvent model. The fact that rigid solvent calculations of the structure of molecular liquids are often in good agreement with experiment provides support for approximation (ii).

Second approximation (ii) is equivalent to neglecting the influence of fluctuations in microscopic TR structure on the V force field. This neglect is realistic if either the vibrational frequencies are sufficiently high or the intramolecular vibrational forces are much stronger than the intermolecular vibrational forces. For both cases the perturbation of the V force field, due to TR fluctuations, is a small part of the total field.

Given approximation (i) $f_{CA}[p_y y]$ may be rewritten as[4]

$$f_{CA}[p_y y] \cong f_{CA}^{(0)}[p_y y]$$

$$= [2\pi k_B T]^{-rN_s}[\det \omega^2]^{1/2}$$

$$\times \exp\left[-\beta\left(\frac{1}{2}p_y^T p_y + \frac{1}{2}y^T \omega^2 y\right)\right]. \tag{3.1}$$

Then the static harmonic mean field model is defined by the following approximate form of Eq. (2.14):

$$f_{CA}[S] \cong f_{CA}^{(0)}[S] = f_{CA}^{(0)}[p_y y]f_{CA}[p_w w; v_0]. \tag{3.2}$$

The superscripts 0 in Eqs. (3.1) and (3.2) indicate the model.

IV. EQUILIBRIUM AVERAGES IN THE HARMONIC MEAN FIELD APPROXIMATION

The advantage of the static harmonic mean field model is that it permits a simple mathematical treatment of the equilibrium properties of the solvent while retaining a considerable measure of physical realism.

We consider in this section evaluation of the equilibrium average of an arbitrary solvent dynamical variable $A[S]$. We use the short-hand notation for dynamical variables and ensemble averages given in Sec. II H.

A. Expansion of dynamical variables

To be consistent with the harmonic level treatment of the solvent vibrational force field we expand $A[S] = A$ about its rigid solvent value $A[p_v = 0v_0, p_w w] = A[v_0]$ to quadratic order in y and p_y. We write this expansion in matrix notation as

$$A = A[v_0] + A^{(v)T}[v_0]y + A^{(p)T}[v_0]p_y + \frac{1}{2}y^T A^{(vv)}[v_0]y$$

$$+ p_y^T A^{(pv)}[v_0]y + \frac{1}{2}p_y^T A^{(pp)}[v_0]p_y. \tag{4.1a}$$

Note that $A^{(v)}[v_0]$, $A^{(vv)}[v_0]$, etc. are mass-weighted vibrational derivatives of A defined in a footnote.[14]

Equation (4.1a) may be recast as

$$A = A[v_0] + A^{(v)T}[v_0]y + A^{(p)T}[v_0]p_y + \frac{1}{2}\text{tr}[A^{(vv)}[v_0]yy^T$$

$$+ A^{(pv)}[v_0]yp_y^T + A^{(pp)}[v_0]p_yp_y^T], \tag{4.1b}$$

where tr denotes a full $(rN_s \times rN_s)$-dimensional trace.

B. Vibrational phase space averages

Next consider an arbitrary vibrational phase space function $a[p_y y]$. We define $\bar{a}$ by

$$\bar{a} \equiv \int f_{CA}^{(0)}[p_y y]a[p_y y]dp_y \, dy, \tag{4.2}$$

where $f_{CA}^{(0)}[p_y y]$ is given by Eq. (3.1).

Comparing Eqs. (3.1) and (4.2) yields

$$\bar{y} = \bar{p}_y = 0,$$

$$\overline{yy^T} = k_B T \omega^{-2},$$

$$\overline{yp_y^T} = 0,$$

$$\overline{p_y p_y^T} = k_B T. \tag{4.3}$$

C. Full equilibrium averages

Combining Eqs. (3.2), (4.1b), and (4.2) yield the following value for the full equilibrium average of A:

$$\langle A \rangle = \langle A \rangle_{v_0} + \langle A^{(v)T} \rangle_{v_0} \bar{y} + \langle A^{(p)T} \rangle_{v_0} \bar{p}_y$$

$$+ \frac{1}{2} \mathrm{tr}[\langle A^{(vv)} \rangle_{v_0} \overline{yy^T} + \langle A^{(pv)} \rangle_{v_0} \overline{yp_y^T}$$

$$+ \langle A^{(pp)} \rangle_{v_0} \overline{p_y p_y^T}], \tag{4.4}$$

where recall $\langle A \rangle_{v_0}$ denotes a rigid solvent model phase space average.

Equation (4.4) may be simplified by using Eq. (4.3). The result is

$$\langle A \rangle = \langle A \rangle_{v_0} + \frac{1}{2} k_B T \, \mathrm{tr}[\langle A^{(vv)} \rangle_{v_0} \omega^{-2} + \langle A^{(pp)} \rangle_{v_0}]. \tag{4.5}$$

D. Reduction of the trace I

Equation (4.5) is intractable as it stands since it involves a trace over matrices of huge dimension, namely $rN_s \times rN_s$.

We next reduce Eq. (4.5) to a tractable trace over matrices of dimension $r \times r$. (Recall r = number of modes of a solvent molecule). This simplification is possible because of the simple form of the matrix structure of ω^2 given in Eq. (2.32).

We begin by considering the trace of an arbitrary $(rN_s \times rN_s)$-dimensional matrix T. The full trace of this matrix is defined by

$$\mathrm{tr}\, T = \sum_{\lambda=1}^{N_s} \sum_{i=1}^{r} [T]_{\lambda\lambda}^{ii}. \tag{4.6}$$

We next define the *inter*molecular trace of T, tr_e, by the $r \times r$ matrix t whose elements are defined by

$$t_{ij} = [\mathrm{tr}_e T]^{ij} = \sum_{\lambda=1}^{N_s} [T]_{\lambda\lambda}^{ij}. \tag{4.7}$$

The *intra*molecular trace tr_a is then defined by

$$\mathrm{tr}_a t = \sum_{i=1}^{r} t_{ii}. \tag{4.8}$$

Comparing Eqs. (4.6)–(4.8) yields

$$\mathrm{tr}\, T = \mathrm{tr}_a \, \mathrm{tr}_e T. \tag{4.9}$$

Since the matrix T is arbitrary we have that the trace may be quite generally factorized as

$$\mathrm{tr} = \mathrm{tr}_a \, \mathrm{tr}_e. \tag{4.10}$$

Equation (4.5) may, therefore, be written as

$$\langle A \rangle = \langle A \rangle_{v_0} + \frac{1}{2} k_B T \, \mathrm{tr}_a$$

$$\times \mathrm{tr}_e[\langle A^{(vv)} \rangle_{v_0} \omega^{-2} + \langle A^{(pp)} \rangle_{v_0}]. \tag{4.11}$$

E. Reduction of the trace II

To make further progress we restrict ourselves to variables A which are symmetric with respect to interchange of the full set of phase space coordinates on an arbitrary pair of solvent molecules λ and λ'.

For this case one may show via arguments similar to those given in Appendix A that the $(rN_s \times rN_s)$-dimensional matrices $\langle A^{(vv)} \rangle_{v_0}$ and $\langle A^{(pp)} \rangle_{v_0}$ have a matrix structure identical to that of ω^2. That is the $r \times r$ subblocks of $\langle A^{(vv)} \rangle_{v_0}$ and $\langle A^{(pp)} \rangle_{v_0}$ have the matrix structure [cf. Eq. (2.32)]:

$$[\langle A^{(vv)} \rangle_{v_0}]_{\lambda\lambda'} = A_D^{(vv)}[v_0]\delta_{\lambda\lambda'} + A_{OD}^{(vv)}[v_0][1 - \delta_{\lambda\lambda'}] \tag{4.12a}$$

and

$$[\langle A^{(pp)} \rangle_{v_0}]_{\lambda\lambda'} = A_D^{(pp)}[v_0]\delta_{\lambda\lambda'} + A_{OD}^{(pp)}[v_0][1 - \delta_{\lambda\lambda'}], \tag{4.12b}$$

where

$$A_{D(OD)}^{(vv)}[v_0] = M_{vv}^{-1/2} \left[\frac{\partial^2 A[S]}{\partial v_1 \partial v_{1(2)}^T} \right]_{\substack{v=v_0 \\ p_s=0}} M_{vv}^{-1/2} \tag{4.13}$$

and

$$A_{D(OD)}^{(pp)}[v_0] = M_{vv}^{1/2} \left[\frac{\partial^2 A[S]}{\partial p_{v_1} \partial p_{v_{1(2)}}^T} \right]_{\substack{v=v_0 \\ p_s=0}} M_{vv}^{-1/2}. \tag{4.14}$$

Also one may readily prove[15] that arbitrary functions of ω^2, $f(\omega^2)$, have the same matrix structure, i.e.,

$$[f[\omega^2]]_{\lambda\lambda'} = [f[\omega^2]]_D \delta_{\lambda\lambda'} + [f[\omega^2]]_{OD}[1 - \delta_{\lambda\lambda'}]. \tag{4.15}$$

Applying Eq. (4.15) to the special case $f[\omega^2] = \omega^{-2}$ yields the following result for the subblocks of ω^{-2}:

$$[\omega^{-2}]_{\lambda\lambda'} = [\omega^{-2}]_D \delta_{\lambda\lambda'} + [\omega^{-2}]_{OD}[1 - \delta_{\lambda\lambda'}]. \tag{4.16}$$

Comparing Eqs. (4.7), (4.12), and (4.16) permits us to evaluate the intermolecular traces appearing in Eq. (4.11). Making this evaluation yields the following result for $\langle A \rangle$ valid in the thermodynamic ($N_s \to \infty$) limit

$$\langle A \rangle = \langle A \rangle_{v_0} + \frac{1}{2} N_s k_B T \, \mathrm{tr}_a \, \mathcal{A}[v_0], \tag{4.17}$$

where $\mathcal{A}[v_0]$ is an $(r \times r)$-dimensional matrix defined by

$$\mathcal{A}[v_0] = A_D^{(vv)}[v_0][\omega^{-2}]_D$$

$$+ N_s A_{OD}^{(vv)}[v_0][\omega^{-2}]_{OD} + A_D^{(pp)}[v_0]. \tag{4.18}$$

F. Final result for $\langle A \rangle$

To complete the harmonic mean field calculation of $\langle A \rangle$ we express $[\omega^{-2}]_D$ and $[\omega^{-2}]_{OD}$ in terms of ω_D^2 and ω_{OD}^2. These latter quantities may be readily calculated from rigid solvent pair correlation functions via Eqs. (2.38).

We show in Appendix C that in the thermodynamic $(N_s \to \infty)$ limit that

$$[\omega^{-2}]_D = [\omega_D^2]^{-1} \tag{4.19a}$$

and

$$[\omega^{-2}]_{OD} = -[\omega_T^2]^{-1}\omega_{OD}^2[\omega_D^2]^{-1}, \tag{4.19b}$$

where

$$\omega_T^2 = \omega_D^2 + N_s\omega_{OD}^2. \tag{4.20}$$

Comparison of Eqs. (2.40) and (4.19) shows that

$$[\omega^{-2}]_D = O(N_s^0), \tag{4.21a}$$

$$[\omega^{-2}]_{OD} = O(N_s^{-1}). \tag{4.21b}$$

Thus all terms appearing in $A[v_0]$ are of order N_s^0.

Comparing Eqs. (4.17)–(4.19) yields our final result for $\langle A \rangle$. This is

$$\langle A \rangle = \langle A \rangle_{v_0} + \frac{1}{2} N_s k_B T \, \mathrm{tr}_a \, \mathcal{A}[v_0], \tag{4.22}$$

where

$$\mathcal{A}[v_0] = A_D^{(vv)}[v_0][\omega_D^2]^{-1} + A_D^{(pp)}[v_0]$$
$$- A_{OD}^{(vv)}[v_0][\omega_T^2]^{-1}[N_s\omega_{OD}^2][\omega_D^2]^{-1}. \tag{4.23}$$

Note that $\langle A \rangle_{v_0}$ is the average value of A for the rigid solvent approximation. The $\mathrm{tr}_a \, \mathcal{A}[v_0]$ term gives the correction to this rigid solvent average due to static vibrational fluctuations.

Also note that *both* the rigid solvent and also the vibrational contributions to $\langle A \rangle$ may be calculated from the rigid solvent pair distribution function $g[w_1 w_2; v_0]$.

Thus the equilibrium properties of the true solvent may be determined from those of the rigid solvent within the static harmonic mean field model.

V. DYNAMIC HARMONIC MEAN FIELD MODEL

We define the dynamic harmonic mean field model in this section. The development of the model as an approximation to exact solvent dynamics is described in Appendix D.

Like its equilibrium analog the dynamic harmonic mean field model is most realistic if the vibrational frequencies of the solvent molecules are sufficiently high and if the intramolecular contribution to the vibrational force $\mathcal{F}_v[v]$ is much larger than the intermolecular contribution. (See Appendix D).

We begin with a description of the exact dynamics of the solvent.

A. Exact Liouville operator of the solvent

The exact Liouville operator of the solvent written in generalized coordinates and expressed in matrix notation is

$$iL = \left[\frac{\partial K[S]}{\partial p_v^T} \frac{\partial}{\partial v} - \frac{\partial K[S]}{\partial v^T} \frac{\partial}{\partial p_v} \right]$$
$$+ \left[\frac{\partial K[S]}{\partial p_w^T} \frac{\partial}{\partial w} - \frac{\partial K[S]}{\partial w^T} \frac{\partial}{\partial p_w} \right]. \tag{5.1}$$

The exact canonical ensemble distribution function of the solvent $f_{CA}[S] = Z^{-1} \exp[-\beta K[S]]$ is the equilibrium solution of the Liouville equation of the solvent. That is it satisfies the equation

$$iL f_{CA}[S] = 0. \tag{5.2}$$

B. Model Liouville operator of the solvent

Equation (5.2) suggests the following definition of the dynamic harmonic mean field model. It is the solvent dynamics generated by a model Liouville operator $L^{(0)}$ which satisfies the equation

$$iL^{(0)} f_{CA}^{(0)}[S] = 0, \tag{5.3}$$

where $f_{CA}^{(0)}[S]$ is the static harmonic mean field approximation [Eq. (3.2)] to the solvent canonical ensemble distribution function.

It follows from Eqs. (3.2) and (5.3) that

$$iL^{(0)} = iL_y^{(0)} + iL[v_0], \tag{5.4}$$

where, in matrix notation,

$$iL_y^{(0)} = p_y^T \frac{\partial}{\partial y} - y^T \omega^2 \frac{\partial}{\partial p_y} \tag{5.5}$$

and where

$$iL[v_0] = \left[\frac{\partial K[p_w w; v_0]}{\partial p_w^T} \frac{\partial}{\partial w} - \frac{\partial K[p_w w; v_0]}{\partial w^T} \frac{\partial}{\partial p_w} \right]. \tag{5.6}$$

The Liouville operator $iL_y^{(0)}$ generates the vibrational dynamics of the solvent within the mean field harmonic approximation.

The Liouville operator $iL[v_0]$ generates its translational-rotational dynamics within the rigid solvent model.

The dynamic harmonic mean field model, defined by Eqs. (5.4)–(5.6), neglects the coupling between V and TR motions. That is according to the dynamic harmonic mean field model energy flows from solvent molecule to solvent molecule only through V–V and TR–TR exchange processes. That is the effects of V-TR exchange are neglected.

The neglect of V-TR processes is realistic if the vibrational frequencies are sufficiently high that the V-TR frequency spectra do not substantially overlap.

VI. TIME CORRELATION FUNCTIONS

This section presents a harmonic mean field construction of solvent time correlation functions $\langle A(t)B \rangle$. The calculation is similar to that of Sec. IV. Thus we will restrict ourselves to a brief outline.

The main result of the analysis, Eq. (6.16) below, provides a separation of $\langle A(t)B \rangle$ into a contribution from rigid solvent TR dynamical fluctuations and a contribution from mean field harmonic dynamical V fluctuations.

This separation permits one to gain an insight into the nature of the frequency spectrum of molecular liquids as discussed in Sec. VII.

A. Time dependence of solvent dynamical variables

We begin by discussing the time dependence of solvent dynamical variables. We first introduce a shorthand notation for the time dependence of dynamical variables in the physical and rigid solvents. This generalizes the notation of Eqs. (2.22) and (2.23).

We define the time dependence of an arbitrary true solvent dynamical variable $A[S] = A$ by

$$A(t) = \exp[iLt]A. \tag{6.1a}$$

We define the time dependence of the corresponding rigid solvent dynamical variable $A [p_v = 0v_0, p_w w] \equiv A[v_0]$ by

$$A[t; v_0] = \exp[iL[v_0]t]A[v_0]. \tag{6.1b}$$

We next evaluate the time dependence of solvent dynamical variables within the harmonic mean field model.

We first note that overtone and combination band contributions to the mean field vibrational eigenvalue spectrum are suppressed when one treats V dynamics in the harmonic approximation. Thus for consistency the overtone and combination band frequencies should not appear in the Fourier decomposition of the time dependence of dynamical variables. These may be removed by approximating these variables by their linear order expansions in y and p_y.

For simplicity, we will restrict ourselves to dynamical variables A, B which are independent of the vibrational momenta p_y. Then the linear order expansions of A and B are

$$A \cong A^{(0)} \equiv A[v_0] + A^{(v)T}[v_0]y, \tag{6.2a}$$

$$B \cong B^{(0)} \equiv B[v_0] + B^{(v)T}[v_0]y, \tag{6.2b}$$

where

$$A^{(v_0)}[v_0] = M^{-1/2} \frac{\partial A[v_0]}{\partial v_0}, \tag{6.3a}$$

$$B^{(v_0)}[v_0] = M^{-1/2} \frac{\partial B[v_0]}{\partial v_0}. \tag{6.3b}$$

The harmonic mean field result for $A(t)$ is then

$$A(t) \cong A^{(0)}(t) = \exp[iL^{(0)}t]A^{(0)}$$

$$= \exp[iL_y^{(0)}t]\exp[iL[v_0]t]A^{(0)}, \tag{6.4}$$

where we have used Eq. (5.4). Comparing Eqs. (6.1), (6.2), and (6.4) then gives

$$A(t) \cong A^{(0)}(t) = A[t; v_0] + A^{(v)T}[t; v_0]y(t), \tag{6.5}$$

where $y(t) = \exp[iL_y^{(0)}t]y$. Using Eq. (5.5) for $iL_y^{(0)}$ gives

$$y(t) = \cos \omega t y + \omega^{-1} \sin \omega t p_y. \tag{6.6}$$

B. Time correlation functions

We define the exact time correlation function of solvent dynamical variables A and B by

$$\langle A(t)B \rangle = \int f_{CA}[S][\exp[iLt]A]BdS. \tag{6.7}$$

We define the corresponding rigid solvent time correlation function by

$$\langle A(t)B \rangle_{v_0} = \int f_{CA}[p_w w; v_0][\exp[iL[v_0]t]$$
$$\times A[v_0]]B[v_0]dp_w \, dw. \tag{6.8}$$

The harmonic mean field approximation to $\langle A(t)B \rangle$ is

$$\langle A(t)B \rangle \cong \int f_{CA}^{(0)}[S][\exp[iL^{(0)}t]A^{(0)}]B^{(0)}dS$$

$$= \int f_{CA}^{(0)}[S]A^{(0)}(t)B^{(0)}dS, \tag{6.9}$$

where $A^{(0)}(t)$ and $B^{(0)}$ denote the linear order expansions of A and B given in Eqs. (6.2) and (6.5).

Equations (6.9) may be reworked to yield the following result for $\langle A(t)B \rangle$ [cf. Eq. (4.11)]

$$\langle A(t)B \rangle = \langle A(t)B \rangle_{v_0} + k_B T \, tr_a$$
$$\times tr_e[\langle B^{(v)}A^{(v)T}(t) \rangle_{v_0} \overline{y(t)y^T}], \tag{6.10}$$

where $\overline{y(t)y^T}$ is the autocorrelation matrix of the solvent vibrational displacements. This autocorrelation matrix may be evaluated using Eqs. (4.3) and (6.6) to yield

$$\overline{y(t)y^T} = k_B T \omega^{-2} \cos \omega t. \tag{6.11}$$

Thus

$$\langle A(t)B \rangle = \langle A(t)B \rangle_{v_0} + k_B T \, tr_a$$
$$\times tr_e[\langle B^{(v)}A^{(v)T}(t) \rangle_{v_0} \omega^{-2} \cos \omega t]. \tag{6.12}$$

We next evaluate the intermolecular trace tr_e analytically as in Sec. IV and reduce Eq. (6.12) to an intramolecular trace over $r \times r$ matrices. This reduction is based on the result that both $\langle B^{(v)}A^{(v)T}(t) \rangle_{v_0}$ and $\omega^{-2} \cos \omega t$ have the same subblock structure as ω^2, Eq. (2.32). We will denote the diagonal and off-diagonal subblocks of $\langle B^{(v)}A^{(v)T}(t) \rangle_{v_0}$ by, respectively,

$$C_D[t; v_0] = \langle B^{(v_1)}A^{(v_1)T}(t) \rangle_{v_0}, \tag{6.13a}$$

$$C_{OD}[t; v_0] = \langle B^{(v_1)}A^{(v_2)T}(t) \rangle_{v_0}, \tag{6.13b}$$

where $A^{(v_\lambda)}$ and $B^{(v_\lambda)}$ are defined by [cf. Eq. (6.3)]:

$$A^{(v_\lambda)}[v_0] = M_{vv}^{-1/2} \frac{\partial A[v_0]}{\partial v_{0_\lambda}}, \tag{6.14a}$$

$$B^{(v_\lambda)}[v_0] = M_{vv}^{-1/2} \frac{\partial B[v_0]}{\partial v_{0_\lambda}}. \tag{6.14b}$$

Thermodynamic limit expressions for the diagonal and off-diagonal subblocks of $[\omega^{-2} \cos \omega t]$ are derived in Appendix C. These results are

$$[\omega^{-2} \cos \omega t]_D = [\omega_D^2]^{-1} \cos \omega_D t, \tag{6.15a}$$

$$[\omega^{-2} \cos \omega t]_{OD} = N_s^{-1}[[\omega_T^2]^{-1} \cos \omega_T t$$
$$- [\omega_D^2]^{-1} \cos \omega_D t], \tag{6.15b}$$

where $\omega_T^2 = \omega_D^2 + N_s\omega_{OD}^2$.

A calculation similar to that presented in Sec. IV then yields the folowing result for $\langle A(t)B \rangle$.

$$\langle A(t)B \rangle = \langle A(t)B \rangle_{v_0} + N_s k_B T \, tr_a \, \mathcal{C}^{AB}[t; v_0], \tag{6.16}$$

where the $(r \times r)$ matrix $\mathcal{C}^{AB}[t; v_0]$ is given by

$$\mathcal{C}^{AB}[t; v_0] = [C_D^{AB}[t; v_0] - C_{OD}^{AB}[t; v_0]][\omega_D^2]^{-1} \cos \omega_D t$$
$$+ C_{OD}^{AB}[t; v_0][\omega_T^2]^{-1} \cos \omega_T t. \qquad (6.17)$$

Equation (6.16) decomposes the solvent time correlation function into a rigid solvent contribution $\langle A(t)B\rangle_{v_0}$ and a vibrational contribution proportional to $\mathrm{tr}_a \, \mathcal{C}^{AB}[t; v_0]$. Notice that both contributions may be constructed from the structure and dynamics of the rigid solvent.

VII. FREQUENCY SPECTRUM OF THE SOLVENT

We next present a qualitative discussion of the nature of the frequency spectrum of molecular liquids based on Eq. (6.16). We hope to present a quantitative treatment for realistic solvent models elsewhere.

We assume for simplicity that the solvent is composed of diatomic molecules. Then the number of normal modes of a solvent molecule $r = 1$. For simplicity we also assume that the dynamical variables A and B are identical. Then Eqs. (6.16) and (6.17) reduce to the following result for the autocorrelation function of a scalar dynamical variable A:

$$\langle A(t)A\rangle = \langle A(t)A\rangle_{v_0} + N_s k_B T \mathcal{C}^{AA}[t; v_0], \qquad (7.1)$$

where

$$\mathcal{C}^{AA}[t; v_0] = [C_D^{AA}[t; v_0] - C_{OD}^{AA}[t; v_0]][\omega_D^2]^{-1} \cos \omega_D t$$
$$+ C_{OD}^{AA}[t; v_0][\omega_T^2]^{-1} \cos \omega_T t. \qquad (7.2)$$

All quantities appearing in Eq. (7.2) are scalars.

We next note that simple considerations based on time reversal symmetry arguments show that all correlation functions appearing in Eqs. (7.1) and (7.2) are even in time.

Thus we may define the frequency spectrum of $\langle A(t)A\rangle$, $\rho(\omega)$, by

$$\rho(\omega) = \frac{2}{\pi} \int_0^\infty \cos \omega t \, \frac{\langle A(t)A\rangle}{\langle A^2\rangle} \, d\omega. \qquad (7.3)$$

It follows from Eq. (7.3) that

$$\int_0^\infty \rho(\omega)d\omega = 1. \qquad (7.4)$$

We may further decompose the spectrum into rigid solvent (TR) and vibrational V parts, i.e.,

$$\rho(\omega) = \rho_{TR}(\omega) + \rho_V(\omega), \qquad (7.5)$$

where

$$\rho_{TR}(\omega) = \frac{2}{\pi} \int_0^\infty \cos \omega t \, \frac{\langle A(t)A\rangle_{v_0}}{\langle A^2\rangle} \, d\omega \qquad (7.6a)$$

and

$$\rho_V(\omega) = \frac{2}{\pi} \langle A^2\rangle^{-1} \int_0^\infty$$
$$\times \cos \omega t [N_s k_B T \mathcal{C}^{AA}[t; v_0]]d\omega. \qquad (7.6b)$$

Comparison of Eqs. (7.4)–(7.6) show that the V and TR spectra are normalized respectively to

$$\int_0^\infty \rho_{TR}(\omega)d\omega = \frac{\langle A^2\rangle_{v_0}}{\langle A^2\rangle} \qquad (7.7a)$$

and

$$\int_0^\infty \rho_V(\omega)d\omega = \frac{\langle A^2\rangle - \langle A^2\rangle_{v_0}}{\langle A^2\rangle}. \qquad (7.7b)$$

We expect that rigid solvent equilibrium averages are reasonably good approximations to true solvent averages for many variables A, i.e., often $\langle A^2\rangle \cong \langle A^2\rangle_{v_0}$. If this is the case, Eqs. (7.7) show that the preponderance of the spectral weight is carried by the TR fluctuations.

To gain a further insight into the frequency spectrum we introduce Gaussian approximations for $\langle A(t)A\rangle_{v_0}$ and $C_{D(OD)}[t; v_0]$. Given the even character of the time correlations functions in Eqs. (7.1) and (7.2) one has that

$$\langle A(t)A\rangle_{v_0} = \langle A^2\rangle_{v_0}\left[1 - \frac{1}{2} F t^2 + \cdots \right]$$
$$\cong \langle A^2\rangle_{v_0} \exp\left[-\frac{1}{2} F t^2 \right] \qquad (7.8a)$$

and

$$C_{D(OD)}^{AA}[t; v_0] = C_{D(OD)}^{AA}[0; v_0]\left[1 - \frac{1}{2} F_{D(OD)} t^2 + \cdots \right]$$
$$\cong C_{D(OD)}^{AA}[0; v_0]\exp\left[-\frac{1}{2} F_{D(OD)} t^2 \right], \qquad (7.8b)$$

where

$$F = \langle A^2\rangle_{v_0}^{-1}\langle \dot{A}^2\rangle_{v_0}, \qquad (7.9a)$$
$$F_D = \langle [A^{(v_1)}]^2\rangle_{v_0}^{-1}\langle [\dot{A}^{(v_1)}]^2\rangle_{v_0}, \qquad (7.9b)$$
$$F_{OD} = \langle A^{(v_1)}A^{(v_2)}\rangle_{v_0}^{-1}\langle \dot{A}^{(v_1)}\dot{A}^{(v_2)}\rangle_{v_0}. \qquad (7.9c)$$

Using the Gaussian approximations of Eqs. (7.8) in Eqs. (7.1) and (7.2) yields the following model for $\langle A(t)A\rangle$:

$$\langle A(t)A\rangle \cong \langle A^2\rangle_{v_0} \exp\left[-\frac{1}{2} F t^2 \right]$$
$$+ N_s k_B T \left[\left[C_D^{AA}[0; v_0]\exp\left[-\frac{1}{2} F_D t^2 \right]\right.\right.$$
$$\left.- C_{OD}^{AA}[0; v_0]\exp\left[-\frac{1}{2} F_{OD} t^2 \right]\right][\omega_D^2]^{-1}$$
$$\times \cos \omega_D t + C_{OD}^{AA}[0; v_0]\exp\left[-\frac{1}{2} F_{OD} t^2 \right]$$
$$\left.\times [\omega_T^2]^{-1} \cos \omega_T t\right]. \qquad (7.10)$$

The frequency spectrum may be readily calculated within the model of Eq. (7.10). Defining the normalized Gaussian function $G[y, \sigma]$ by

$$G[y, \sigma] = [2\pi\sigma]^{-1/2} \exp\left[-\frac{1}{2} \frac{y^2}{\sigma} \right], \qquad (7.11)$$

one may write the Gaussian model rigid solvent spectrum as

$$\rho_{TR}(\omega) = 2 \frac{\langle A^2 \rangle_{v_0}}{\langle A^2 \rangle} G[\omega, F]. \tag{7.12a}$$

The vibrational frequency spectrum may correspondingly be written as

$$\rho_V(\omega) = \frac{N_s k_B T}{\langle A^2 \rangle} [[\omega_D^2]^{-1} C_D^{AA}[0; v_0] G[\omega - \omega_D, F_D]$$

$$- [\omega_D^2]^{-1} C_{OD}^{AA}[0; v_0] G[\omega - \omega_D, F_{OD}]]$$

$$+ [\omega_T^2]^{-1} C_{OD}^{AA}[0; v_0] G[\omega - \omega_T, F_{OD}]]. \tag{7.12b}$$

We next discuss Eq. (7.12b). First assume that liquid state effects on ω^2 can be ignored. Then $\omega_D^2 = \omega_g^2$, $\omega_{OD}^2 = 0$, and $\omega_T^2 = \omega_D^2 = \omega_g^2$. Equation (7.12b) reduces to a single band centered at frequency ω_g. This is broadened from the gas phase δ function by solvent TR motion. The Gaussian width of the band is $F_D^{1/2}$. When liquid state effects are reinstated, the peak of this band is shifted from ω_g to ω_D. Moreover superimposed on the original band is a second band. This band has negative spectral weight. Within the Gaussian model the width of this second band is $F_{OD}^{1/2}$.

Finally a second vibrational band of positive weight centered at ω_T appears.

VIII. SUMMARY

This paper has dealt with the development of a liquid state analog of the harmonic oscillator-rigid top model for isolated molecule dynamics. This analog, which we call the harmonic mean field model, provides a treatment of static and dynamic fluctuations in molecular solvents which is analytically simple and which preserves a reasonable measure of physical realism.

The model is most realistic if: (i) the vibrational (V) frequencies of the solvent molecules are sufficiently large that they occur well outside the translational-rotational (TR) spectrum; (ii) The intramolecular forces acting on the vibrational coordinates are much larger than the intermolecular forces.

We consider a solvent composed of N_s molecules each with r normal modes. Then the static harmonic mean field model is defined as the following approximation to $f_{CA}[S]$, the full solvent canonical ensemble distribution function

$$f_{CA}^{(0)}[S] = f_{CA}^{(0)}[p_y, y] f_{CA}[p_w, w; v_0]. \tag{8.1}$$

Note that $f_{CA}[p_w, w; v_0]$ is the canonical ensemble distribution function of the rigid solvent model and that

$$f_{CA}^{(0)}[p_y, y] \sim \exp\left[-\beta \left(\frac{1}{2} p_y^T p_y + \frac{1}{2} y^T \omega^2 y \right) \right] \tag{8.2}$$

is an effective phase space distribution function for the rN_s vibrational displacements y of the solvent and their conjugate momenta p_y.

The quantity ω^2 is the $(rN_s \times rN_s)$-dimensional mean field dynamical matrix of the solvent. It may be partitioned into N_s^2 subblocks each of dimension $r \times r$. The dynamical matrix ω^2 has the property that all of the diagonal subblocks are identical and all of the off-diagonal subblocks are identical. That is ω^2 has the matrix structure

$$\omega^2 = \begin{bmatrix} \omega_D^2 & \omega_{OD}^2 & \omega_{OD}^2 & \cdots \\ \omega_{OD}^2 & \omega_D^2 & \omega_{OD}^2 & \cdots \\ \omega_{OD}^2 & \omega_{OD}^2 & \omega_D^2 & \cdots \\ \vdots & & & \end{bmatrix}. \tag{8.3}$$

The diagonal subblocks ω_D^2 govern the liquid state intramolecular force fields. The off-diagonal subblocks govern intermolecular vibrational coupling.

The $r \times r$ matrices ω_D^2 and ω_{OD}^2 may be computed from the structure of the liquid within the rigid solvent model via Eqs. (2.31) or (2.35).

The canonical ensemble average value of a dynamical variable A for the vibrating solvent, which we denote by $\langle A \rangle$, may be constructed from Eq. (8.1) as

$$\langle A \rangle = \langle A \rangle_{v_0} + \frac{1}{2} N_s k_B T \, \text{tr}_a \, \mathcal{A}[v_0]. \tag{8.4}$$

Note that $\langle A \rangle_{v_0}$ is the average of A within the rigid solvent model and the term proportional to $\text{tr}_a \, \mathcal{A}[v_0]$ gives the correction due to vibrational fluctuations. The quantity $\mathcal{A}[v_0]$ is the following $(r \times r)$ matrix:

$$\mathcal{A}[v_0] = A_D^{(vv)}[v_0][\omega_D^2]^{-1} + A_D^{(pp)}[v_0]$$

$$- A_{OD}^{(vv)}[v_0][\omega_T^2]^{-1} [N_s \omega_{OD}^2][\omega_D^2]^{-1}, \tag{8.5}$$

where $\omega_T^2 = \omega_D^2 + N_s \omega_{OD}^2$ and where $A_D^{(vv)}[v_0]$, etc. are vibrational phase space derivative of A defined in Eqs. (4.13) and (4.14).

The exact Liouville operator of the solvent satisfies the equation $L f_{CA}[S] = 0$. The Liouville operator $L^{(0)}$ of the dynamical harmonic mean field model satisfies the equation $L^{(0)} f_{CA}^{(0)}[S] = 0$. This model Liouville operator is given by

$$iL^{(0)} = iL_y^{(0)} + iL[v_0], \tag{8.6}$$

where

$$iL_y^{(0)} = p_y^T \frac{\partial}{\partial y} - y^2 \omega^2 \frac{\partial}{\partial p_y} \tag{8.7}$$

generates the V dynamics within the mean field harmonic approximation and where $iL[v_0]$ generates the TR dynamics within the rigid solvent model.

The model solvent dynamics generated by $iL^{(0)}$ yields the following result for solvent time correlation functions $\langle A(t)B \rangle$:

$$\langle A(t)B \rangle = \langle A(t)B \rangle_{v_0} + N_s k_B T \, \text{tr}_a \, \mathcal{C}^{AB}[t; v_0], \tag{8.8}$$

where $\langle A(t)B \rangle_{v_0}$ is the rigid solvent model approximation to $\langle A(t)B \rangle$ and where the term proportional to $\text{tr}_a \, \mathcal{C}^{AB}[t; v_0]$ gives the correction due to vibrational fluctuations. This correction leads to qualitative modifications of the solvent vibrational frequency spectrum as discussed below.

The quantity $\mathcal{C}^{AB}[t; v_0]$ is defined by

$$\mathcal{C}^{AB}[t; v_0] = [C_D^{AB}[t; v_0] - C_{OD}^{AB}[t; v_0]][\omega_D^2]^{-1} \cos \omega_D t$$

$$+ C_{OD}^{AB}[t; v_0][\omega_T^2]^{-1} \cos \omega_T t, \tag{8.9}$$

where $C_{D(OD)}[t; v_0]$ are rigid solvent time correlation functions defined in Eqs. (6.13) and where $\omega_T^2 = \omega_D^2 + N_s\omega_{OD}^2$.

The frequency spectrum of the autocorrelation function $\langle A(t)A \rangle$ for a diatomic solvent ($r = 1$) may be readily calculated from Eqs. (8.8) and (8.9) if one additionally assumes that the Gaussian approximation holds for all time correlation functions.

This frequency spectrum may be qualitatively described as follows. It contains three bands. The first is a strong band peaked at $\omega = 0$ arising from solvent TR fluctuations. Outside of this TR band are two V bands. The first is peaked at ω_D, which is the shifted vibrational frequency of the diatomic molecule. This band, within the simplest model, is a superposition of a positive Gaussian and a negative Gaussian. The second V band is positive and is centered at $\omega_T = [\omega_D^2 + N_s\omega_{OD}^2]^{1/2}$.

ACKNOWLEDGMENT

APPENDIX A. PROOF OF SYMMETRY PROPERTIES

In this Appendix we: (i) Prove the rigorous symmetry property of $W[v]$, Eq. (2.21); (ii) Prove that ω^2 has the matrix structure given in Eq. (2.32).

We begin by rewriting the partition function $Z[v]$ as

$$Z[v] = [2\pi k_B T]^{\frac{1}{2} sN_s} \int d\bar{w}$$
$$\times \exp\left[-\beta\left(\sum_{\lambda=1}^{N_s} K_V[v_\lambda w_\lambda] + K_{VV}[vw] \right) \right], \quad \text{(A1)}$$

where

$$d\bar{w} = \prod_{\lambda=1}^{N_s} [\det M_{ww}[v_\lambda w_\lambda]]^{1/2} dw_\lambda. \quad \text{(A2)}$$

Equation (A1) follows by combining Eqs. (2.9) and (2.16) and analytically performing the Gaussian integrals over p_w.

Because all solvent molecules are identical the integrand in Eq. (A1) is symmetric with respect to interchange of the full set of solvent coordinates $v_\lambda w_\lambda$ and $v_{\lambda'} w_{\lambda'}$ on any pair of molecules λ and λ'. An immediate consequence is that $Z[v] = Z[v_1 \cdots v_\lambda \cdots v_{\lambda'} \cdots v_{N_s}]$ is symmetric with respect to the interchange of v_λ and $v_{\lambda'}$, i.e.,

$$Z[v_1 \cdots v_\lambda \cdots v_{\lambda'} \cdots v_{N_s}]$$
$$= Z[v_1 \cdots v_{\lambda'} \cdots v_\lambda \cdots v_{N_s}]. \quad \text{(A3)}$$

Equation (2.21) follows immediately from Eqs. (A3) and (2.18).

We next prove Eq. (2.32). We begin with Eq. (2.29) which we rewrite as

$$W[v] = W[v_0] + \frac{1}{2} \sum_{\lambda=1}^{N_s} \sum_{\lambda'=1}^{N_s} y_\lambda^T[\omega^2]_{\lambda\lambda'} y_{\lambda'}. \quad \text{(A4)}$$

We will assume that all vibrational coordinates are fixed at equilibrium except coordinates, ijk and l, i.e.,

$$y_\lambda = 0 \quad \text{unless} \quad \lambda = ijk \text{ or } l. \quad \text{(A5)}$$

Then Eq. (A4) becomes

$$W[v] = W[v_0] + \frac{1}{2} y_i^T[\omega^2]_{ii} y_i + \frac{1}{2} y_j^T[\omega^2]_{jj} y_j$$
$$+ \frac{1}{2} y_k^T[\omega^2]_{kk} y_k + \frac{1}{2} y_l^T[\omega^2]_{ll} y_l + y_i^T[\omega^2]_{ij} y_j$$
$$+ y_i^T[\omega^2]_{ik} y_k + y_i^T[\omega^2]_{il} y_l + y_j^T[\omega^2]_{jk} y_k$$
$$+ y_j^T[\omega^2]_{jl} y_l + y_k^T[\omega^2]_{kl} y_l. \quad \text{(A6)}$$

Making the interchange $i \rightleftarrows k$ and $j \rightleftarrows l$ and using the fact that $W[v]$ is symmetric under this interchange, Eq. (2.21), yields the following alternative expression for $W[v]$:

$$W[v] = W[v_0] + \frac{1}{2} y_k^T[\omega^2]_{ii} y_k + \frac{1}{2} y_l^T[\omega^2]_{jj} y_l$$
$$+ \frac{1}{2} y_i^T[\omega^2]_{kk} y_i + \frac{1}{2} y_j^T[\omega^2]_{ll} y_j + y_k^T[\omega^2]_{ij} y_l$$
$$+ y_i^T[\omega^2]_{ik} y_k + y_k^T[\omega^2]_{il} y_j + y_i^T[\omega^2]_{jk} y_i$$
$$+ y_j^T[\omega^2]_{jl} y_l + y_i^T[\omega^2]_{kl} y_l. \quad \text{(A7)}$$

Equating Eqs. (A6) and (A7) and setting $y_i = 1$ and $y_j = y_k = y_l = 0$ yields

$$[\omega^2]_{ii} = [\omega^2]_{kk} \equiv \omega_D^2. \quad \text{(A8)}$$

Thus we have shown all diagonal subblocks of ω^2 are equal. Given this result, equating Eqs. (A6) and (A7) yields the following relationship:

$$y_i^T[\omega^2]_{ij} y_j + y_i^T[\omega^2]_{il} y_l + y_j^T[\omega^2]_{jk} y_k + y_k^T[\omega^2]_{kl} y_l$$
$$= y_k^T[\omega^2]_{ij} y_l + y_k^T[\omega^2]_{il} y_j + y_i^T[\omega^2]_{jk} y_i + y_i^T[\omega^2]_{kl} y_l. \quad \text{(A9)}$$

Setting $y_i = y_j = 0$ and $y_k = y_l = 1$ in Eq. (A9) yields

$$[\omega^2]_{kl} = [\omega^2]_{ij} \equiv [\omega^2]_{OD}. \quad \text{(A10)}$$

Thus we have shown all off-diagonal subblocks of ω^2 are equal.

We have therefore proven Eq. (2.32).

APPENDIX B. APPROXIMATE RESULTS FOR ω^2 AND Δ

In this Appendix, we develop the approximate results given in Eqs. (2.35) and (2.42) for ω_D^2, ω_{OD}^2, and Δ.

We assume that the intramolecular contribution to the vibrational forces $\mathcal{F}_{v_\lambda}$ is much stronger than the intermolecular contribution. We make an evaluation of ω_D^2, ω_{OD}^2, and Δ which is valid to linear order in the intermolecular forces.

It is straightforward to show that the leading contribution to $\langle \mathcal{F}_v \mathcal{F}_v^T \rangle_{v=v_0}$ is bilinear in the intermolecular forces. Thus for the present linear order evaluation we

apply the approximate form for ω^2 given in Eq. (2.33). This gives the following results for ω_D^2 and ω_{OD}^2:

$$\omega_D^2 = -M_{vv}^{-1/2} \left\langle \frac{\partial \mathcal{F}_{v_1}^T}{\partial v_1} \right\rangle_{v_0} M_{vv}^{-1/2}, \tag{B1a}$$

$$\omega_{OD}^2 = -M_{vv}^{-1/2} \left\langle \frac{\partial \mathcal{F}_{v_2}^T}{\partial v_1} \right\rangle_{v_0} M_{vv}^{-1/2}. \tag{B1b}$$

To derive Eqs. (2.35) from Eqs. (B1) we additionally make the following simplifying assumptions:

(i) $K_{VV}[vw]$ is pairwise additive and given by Eq. (2.34).

(ii) Centripetal force contributions to $\mathcal{F}_{v_\lambda}$ are negligible. This is most realistic if the solvent rotational kinetic energy is either small or rapidly fluctuating about zero. The latter condition is expected to hold for liquids because of cage hindrance of rotational motion.

(iii) The intramolecular potential energy function $K_V[v_\lambda w_\lambda]$ is independent of w_λ and, moreover, may be replaced by its harmonic approximation, i.e.,

$$K_V[v_\lambda w_\lambda] \cong K_V[v_\lambda], \tag{B2}$$

where

$$K_V[v_\lambda] \cong K_V[v_{g\lambda}] + \frac{1}{2} [v_\lambda - v_{g\lambda}]^T$$
$$\times M_{vv}^{1/2} \omega_g^2 M_{vv}^{1/2} [v_\lambda - v_{g\lambda}]. \tag{B3}$$

Recall $v_{g\lambda}$ is the gas phase value of the equilibrium vibrational coordinates and ω_g^2 is the $r \times r$ gas phase dynamical matrix of a solvent molecular defined by Eq. (B3).

Equation (B2) is exact if v_λ and w_λ are actually the V and TR coordinates of a solvent molecule. Equation (B2) is consistent with the harmonic model for solvent vibrations used throughout this paper. Given these assumptions it follows from Eq. (2.25) that

$$\mathcal{F}_{v_1}[v] = -M_{vv}^{1/2} \omega_g^2 M_{vv}^{1/2} [v_1 - v_{g1}]$$
$$- \frac{\partial}{\partial v_1} \sum_{\lambda=2}^{N_s} k_{VV}[v_1 w_1, v_\lambda w_\lambda]. \tag{B4}$$

Differentiating Eq. (B4) with respect to v_1 and v_2 yields

$$\frac{\partial \mathcal{F}_{v_1}^T}{\partial v_1} = -\left[M_{vv}^{1/2} \omega_g^2 M_{vv}^{1/2} \right.$$
$$\left. + \frac{\partial}{\partial v_1 \partial v_1^T} \sum_{\lambda=2}^{N_s} k_{VV}[v_1 w_1, v_\lambda w_\lambda] \right] \tag{B5a}$$

$$\frac{\partial \mathcal{F}_{v_1}^T}{\partial v_2} = -\frac{\partial^2 k_{VV}[v_1 w_1, v_2 w_2]}{\partial v_1 \partial v_2^T}. \tag{B5b}$$

Combining Eqs. (B1) and (B5) yields Eq. (2.35) for ω_D^2 and ω_{OD}^2.

We next develop Eq. (2.42) for Δ. We begin with the relationship

$$M_{vv}^{1/2} \omega_g^2 \Delta = \frac{\partial K_V[v_{01}]}{\partial v_{01}}, \tag{B6}$$

which follows from Eqs. (2.41) and (B3).

From Eq. (B4) it follows that

$$\mathcal{F}_{v_1}[v_0] = -M_{vv}^{1/2} \omega_g^2 \Delta - \frac{\partial}{\partial v_{01}} \sum_{\lambda=2}^{N_s} k_{VV}[v_{01} w_1, v_{0\lambda} w_\lambda]. \tag{B7}$$

Comparing Eqs. (2.26) and (B7) and using $\langle \mathcal{F}_{v_1} \rangle_{v_0} = 0$ [Eq. (2.28)] yields the following relationship for Δ:

$$\Delta = -\omega_g^{-2} \sum_{\lambda=2}^{N_s} \int M_{vv}^{-1/2} \left[\frac{\partial k_{VV}[v_{01} w_1, v_{0\lambda} w_\lambda]}{\partial v_{01}} \right]$$
$$\times f_{CA}[p_w w; v_0] dp_w \, dw. \tag{B8}$$

Equation (B8) is equivalent to Eq. (2.42) in the thermodynamic ($N_s \rightarrow \infty$) limit.

APPENDIX C. THERMODYNAMIC LIMIT RESULTS

We develop in this Appendix the thermodynamic limit results for $[\omega^{-2}]_D$ and $[\omega^{-2}]_{OD}$ quoted in Eqs. (4.19) and the corresponding results for $[\omega^{-2} \cos \omega t]_D$ and $[\omega^{-2} \times \cos \omega t]_{OD}$ quoted in Eqs. (6.15).

We begin by noting that since $\cos \omega t$ and $z(z^2 + \omega^2)^{-1}$ are Laplace transform pairs one has that

$$[\cos \omega t]_D = \int_C \exp[zt] z[(z^2 + \omega^2)^{-1}]_D dz \tag{C1a}$$

and

$$[\cos \omega t]_{OD} = \int_C \exp[zt] z[(z^2 + \omega^2)^{-1}]_{OD} dz, \tag{C1b}$$

where C is the Laplace inversion contour and where $z^2 = z^2 \bar{1}$ where $\bar{1}$ is the $rN_s \times rN_s$-dimensional unit matrix.

To evaluate Eq. (C1) we must relate $[z^2 + \omega^2]^{-1}$ to ω^2 which, recall, may be calculated from rigid solvent pair correlation functions, Eqs. (2.38).

We begin with the matrix relationship

$$[z^2 + \omega^2][z^2 + \omega^2]^{-1} = \bar{1}. \tag{C2}$$

This may be rewritten in subblock form as

$$\sum_{\lambda=1}^{N_s} \sum_{\lambda'=1}^{N_s} [z^2 + \omega^2]_{\lambda\lambda'}[(z^2 + \omega^2)^{-1}]_{\lambda'\lambda} = 1 \tag{C3a}$$

and ($\mu \neq \lambda$),

$$\sum_{\lambda=1}^{N_s} \sum_{\lambda'=1}^{N_s} [z^2 + \omega^2]_{\lambda\lambda'}[(z^2 + \omega^2)]_{\lambda'\mu}^{-1} = 0, \tag{C3b}$$

where 1 and 0 are, respectively, the unit and null matrices of dimension $r \times r$.

Using Eq. (4.15), Eq. (C3) may be simplified to

$$[z^2 + \omega^2]_D[(z^2 + \omega^2)^{-1}]_D + (N_s - 1)$$
$$\times [z^2 + \omega^2]_{OD}[(z^2 + \omega^2)^{-1}]_{OD} = 1, \tag{C4a}$$

$$[z^2 + \omega^2]_D[(z^2 + \omega^2)^{-1}]_{OD} + [z^2 + \omega^2]_{OD}[(z^2 + \omega^2)^{-1}]_D$$
$$+ (N_s - 2)[z^2 + \omega^2]_{OD}[(z^2 + \omega^2)^{-1}]_{OD} = 0. \tag{C4b}$$

We have additionally that

$$[z^2 + \omega^2]_D = z^2 1 + \omega_D^2 \equiv z^2 + \omega_D^2 \tag{C5a}$$

and

$$[z^2 + \omega^2]_{OD} = \omega_{OD}^2. \tag{C5b}$$

Using Eqs. (C5), Eqs. (C4) may be written as

$$[z^2 + \omega_D^2][(z^2 + \omega^2)^{-1}]_D + (N_s - 1)$$
$$\times [\omega_{OD}^2][(z^2 + \omega^2)^{-1}]_{OD} = 1, \tag{C6a}$$

$$[z^2 + \omega_D^2][(z^2 + \omega^2)^{-1}]_{OD} + [z^2 + \omega_{OD}^2][(z^2 + \omega^2)^{-1}]_D$$
$$+ (N_s - 2)\omega_{OD}^2[(z^2 + \omega^2)^{-1}]_{OD} = 0. \tag{C6b}$$

Solving Eq. (C4b) for $[(z^2 + \omega^2)^{-1}]_{OD}$ then yields in the thermodynamic $(N_s \to \infty)$ limit

$$[(z^2 + \omega^2)^{-1}]_{OD} = -[z^2 + \omega_T^2]^{-1}\omega_{OD}^2[(z^2 + \omega_D^2)^{-1}], \tag{C7}$$

where ω_T^2 is defined in Eq. (3.23). Since $[z^2 + \omega_T^2]^{-1}$ and $[(z^2 + \omega_D^2)^{-1}]_D$ are of order N_s^0 and since ω_{OD}^2 is of order N_s^{-1}, it follows from Eq. (C7) that

$$[(z^2 + \omega^2)^{-1}]_{OD} = O(N_s^{-1}). \tag{C8}$$

Using Eq. (C8), Eq. (C6a) may now be solved in the thermodynamic limit to yield

$$[(z^2 + \omega^2)^{-1}]_D = [z^2 + \omega_D^2]^{-1}. \tag{C9}$$

Setting $z = 0$ in Eqs. (C9) and (C7) yields Eqs. (4.19) for $[\omega^{-2}]_D$ and $[\omega^{-2}]_{OD}$.

We next evaluate $[\cos \omega t]_D$ and $[\cos \omega t]_{OD}$. Combining Eq. (C1a) and Eq. (C9) yields after Laplace inversion

$$[\cos \omega t]_D = \cos \omega_D t. \tag{C10a}$$

Similarily combining Eqs. (C1b) and (C7) yields

$$[\cos \omega t]_{OD} = -\int_C dz \, \exp[zt] z [z^2 + \omega_T^2]^{-1}$$
$$\times \omega_{OD}^2[(z^2 + \omega_D^2)^{-1}]. \tag{C11}$$

Using the partial fraction decomposition

$$[z^2 + \omega_T^2]^{-1}\omega_{OD}^2[(z^2 + \omega_D^2)$$
$$= N_s^{-1}[(z^2 + \omega_T^2)^{-1} - (z^2 + \omega_D^2)^{-1}],$$

the Laplace inversion in Eq. (C11) may be readily performed to yield

$$[\cos \omega t]_{OD} = N_s^{-1}[\cos \omega_T t - \cos \omega_D t]. \tag{C10b}$$

Derivation of Eqs. (6.15) from Eqs. (3.10) is straightforward so we will only provide a brief outline. We rewrite $\omega^{-2} \cos \omega t$ in subblock form as

$$[\omega^{-2} \cos \omega t]_{\lambda\mu} = \sum_{\lambda=1}^{N_s} \sum_{\lambda'=1}^{N_s} [\omega^{-2}]_{\lambda\lambda'}[\cos \omega t]_{\lambda'\mu}. \tag{C.12}$$

Following steps like those which lead from Eq. (C3) to Eqs. (C7) and (C9), Eq. (C12) may be evaluated to yield the results for $[\omega^{-2} \cos \omega t]_D$ and $[\omega^{-2} \cos \omega t]_{OD}$ quoted in Eqs. (6.15).

APPENDIX D. DEVELOPMENT OF THE DYNAMIC HARMONIC MEAN FIELD MODEL

In this Appendix we develop the model solvent Liouville operator $iL^{(0)}$ [Eq. (5.4)] from the exact solvent Liouville operator iL [Eq. (5.1)].

We begin with the following *exact* recasting of Eq. (5.1):

$$iL = iL_y + iL[v]. \tag{D1}$$

Note that L_y is the exact V Liouville operator defined by

$$iL_y = p_y^T \frac{\partial}{\partial y} + \mathcal{F}_v^T[v]M^{-1/2}\frac{\partial}{\partial p_y}, \tag{D2}$$

where $\mathcal{F}_v[v]$ is the vibrational force [see Eq. (2.25)]. The quantity $L[v]$ is the exact TR Liouville operator defined by

$$iL[v] = \left[\frac{\partial K[p_w w; v]}{\partial p_w^T}\frac{\partial}{\partial w} - \frac{\partial K[p_w w; v]}{\partial w^T}\frac{\partial}{\partial p_w}\right]. \tag{D3}$$

Note that iL contains the full effects of V-TR coupling since the w coordinates enter Eq. (D2) through $\mathcal{F}_v[v]$ and the V coordinates enter Eq. (D3) through $K[p_w w; v]$.

The V-TR coupling is suppressed in the dynamic harmonic mean field model. We next develop this model via approximations to Eqs. (D2) and (D3).

We assume the harmonic model for solvent vibrations. Thus we expand

$$\mathcal{F}[v] = \mathcal{F}[v_0] + \frac{\partial \mathcal{F}_v^T[v_0]}{\partial v_0}M^{-1/2}y. \tag{D4}$$

Using Eq. (D4) in Eq. (D2) yields

$$iL_y = p_y^T \frac{\partial}{\partial y}$$
$$+ \left[\mathcal{F}_v^T[v_0] + y^T M^{-1/2}\frac{\partial \mathcal{F}_v^T[v_0]}{\partial v_0}\right]M^{-1/2}\frac{\partial}{\partial p_y}. \tag{D5}$$

We next assume that intramolecular contributions to $\mathcal{F}_v[v]$ are much larger than intermolecular contributions. This implies that the average and instantaneous vibrational forces are nearly identical. An immediate consequence is that

$$\mathcal{F}_v[v_0] \cong \langle \mathcal{F}_v \rangle_{v_0} = 0 \tag{D6a}$$

and

$$\frac{\partial \mathcal{F}_v}{\partial v_0}[v_0] \cong \left\langle \frac{\partial \mathcal{F}_v^T}{\partial v} \right\rangle_{v_0}. \tag{D6b}$$

Using Eqs. (D6) in Eq. (D5) yields

$$iL_y \cong p_y^T \frac{\partial}{\partial y} + y^T M^{-1/2}\left\langle \frac{\partial \mathcal{F}_v^T}{\partial v} \right\rangle_{v_0} M^{-1/2}\frac{\partial}{\partial p_y}. \tag{D7}$$

Given our assumption about the relative magnitudes of intra- and intermolecular vibrational forces, the approximate form for ω^2 given in Eq. (2.33) holds. Using

this form to eliminate $\langle \partial \mathcal{F}_v^T / \partial v \rangle_{v_0}$ in favor of ω^2 from Eq. (D7) gives

$$iL_y \cong iL_y^{(0)} = p_y^T \frac{\partial}{\partial y} - y^T \omega^2 \frac{\partial}{\partial p_y} \tag{D8}$$

The approximations used to develop the model for iL_y given in Eq. (D8) have made the V motion independent of the TR coordinates w. Thus the effects of V-TR energy transfer are removed from the vibrational dynamics.

In order to preserve detailed balance, the effects of V-TR energy transfer must also be removed from the translational-rotational dynamics. This suppression may be accomplished by removing the instantaneous vibrational coordinate v from $iL[v]$ by setting $v = v_0$. This yields

$$iL[v] \cong iL[v_0]. \tag{D9}$$

Comparing Eqs. (D1), (D8), and (D9) yields Eq. (5.4).

[1] See, for example, G. Herzberg, *Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1950). Also see E. Bright Wilson, Jr., J. C. Decius, and P. C. Cross, *Molecular Vibrations: The Theory of Infrared and Raman Spectra* (Dover, New York, 1965).

[2] See, for example, R. D. Levine and R. B. Bernstein, *Molecular Reaction Dynamics* (Clarendon, Oxford, 1974).

[3] See, for example, D. A. McQuarrie, *Statistical Mechanics* (Harper and Row, New York, 1976).

[4] The first part is S. A. Adelman and M. W. Balk, J. Chem. Phys. **81**, 5117 (1984).

[5] S. A. Adelman, Adv. Chem. Phys. **53**, 61 (1983).

[6] The equations of motion developed in Ref. 5 when truncated retain only the first few moments of the frequency spectrum of the autocorrelation function of the random part of the solvent force exerted on the reagents. This formulation is sufficient to describe the influence of the "acoustic" branches of the spectrum, which arise from solvent translational-rotational fluctuations. However to realistically describe the influence of the "optical" branches, which are due to vibrational fluctuations, an extended formulation, which will be developed in this series of papers, is required.

[7] For molecular dynamics simulations of frequency spectra of time correlation functions of molecular solvents see P. Bado, P. H. Berens, J. P. Bergsma, M. H. Coladonto, C. G. Dupery, P. M. Edelsten, J. D. Kahn, and K. R. Wilson, *Proceedings of the International Conference on Photochemistry and Photobiology*, edited by A. Zewail (Harwood Academic, New York, 1983).

[8] For molecular dynamics studies of I_2 photolysis see, for example, Ref. 8.

[9] D. J. Nesbitt and J. T. Hynes, J. Chem. Phys. **77**, 2130 (1982).

[10] C. L. Brooks III, M. W. Balk, and S. A. Adelman, J. Chem. Phys. **79**, 784 (1983); M. W. Balk, C. L. Brooks III, and S. A. Adelman, *ibid.* **79**, 804 (1983).

[11] S. A. Adelman and M. W. Balk (unpublished calculations).

[12] The Cartesian phase space coordinates of solvent molecule λ will be denoted, respectively, by the $3n_s$-dimensional column vectors $q_\lambda = (q_{\lambda 1} q_{\lambda 2} \cdots q_{\lambda n_s})$, $p_{q\lambda} = (p_{q\lambda 1} p_{q\lambda 2} \cdots p_{q\lambda n_s})$. The full set of Cartesian coordinates of the solvent will correspondingly be denoted by the $3n_s N_s$-dimensional column vectors $q = (q_1 q_2 \cdots q_{N_s})$ and $p_q = (p_{q1} p_{q2} \cdots p_{qN_s})$. Similarily $v_\lambda = (v_{\lambda 1} v_{\lambda 2} \cdots v_{\lambda r})$, $p_{v\lambda} = (p_{v\lambda 1} p_{v\lambda 2} \cdots p_{v\lambda r})$, $v = (v_1 v_2 \cdots v_{N_s})$, $p_v = (p_{v1} p_{v2} \cdots p_{vN_s})$, $w_\lambda = (w_{\lambda 1} w_{\lambda 2} \cdots w_{\lambda s})$, $p_{w\lambda} = (p_{w\lambda 1} p_{w\lambda 2} \cdots p_{w\lambda s})$, $w = (w_1 w_2 \cdots w_{N_s})$, $p_w = (p_{w1} p_{w2} \cdots p_{wN_s})$. The mass matrix $M[q_\lambda]$ is defined by

$$M[q_\lambda] = \begin{bmatrix} M_1 & & & & & & & & \\ & M_1 & & & & & & \bigcirc & \\ & & M_1 & & & & & & \\ & & & M_2 & & & & & \\ & & & & \ddots & & & & \\ & & & & & M_{N_s-1} & & & \\ & & & & & & M_{N_s} & & \\ & \bigcirc & & & & & & M_{N_s} & \\ & & & & & & & & M_{N_s} \end{bmatrix}$$

[13] For a discussion of generalized coordinates and related topics see, for example, H. Goldstein, *Classical Mechanics* (Addison–Wesley, Reading, MA, 1980).

[14] $A^{(v)}[v_0]$ and $A^{(p)}[v_0]$ are rN_s-dimensional column vectors defined, respectively, by

$$A^{(v)}[v_0] = M^{-1/2} \left[\frac{\partial A[S]}{\partial v} \right]_{\substack{v=v_0 \\ p_v=0}}$$

and

$$A^{(p)}[v_0] = M^{1/2} \left[\frac{\partial A[S]}{\partial p_v} \right]_{\substack{v=v_0 \\ p_v=0}}.$$

$A^{(vv)}[v_0]$, $A^{(pv)}[v_0]$, $A^{(pp)}[v_0]$, are $(rN_s \times rN_s)$-dimensional matrices defined by

$$A^{(vv)}[v_0] = M^{-1/2} \left[\frac{\partial^2 A[S]}{\partial v \partial v^T} \right]_{\substack{v=v_0 \\ p_v=0}} M^{-1/2},$$

$$A^{(pv)}[v_0] = M^{1/2} \left[\frac{\partial^2 A[S]}{\partial p_v \partial v^T} \right]_{\substack{v=v_0 \\ p_v=0}} M^{-1/2},$$

$$A^{(pp)}[v_0] = M^{1/2} \left[\frac{\partial^2 A[S]}{\partial p_v \partial p_v^T} \right]_{\substack{v=v_0 \\ p_v=0}} M^{1/2}.$$

[15] Equation (4.15) may be proven by expanding $f[\omega]$ in a power series in ω^2 and using Eqs. (2.32) and (2.40).