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# Generalized Langevin theory for many-body problems in chemical dynamics: Formulation for molecular solvents, equilibrium aspects

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This paper deals with equilibrium statistical mechanical aspects of the extension of the MTGLE approach for chemical reaction dynamics in liquids [S. A. Adelman, Adv. Chem. Phys. **53**, 611 (1983)] so that it is applicable to molecular as well as monatomic solvents. This extension is necessary in order to conveniently treat energy exchange between the solute molecules and the solvent vibrational degrees of freedom. The analysis yields a separation of equilibrium solvent density fluctuations into translation-rotational (TR) and vibrational (V) contributions. The TR fluctuations are treated within the rigid solvent molecule model. The V fluctuations are treated within the harmonic oscillator approximation. The analysis is carried out in terms of a set of generalized solvent phase space coordinates  $S = p_v v p_w w$  where  $v$  and  $w$  are, respectively, the V and TR coordinates and where  $p_v$  and  $p_w$  are the corresponding conjugate momenta. In this coordinate system, canonical ensemble distribution function for the solvent given that the solute is fixed at configuration point  $r_0$ , denoted by  $f_{CA}[S; r_0]$ , may be factorized as  $f_{CA}[S; r_0] = f_{CA}[p_v v] f_{CA}[p_w w; v_0 r_0]$  where  $f_{CA}[p_w w; v_0 r_0]$  and  $f_{CA}[p_v v]$  are respectively: the rigid solvent model approximation to  $f_{CA}[S; r_0]$ ; a vibrational phase space probability distribution function which governs equilibrium mean field V fluctuations in the *pure solvent*. This vibrational probability distribution function may be written as  $f_{CA}[p_v v] = Z^{-1} \exp[-\beta(T_v + W(v))]$  where  $Z$  = pure solvent partition function, where  $T_v$  = pure solvent kinetic energy, and where  $W[v]$  is a vibrational potential of mean force. The above factorization of  $f_{CA}[S; r_0]$  holds if: (i) Coriolis coupling between the  $v$  and  $w$  coordinates is ignored; (ii) The solvent vibrational frequencies are sufficiently high. Within the harmonic approximation to  $W[v]$ ,  $f_{CA}[p_v v] = [2\pi k_B T]^{-rN_s} \det \omega^2 \exp[-\beta(T_v + \frac{1}{2} y^T \omega^2 y)]$  where  $y$  are the mass-weighted displacements of the  $v$  coordinates from equilibrium, where  $rN_s$  = number of solvent normal modes, and where  $\omega^2$  is an  $(rN_s \times rN_s)$ -dimensional dynamical matrix which determines the vibrational frequency spectrum of the pure solvent within the harmonic approximation. This dynamical matrix may be constructed from the canonical ensemble distribution function of the pure rigid molecule solvent. Thus given the harmonic approximation to  $W[v]$  the canonical ensemble distribution function of the nonrigid solvent  $f_{CA}[S; r_0]$  may be constructed from the equilibrium properties of the rigid molecule solvent.

## I. INTRODUCTION

This paper is the first in a three-part series which will extend the MTGLE approach for chemical reaction dynamics in liquids<sup>1</sup> so that it is conveniently applicable to molecular as well as monatomic solvents.

The motivation for the present work arose, in part, from the results of recent applications of the theory to several problems in condensed phase chemical kinetics.<sup>2-5</sup> These first applications brought out the basic role played by temporal density fluctuations in the solvation shells in influencing the rate of solute-solvent energy exchange and hence the course of liquid state chemical events. Qualitatively speaking, this energy exchange is efficient if the solute frequencies relevant for the process of interest<sup>6</sup> have substantial resonance overlap with the frequency spectrum which characterizes solvation shell density fluctuations.

The presently developed theory provides a rigorously based set of solute equations of motion which permits one to simulate the influence of density fluctuations arising from

hindered *translational* motion in the solvation shells. These equations of motion describe either the full solute dynamics<sup>1</sup> or the dynamics of a set of solute generalized coordinates<sup>7</sup> whose motions govern the rates of processes of interest.<sup>6</sup>

Our MTGLE simulation work on molecular iodine photolysis<sup>2</sup> and also the complementary work of Wilson and co-workers<sup>8</sup> and Nesbitt and Hynes<sup>9</sup> show that in molecular solvents local density fluctuations arising from molecular vibrations can qualitatively change the course of liquid state chemical events.

This is because these vibrational density fluctuations introduce condensed phase broadened vibrational bands<sup>10</sup> in the solvation shell frequency spectra. If resonance overlap occurs between the solute frequencies relevant for a given process<sup>6</sup> and one of these vibrational bands, then efficient energy exchange between the solute and solvent vibrational motions can greatly modify the reaction dynamics from that expected in monatomic or rigid molecular solvents.

This series of papers is aimed at the development of a set of rigorously founded equations of motion for solute dynamics in molecular solvents. These equations of motion separate the effects of solvent translational-rotational and sol-

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vent vibrational motion on solute dynamics in a practically useful and physically clear manner. The equations of motion, e.g., permit one to conveniently model the complex fluctuation spectrum characteristic of a molecular solvent<sup>10</sup> in a manner which realistically preserves its influence on solute motion.

This paper is concerned with equilibrium statistical mechanical aspects of the problem. We present, in particular, a method for factorizing the equilibrium solvent phase space probability distribution function into translational-rotational and vibrational components. We also present an analysis which provides insight into the nature of the vibrational frequency spectrum in molecular liquids.

The equilibrium analysis present in this paper is basic to subsequent developments. This is because the effects of the temporal solvent density fluctuations which “drive” the solute motions may be largely constructed from the equilibrium results present here. The next two papers will concern, respectively, the development of equations of motion for full solute dynamics and for the dynamics of generalized coordinates whose motions govern the rates of important elementary processes.<sup>6</sup> Applications of these equations of motion to specific processes in molecular solvents will appear in subsequent papers.

The plan of this paper is as follows. The main results of the analysis are summarized in Sec. II. The liquid solution is specified in Sec. III. The theoretical development is presented in Sec. IV and in the Appendix.

## II. SUMMARY OF MAIN RESULTS

We begin with a brief summary of the main results of this paper.

We will analyze the equilibrium statistical mechanics of the solvent using a set of generalized phase space coordinates  $S = p_v v p_w w$ . The coordinates  $v$  describe the high frequency motion of the solvent. They will usually be taken as the normal mode coordinates of the solvent molecules when isolated. These high frequency coordinates will be treated within the harmonic approximation. The coordinates  $w$  describe the low frequency motions of the solvent. They will usually be taken as the translational-rotational coordinates of the solvent. Highly anharmonic low frequency vibrational modes may, however, also be included in the set  $w$ . This device permits one to properly account for overtone and combination band contribution of these low frequency modes to the solvent fluctuation spectrum.

To calculate the dynamic response of the solvent to solute motion when the solute is located at configuration point  $r_0$ , one requires the canonical ensemble phase space distribution function of the solvent conditional that the solute is fixed at point  $r_0$ . We will denote this phase space probability distribution function (pdf) by  $f_{CA}[S; r_0]$ . We will show below that this phase space pdf may be approximately factorized as

$$f_{CA}[S; r_0] = f_{CA}[p_v v] f_{CA}[p_w w; v_0 r_0]. \quad (2.1)$$

The pdf  $f_{CA}[p_w w; v_0 r_0]$  is the *rigid solvent model* approximation to  $f_{CA}[S; r_0]$ . The rigid solvent model is defined by fixing all solvent vibrational coordinates at their equilibri-

um values  $v_0$ . These equilibrium values are defined in Eq. (4.35).

The effects of solvent equilibrium vibrational fluctuations are accounted for by the vibrational phase space pdf  $f_{CA}[p_v v]$ . This pdf describes mean field vibrational fluctuations in the *pure solvent*. (The term mean field refers to the fact that the effects of statistical fluctuations in the values of the low frequency coordinates on the vibrational phase space pdf are integrated out in the definition of  $f_{CA}[p_v v]$ .)

The approximate factorization of  $f_{CA}[S; r_0]$  given in Eq. (2.1) holds if: (i) the oscillation frequencies of the  $v$  coordinates are sufficiently high. (For this case, quantum statistical effects can become important. A simple method for incorporating these will be presented elsewhere.) (ii) The Coriolis coupling between the  $v$  and  $w$  coordinates can be neglected.

The mean field vibrational phase space pdf takes the following form:  $[\beta = (k_B T)^{-1}]$ ,

$$f_{CA}[p_v v] = Z^{-1} \exp[-\beta T_v + W(v)]. \quad (2.2)$$

Note that  $Z$  is the pure solvent partition function,  $T_v$  is the solvent vibrational kinetic energy, and  $W[v]$  is the vibrational potential of mean force.

The vibrational potential of mean force is defined by the relationship

$$Z[v] = \exp[-\beta W(v)], \quad (2.3)$$

where  $Z[v]$  is the partition function of the pure solvent conditional that the vibrational coordinates are fixed at some value  $v$ .

The potential of mean force in the harmonic approximation is

$$W[v] = W[v_0] + \frac{1}{2} y^T \omega^2 y, \quad (2.4)$$

where  $y = M^{1/2}[v - v_0]$  is a set of mass-weighted vibrational displacements and where  $\omega^2$  is the mean field vibrational frequency matrix of the pure solvent. This has the matrix structure

$$\omega^2 = \begin{pmatrix} \omega_D^2 & \omega_{OD}^2 & \omega_{OD}^2 & \cdots \\ \omega_{OD}^2 & \omega_D^2 & \omega_{OD}^2 & \cdots \\ \omega_{OD}^2 & \omega_{OD}^2 & \omega_D^2 & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}. \quad (2.5)$$

The diagonal elements describe the liquid state intramolecular vibrational force fields. The off-diagonal elements describe the intermolecular couplings which broaden gas phase vibrational lines into liquid state vibrational bands.

The vibrational frequency matrix  $\omega^2$  may be calculated from the equilibrium structure of the pure rigid solvent via

$$\omega^2 = -M^{-1/2} \cdot \left[ \left\langle \frac{\partial F_v^T}{\partial v} \right\rangle_{v_0} + \beta \langle F_v F_v^T \rangle_{v_0} \right] \cdot M^{-1/2}, \quad (2.6)$$

where all quantities and canonical ensemble averages are to be evaluated for the rigid solvent model.

Given the harmonic approximation, the full solvent partition function  $Z$  and the rigid solvent partition function  $Z[v_0]$  may be related by

$$Z = [2\pi k_B T]^{r_N} [\det \omega^2]^{-1/2} Z[v_0], \quad (2.7)$$

where  $rN_s$  is the number of normal modes of the solvent. Comparison of Eqs. (2.1)–(2.4) and (2.7) then yields the following result for  $f_{CA}[S;r_0]$  within the harmonic approximation for the solvent vibrational motions:

$$f_{CA}[S;r_0] = [2\pi k_B T]^{-rN_s} [\det \omega^2]^{1/2} \times \exp[-\beta(T_v + \frac{1}{2} y^T \omega^2 y)] f_{CA}[p_w w; \dot{v}_0 r_0]. \quad (2.8)$$

Equations (2.6) and (2.8) show that within the harmonic approximation for the solvent vibrational motions the full canonical ensemble distribution function of the solvent may be constructed from the canonical ensemble distribution function of the rigid solvent.

### III. SPECIFICATION OF THE LIQUID SOLUTION

We begin with a specification of the liquid solution. We assume a one-component polyatomic solvent composed of  $N_s$  molecules. Each solvent molecule is composed of  $n_s$  atoms. The thermodynamic state of the solvent is specified by its number density  $\rho = N_s/V$ , where  $V$  = volume of the solution, and by its Kelvin temperature  $T$ . Immersed at infinite dilution in the polyatomic solvent is an  $n$ -atom solute system.

For brevity we will employ a short-hand matrix and vector notation similar to that employed elsewhere<sup>11</sup> to designate the masses and phase space coordinates of the particles in the liquid solution. Specifically we will denote the Cartesian phase space coordinates of solvent molecule  $\lambda$  by  $q_\lambda$  and  $p_{q_\lambda}$ , of the full solvent by  $q$  and  $p_q$ , and of the solute system by  $r_0$  and  $p_0$ .

The masses of the atoms of solvent molecule  $\lambda$  will be denoted by the diagonal matrix  $M[q_\lambda]$ ; those of the solute system will analogously be denoted by the diagonal matrix  $m$ .

The potential energy functions describing interactions in the solution will be denoted by  $U_{UU}[r_0]$  = gas phase solute potential,  $U_V[q_\lambda]$  = gas phase potential of solvent molecule  $\lambda$ ,  $U_{VV}[q]$  = solvent intermolecular potential,  $U_{VV}[qr_0]$  = solute-solvent potential.

### IV. SEPARATION OF VIBRATIONAL AND TRANSLATIONAL-ROTATIONAL EQUILIBRIUM FLUCTUATIONS

In this section we will develop the results summarized in Sec. II. This development is most conveniently carried out by describing the solvent in generalized as opposed to Cartesian phase space coordinates. So we begin by discussing the transformation to generalized coordinates.

#### A. Generalized coordinates

We will collectively denote<sup>11</sup> the  $3N_s$  generalized coordinates for solvent molecule  $\lambda$  by the column vector  $u_\lambda$ . The conjugate momenta will be denoted by the vector  $p_{u_\lambda}$ . We will correspondingly denote<sup>11</sup> the  $3n_s N_s$  generalized coordinates for the full solvent by the column vectors  $u$  and  $p_u$ .

We assume the Cartesian and generalized coordinates for solvent molecule  $\lambda$  are related by a time-independent

point canonical transformation<sup>12</sup>  $u$  which is the same for all solvent molecules.

That is,

$$u_\lambda = u[q_\lambda]. \quad (4.1)$$

From Eq. (4.1) it is straightforward<sup>13</sup> to show that the kinetic energy of solvent molecule  $\lambda$  written in terms of the generalized coordinates is

$$T = \frac{1}{2} \dot{u}_\lambda^T M[u_\lambda] \dot{u}_\lambda = \frac{1}{2} p_{u_\lambda}^T M^{-1}[u_\lambda] p_{u_\lambda}, \quad (4.2)$$

where  $p_{u_\lambda} = M[u_\lambda] \dot{u}_\lambda$  is the generalized momentum conjugate to  $u_\lambda$  and where  $M[u_\lambda]$  as the  $(3n_s \times 3n_s)$ -dimensional mass matrix defined by

$$M[u_\lambda] = \left[ \frac{\partial q_\lambda}{\partial u_\lambda} \right]^T M[q_\lambda] \left[ \frac{\partial q_\lambda}{\partial u_\lambda} \right]. \quad (4.3)$$

#### B. Low and high frequency coordinates

We next partition the  $3N_s$  generalized coordinates of solvent molecule  $\lambda$  into a set of  $r$  high frequency coordinates  $v_\lambda$  and a set of  $s = 3n_s - r$  low frequency coordinates  $w_\lambda$ . That is,

$$u_\lambda = \begin{pmatrix} v_\lambda \\ w_\lambda \end{pmatrix}. \quad (4.4)$$

The  $3n_s N_s$  generalized coordinates of the full solvent  $u$  will be analogously partitioned as

$$u = \begin{pmatrix} v \\ w \end{pmatrix}. \quad (4.5)$$

In practice, we will usually choose the set  $v_\lambda$  to be the normal mode vibrational (V) coordinates of solvent molecule  $\lambda$  and the set  $w_\lambda$  to be its translational-rotational (TR) coordinates. This specific choice, however, is not essential for the validity of the development to be presented below. Corresponding to the partitioning of Eq. (4.5), the mass matrix  $M[u_\lambda]$  partitions as

$$M[u_\lambda] = \begin{bmatrix} M_{vv}[v_\lambda w_\lambda] & M_{vw}[v_\lambda w_\lambda] \\ M_{wv}[v_\lambda w_\lambda] & M_{ww}[v_\lambda w_\lambda] \end{bmatrix}, \quad (4.6)$$

where

$$M_{vv}[u_\lambda w_\lambda] = \left[ \frac{\partial q_\lambda}{\partial v_\lambda} \right]^T M[u_\lambda] \left[ \frac{\partial q_\lambda}{\partial v_\lambda} \right], \text{ etc.} \quad (4.7)$$

The kinetic energy of solvent molecule  $\lambda$  may be written in the following two equivalent forms:

$$T_\lambda = \left[ \frac{1}{2} \dot{v}_\lambda^T M_{vv}[v_\lambda w_\lambda] \dot{v}_\lambda + \dot{v}_\lambda^T M_{vw}[v_\lambda w_\lambda] \dot{w}_\lambda + \frac{1}{2} \dot{w}_\lambda^T M_{ww}[v_\lambda w_\lambda] \dot{w}_\lambda \right] \quad (4.8a)$$

and

$$T_\lambda = \left[ \frac{1}{2} p_{v_\lambda}^T [M^{-1}[v_\lambda w_\lambda]]_{vv} p_{v_\lambda} + p_{v_\lambda}^T [M^{-1}[v_\lambda w_\lambda]]_{vw} p_{w_\lambda} + \frac{1}{2} p_{w_\lambda}^T [M^{-1}[v_\lambda w_\lambda]]_{ww} p_{w_\lambda} \right]. \quad (4.8b)$$

The generalized momenta  $p_{v_\lambda}$  and  $p_{w_\lambda}$  conjugate to the generalized coordinates  $v_\lambda$  and  $w_\lambda$  are given by

$$\begin{aligned} p_{v_\lambda} &= \mathbf{M}_{vv} [v_\lambda w_\lambda] \dot{v}_\lambda + \mathbf{M}_{vw} [v_\lambda w_\lambda] \dot{w}_\lambda, \\ p_{w_\lambda} &= \mathbf{M}_{wv} [v_\lambda w_\lambda] \dot{v}_\lambda + \mathbf{M}_{ww} [v_\lambda w_\lambda] \dot{w}_\lambda. \end{aligned} \quad (4.9)$$

### C. Short-hand notation

For brevity we will often use the following short-hand notation for the high and low frequency generalized coordinates:

$$S_\lambda = (p_{v_\lambda} v_\lambda, p_{w_\lambda} w_\lambda), \quad (4.10a)$$

$$S = (p_v v, p_w w). \quad (4.10b)$$

The corresponding phase space volume elements will be defined by

$$dS_\lambda = dp_{v_\lambda} dv_\lambda dp_{w_\lambda} dw_\lambda, \quad (4.11a)$$

$$dS = dp_v dv dp_w dw. \quad (4.11b)$$

### D. Hamiltonian of the solvent

To determine the solvent influence on reagent dynamics when the reagent atoms are located at configuration point  $r_0$ , we will require the Hamiltonian of the solvent conditional that the reagent atoms are *fixed* at point  $r_0$ .

This solvent Hamiltonian expressed in the generalized phase space coordinates  $S$  will be denoted by  $K[S; r_0]$ . Defining the potential energy functions in generalized coordinates via  $K_V[v_\lambda w_\lambda] = U_V[q_\lambda]$ ,  $K_{VV}[vw] = U_{VV}[q]$ ,  $K_{VU}[vwr_0] = U_{VU}[qr_0]$ , the solvent Hamiltonian may be written as

$$\begin{aligned} K[S; r_0] &= \sum_{\lambda=1}^{N_s} [T_\lambda + K_V[v_\lambda w_\lambda]] \\ &\quad + K_{VV}[vw] + K_{VU}[vwr_0]. \end{aligned} \quad (4.12)$$

### E. Canonical ensemble distribution function of the solvent

The canonical ensemble distribution function of the solvent given that the solute is fixed at  $r_0$  is given by

$$f_{CA}[S; r_0] = [Z[r_0]]^{-1} \exp[-\beta K(S; r_0)], \quad (4.13)$$

where  $Z(r_0)$ , the partition function of the solvent in the presence of the fixed solute, is given by

$$Z[r_0] = \int \exp[-\beta K(S; r_0)] dS. \quad (4.14)$$

### F. Clamping of solvent vibrations

To separate the effects of solvent V fluctuations from those of solvent TR fluctuations, it will prove convenient to introduce the mathematical device of *fixing* the  $V$  coordinates of each solvent molecule at some value  $v_\lambda$ . (This value can be different for different solvent molecules.)

If the  $V$  coordinates are fixed, then  $\dot{v}_\lambda = 0$  and Eqs. (4.8) and (4.9) yield the following result for the kinetic energy of solvent molecule  $\lambda$ :

$$\begin{aligned} T_\lambda^{(0)} &= \frac{1}{2} \dot{w}_\lambda \mathbf{M}_{ww} [v_\lambda w_\lambda] \dot{w}_\lambda \\ &= \frac{1}{2} p_{w_\lambda}^T \mathbf{M}_{ww}^{-1} [v_\lambda w_\lambda] p_{w_\lambda}. \end{aligned} \quad (4.15)$$

The Hamiltonian of the solvent in the presence of the fixed solute and with the vibrations also fixed will be denoted

by  $K[p_w w; vr_0]$ . This Hamiltonian may be obtained by replacing  $T_\lambda$  in Eq. (4.12) by  $T_\lambda^{(0)}$  to give

$$\begin{aligned} K[p_w w; vr_0] &= \sum_{\lambda=1}^{N_s} [T_\lambda^{(0)} + K_V[v_\lambda w_\lambda]] \\ &\quad + K_{VV}[vw] + K_{VU}[vwr_0]. \end{aligned} \quad (4.16)$$

The corresponding canonical ensemble distribution function is

$$f_{CA}[p_w w; vr_0] = [Z[vr_0]]^{-1} \exp[-K(p_w w; vr_0)], \quad (4.17)$$

where

$$Z[vr_0] = \int \exp[-\beta K(p_w w; vr_0)] dp_w dw \quad (4.18)$$

is the partition function of the solvent given that the solute is fixed at configuration point  $r_0$  and that the  $V$  coordinates are fixed at point  $v$ .

### G. Approximate mass matrix

We next assume that the off-diagonal solvent mass matrix elements are much smaller than the diagonal elements and that  $\mathbf{M}_{vv}[v_\lambda w_\lambda]$  is independent of the generalized coordinates. Explicitly,

$$\mathbf{M}[v_\lambda w_\lambda] = \begin{pmatrix} \mathbf{M}_{vv} & \mathbf{O} \\ \mathbf{O} & \mathbf{M}_{ww}[v_\lambda w_\lambda] \end{pmatrix}. \quad (4.19)$$

This assumed form of the mass matrix will greatly simplify the subsequent analysis. This assumed form is rigorously correct if: (i) The high and low frequency coordinates are actually the normal mode and TR coordinates of the molecule; (ii) the Coriolis coupling<sup>14</sup> between vibrations and rotations is ignored.

### H. Separation of equilibrium fluctuations

Given Eq. (4.19), it is straightforward to show that the full solvent Hamiltonian and the solvent Hamiltonian with the vibrations fixed are related by

$$K[S; r_0] = \sum_{\lambda=1}^{N_s} \frac{1}{2} p_{v_\lambda}^T \mathbf{M}_{vv}^{-1} p_{v_\lambda} + K[p_w w; vr_0]. \quad (4.20)$$

A consequence<sup>15</sup> of Eq. (4.20) is that the full solvent phase space probability distribution function (pdf) rigorously factorizes into a pdf for the equilibrium V fluctuations and a pdf for the equilibrium TR fluctuations. Explicitly,

$$f_{CA}[S; r_0] = f_{CA}[p_v v; r_0] f_{CA}[p_w w; vr_0], \quad (4.21)$$

where  $f_{CA}[p_v v; r_0]$  is a unit normalized effective phase space pdf for the V fluctuations. This is defined by

$$f_{CA}[p_v v; r_0] = \int f_{CA}[S; r_0] dp_w dw. \quad (4.22)$$

Comparison of Eqs. (4.13), (4.17), and (4.20) with the above definition of  $f_{CA}[p_v v; r_0]$  yields the following alternative expression for this vibrational pdf:

$$f_{CA}[p_v v; r_0] = \left[ \frac{Z[vr_0]}{Z[r_0]} \right] \exp \left[ -\beta \sum_{\lambda=1}^{N_s} \frac{1}{2} p_{v_\lambda}^T \mathbf{M}_{vv}^{-1} p_{v_\lambda} \right]. \quad (4.23)$$

The factorization identity Eq. (4.21) is the first step in

separating the effects of solvent fluctuations on solute motion into V and TR parts. This separation is, however, not yet complete since  $f_{CA} [p_w w; v r_0]$ , the phase space pdf for the TR fluctuations, depends on the vibrational coordinate  $v$ .

### I. Vibrational potential of mean force

The vibrational potential of mean force  $W[v r_0]$  is defined by

$$Z[v r_0] = \exp[-\beta W(v r_0)], \quad (4.24)$$

where  $Z[v r_0]$  is defined in Eq. (4.18).

Comparing Eqs. (4.23) and (4.24) yields the following form for the vibrational phase space pdf:

$$\begin{aligned} f_{CA} [p_v v; r_0] \\ = [Z[r_0]]^{-1} \\ \times \exp \left[ -\beta \left( \sum_{\lambda=1}^{N_s} \frac{1}{2} p_{v\lambda}^T M_{vv}^{-1} p_{v\lambda} + W[v r_0] \right) \right]. \end{aligned} \quad (4.25)$$

Given Eq. (4.25), it is clear that the partition function  $Z[r_0]$ , which is defined as a full solvent phase space integral in Eq. (4.14), may be rewritten as the following vibrational phase space integral:

$$\begin{aligned} Z[r_0] = \int dp_v dv \\ \times \left[ \exp \left[ -\beta \left( \sum_{\lambda=1}^{N_s} \frac{1}{2} p_{v\lambda}^T M_{vv}^{-1} p_{v\lambda} + W(v r_0) \right) \right] \right]. \end{aligned} \quad (4.26)$$

Given the definition of  $f_{CA} [p_v v; r_0]$ , Eq. (4.22), it is clear that this phase space pdf describes V fluctuations with the effects of microscopic TR fluctuations averaged out. Thus  $W[v r_0]$  describes mean field vibrational fluctuations.

From the definition of  $W[v r_0]$  as a mean field quantity, it follows that  $W[v r_0]$  is a symmetric function with respect to interchange of the full set of vibrational coordinates on different molecules. That is,

$$W[v r_0] = W[v_1 v_2 \dots v_{N_s} r_0] = W[v_2 v_1 \dots v_{N_s} r_0] = \dots \quad (4.27)$$

The simplest approximate model for the vibrational potential of mean force, which satisfies the rigorous symmetry property Eq. (4.27), is

$$W[v r_0] = \sum_{\lambda=1}^{N_s} w[v_\lambda r_0], \quad (4.28)$$

where  $w[v_\lambda r_0]$  is a single molecule vibrational potential of mean force.

Within the model of Eq. (4.28), coupling of normal mode fluctuations on different molecules due to liquid state effects is neglected and  $f_{CA} [p_v v; r_0]$  factorizes into single molecule vibrational pdf's.

### J. Canonical ensemble averages

We will denote the canonical ensemble average of an arbitrary solvent phase space variable  $A[S; r_0]$  by  $\langle A \rangle_{r_0}$ , where

$$\langle A \rangle_{r_0} = \int f_{CA} [S; r_0] A[S; r_0] dS. \quad (4.29)$$

Because of the identity of Eq. (4.21), the above average may be rewritten as

$$\langle A \rangle_{r_0} = \int f_{CA} [p_v v; r_0] \langle A \rangle_{p_v v r_0} dp_v dv, \quad (4.30)$$

where

$$\langle A \rangle_{p_v v r_0} = \int f_{CA} [p_w w; v r_0] A[S; r_0] dp_w dw. \quad (4.31)$$

Note that  $\langle A \rangle_{p_v v r_0}$  is the contribution to  $\langle A \rangle_{r_0}$  from pure TR fluctuations, i.e., the contribution with the effects of V fluctuations removed. Thus comparison of  $\langle A \rangle_{r_0}$  and  $\langle A \rangle_{p_v v r_0}$  permits one to assess the relative contribution of TR and V fluctuations to canonical ensemble averages. Finally if  $A[S; r_0]$  is independent of  $p_v$  then for brevity we will denote  $\langle A \rangle_{p_v v r_0}$  by  $\langle A \rangle_{v r_0}$ .

### K. Mean forces

The generalized force exerted on the solute atoms by the solvent is defined by

$$F_{r_0} = - \frac{\partial K[S; r_0]}{\partial r_0}. \quad (4.32a)$$

The analogous generalized force exerted on the vibrational coordinates is defined by

$$F_v = - \frac{\partial K[S; r_0]}{\partial v}. \quad (4.32b)$$

Next consider the mean forces  $\langle F_v \rangle_{v r_0}$  and  $\langle F_{r_0} \rangle_{v r_0}$ . These may be rigorously determined from the vibrational potential of mean force via the relations<sup>16</sup>

$$\langle F_{r_0} \rangle_{v r_0} = - \frac{\partial W[v r_0]}{\partial r_0} \quad (4.33)$$

and

$$\langle F_v \rangle_{v r_0} = - \frac{\partial W[v r_0]}{\partial v}. \quad (4.34)$$

### L. Rigid solvent model

We next define the rigid solvent model as the model for which the vibrational coordinates are fixed at their equilibrium values  $v_0$ . These equilibrium values are defined by the relations

$$\langle F_v \rangle_{v_0 r_0} = - \frac{\partial W[v_0 r_0]}{\partial v_0} = 0. \quad (4.35)$$

The equilibrium values of the vibrational coordinates are expected to be the same for all molecules. This may be proven from the symmetry property [Eq. (4.27)].

We will later require the canonical ensemble phase space pdf for the rigid solvent model. From Eq. (4.17) this is  $f_{CA} [p_w w; v_0 r_0] = [Z[v_0 r_0]]^{-1} \exp[-\beta K(p_w w; v_0 r_0)]$ .

(4.36)

Note that  $Z[v_0 r_0]$  is the partition function of the rigid solvent model.

### M. Vibrational frequency matrix

We next examine the frequency matrix  $\omega^2(r_0)$  which governs mean field vibrational fluctuations in the liquid.

We begin by defining the mass-weighted vibrational displacement  $y$  of the  $V$  coordinates of solvent molecule  $\lambda$  by

$$y_\lambda = M_{vv}^{1/2} [v_\lambda - v_{0\lambda}]. \quad (4.37)$$

We may correspondingly define the mass-weighted displacements of the full solvent by

$$y = M^{1/2} [v - v_0], \quad (4.38)$$

where  $M$  is the  $(rN_s \times rN_s)$ -dimensional mass matrix defined by

$$M = \begin{pmatrix} M_{vv} & & & \\ & M_{vv} & & \\ & & \ddots & \\ & & & M_{vv} \end{pmatrix}. \quad (4.39)$$

Expanding  $W[vr_0]$  about the rigid solvent value  $W[v_0r_0]$  and retaining only quadratic order terms yields

$$W[vr_0] = W[v_0r_0] + \frac{1}{2} y^T \omega^2(r_0) y, \quad (4.40)$$

where

$$\omega^2(r_0) = M^{-1/2} \left[ \frac{\partial^2 W[vr_0]}{\partial v \partial v^T} \right]_{v=v_0} M^{-1/2} \quad (4.41)$$

is the dynamical matrix which governs the mean field vibrational motions of the solvent.

From the symmetry property [Eq. (4.27)] it is straightforward to show that the matrix structure of  $\omega^2(r_0)$  is

$$\omega^2(r_0) = \begin{pmatrix} \omega_D^2(r_0) & \omega_{OD}^2(r_0) & \omega_{OD}^2(r_0) & \cdots \\ \omega_{OD}^2(r_0) & \omega_D^2(r_0) & \omega_{OD}^2(r_0) & \cdots \\ \omega_{OD}^2(r_0) & \omega_{OD}^2(r_0) & \omega_D^2(r_0) & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}. \quad (4.42)$$

The submatrix  $\omega_D(r_0)$  describes the mean field intramolecular force field of a particular solvent molecule in the liquid. It may be decomposed into a gas phase part and a liquid state correction as follows:

$$\omega_D(r_0) = \omega_D^{(g)}(r_0) + \omega_D^{(l)}(r_0). \quad (4.43)$$

The gas-phase part  $\omega_D^{(g)}$  is the diagonal matrix of normal mode frequencies of an isolated solvent molecule. The diagonal elements of the liquid state correction  $\omega_D^{(l)}(r_0)$  account for condensed phase shifts of the normal mode frequencies. The off-diagonal elements of  $\omega_D^{(l)}(r_0)$  describe the solvent induced coupling of normal modes on a given molecule.

The submatrix  $\omega_{OD}^2(r_0)$  describes the coupling of normal modes on two different solvent molecules. It thus describes the exciton-like broadening of gas-phase vibrational lines into liquid state vibrational bands.

The explicit formulas for  $\omega_D^2(r_0)$  and  $\omega_{OD}^2(r_0)$  are

$$\omega_D^2(r_0) = M_{vv}^{-1/2} \left[ \frac{\partial^2 W[vr_0]}{\partial v_1 \partial v_1^T} \right]_{v=v_0} M_{vv}^{-1/2}, \quad (4.44a)$$

$$\omega_{OD}^2(r_0) = M_{vv}^{-1/2} \left[ \frac{\partial^2 W[vr_0]}{\partial v_1 \partial v_2^T} \right]_{v=v_0} M_{vv}^{-1/2}. \quad (4.44b)$$

## N. Vibrational spectral density of the liquid

We next discuss the spectral density associated with the high frequency motion of the solvent. We begin by noting

that since the dynamical matrix is symmetric it may be diagonalized by an orthogonal matrix to yield a diagonal matrix  $\omega_D^2(r_0) = U^T(r_0) \omega^2(r_0) U(r_0)$  whose elements are the  $rN_s$  normal mode frequencies associated with the  $V$  motion of the solvent. Explicitly  $\omega_D^2(r_0)$  is given by

$$\omega_D^2(r_0) = \begin{pmatrix} \omega_1^2(r_0) & & & \\ & \omega_2^2(r_0) & & \\ & & \ddots & \\ & & & \omega_{rN_s}^2(r_0) \end{pmatrix}. \quad (4.45)$$

In the low density limit the  $rN_s$  normal mode frequencies become the  $r$  isolated solvent molecule vibrational frequencies. Each of these isolated molecule frequencies is  $N_s$ -fold degenerate. The degeneracy is split by solvent molecule interactions in the liquid. This splitting produces  $r$  vibrational bands which may or may not be overlapping.

The spectral density describing these vibrational bands is defined in terms of the normal mode frequencies  $\omega_1(r_0), \omega_2(r_0), \dots, \omega_{rN_s}(r_0)$  by

$$\rho(\omega; r_0) = \sum_{k=1}^{rN_s} \delta[\omega - \omega_k(r_0)]. \quad (4.46)$$

## O. Molecular expression for the vibrational frequency matrix

The vibrational frequency matrix may be calculated from the structure of the liquid within the rigid solvent model. (Here and below the subscript  $v_0r_0$  indicates that all quantities and averages are to be evaluated for this model.) A straightforward calculation<sup>17</sup> yields the following molecular expression for  $\omega^2(r_0)$ :

$$\omega^2(r_0) = -M^{-1/2} \cdot \left[ \left\langle \frac{\partial F_v^T}{\partial v} \right\rangle_{v_0r_0} + \beta \langle F_v F_v^T \rangle_{v_0r_0} \right] \cdot M^{-1/2}. \quad (4.47)$$

## P. Relationship between the true and rigid solvent model partition functions

Given the harmonic approximation to  $W[vr_0]$  [Eq. (4.40)] one may develop a rigorous relationship between the true solvent partition function  $Z[r_0]$  and the partition function of the rigid solvent model  $Z[v_0r_0]$ . This relationship follows from Eqs. (4.24), (4.26), and (4.40). It is

$$Z[r_0] = z(r_0) Z[v_0r_0], \quad (4.48)$$

where  $z(r_0)$ , the correction due to vibrational fluctuations, is

$$z(r_0) = [2\pi k_B T]^{rN_s} [\det \omega^2(r_0)]^{-1/2}. \quad (4.49)$$

The correction  $z(r_0)$  may be reexpressed in terms of the vibrational spectral density. This follows because  $\det \omega^2(r_0)$  may be expressed as

$$\det \omega^2(r_0) = \exp \left[ \int_0^\infty \ln \omega^2 \rho(\omega; r_0) d\omega \right].$$

Comparing the above two equations yields

$$z(r_0) = [2\pi k_B T]^{rN_s} \exp \left[ - \int_0^\infty \ln \omega \rho(\omega; r_0) d\omega \right]. \quad (4.50)$$

### Q. Vibrational phase space pdf in the harmonic approximation

Within the harmonic approximation to  $W[vr_0]$ , the rigid solvent partition function can be cancelled from the vibrational phase space pdf to yield

$$f_{CA}[p_v v; r_0] = [z(r_0)]^{-1} \exp \left[ -\beta \left( \frac{1}{2} p_{v\lambda}^T M_{vv}^{-1} p_{v\lambda} + \frac{1}{2} y^T \omega^2(r_0) y \right) \right]. \quad (4.51)$$

Equation (4.51) follows from Eqs. (4.24), (4.25), (4.40), and (4.48).

### R. High frequency limit of $f_{CA}[S; r_0]$

We next develop a simple approximate form for  $f_{CA}[S; r_0]$  which is valid in the high frequency limit.

We begin by relating the exact phase space pdf  $f_{CA}[p_w w; v; r_0]$  for the TR fluctuations to the rigid solvent model pdf  $f_{CA}[p_w w; v_0; r_0]$  for these fluctuations. A brief calculation based on Eqs. (4.17), (4.18), and (4.47) yields

$$f_{CA}[p_w w; v; r_0] = f_{CA}[p_w w; v_0; r_0] \times \{1 + \beta y^T M^{-1/2} F_v + \frac{1}{2} \beta y^T [\omega^2(r_0) - \Omega^2(r_0)] y\}, \quad (4.52)$$

where

$$\Omega^2(r_0) = -M^{-1/2} \cdot \left[ \frac{\partial F_v^T}{\partial v} + \beta F_v F_v^T \right]_{v=v_0} \cdot M^{-1/2}. \quad (4.53)$$

Note that  $\Omega^2(r_0)$  is the instantaneous vibrational frequency matrix of the solvent. This vibrational frequency matrix includes the effects of microscopic solvent TR fluctuations on the vibrational motions of the solvent molecules. If one averages these fluctuations over the rigid solvent canonical ensemble distribution function then comparison of Eqs. (4.47) and (4.53) shows that the mean field vibrational frequency is recovered. That is,

$$\omega^2(r_0) = \langle \Omega^2(r_0) \rangle_{v_0 r_0}. \quad (4.54)$$

Equation (4.52) shows that the deviation of  $f_{CA}[p_w w; v; r_0]$  from the rigid solvent result is due to fluctuations of the generalized force  $F_v$  from its most probable value  $\langle F_v \rangle_{v_0 r_0} = 0$  and from fluctuations of the frequency matrix from its most probable value  $\omega^2(r_0)$ . A careful analysis shows that the effects of these fluctuations on the TR phase space distribution function is negligible in the high vibrational frequency limit. Thus in this limit one may approximate

$$f_{CA}[p_w w; v; r_0] = f_{CA}[p_w w; v_0; r_0]. \quad (4.55)$$

Comparison of Eqs. (4.21) and (4.55) shows that the following approximate form of  $f_{CA}[S; r_0]$  holds in the high frequency limit:

$$f_{CA}[S; r_0] = f_{CA}[p_v v; r_0] f_{CA}[p_w w; v_0; r_0], \quad \text{high frequency limit.} \quad (4.56)$$

### S. Notational conventions for the pure solvent

We next introduce a notational convention for the pure solvent analogous to our notation for the solvent in the presence of the fixed solute.

Consider a quantity  $A[r_0]$  which describes the solvent in the presence of the solute fixed at configuration point  $r_0$ . The corresponding pure solvent property will be denoted by  $A$ . Thus, for example, the pure solvent quantities which correspond to  $K[S; r_0]$  and  $K[p_w w; v; r_0]$  will be denoted by  $K[S]$  and  $K[p_w w; v]$ . These latter quantities are respectively the full Hamiltonian of the pure solvent and the pure solvent Hamiltonian given that the vibrational coordinates are fixed at  $v$ . As a second example, the dynamical matrix of the solvent in the presence of the fixed solute is  $\omega^2(r_0)$  given by Eq. (4.42). The corresponding dynamical matrix of the pure solvent  $\omega^2$  is given by Eq. (2.5).

We will introduce an analogous notation for canonical ensemble averages in the pure solvent. Corresponding to Eqs. (4.31) one has

$$\langle A \rangle_{p_v v} = \int f_{CA}[p_w w; v] A[S] dp_w dw. \quad (4.57)$$

Also we will denote  $\langle A \rangle_{p_v v}$  by  $\langle A \rangle_v$  if  $A[S]$  is independent of  $p_v$ .

### T. Replacement of $f_{CA}[p_v v; r_0]$ by $f_{CA}[p_v v]$

The vibrational phase space pdf  $f_{CA}[p_v v; r_0]$  for the solution may be replaced by the corresponding pure solvent quantity  $f_{CA}[p_v v]$  if derivatives of  $f_{CA}[p_v v; r_0]$  with respect to  $r_0$  are not required. That is,

$$f_{CA}[p_v v; r_0] \doteq f_{CA}[p_v v], \quad (4.58)$$

where the symbol  $\doteq$  indicates equality subject to the condition on derivatives. An immediate consequence of Eq. (4.58) is that the solution and pure solvent vibrational potentials of mean force are also related by

$$W[vr_0] \doteq W[v]. \quad (4.59)$$

From Eq. (4.59) it follows that the mean vibrational forces and the equilibrium values of the vibrational coordinates  $v_0$  are identical in the solution and the pure solvent.

We next present a brief justification for Eqs. (4.58) and (4.59). An amplification of the argument is given in the Appendix.

The justification is evident from the definition [Eq. (4.22)] of  $f_{CA}[p_v v; r_0]$  as a mean field quantity. The phase space pdf  $f_{CA}[S; r_0]$  differs from  $f_{CA}[S]$  only for regions of  $w$  space for which the solute-solvent potential  $K_{vv}[vwr_0]$  is nonnegligible. If we denote the molecular scale volume within which the solute and a solvent molecule interact by  $v_{\text{MOL}}$ , then the fraction of  $w$  space for which  $f_{CA}[S; r_0]$  and  $f_{CA}[S]$  differ is of order  $[v_{\text{MOL}}/V]^{N_s}$ .

Thus  $f_{CA}[p_v v; r_0]$  and  $f_{CA}[p_v v]$  differ only negligibly and the difference can be ignored unless derivatives with respect to  $r_0$  are required. (Such derivatives are needed to construct  $\langle F_v \rangle_{v_0 r_0}$ .)

Given Eqs. (4.58) and (4.59), the notational conventions of Sec. III S, and the other results derived in this section, the results quoted in Sec. II follow immediately.

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## APPENDIX

In this Appendix we provide a more detailed justification of Eq. (4.58). The pure solvent vibrational pdf may be written using the notation of Sec. IV R as [cf. Eq. (4.25)]

$$f_{CA} [p_v v] = Z^{-1} \exp \left[ -\beta \left( \sum_{\lambda=1}^{N_s} \frac{1}{2} \right. \right. \\ \left. \left. \times p_{v_\lambda}^T M_{vv}^{-1} p_{v_\lambda} + W(v) \right) \right], \quad (\text{A1})$$

where  $Z$  is the pure solvent partition function. The vibrational potential of mean force  $W[v]$  is related to the pure solvent partition function with the vibrations fixed,  $Z[v]$ , via [cf. Eq. (4.24)]

$$Z[v] = \exp[-\beta W(v)] \quad (\text{A2a})$$

or

$$W[v] = -\beta^{-1} \ln Z[v]. \quad (\text{A2b})$$

Now since  $K[p_w w; v r_0] = K[p_w w; v] + K_{vU}[v w r_0]$  one has that

$$\exp[-\beta K(p_w w; v r_0)] \\ = \exp[-\beta K(p_w w; v)] [1 + F_{vU}[v w r_0]], \quad (\text{A3})$$

where

$$F_{vU}[v w r_0] = \exp[-\beta K_{vU}[v w r_0]] - 1. \quad (\text{A4})$$

Integration of the above relationship over the TR phase space volume element  $dp_w dw$  yields the relationship

$$Z[v r_0] = Z[v] [1 + \langle F_{vU} \rangle_v]. \quad (\text{A5})$$

A straightforward analysis of  $\langle F_{vU} \rangle_v$  shows that it is of the form

$$\langle F_{vU} \rangle_v = F[v r_0] [v_{\text{MOL}}/V]^{N_s}, \quad (\text{A6})$$

where  $F[v r_0]$  is a function of order unity. Comparison of Eqs. (A2b), (A5), and (A6) yields the following relationship between the vibrational potentials of mean force of the solution and the pure solvent:

$$W[v r_0] = W[v] - \beta^{-1} F[v r_0] [v_{\text{MOL}}/V]^{N_s}. \quad (\text{A7})$$

Equation (A7) shows that if derivatives with respect to  $r_0$  are not required then  $W[v r_0]$  and  $W[v]$  differ only negligibly. Thus Eqs. (4.59) and hence (4.58) are justified.

<sup>1</sup>S. A. Adelman, *Adv. Chem. Phys.* **53**, 61 (1983). Also see references to earlier work cited in this article.

<sup>2</sup>For application of the MTGLE theory to molecular iodine photolysis see C. L. Brooks III, M. W. Balk, and S. A. Adelman, *J. Chem. Phys.* **79**, 784 (1983); M. W. Balk, C. L. Brooks III, and S. A. Adelman, *ibid.* **79**, 804 (1983).

<sup>3</sup>For application of the MTGLE theory to single ion dynamics see H. L. Nguyen and S. A. Adelman, *J. Chem. Phys.* (to be published).

<sup>4</sup>For application of the MTGLE theory to superionic conduction see M. Olson and S. A. Adelman, *Phys. Rev.* (to be published).

<sup>5</sup>For application of the MTGLE theory to butane isomerization see R. Stote and S. A. Adelman (unpublished calculations).

<sup>6</sup>The relevant solute frequencies and associated generalized coordinates depend on the process of interest. For example, for vibrational energy relaxation in liquids the relevant frequency is the vibrational frequency of the relaxing normal mode and the associated generalized coordinate is the normal mode coordinate. For activated barrier crossing in liquids, the relevant frequency is the barrier crossing frequency and the associated generalized coordinate is the reaction coordinate.

<sup>7</sup>For a formulation of the MTGLE theory in generalized coordinates which is valid for monatomic solvents see S. A. Adelman, *J. Chem. Phys.* (in press).

<sup>8</sup>See, for example, 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).

<sup>9</sup>D. J. Nesbitt and J. T. Hynes, *J. Chem. Phys.* **77**, 2130 (1982).

<sup>10</sup>For an illustration of the effects of vibrational bands on solvent fluctuation spectra see Fig. 9 of Ref. 8.

<sup>11</sup>For a specification of this notation see Ref. 25 of Ref. 7.

<sup>12</sup>For a complete description of the theory of canonical transformations see, for example, H. Goldstein, *Classical Mechanics* (Addison-Wesley, Reading, MA, 1980).

<sup>13</sup>Equation (4.2) may readily be derived from the results presented in Chap. 1 of Ref. 12.

<sup>14</sup>The neglect of vibrational-rotational Coriolis coupling is a familiar approximation in molecular spectroscopy. For a discussion, see E. B. Wilson, J. C. Decius, and P. C. Cross, *Molecular Vibrations, The Theory of Infrared and Raman Spectra* (Dover, New York, 1965).

<sup>15</sup>Equation (4.21) may be derived by following the method used to derive Eq. (C6) of Ref. 7.

<sup>16</sup>Equations (4.33) and (4.44) may be derived by following the method used to derive Eq. (C10) of Ref. 7.

<sup>17</sup>To prove Eq. (4.47), one expands the Boltzmann factor  $\exp[-\beta K(p_w w; v r_0)]$  to quadratic order about its rigid solvent value and then integrates over  $p_w w$ . Using the result  $\langle F_v \rangle_{v, r_0} = 0$  yields the following expansion of  $Z[v r_0]$ ,

$$Z[v r_0] = Z[v_0 r_0] \left[ 1 + \frac{1}{2} \beta y^T M^{-1/2} \cdot \left( \left\langle \frac{\partial F_v}{\partial v} \right\rangle_{v, r_0} \right. \right. \\ \left. \left. + \beta \langle F_v F_v^T \rangle_{v, r_0} \right) \cdot M^{-1/2} y \right].$$

Comparing the above expression with  $Z[v r_0] = Z[v_0 r_0] \exp[-\beta \frac{1}{2} y^T \omega^2(r_0) y] = Z[v_0 r_0] [1 - \frac{1}{2} \beta y^T \omega^2(r_0) y]$  yields Eq. (4.47).