

# The statistical mechanics of the electro-acoustic effects of liquids

T. Yamaguchi,<sup>a)</sup> T. Matsuoka, and S. Koda

*Department of Molecular Design and Engineering, Graduate School of Engineering, Nagoya University, Chikusa, Nagoya, Aichi 464-8603, Japan*

(Received 5 March 2003; accepted 28 May 2003)

The ultrasonic vibration potential (UVP) and the electrokinetic sonic amplitude (ESA) are described in terms of equilibrium time-correlation functions using the linear response theory. The reciprocal relationship between UVP and ESA is shown based on the formulation. By introducing the generalized Langevin theory and taking the hydrodynamic limit, it is discussed how the effective volume of ions in the UVP measurement is related to their partial molar thermodynamic quantities. The effective volume is proven exactly equal to the isothermal partial molar volume in the isothermal formulation. The effect of the adiabaticity of sound wave is also investigated. © 2003 American Institute of Physics. [DOI: 10.1063/1.1592797]

## I. INTRODUCTION

The alternating electric potential is induced when the ultrasonic wave passes through the electrolyte solution. This phenomenon is called “ultrasonic vibrational potential” (UVP), and first predicted theoretically by Debye in 1933.<sup>1</sup> The existence of UVP is later proven experimentally by Yeager *et al.* in 1949.<sup>2</sup> Since the effect of the excluded volume of ions is included in UVP, it has been utilized as the unique method that can divide the apparent partial molar volume of electrolytes into the contributions of individual ions without *extrathermodynamic* assumptions.<sup>3–8</sup>

The reciprocal phenomenon can also be observed. The ultrasonic wave is generated by the application of the alternating electric field, which is called “electrokinetic sonic amplitude” (ESA). The equipment to measure the ESA was patented by Oja *et al.*,<sup>9</sup> and it is now commercially available. The reciprocal relationship exists between the UVP and ESA signals as an example of the Onsager’s reciprocal relationship. It is proven theoretically first by O’Brien *et al.* for colloidal dispersions in terms of fluid mechanics,<sup>10,11</sup> and later shown experimentally for various systems including simple ions, polyelectrolytes, and colloids.<sup>12</sup> In this work, we use the name of “electro-acoustic effect” for the coupling effect between the sound wave and the electric potential generally, including UVP and ESA.

In spite of the great use of the electro-acoustic effect of liquids and solutions, we consider its microscopic basis is quite weak. In the formulation used by Zana *et al.*, the ionic vibrational potential was treated in terms of the equation-of-motion of individual ions, and the relationship between the ionic vibrational potential and the ionic partial molar volume has been given only in intuitive ways.<sup>1,3,13–16</sup> For instance, some included the buoyancy term into the equation-of-motion, and the excluded volume effective to the buoyancy was related to the partial molar volume. Some considered the force proportional to the pressure gradient, in which the proportionality coefficient was taken to be the partial molar vol-

ume. Others considered that the mass of ions are *effectively* increased because solvated solvent molecules move together with ions. In all the ideas, however, the meanings of the buoyancy, the pressure gradient, or the solvation number were not clarified at the molecular level, and the effective volume in these ideas was not guaranteed equivalent to the *thermodynamic* partial molar volume.<sup>16</sup>

In addition, the apparent *isothermal* partial molar volume of electrolytes is used as the sum of the volume of ions in the analysis of UVP, whereas the *adiabatic* partial molar volume is effective to the ultrasonic relaxation. Although the difference between the isothermal and adiabatic partial molar volumes may not be important in aqueous solution due to the small thermal expansion of water, the UVP method has also been used to determine the partial molar volume of individual ions in organic solvents.<sup>4–7</sup>

In this work, we first describe both UVP and ESA in terms of the equilibrium time-correlation functions using the linear response theory. Since our formulation is quite general, we believe our present formulation will give a theoretical foundation of how the slow dynamics of complex systems such as concentrated electrolyte solutions, polyelectrolyte ones, or electrolyte gels appears in their electro-acoustic properties. The reciprocal relationship between them is proven for general systems including simple electrolytes and polyelectrolytes. Then, the UVP signal is related to the site–site dynamic structure factor. By introducing the generalized Langevin equation for the site–site dynamic structure factor and taking the hydrodynamic limit, we show that the effective volume of ions in UVP is equivalent to the partial molecular volume given by the Kirkwood–Buff theory in the isothermal case. The expression derived by Debye<sup>1</sup> and used by Zana and Yeager<sup>3</sup> is also reproduced for simple ionic solutions. We consider our present result gives a microscopic validation to the experimental determination of the partial molar volume of individual ions by UVP measurement. We further include the energy density as the slow variable in the generalized Langevin equation, and its effect on the effective volume in UVP will be discussed.

<sup>a)</sup>Electronic mail: tyama@nuce.nagoya-u.ac.jp

## II. STATISTICAL MECHANICAL FORMULATION OF UVP AND ESA

### A. Ultrasonic vibrational potential

The response function of UVP in the time-domain, denoted as  $\Phi_{\text{UVP}}(k, t)$ , is expressed in terms of the relationship between the electrostatic potential,  $[\langle \phi(k, t) \rangle_{\text{ne}} / V]$ , and the center-of-mass velocity field,  $[\langle j_{m,z}(k, t) \rangle_{\text{ne}} / \rho_m V]$ , as

$$\left[ \frac{1}{V} \langle \phi(k, t) \rangle_{\text{ne}} \right] = \int_{-\infty}^t dt' \Phi_{\text{UVP}}(k, t-t') \times \left[ \frac{1}{\rho_m V} \langle j_{m,z}(k, t') \rangle_{\text{ne}} \right], \quad (1)$$

where ne stands for the statistical average under the applied sound field whose wave number is  $k$ . The direction of the sound wave is taken parallel to  $z$  axis. The total volume of the system and the mass density are denoted as  $V$  and  $\rho_m$ , respectively.  $\phi(k, t)$  and  $\mathbf{j}_m(k, t)$  represent the electrostatic potential and the mass current, respectively.

In order to apply the linear response theory, one should express the applied field as the perturbative Hamiltonian, which is not a trivial problem in the case of ultrasonic wave. In this work, we use the expression of the perturbation as

$$-\sigma_{zz}(k) f_0 e^{-i\omega t}, \quad (2)$$

where  $\sigma(k)$  and  $\omega$  mean the wave-number-dependent stress tensor and the angular frequency of the applied sound, respectively, and  $f_0$  is the proportionality coefficient. In actual experiments, the piezoelectric transducer changes the volume of the liquid near its surface according to the applied alternating voltage. Since the pressure is the physical quantity conjugate to the volume, the change of the volume can be interpreted as the external force proportional to the pressure, which rationalizes our definition of the perturbation.

Based on Eq. (2), the nonequilibrium averages of the electrostatic potential and mass current are obtained by the linear response theory<sup>17</sup> as follows:

$$\langle \phi(k, t) \rangle_{\text{ne}} = -\frac{f_0 e^{-i\omega t}}{\epsilon_0 k_B T k^4} \int_0^\infty dt' \langle \dot{\rho}_m^*(k) \dot{\rho}_e(k, t') \rangle e^{i\omega t'}, \quad (3)$$

$$\langle j_{m,z}(k, t) \rangle_{\text{ne}} = \frac{f_0 e^{-i\omega t}}{i k_B T k^3} \int_0^\infty dt' \langle \dot{\rho}_m^*(k) \dot{\rho}_m(k, t') \rangle e^{i\omega t'}, \quad (4)$$

where  $\epsilon_0$ ,  $k_B$ ,  $T$  denote the dielectric constant of the vacuum, the Boltzmann constant, and the absolute temperature, respectively, and  $\rho_m(k, t)$  and  $\rho_e(k, t)$  means the mass and charge-density fields, respectively. The dots represent the derivation with respect to the time. In the derivation of the above-mentioned equations, we used the relationships as

$$\sigma_{zz}(k, t) = \frac{1}{-ik} \dot{j}_{m,z}(k, t) = -\frac{1}{k^2} \dot{\rho}_m(k, t), \quad (5)$$

$$\phi(k) = \frac{1}{\epsilon_0 k^2} \rho_e(k), \quad (6)$$

which are called continuity equations and the Poisson one, respectively.

Substituting Eqs. (3) and (4) into Eq. (1), the UVP response function in the frequency domain is given by

$$\begin{aligned} \tilde{\Phi}_{\text{UVP}}(k, \omega) &\equiv \int_0^\infty dt \Phi_{\text{UVP}}(k, t) e^{i\omega t} \\ &= -\frac{i \rho_m \int_0^\infty dt \langle \dot{\rho}_m^*(k) \dot{\rho}_e(k, t) \rangle e^{i\omega t}}{\epsilon_0 k \int_0^\infty dt \langle \dot{\rho}_m^*(k) \dot{\rho}_m(k, t) \rangle e^{i\omega t}}. \end{aligned} \quad (7)$$

### B. Electrokinetic sonic amplitude

According to the phenomenological treatment described in Appendix A, the ESA response function in the time domain, denoted as  $\Phi_{\text{ESA}}(k, t)$ , is given by

$$\begin{aligned} \frac{1}{V} \langle j_{m,z}(k, t) \rangle_{\text{ne}} &= k^2 \int_{-\infty}^t dt' \frac{\langle j_{m,z}^*(k) j_{m,z}(k, t-t') \rangle}{\langle j_{m,z}^*(k) j_{m,z}(k) \rangle} \\ &\times \left[ \int_{-\infty}^{t'} dt'' \Phi_{\text{ESA}}(k, t'-t'') \left\langle \frac{\phi(k, t'')}{V} \right\rangle_{\text{ne}} \right]. \end{aligned} \quad (8)$$

In this section, ne stands for the average under the applied electric field. The above-given definition means that the electric field is converted into the external force on the acoustic field by the ESA mechanism, and the generated sound wave travels to the detector.

The perturbative Hamiltonian of ESA is denoted as

$$\phi_{\text{ex}} \rho_e(k) e^{-i\omega t}, \quad (9)$$

where  $\phi_{\text{ex}}$  stands for the external electric potential. Due to the presence of the external field, the total electrostatic potential is given by

$$\phi(k, t) = \frac{1}{\epsilon_0 k^2} \rho_e(k, t) + V \phi_{\text{ex}} e^{-i\omega t}. \quad (10)$$

According to the linear response theory, the mass current density is given by

$$\langle j_{m,z}(k, t) \rangle_{\text{ne}} = -\frac{\phi_{\text{ex}} e^{-i\omega t}}{i k_B T k} \int_0^\infty dt' \langle \rho_e^*(k) \dot{\rho}_m(k, t') \rangle e^{i\omega t'}. \quad (11)$$

In a similar way, the electrostatic potential is derived as

$$\frac{1}{V} \langle \phi(k, t) \rangle_{\text{ne}} = \frac{\epsilon_0 \phi_{\text{ex}} e^{-i\omega t}}{\tilde{\epsilon}^*(k, \omega)}, \quad (12)$$

where  $\tilde{\epsilon}(k, \omega)$  is the frequency- and wave-number-dependent dielectric function given by<sup>18</sup>

$$\frac{1}{\epsilon_0 k_B T k^2 V} \langle |\rho_e(k)|^2 \rangle = 1 - \frac{\epsilon_0}{\tilde{\epsilon}(k, \omega=0)}, \quad (13)$$

$$\begin{aligned} &-\frac{i\omega}{\epsilon_0 k_B T k^2 V} \int_0^\infty dt \langle \rho_e^*(k) \rho_e(k, t) \rangle e^{i\omega t} \\ &= \frac{\epsilon_0}{\tilde{\epsilon}^*(k, \omega)} - \frac{\epsilon_0}{\tilde{\epsilon}(k, \omega=0)}. \end{aligned} \quad (14)$$

The self-correlation functions of mass-current density are easily calculated as

$$\langle |j_{m,z}(k)|^2 \rangle = \rho_m k_B T V, \tag{15}$$

$$\langle j_{m,z}^*(k) j_{m,z}(k, t) \rangle = \frac{1}{k^2} \langle \dot{\rho}_m^*(k) \dot{\rho}_m(k, t) \rangle. \tag{16}$$

The ESA response function in the frequency domain is given by substituting Eqs. (11), (12), (15), and (16) into Eq. (8) as

$$\begin{aligned} \tilde{\Phi}_{\text{ESA}}(k, \omega) &\equiv \int_0^\infty dt \Phi_{\text{ESA}}(k, t) e^{i\omega t} \\ &= - \frac{\rho_m \tilde{\epsilon}^*(k, \omega) \int_0^\infty dt \langle \rho_e^*(k) \dot{\rho}_m(k, t) \rangle e^{i\omega t}}{i k \epsilon_0 \int_0^\infty dt \langle \dot{\rho}_m^*(k) \dot{\rho}_m(k, t) \rangle e^{i\omega t}}. \end{aligned} \tag{17}$$

**C. Reciprocal relationship between UVP and ESA**

The numerator and denominator of Eq. (17) are, respectively, transformed as follows:

$$\begin{aligned} \int_0^\infty dt \langle \rho_e^*(k) \dot{\rho}_m(k, t) \rangle e^{i\omega t} &= - \frac{1}{i\omega} \langle \ddot{\rho}_m^*(k) \rho_e(k) \rangle \\ &\quad - \frac{1}{i\omega} \int_0^\infty dt \langle \dot{\rho}_m^*(k) \dot{\rho}_e(k, t) \rangle e^{i\omega t} \\ &\simeq - \frac{1}{i\omega} \int_0^\infty dt \langle \dot{\rho}_m^*(k) \dot{\rho}_e(k, t) \rangle e^{i\omega t}, \end{aligned} \tag{18}$$

$$\begin{aligned} \int_0^\infty dt \langle \dot{\rho}_m^*(k) \dot{\rho}_m(k, t) \rangle e^{i\omega t} &= \frac{1}{\omega^2} \langle |\dot{\rho}_m^*(k)|^2 \rangle \\ &\quad + \frac{1}{\omega^2} \int_0^\infty dt \langle \ddot{\rho}_m^*(k) \ddot{\rho}_m(k, t) \rangle e^{i\omega t} \\ &\simeq \frac{1}{\omega^2} \int_0^\infty dt \langle \ddot{\rho}_m^*(k) \ddot{\rho}_m(k, t) \rangle e^{i\omega t}. \end{aligned} \tag{19}$$

Here, we used the equation as

$$\langle \rho_e^*(k) \rho_m(k, t) \rangle = \langle \rho_m^*(k) \rho_e(k, t) \rangle, \tag{20}$$

which is based on the invariance of the system under the space and time inversion. The first terms of Eqs. (18) and (19) can be neglected because the second terms have the acoustic resonance structures whereas the first ones do not, as will be shown in the next section.

According to Eqs. (7) and (17)–(19), we can find the relationship between the UVP and ESA response functions as

$$\tilde{\Phi}_{\text{ESA}}(k, \omega) \simeq -i\omega \tilde{\epsilon}^*(k, \omega) \tilde{\Phi}_{\text{UVP}}(k, \omega). \tag{21}$$

The complex specific electric conductivity,  $\tilde{\sigma}_e(k, \omega)$ , is related to the dielectric function as

$$\tilde{\epsilon}(k, \omega) = \frac{\tilde{\sigma}(k, \omega)}{i\omega}. \tag{22}$$

Using Eq. (22), Eq. (21) is transformed as

$$\tilde{\Phi}_{\text{ESA}}(k, \omega) \simeq \tilde{\sigma}^*(k, \omega) \tilde{\Phi}_{\text{UVP}}(k, \omega). \tag{23}$$

This equation corresponds to the reciprocal relationship between UVP and ESA proven by O’Brien in a hydrodynamic way.<sup>10,11</sup> However, it should be noted that our derivation is quite general, not restricted to colloidal dispersions.

**D. UVP response function in terms of site–site dynamic structure factor**

Hereafter we consider the isotropic liquid that consists of interaction sites (atoms)  $\alpha, \gamma, \dots$ . At present, it does not matter whether the sites are bound to each other by chemical bonds. The mass, charge, and number density of the site  $\alpha$  are denoted as  $m_\alpha, z_\alpha,$  and  $\rho_\alpha$ , respectively. The density field and the current density of site  $\alpha$ , denoted as  $\rho_\alpha(\mathbf{k}, t)$  and  $\mathbf{j}_\alpha(\mathbf{k}, t)$ , respectively, are defined as

$$\rho_\alpha(\mathbf{k}, t) = \sum_{i \in \alpha} e^{i\mathbf{k} \cdot \mathbf{r}_i(t)}, \tag{24}$$

$$\mathbf{j}_\alpha(\mathbf{k}, t) = \sum_{i \in \alpha} \mathbf{v}_i(t) e^{i\mathbf{k} \cdot \mathbf{r}_i(t)}. \tag{25}$$

Here,  $i$  is the index for individual sites, and  $\mathbf{r}_i(t)$  and  $\mathbf{v}_i(t)$  stand for the position and the velocity, respectively, of site  $i$  at time  $t$ .

In this work, we define the site–site dynamic structure factor,  $F^{\alpha\gamma}(k, t)$ , as follows:

$$F^{\alpha\gamma}(k, t) \equiv \frac{1}{V} \langle \rho_\alpha^*(k) \rho_\gamma(k, t) \rangle. \tag{26}$$

Be careful to the difference in the normalization factor among the literatures, which leads to the different appearance of equations hereafter. The static structure factor,  $\chi^{\alpha\gamma}(k)$ , and static current-correlation function,  $J^{\alpha\gamma}(k)$ , are defined as

$$\chi^{\alpha\gamma}(k) \equiv \frac{1}{V} \langle \rho_\alpha^*(k) \rho_\gamma(k) \rangle = F^{\alpha\gamma}(k, t=0), \tag{27}$$

$$J^{\alpha\gamma}(k) \equiv \frac{1}{V} \langle j_{\alpha,z}^*(k) j_{\gamma,z}(k) \rangle = - \frac{1}{k^2} \ddot{F}^{\alpha\gamma}(k, t=0). \tag{28}$$

The mass and charge densities are given by the site density as

$$\rho_m(k, t) = \sum_\alpha m_\alpha \rho_\alpha(k, t), \tag{29}$$

$$\rho_e(k, t) = \sum_\alpha z_\alpha \rho_\alpha(k, t). \tag{30}$$

Here, we neglected the electronic polarization of atoms. Using Eqs. (29) and (30), the UVP response function, Eq. (7) is transformed as

$$\tilde{\Phi}_{\text{UVP}}(k, \omega) = - \frac{i \rho_m \int_0^\infty dt' \sum_{\alpha\gamma} m_{\alpha z_\gamma} (d^3/dt'^3) F^{\alpha\gamma}(k, t') e^{i\omega t'}}{\epsilon_0 k \int_0^\infty dt' \sum_{\alpha\gamma} m_{\alpha m_\gamma} (d^4/dt'^4) F^{\alpha\gamma}(k, t') e^{i\omega t'}} = \frac{\rho_m \sum_{\alpha\gamma} m_{\alpha z_\gamma} [k^2 J^{\alpha\gamma}(k) + \omega^2 \chi^{\alpha\gamma}(k) + i\omega^3 \tilde{F}^{\alpha\gamma}(k, \omega)]}{\epsilon_0 \omega k \sum_{\alpha\gamma} m_{\alpha m_\gamma} [k^2 J^{\alpha\gamma}(k) + \omega^2 \chi^{\alpha\gamma}(k) + i\omega^3 \tilde{F}^{\alpha\gamma}(k, \omega)]}, \quad (31)$$

where  $\tilde{\mathbf{F}}(k, \omega)$  represents the site–site dynamic structure factor in the frequency domain defined as

$$\tilde{\mathbf{F}}(k, \omega) = \int_0^\infty dt \mathbf{F}(k, t) e^{i\omega t}. \quad (32)$$

### III. ISOTHERMAL FORMULATION OF UVP

#### A. Site–site generalized Langevin equation

Considering that only  $\{\rho_\alpha(k, t)\}$  and  $\{\mathbf{j}_\alpha(k, t)\}$  are the slow variables, we can derive the site–site generalized Langevin equation in a standard method as<sup>19</sup>

$$\begin{aligned} \ddot{\mathbf{F}}(k, t) + k^2 \mathbf{J}(k) \cdot \chi^{-1}(k) \cdot \mathbf{F}(k, t) + \int_0^t dt' \mathbf{K}(k, t-t') \cdot \dot{\mathbf{F}}(k, t') \\ = 0. \end{aligned} \quad (33)$$

Equation (33) is the matrix equation, whose indices are interaction sites. Here,  $\mathbf{K}(k, t)$  is the memory function matrix defined as

$$[\mathbf{K}(k, t) \mathbf{J}(k)]_{\alpha\gamma} \equiv \frac{1}{V} \langle \mathcal{Q} j_\alpha(k) e^{i\mathcal{Q}\mathcal{L}\mathcal{Q}t} \mathcal{Q} j_\gamma(k) \rangle, \quad (34)$$

where  $\mathcal{L}$  is the Liouvillian,  $\mathcal{Q}$  equals  $1 - \mathcal{P}$ , and  $\mathcal{P}$  stands for the projection operator to the space of slow variables. In the frequency domain, Eq. (33) can be solved formally as

$$\tilde{\mathbf{F}}(k, \omega) = \mathbf{Y}^{-1}(k, \omega) [\mathbf{J}^{-1}(k) \tilde{\mathbf{K}}(k, \omega) - i\omega \mathbf{J}^{-1}(k)] \chi(k), \quad (35)$$

where  $\tilde{\mathbf{K}}(k, \omega)$  and  $\mathbf{Y}(k, \omega)$  are given by

$$\tilde{\mathbf{K}}(k, \omega) = \int_0^\infty dt \mathbf{K}(k, t) e^{i\omega t}, \quad (36)$$

$$\mathbf{Y}(k, \omega) = k^2 \chi^{-1}(k) - i\omega \mathbf{J}^{-1}(k) \tilde{\mathbf{K}}(k, \omega) - \omega^2 \mathbf{J}^{-1}(k). \quad (37)$$

By substituting Eq. (35) into Eq. (31),  $\tilde{\Phi}_{\text{UVP}}(k, \omega)$  is written as

$$\tilde{\Phi}_{\text{UVP}}(k, \omega) = \frac{\rho_m \sum_{\alpha\gamma} m_{\alpha z_\gamma} [\mathbf{J}(k) + \omega^2 \mathbf{Y}^{-1}(k, \omega)]_{\alpha\gamma}}{\epsilon_0 k \omega \sum_{\alpha\gamma} m_{\alpha m_\gamma} [\mathbf{J}(k) + \omega^2 \mathbf{Y}^{-1}(k, \omega)]_{\alpha\gamma}}. \quad (38)$$

#### B. Hydrodynamic limit of various correlation functions

In actual measurements of the electro-acoustic effect of liquids, the characteristic frequency of the sound wave is about 1 MHz, which corresponds to the wavelength around 1 mm in aqueous solutions. Since the wavelength of the sound is far larger than the size of molecules, we can take the long-wavelength ( $k \rightarrow 0$ ) limit of the response function. Because the UVP response function is given by the site–site dynamic structure factor in Eq. (38), we have to know how the site–site dynamic structure factor behaves in the  $k \rightarrow 0$

limit. It should be noted here that the relationship  $\omega = ck$  must be maintained in the limiting procedure, where  $c$  refers to the sound velocity.

Since we are interested in the correlation functions in the hydrodynamic limit, one may consider that the thermodynamically constructed hydrodynamic theory is sufficient, without resorting to the statistical mechanics. In the case of atomic liquids, in fact, phenomenological consideration formally leads to the equation similar to Eq. (33) if we choose the atomic densities and currents as the set of slow variables. The memory kernel becomes Markovian and  $\chi^{-1}(k)$  is replaced by the second derivative of the free energy. However, the second derivative of the free energy,  $\partial^2 A / \partial \rho_\alpha \partial \rho_\gamma$ , is divergent if  $\alpha$  or  $\gamma$  is the charged particle. It means that the number densities of charged particles cannot be varied independently due to the charge neutrality, which is just the reason why we cannot measure the individual ionic partial molar volume directly in thermodynamic ways. Even if the Coulombic parts are treated separately to remove the divergence, we have no means to relate the residual chemical potential (which is *assumed* to be convergent within the phenomenological treatment!) with the microscopic solution structure. In the solution chemistry, the individual ionic partial molar volume is of no use if it is not related to the solvation structure of the ion. It is therefore necessary to construct the theory valid for finite wave numbers and to take the hydrodynamic limit properly. Moreover, since our formulation is not limited to atomic liquids, we can treat the effect of the internal modes of flexible molecules consistently.

In the following part of this paper, it is assumed that both  $k^2 \chi^{-1}(k)$  and  $\mathbf{J}^{-1}(k)$  are finite in the long-wavelength limit. In the case of liquid composed of rigid molecules, it means that the number of sites in a molecule is no more than two, three, and four for linear, planar, and nonplanar molecules, respectively. Although we consider that this condition is not necessary, we introduced it here for simplicity.

The dynamic structure factor,  $\mathbf{F}(k, t)$ , is the matrix on the vector space,  $V$ , defined as

$$V = \{(a_\alpha, a_\gamma, \dots) | a_\alpha \in \mathbf{R}\}, \quad (39)$$

where  $\mathbf{R}$  stands for the real number. Here, we decompose  $V$  into the direct sum of three subspaces, denoted as  $V_1$ ,  $V_2$ , and  $V_3$  defined as follows: First,  $V_1$  is the space on which  $\lim_{k \rightarrow 0} k^2 \chi^{-1}(k)$  is finite. Second,  $V_3$  consists of the vector proportional to  $(\rho_\alpha, \rho_\gamma, \dots)$ . Finally,  $V_2$  is defined as the space orthogonal to both  $V_1$  and  $V_3$ . Physically speaking,  $V_1$  stands for the reorientation and the charge fluctuation, since the charge density is fixed due to the charge neutrality and sites within a molecule are bound by chemical bonds in the

hydrodynamic limit.  $V_3$  represents the acoustic wave, because it is the translational motion of the liquid as a whole. The remaining  $V_2$  corresponds to the mutual diffusion. Their meanings in actual systems will appear in Secs. III E–III G.

Here we define the projection operators to  $V_1$  and  $V_3$ , denoted as  $\mathcal{P}_1$  and  $\mathcal{P}_3$ , respectively. In particular,  $\mathcal{P}_3$  is given by

$$\mathcal{P}_3^{\alpha\gamma} = \frac{\rho_\alpha \rho_\gamma}{\sum_\alpha \rho_\alpha^2}. \quad (40)$$

In definition,  $\chi(k)$  and  $\chi^{-1}(k)$  behave in the  $k \rightarrow 0$  limit as

$$\chi(k) = \begin{matrix} & V_1 & V_2 \oplus V_3 \\ \begin{matrix} V_1 \\ V_2 \oplus V_3 \end{matrix} & \begin{pmatrix} \mathcal{O}(k^2) & \mathcal{O}(k^2) \\ \mathcal{O}(k^2) & \mathcal{O}(1) \end{pmatrix} \end{matrix}, \quad (41)$$

$$\chi^{-1}(k) = \begin{matrix} & V_1 & V_2 \oplus V_3 \\ \begin{matrix} V_1 \\ V_2 \oplus V_3 \end{matrix} & \begin{pmatrix} \mathcal{O}(k^{-2}) & \mathcal{O}(1) \\ \mathcal{O}(1) & \mathcal{O}(1) \end{pmatrix} \end{matrix}. \quad (42)$$

In particular, their 11 components are related to each other as

---


$$\mathbf{Y}(k, \omega) \rightarrow \begin{matrix} & V_1 & V_2 & V_3 \\ \begin{matrix} V_1 \\ V_2 \\ V_3 \end{matrix} & \begin{pmatrix} [k^2 \chi^{-1}(k)]_{11} & -i\omega [\mathbf{J}^{-1}(k) \tilde{\mathbf{K}}(k, \omega)]_{12} & [k^2 \chi^{-1}(k) - \omega^2 \mathbf{J}^{-1}(k)]_{13} \\ -i\omega [\mathbf{J}^{-1}(k) \tilde{\mathbf{K}}(k, \omega)]_{21} & -i\omega [\mathbf{J}^{-1}(k) \tilde{\mathbf{K}}(k, \omega)]_{22} & [k^2 \chi^{-1}(k) - \omega^2 \mathbf{J}^{-1}(k)]_{23} \\ [k^2 \chi^{-1}(k) - \omega^2 \mathbf{J}^{-1}(k)]_{31} & [k^2 \chi^{-1}(k) - \omega^2 \mathbf{J}^{-1}(k)]_{32} & [k^2 \chi^{-1}(k) - \omega^2 \mathbf{J}^{-1}(k)]_{33} \end{pmatrix} \end{matrix}$$

$$\sim \begin{matrix} & V_1 & V_2 & V_3 \\ \begin{matrix} V_1 \\ V_2 \\ V_3 \end{matrix} & \begin{pmatrix} \mathcal{O}(1) & \mathcal{O}(k) & \mathcal{O}(k^2) \\ \mathcal{O}(k) & \mathcal{O}(k) & \mathcal{O}(k^2) \\ \mathcal{O}(k^2) & \mathcal{O}(k^2) & \mathcal{O}(k^2) \end{pmatrix} \end{matrix}. \quad (46)$$

Therefore, the inverse matrix,  $\mathbf{Y}^{-1}(k, \omega)$  behaves as

$$\mathbf{Y}^{-1}(k, \omega) \rightarrow \begin{matrix} & V_1 & V_2 & V_3 \\ \begin{matrix} V_1 \\ V_2 \\ V_3 \end{matrix} & \begin{pmatrix} \mathcal{O}(1) & \mathcal{O}(1) & \mathcal{O}(1) \\ \mathcal{O}(1) & \mathcal{O}(k^{-1}) & \mathcal{O}(k^{-1}) \\ \mathcal{O}(1) & \mathcal{O}(k^{-1}) & \mathcal{O}(k^{-2}) \end{pmatrix} \end{matrix}. \quad (47)$$

Their 33 components are related to each other as

$$[\lim_{k \rightarrow 0} k^{-2} [\mathbf{Y}(k, \omega)]_{33}]^{-1} = \lim_{k \rightarrow 0} k^2 [\mathbf{Y}^{-1}(k, \omega)]_{33}. \quad (48)$$

### C. Acoustic resonance condition

According to its derivation, the denominator of the right-hand side of Eq. (38) is proportional to the response of the center-of-mass velocity to the applied acoustic field. Its hydrodynamic limit is given by

$$\sum_{\alpha\gamma} m_\alpha m_\gamma [\mathbf{J}(k) + \omega^2 \mathbf{Y}^{-1}(k, \omega)]_{\alpha\gamma} \rightarrow \rho_m k_B T + \frac{\omega^2 (\sum_\alpha m_\alpha \rho_\alpha)^2}{\sum_{\alpha\gamma} \rho_\alpha [k^2 \chi^{-1}(k) - \omega^2 \mathbf{J}^{-1}(k)]_{\alpha\gamma} \rho_\gamma}, \quad (49)$$

$$[\lim_{k \rightarrow 0} k^{-2} [\chi(k)]_{11}]^{-1} = \lim_{k \rightarrow 0} k^2 [\chi^{-1}(k)]_{11}, \quad (43)$$

where the suffix 11 means the submatrix on  $V_1 \times V_1$ .

In assumption, both  $\mathbf{J}(k)$  and  $\mathbf{J}^{-1}(k)$  are regular in the  $k \rightarrow 0$  limit. In particular, as is shown in Appendix B, the following relationship holds as

$$\sum_\alpha \rho_\alpha \mathbf{J}^{-1, \alpha\gamma}(k=0) = \frac{m_\gamma}{k_B T}. \quad (44)$$

The memory function behaves in the hydrodynamic limit as<sup>20</sup>

$$[\mathbf{J}^{-1}(k) \tilde{\mathbf{K}}(k, t)] \rightarrow \begin{matrix} & V_1 \oplus V_2 & V_3 \\ \begin{matrix} V_1 \oplus V_2 \\ V_3 \end{matrix} & \begin{pmatrix} \mathcal{O}(1) & \mathcal{O}(k^2) \\ \mathcal{O}(k^2) & \mathcal{O}(k^2) \end{pmatrix} \end{matrix}, \quad (45)$$

which is due to the momentum conservation, as shown in Appendix C.

From the above-given equations, the hydrodynamic limit of the matrix,  $\mathbf{Y}(k, \omega)$ , is given by

---

where Eqs. (44) and (48) are used in the derivation. The hydrodynamic limit of the static structure factor is related to the isothermal compressibility,  $\chi_T$ , as<sup>21</sup>

$$\lim_{k \rightarrow 0} \sum_{\alpha\gamma} \rho_\alpha \chi^{-1, \alpha\gamma}(k) \rho_\gamma = \frac{1}{k_B T \chi_T}. \quad (50)$$

Therefore, the right-hand side of Eq. (49) is further transformed as

$$\sum_{\alpha\gamma} m_\alpha m_\gamma [\mathbf{J}(k) + \omega^2 \mathbf{Y}^{-1}(k, \omega)]_{\alpha\gamma} \rightarrow \frac{\rho_m k_B T c_T^2}{c_T^2 - c^2}, \quad (51)$$

where  $c_T$  is the isothermal sound velocity given by

$$c_T^2 = \frac{1}{\rho_m \chi_T}. \quad (52)$$

Equation (51) diverges when  $c = \omega/k$  is equal to  $c_T$ , which is the resonance condition of the sound wave. The sound velocity is equal to  $c_T$  in the present treatment, which is different from the adiabatic sound velocity derived in the hydro-

dynamic way. It is because the energy conservation is not considered at present,<sup>22</sup> and we will improve our treatment in the next section.

### D. Effective mass for UVP

The numerator of Eq. (38) stands for the coupling between the acoustic and charge-density modes. Here,  $(z_\alpha, z_\gamma, \dots)$  belongs to  $V_1$  due to the charge-neutral condition. On the other hand,  $(m_\alpha, m_\gamma, \dots)$  contains components of  $V_1$ ,  $V_2$ , and  $V_3$  in general. In the lowest order of  $k$ , the submatrices of  $\mathbf{Y}^{-1}(k, \omega)$  are given by

$$[\mathbf{Y}^{-1}(k, \omega)]_{11} \rightarrow [k^{-2}\boldsymbol{\chi}(k)], \quad (53)$$

$$[\mathbf{Y}^{-1}(k, \omega)]_{21} \rightarrow -[\mathbf{Y}^{-1}(k, \omega)]_{22}[\mathbf{Y}(k, \omega)]_{21}[\mathbf{Y}^{-1}(k, \omega)]_{11}, \quad (54)$$

$$[\mathbf{Y}^{-1}(k, \omega)]_{31} \rightarrow -[\mathbf{Y}^{-1}(k, \omega)]_{33}\{[\mathbf{Y}(k, \omega)]_{31}[\mathbf{Y}^{-1}(k, \omega)]_{11} + [\mathbf{Y}(k, \omega)]_{32}[\mathbf{Y}^{-1}(k, \omega)]_{21}\}. \quad (55)$$

Since we consider the condition that  $c = \omega/k$  is close to  $c_T$ , we have to consider only the term containing  $1/(c^2 - c_T^2)$ , that is,  $[\mathbf{Y}^{-1}(k, \omega)]_{33}$ . From Eq. (46), the hydrodynamic limit of  $[\mathbf{Y}^{-1}(k, \omega)]_{31}$  is given by

$$\begin{aligned} [\mathbf{Y}^{-1}(k, \omega)]_{31} \rightarrow & -[[k^2\boldsymbol{\chi}^{-1}(k) - \omega^2\mathbf{J}^{-1}(k)]_{33}]^{-1} \\ & \cdot [k^2\boldsymbol{\chi}^{-1}(k) - \omega^2\mathbf{J}^{-1}(k)]_{3,1\oplus 2} \\ & \cdot [\{\mathbf{J}^{-1}(k)\tilde{\mathbf{K}}(k, \omega)\}^{-1}]_{1\oplus 2,1} \\ & \cdot [[\{\mathbf{J}^{-1}(k)\tilde{\mathbf{K}}(k, \omega)\}^{-1}]_{11}]^{-1}[k^{-2}\boldsymbol{\chi}(k)]_{11} \end{aligned} \quad (56)$$

$$\begin{aligned} \rightarrow & -\frac{k_B T \sum_\alpha \rho_\alpha^2}{\rho_m k^2 (c_T^2 - c^2)} \mathcal{P}_3 [k^2\boldsymbol{\chi}^{-1}(k) - \omega^2\mathbf{J}^{-1}(k)] \\ & \cdot (1 - \mathcal{P}_3) [\mathbf{J}^{-1}\tilde{\mathbf{K}}(k, \omega)]^{-1} \cdot [k^2\boldsymbol{\chi}^{-1}(k)] \\ & \cdot [k^{-2}\tilde{\mathbf{F}}(k, \omega)] \mathcal{P}_1, \end{aligned} \quad (57)$$

where we used the relationships as

$$\lim_{k \rightarrow 0, \omega = ck} [k^{-2}\tilde{\mathbf{F}}(k, \omega)]_{11} = \lim_{k \rightarrow 0, \omega = ck} \{[\mathbf{Y}^{-1}(k, \omega)\mathbf{J}^{-1}(k) \cdot \tilde{\mathbf{K}}(k, \omega)k^{-2}\boldsymbol{\chi}(k)]^{-1}\}_{11}^{-1}, \quad (58)$$

$$[k^2\boldsymbol{\chi}^{-1}(k) - \omega^2\mathbf{J}^{-1}(k)]_{33} = \frac{\rho_m k^2}{k_B T \sum_\alpha \rho_\alpha^2} (c_T^2 - c^2). \quad (59)$$

The isothermal partial molecular volume of the interaction-site,  $v_\alpha$ , is defined by the RISM/KB theory as<sup>21,23</sup>

$$v_\alpha = k_B T \chi_T \sum_\gamma \rho_\gamma \lim_{k \rightarrow 0} \chi^{-1, \gamma\alpha}(k). \quad (60)$$

Using Eqs. (44), (40), and (60), the second factor of Eq. (57) is given by

$$[\mathcal{P}_3 [k^2\boldsymbol{\chi}^{-1}(k) - \omega^2\mathbf{J}^{-1}(k)]]_{\alpha\gamma} \rightarrow -\frac{\rho_\alpha c^2 k^2}{\sum_\mu \rho_\mu^2 k_B T} m_{\text{eff}, \gamma}^{\alpha}, \quad (61)$$

where  $m_{\text{eff}, \gamma}$  is the effective mass of the site  $\gamma$  defined as

$$m_{\text{eff}, \gamma} = m_\gamma - \rho_m v_\gamma. \quad (62)$$

The effective site mass defined here is the same as that phenomenologically introduced in previous literature,<sup>2,3,24,25</sup> which validates the UVP determination of the partial molar volume of individual ions.

Using Eqs. (57) and (61), the numerator of Eq. (38) is described as

$$\begin{aligned} \sum_{\alpha\gamma} m_{\alpha z_\gamma} [\mathbf{Y}^{-1}(k, \omega)]_{\alpha\gamma} \rightarrow & \sum_{\alpha\gamma} m_{\alpha z_\gamma} [\mathcal{P}_3 \mathbf{Y}^{-1}(k, \omega) \mathcal{P}_1]_{\alpha\gamma} \\ \rightarrow & \frac{c^2}{c_T^2 - c^2} \sum_{\alpha\gamma} m_{\text{eff}, \alpha z_\gamma} [(1 - \mathcal{P}_3) \\ & \cdot [\mathbf{J}^{-1}(k)\tilde{\mathbf{K}}(k, \omega)]^{-1} [k^2\boldsymbol{\chi}^{-1}(k)] \\ & \cdot [k^{-2}\tilde{\mathbf{F}}(k, \omega)]]_{\alpha\gamma}. \end{aligned} \quad (63)$$

Substituting Eqs. (51) and (63) into Eq. (38), the hydrodynamic limit of the UVP response function is described as

$$\begin{aligned} \lim_{k \rightarrow 0, \omega = ck} \tilde{\Phi}_{\text{UVP}}(k, \omega) \\ = & \frac{c}{\epsilon_0 k_B T} \sum_{\alpha\gamma} m_{\text{eff}, \alpha z_\gamma} \lim_{k \rightarrow 0, \omega = ck} [(1 - \mathcal{P}_3) \\ & \cdot [\mathbf{J}^{-1}(k)\tilde{\mathbf{K}}(k, \omega)]^{-1} \cdot [k^2\boldsymbol{\chi}^{-1}(k)] [k^{-2}\tilde{\mathbf{F}}(k, \omega)]]_{\alpha\gamma}. \end{aligned} \quad (64)$$

In Secs. III E–III G we will apply this formula to various systems.

### E. Simple dilute ionic solution

In this section, we reproduce the expression of the UVP response function derived first by Debye.<sup>1</sup> We consider here the simplest system as follows: First, the liquid consists of monoatomic molecules. One species denoted as “S” is the solvent, and others are solute ions. The latter are sufficiently dilute, that is,

$$\rho_S \gg \rho_\alpha \quad (\alpha \neq S). \quad (65)$$

Under these conditions,  $V_1$  is proportional to  $(z_\alpha, z_\gamma, \dots)$ , and  $V_3$  represents the motion of solvent.

From the Coulombic asymptotics of the direct correlation function,<sup>22</sup> the hydrodynamic limit of the static structure factor is given by

$$\lim_{k \rightarrow 0} k^2 \chi^{-1, \alpha\gamma}(k) = \frac{z_\alpha z_\gamma}{\epsilon_0 k_B T}. \quad (66)$$

Since the random forces on different ions are not correlated in the dilute solution, the memory function is reduced to the simple form as

$$[\mathbf{J}^{-1}(k)\tilde{\mathbf{K}}(k, \omega)]_{\alpha\gamma} \rightarrow \frac{\delta_{\alpha\gamma}}{\rho_\alpha D_\alpha} \quad (\alpha, \gamma \neq S), \quad (67)$$

where  $D_\alpha$  stands for the self-diffusion coefficient of ion  $\alpha$ , and we used here the Einstein relationship for the diffusion coefficient.

The substitution of Eqs. (66) and (67) yields

$$\begin{aligned} \lim_{k \rightarrow 0, \omega = ck} \tilde{\Phi}_{\text{UVP}}(k, \omega) &= \frac{c}{\epsilon_0 k_B T} \sum_{\alpha \in S} m_{\text{eff}, \alpha} \rho_{\alpha} D_{\alpha} \lim_{k, \omega \rightarrow 0} \frac{1}{\epsilon_0 k_B T k^2} \\ &\quad \times \sum_{\mu\nu} z_{\mu} z_{\nu} \tilde{F}^{\mu\nu}(k, \omega). \end{aligned} \quad (68)$$

From Eqs. (14) and (22) the hydrodynamic static specific conductivity, denoted as  $\sigma$ , is given by<sup>22</sup>

$$\frac{\epsilon_0}{\sigma} = \lim_{k, \omega \rightarrow 0} \frac{1}{\epsilon_0 k_B T k^2} \sum_{\mu\nu} \tilde{F}^{\mu\nu}(k, \omega). \quad (69)$$

On the other hand,  $\sigma$  is related to the self-diffusion coefficients of ions in the dilution limit by the Nernst–Einstein relationship as<sup>22</sup>

$$\sigma = \frac{\sum_{\alpha} \rho_{\alpha} z_{\alpha}^2 D_{\alpha}}{k_B T}. \quad (70)$$

Using Eqs. (68)–(70), the UVP response function is given by

$$\lim_{k \rightarrow 0, \omega = ck} \tilde{\Phi}_{\text{UVP}}(k, \omega) = c \frac{\sum_{\alpha} m_{\text{eff}, \alpha} \rho_{\alpha} z_{\alpha} D_{\alpha}}{\sum_{\alpha} \rho_{\alpha} z_{\alpha}^2 D_{\alpha}}, \quad (71)$$

which is just the expression derived by Debye<sup>1</sup> and used by Zana and Yeager.<sup>3</sup>

### F. Neat binary molten salt

Contrary to the dilute solution treated in Sec. III E, we consider the extremely concentrated case, that is, the liquids composed of ions. For simplicity, we suppose that all the ions are monoatomic, and the number of ionic species is two, i.e., the anion (+) and the cation (–).

In this case,  $V_1$  is proportional to  $(z_+, z_-)$ , and  $V_2$  is absent. Due to the absence of  $V_2$ ,  $[\mathbf{Y}^{-1}(k, \omega)]_{31}$  is described from Eq. (57) as

$$\begin{aligned} [\mathbf{Y}^{-1}(k, \omega)]_{31} &= -[[k^2 \chi(k) - \omega^2 \mathbf{J}^{-1}(k)]_{33}]^{-1} \\ &\quad \cdot [k^2 \chi(k) - \omega^2 \mathbf{J}^{-1}(k)]_{31} [k^{-2} \chi(k)]_{11}. \end{aligned} \quad (72)$$

The UVP response function is thus given by

$$\begin{aligned} \lim_{k \rightarrow 0, \omega = ck} \tilde{\Phi}_{\text{UVP}}(k, \omega) &= \frac{c}{\epsilon_0 k_B T} \sum_{\alpha\gamma} m_{\text{eff}, \alpha} z_{\alpha} z_{\gamma} \lim_{k, \omega \rightarrow 0} [k^{-2} \mathcal{P}_1 \chi(k)]_{\alpha\gamma} \\ &= c \frac{\sum_{\alpha} m_{\text{eff}, \alpha} z_{\alpha}}{\sum_{\alpha} z_{\alpha}^2}, \end{aligned} \quad (73)$$

where we used the expression of  $\mathcal{P}_1$  as

$$\mathcal{P}_1^{\alpha\gamma} = \frac{z_{\alpha} z_{\gamma}}{\sum_{\alpha} z_{\alpha}^2}, \quad (74)$$

and the hydrodynamic limit of the static structure factor as

$$\frac{1}{\epsilon_0 k_B T k^2} \sum_{\alpha\gamma} z_{\alpha} z_{\gamma} \chi^{\alpha\gamma}(k) \rightarrow 1. \quad (75)$$

According to Eq. (73), the UVP measurement can be used in order to divide the partial molar volume of binary molten salts into ionic contributions. It should be noted in particular that no dynamic information is required to analyze the UVP experiment in the zero-frequency limit.

### G. Neat water

In the early days of UVP measurement, it is sometimes observed that the UVP signal of aqueous electrolytes *increased* with decreasing the concentration of salts. Based on these observations, Hunter *et al.* proposed that the neat water can generate the vibrational potential in the absence of salts,<sup>24,25</sup> and Weinmann formulated the UVP intensity of neat polar liquids.<sup>26,27</sup> On the other hand, Zana and Yeager showed later experimentally that the UVP signal of the dilute electrolyte solution can be reduced by improving the structure of the electrode, and they proposed that the piezoelectric effect of electrodes largely affect the observed UVP response of dilute electrolyte solutions.<sup>3</sup> They also showed that the effect of electrodes is small in the concentration range of ordinary measurement (~10–100 mM). However, their experiment does not exclude the *existence* of the UVP in neat water.

Here we consider the three-site model of water, that is, the water molecule is composed of three sites denoted as O, H<sub>1</sub>, and H<sub>2</sub>. In this case, the dimension of  $V_1$  is 2, and its bases are (2, –1, –1) and (0, 1, –1), which represent the reorientational modes.  $V_3$  is proportional to (1, 1, 1) (translation), and  $V_2$  does not exist. Due to the absence of  $V_2$ , the UVP response function is obtained as is done in Sec. III F as

$$\lim_{k \rightarrow 0, \omega = ck} \tilde{\Phi}_{\text{UVP}}(k, \omega) = c \left( 1 - \frac{\epsilon_0}{\epsilon} \right) \frac{\sum_{\alpha} m_{\text{eff}, \alpha} z_{\alpha}}{\sum_{\alpha} z_{\alpha}^2}, \quad (76)$$

where we used the expression of the dielectric constant,  $\epsilon = \tilde{\epsilon}(k=0, \omega=0)$ , given by Eq. (13). Equation (76) indicates that the water can generate the vibrational potential without electrolytes, although we cannot estimate its magnitude because of the lack of information on the isothermal partial molar volume of *individual interaction sites*. In addition, we have to handle the effect of solvent partial charges in the presence of ions in order to resolve its effects on the determination of the ionic partial volumes.

### IV. ADIABATIC TREATMENT OF UVP

In the generalized Langevin theory, we need to consider explicitly all the slow variables in order that the resulting equation has the Langevin character. Since the conservation law guarantees the slow relaxation of conserved quantities, we have to take the densities of all conserved quantities into account.<sup>20</sup> However, the energy density is not considered explicitly in our treatment in Sec. III. As shown in Sec. III C, one of the largest defects is the disagreement of the sound velocity. According to the hydrodynamics, the sound veloc-

ity,  $c$ , is described as  $c = c_S \equiv 1/\sqrt{\rho_m \chi_S}$ , where  $\chi_S$  is the adiabatic compressibility, whereas  $\chi_S$  is replaced by  $\chi_T$  in our treatment.

The ultrasonic relaxation measurement of solution probes the relaxation of the *adiabatic* partial molar volume of solutes. In this analogy, one may infer that the isothermal partial molar volume will be replaced by the adiabatic one in the adiabatic treatment of UVP. Although their difference is small in water because its thermal expansion is small, it is theoretically interesting to investigate the above-mentioned idea, and it is also important quantitatively for nonaqueous solutions.

### A. Generalized Langevin equation under the adiabatic condition

In this section, we consider the site densities,  $\{\rho_\alpha(k, t)\}$ , site-current densities,  $\{\mathbf{j}_\alpha(k, t)\}$ , and the energy density,  $\rho_\epsilon(k, t)$ , as the set of slow variables. We define the energy-current density, denoted as  $\mathbf{j}_\epsilon(k, t)$ , by the continuity equation as

$$\dot{\rho}_\epsilon(\mathbf{k}, t) = i\mathbf{k} \cdot \mathbf{j}_\epsilon(\mathbf{k}, t). \quad (77)$$

We also define here the new variable,  $\rho_q(k)$  as<sup>20</sup>

$$\rho_q(k) = \rho_\epsilon(k) - \frac{1}{V} \sum_{\alpha\gamma} \langle \rho_\epsilon(k) \rho_\gamma^*(k) \rangle \chi^{-1, \alpha\gamma}(k) \rho_\alpha(k), \quad (78)$$

so that  $\rho_q(k)$  is orthogonal to site densities as

$$\langle \rho_q^*(k) \rho_\alpha(k) \rangle = 0. \quad (79)$$

The current density of  $\rho_q(k)$ , denoted as  $\mathbf{j}_q(k)$ , is given by

$$\mathbf{j}_q(k) = \mathbf{j}_\epsilon(k) - \frac{1}{V} \sum_{\alpha\gamma} \langle \rho_\epsilon(k) \rho_\gamma^*(k) \rangle \chi^{-1, \alpha\gamma}(k) \mathbf{j}_\alpha(k). \quad (80)$$

Considering that  $\{\rho_\alpha(k), \mathbf{j}_\alpha(k), \rho_q(k)\}$  is the set of slow variables, by the standard method of the generalized Langevin theory<sup>20</sup> we can derive the following equation-of-motion as

$$\begin{aligned} & \ddot{F}^{\alpha\gamma}(k, t) + k^2 [\mathbf{J}(k) \chi^{-1}(k) \mathbf{F}(k, t)]_{\alpha\gamma} \\ & + \int_0^t d\tau [\mathbf{K}(k, t - \tau) \dot{\mathbf{F}}(k, \tau)]_{\alpha\gamma} - \left[ \frac{1}{V} \langle \dot{\rho}_\gamma^*(k) \rho_q(k) \rangle \right] \\ & \times \left[ \frac{1}{V} \langle |\rho_q(k)|^2 \rangle \right]^{-1} \left[ \frac{1}{V} \langle \rho_\alpha^*(k) \rho_q(k, t) \rangle \right] = 0, \end{aligned} \quad (81)$$

$$\begin{aligned} \frac{1}{V} \langle \rho_\alpha^*(k) \dot{\rho}_q(k, t) \rangle &= \sum_{\gamma\nu} \dot{F}^{\alpha\gamma}(k, t) J^{-1, \gamma\nu}(k) \left[ \frac{1}{V} \langle j_\nu^*(k) j_q(k) \rangle \right] \\ & + \int_0^t d\tau K_{qq}(k, t - \tau) \\ & \times \left[ \frac{1}{V} \langle \rho_q^*(k) \rho_\alpha(k, \tau) \rangle \right]. \end{aligned} \quad (82)$$

The cross-term of the memory function between the energy and mass modes is neglected, since it behaves as  $\mathcal{O}(k^2)$  due to the symmetry of the system under the space and time inversion and the energy conservation law.<sup>20</sup>

The last term of Eq. (82) describes the heat diffusion. Since the heat diffusion is sufficiently slow compared with the acoustic frequency, this term can be neglected to yield

$$\begin{aligned} \frac{1}{V} \langle \rho_\alpha^*(k) \dot{\rho}_q(k, t) \rangle &= \sum_{\gamma\nu} \dot{F}^{\alpha\gamma}(k, t) J^{-1, \gamma\nu}(k) \\ & \times \left[ \frac{1}{V} \langle j_\nu^*(k) j_q(k) \rangle \right]. \end{aligned} \quad (83)$$

Integrating this equation from 0 to  $t$ ,

$$\begin{aligned} \frac{1}{V} \langle \rho_\alpha^*(k) \rho_q(k, t) \rangle &= \sum_{\gamma\nu} \{ F^{\alpha\gamma}(k, t) - \chi^{\alpha\gamma}(k) \} J^{-1, \gamma\nu}(k) \\ & \times \left[ \frac{1}{V} \langle j_\nu^*(k) j_q(k) \rangle \right], \end{aligned} \quad (84)$$

where we used Eq. (79). From Eqs. (81) and (84), the time development of  $F^{\alpha\gamma}(k, t)$  is given by

$$\begin{aligned} & \ddot{F}^{\alpha\gamma}(k, t) + k^2 [\mathbf{J}(k) \chi^{-1}(k) \mathbf{F}(k, t)]_{\alpha\gamma} \\ & + k^2 [\mathbf{J}(k) \mathbf{B}(k) \{ \mathbf{F}(k, t) - \chi(k) \}]_{\alpha\gamma} \\ & + \int_0^t d\tau [\mathbf{K}(k, t - \tau) \dot{\mathbf{F}}(k, \tau)]_{\alpha\gamma} = 0, \end{aligned} \quad (85)$$

where  $\mathbf{B}(k)$  is defined as

$$\begin{aligned} B^{\alpha\gamma}(k) &= \sum_{\nu\nu'} J^{-1, \alpha\nu}(k) \left[ \frac{1}{V} \langle j_\nu^*(k) j_q(k) \rangle \right] \\ & \times \left[ \frac{1}{V} \langle |\rho_q(k)|^2 \rangle \right]^{-1} \left[ \frac{1}{V} \langle j_q^*(k) j_{\nu'}(k) \rangle \right] J^{-1, \nu'\gamma}(k). \end{aligned} \quad (86)$$

The solution of Eq. (85) is formally described as

$$\tilde{\mathbf{F}}(k, \omega) = \frac{1}{i\omega} \mathbf{Y}'^{-1}(k, \omega) [k^2 \chi^{-1}(k) - \mathbf{Y}'(k, \omega)] \chi(k), \quad (87)$$

where  $\mathbf{Y}'(k, \omega)$  is given by

$$\begin{aligned} \mathbf{Y}'(k, \omega) &= k^2 \chi^{-1}(k) + k^2 \mathbf{B}(k) - i\omega \mathbf{J}^{-1}(k) \tilde{\mathbf{K}}(k, \omega) \\ & - \omega^2 \mathbf{J}^{-1}(k). \end{aligned} \quad (88)$$

Using Eqs. (31) and (87), the UVP response function is given by

$$\tilde{\Phi}_{\text{UVP}}(k, \omega) = \frac{\rho_m \sum_{\alpha\gamma} m_{\alpha\gamma} \chi_{\alpha\gamma} [\mathbf{J}(k) + \omega^2 \mathbf{Y}'^{-1}(k, \omega)]_{\alpha\gamma}}{\epsilon_0 k \omega \sum_{\alpha\gamma} m_{\alpha\gamma} m_{\gamma} [\mathbf{J}(k) + \omega^2 \mathbf{Y}'^{-1}(k, \omega)]_{\alpha\gamma}}. \quad (89)$$

Compared with Eq. (38),  $\mathbf{Y}(k, \omega)$  is replaced by  $\mathbf{Y}'(k, \omega)$  in the adiabatic treatment.

### B. Adiabatic sound velocity

In a similar way to Sec. III C, the resonance condition of the sound wave is proven to be the one as follows:

$$\lim_{k \rightarrow 0} \sum_{\alpha\gamma} \rho_\alpha [\chi^{-1}(k) + \mathbf{B}(k) - c^2 \mathbf{J}^{-1}(k)]_{\alpha\gamma} \rho_\gamma = 0. \quad (90)$$

According to Appendix D, the second term on the left-hand side of Eq. (90) is given by

$$\sum_{\alpha\gamma} \rho_\alpha B^{\alpha\gamma}(k) \rho_\gamma \rightarrow -\frac{V}{k_B T} \left( \frac{\partial T}{\partial V} \right)_{S,N} \left( \frac{\partial P}{\partial T} \right)_{V,\rho}, \quad (91)$$

where  $\mathbf{N}$  and  $\boldsymbol{\rho}$  stand for  $\{N_\alpha, \dots\}$  ( $N_\alpha$  means the number of  $\alpha$  site) and  $\{\rho_\alpha, \dots\}$ , respectively.

From Eqs. (44), (50), (90), and (91), the acoustic resonance condition in the adiabatic case is given by

$$c = c_S \equiv \frac{1}{\sqrt{\rho_m \chi_S}}, \quad (92)$$

which agrees with that obtained by the hydrodynamics.

### C. Effective mass for UVP under the adiabatic condition

By the procedure used in Sec. III D, we can derive the hydrodynamic limit of the UVP response function under the adiabatic condition as

$$\begin{aligned} \lim_{k \rightarrow 0, \omega = ck} \Phi_{\text{UVP}}(k, \omega) &= \frac{c}{\epsilon_0 k_B T} \sum_{\alpha\gamma} m'_{\text{eff}, \alpha z \gamma} \lim_{k \rightarrow 0, \omega = ck} [(1 - \mathcal{P}_3) \\ &\cdot [\mathbf{J}^{-1}(k) \tilde{\mathbf{K}}(k, \omega)]^{-1} \cdot [k^2 \chi^{-1}(k)] \\ &\cdot [k^{-2} \tilde{\mathbf{F}}(k, \omega)]]_{\alpha\gamma}, \end{aligned} \quad (93)$$

which is the same as Eq. (64) except for the replacement of  $m_{\text{eff}, \alpha}$  by  $m'_{\text{eff}, \alpha}$  defined by

$$\begin{aligned} m'_{\text{eff}, \alpha} &= m_\alpha - \rho_m v_{U, \alpha} \\ &\equiv m_\alpha - \rho_m \left[ \frac{\chi_S}{\chi T} v_\alpha + \chi_S k_B T \sum_\nu \rho_\nu B^{\nu\alpha}(0) \right]. \end{aligned} \quad (94)$$

The second term of Eq. (94) can be calculated in a similar way to Appendix D as

$$\sum_\nu \rho_\nu B^{\nu\alpha}(0) = \frac{V}{k_B T^2} \left( \frac{\partial T}{\partial V} \right)_{S,N} \left[ X_\gamma - \left( \frac{\partial U}{\partial N_\gamma} \right)_{T, V, N_\nu (\nu \neq \gamma)} \right], \quad (95)$$

where  $X_\gamma$  is defined as

$$X_\gamma = \frac{1}{V} \sum_\alpha \langle j_{\epsilon, z}^*(0) j_{\alpha z}(0) \rangle J^{-1, \alpha\gamma}(0). \quad (96)$$

The effective partial molecular volume for UVP under the adiabatic condition, denoted as  $v_{U, \alpha}$ , is obtained by substituting Eq. (95) into Eq. (94) as

$$v_{U, \alpha} = \left( \frac{\partial \mu_\alpha}{\partial P} \right)_{S,N} + \left( \frac{\partial T}{\partial P} \right)_{S,N} \frac{X_\alpha - \mu_\alpha}{T}. \quad (97)$$

The first term is the adiabatic partial molecular volume as is expected, but there is an additional term that includes  $X_\alpha$ .

### D. Sum rule of $X_\alpha$

Although individual  $X_\alpha$  is not obtained without the specification of  $\mathbf{j}_\epsilon(0)$ , we can show the sum rule of  $X_\alpha$  as

$$\sum_\alpha \rho_\alpha X_\alpha = \frac{H}{V}, \quad (98)$$

where  $H$  stands for enthalpy. The proof of Eq. (98) is given in Appendix E.

From Eq. (98), we can show the relationship as

$$\sum_\alpha N_\alpha v_{U, \alpha} = V. \quad (99)$$

The same relationship holds for the *isothermal* partial molecular volume, but not for the *adiabatic* one. It can therefore be said that the simple replacement of the former by the latter does not lead to the adiabatic expression of UVP. Although we will not show the detailed explanation, the sum rule corresponds to the requirement that the total forces acting on a unit volume is equal to the pressure gradient in the hydrodynamic limit.

Equation (98) means that  $X_\alpha$  gives the division of enthalpy into the contribution of each site. Assuming that  $X_\alpha$  is equal to the partial molecular enthalpy as

$$X_\alpha = \left( \frac{\partial H}{\partial N_\alpha} \right)_{T, P, N_\nu (\nu \neq \alpha)}, \quad (100)$$

by substituting Eq. (100) into Eq. (97), we can show that  $v_{U, \alpha}$  is equal to the *isothermal* partial molecular volume.

### E. $X_\gamma$ by the conventional expression of the energy-current density

In this section, we consider the liquid composed of monoatomic molecules. The expression of the energy current,  $\mathbf{j}_\epsilon(k=0)$ , conventionally used in the molecular dynamics simulation of heat conductivity is written as<sup>28</sup>

$$\begin{aligned} j_{\epsilon, z}(0) &= \sum_i \left[ \frac{1}{2} m_i \dot{r}_{i,z} |\dot{\mathbf{r}}_i|^2 + \frac{1}{2} \sum_j \phi_{ij}(r_{ij}) \dot{r}_{i,z} \right. \\ &\quad \left. - \frac{1}{2} \sum_j \frac{\partial \phi_{ij}(r_{ij})}{\partial r_{ij}} \frac{r_{ij,z}}{r_{ij}} \mathbf{r}_{ij} \cdot \dot{\mathbf{r}}_i \right], \end{aligned} \quad (101)$$

where  $\phi_{ij}(r_{ij})$  stands for the interaction between atoms  $i$  and  $j$ .

From Eqs. (96) and (101),  $X_\alpha$  is given by

$$\begin{aligned} X_\alpha &= \frac{5}{2} k_B T + \frac{1}{2} \sum_\gamma \rho_\gamma \int_0^\infty dr 4\pi r^2 \phi_{\alpha\gamma}(r) g_{\alpha\gamma}(r) \\ &\quad - \frac{1}{6} \sum_\gamma \rho_\gamma \int_0^\infty dr 4\pi r^3 \frac{\partial \phi_{\alpha\gamma}(r)}{\partial r} g_{\alpha\gamma}(r). \end{aligned} \quad (102)$$

The sum rule, Eq. (98), can be shown as

$$\begin{aligned} \sum_{\alpha} \rho_{\alpha} X_{\alpha} = & \left[ \sum_{\alpha} \frac{3}{2} \rho_{\alpha} k_B T + \frac{1}{2} \sum_{\alpha\gamma} \rho_{\alpha} \rho_{\gamma} \right. \\ & \times \int_0^{\infty} dr 4\pi r^2 \phi_{\alpha\gamma}(r) g_{\alpha\gamma}(r) \left. + \left[ \sum_{\alpha} \rho_{\alpha} k_B T \right. \right. \\ & \left. \left. - \frac{1}{6} \sum_{\alpha\gamma} \rho_{\alpha} \rho_{\gamma} \int_0^{\infty} dr 4\pi r^3 \frac{\partial \phi_{\alpha\gamma}(r)}{\partial r} g_{\alpha\gamma}(r) \right] \right], \end{aligned} \quad (103)$$

where the first and the second brackets correspond to the internal energy density and the virial pressure, respectively.<sup>22</sup>

However,  $X_{\alpha}$  obtained in Eq. (102) does not correspond to the partial molecular enthalpy. The partial molar enthalpy involves the derivative of enthalpy, the right-hand side of Eq. (103), with respect to  $\rho_{\alpha}$ . So long as  $g_{\alpha\gamma}(r)$  is the function of  $\rho_{\alpha}$ , the derivative does not reduce to the right-hand side of Eq. (102). If we regard  $\alpha$  as a solute, for example, the solvent-solvent contribution to enthalpy is not included in Eq. (102). In other words, the modification of the solvent structure around the solute affects the partial molecular enthalpy of the solute, but not  $X_{\gamma}$  in Eq. (102). We consider that it is because the division of the energy into molecules employed in Eq. (101) is not consistent with thermodynamics.

## V. CONCLUSION

In this work, we derived microscopic expressions of the electro-acoustic effects, UVP and ESA, of liquids using the linear response theory. The reciprocal relationship between UVP and ESA was also proven in a quite general way. We are now intending to extend our theory to concentrated electrolyte solutions and polyelectrolyte ones using our present general expression, so as to clarify how the correlated motion of ions appears in the frequency dependence of the electro-acoustic properties.

The site-site generalized Langevin theory was applied to the time-correlation functions that appear in the expression of the UVP response function. In the isothermal formulation, we showed that the volume effective to the electro-acoustic effects coincides with the isothermal partial molecular volume in the hydrodynamic limit. In addition, the expression used by Zana and Yeager<sup>3</sup> was reproduced in the simplest case.

We also extended our theory to include the adiabatic character of sound wave. It was shown that the replacement of the isothermal partial molecular volume to the adiabatic one does not lead to the adiabatic expression of the UVP response function. Rather, the effective volume remained the isothermal one under a particular condition given by Eq. (100). However, with the conventional expression of the energy-current density, the effective volume did not agree with partial thermodynamic quantities, which was tentatively attributed to the inconsistency between the energy division employed in Eq. (101) and thermodynamics.

## APPENDIX A: PHENOMENOLOGICAL TREATMENT OF ESA

In the absence of the electro-acoustic effect, the conserved variables  $\rho_m(k, t)$ ,  $j_{m,z}(k, t)$ ,  $\rho_{\epsilon}(k, t)$  follow the closed linear equation of motion in the hydrodynamic limit as

$$\frac{d}{dt} \begin{pmatrix} \rho_m(k, t) \\ j_{m,z}(k, t) \\ \rho_{\epsilon}(k, t) \end{pmatrix} = \mathbf{U}(k) \begin{pmatrix} \rho_m(k, t) \\ j_{m,z}(k, t) \\ \rho_{\epsilon}(k, t) \end{pmatrix}, \quad (A1)$$

where  $\rho_{\epsilon}(k, t)$  stands for the energy-density field. The matrix  $\mathbf{U}(k)$  governs the time development of these variables, which we will not specify here.<sup>22</sup>

By multiplying  $(\rho_m^*(k), j_{m,z}^*(k), \rho_{\epsilon}^*(k))$  from the right, Eq. (A1) is formally solved as

$$\mathbf{C}(k, t) = \exp(\mathbf{U}(k)t) \cdot \mathbf{C}(k, 0), \quad (A2)$$

where  $\mathbf{C}(k, t)$  is the correlation-function matrix given by

$$\mathbf{C}(k, t) \equiv \begin{pmatrix} \langle \rho_m^*(k) \rho_m(k, t) \rangle & \langle j_{m,z}^*(k) \rho_m(k, t) \rangle & \langle \rho_{\epsilon}^*(k) \rho_m(k, t) \rangle \\ \langle \rho_m^*(k) j_{m,z}(k, t) \rangle & \langle j_{m,z}^*(k) j_{m,z}(k, t) \rangle & \langle \rho_{\epsilon}^*(k) j_{m,z}(k, t) \rangle \\ \langle \rho_m^*(k) \rho_{\epsilon}(k, t) \rangle & \langle j_{m,z}^*(k) \rho_{\epsilon}(k, t) \rangle & \langle \rho_{\epsilon}^*(k) \rho_{\epsilon}(k, t) \rangle \end{pmatrix}. \quad (A3)$$

From Eq. (A2), the time-propagator,  $\exp(\mathbf{U}(k)t)$ , is formally described as

$$\exp(\mathbf{U}(k)t) = \mathbf{C}(k, t) \cdot \mathbf{C}^{-1}(k, 0). \quad (A4)$$

In particular, the 22 component is given by

$$[\exp(\mathbf{U}(k)t)]_{22} = \frac{\langle j_{m,z}^*(k) j_{m,z}(k, t) \rangle}{\langle |j_{m,z}(k)|^2 \rangle}. \quad (A5)$$

Here we used the independence of the momentum and the variables in the coordinate space at  $t=0$ .

In the presence of the electro-acoustic effect, the time development of the acoustic field is given by

$$\frac{d}{dt} \begin{pmatrix} \langle \rho_m(k, t) \rangle_{ne} \\ \langle j_{m,z}(k, t) \rangle_{ne} \\ \langle \rho_{\epsilon}(k, t) \rangle_{ne} \end{pmatrix} = \mathbf{U}(k) \begin{pmatrix} \langle \rho_m(k, t) \rangle_{ne} \\ \langle j_{m,z}(k, t) \rangle_{ne} \\ \langle \rho_{\epsilon}(k, t) \rangle_{ne} \end{pmatrix} + \begin{pmatrix} 0 \\ ikP_{ESA}(k, t) \\ 0 \end{pmatrix}, \quad (A6)$$

where  $\overline{\phantom{x}}$  stands for the statistical average in the presence of the electric field, and  $P_{\text{ESA}}(k,t)$  represents the pressure induced by the ESA mechanism as

$$P_{\text{ESA}}(k,t) = -ik \int_{-\infty}^t dt' \Phi_{\text{ESA}}(k,t-t') \langle \phi(k,t') \rangle_{\text{ne}}. \quad (\text{A7})$$

From Eqs. (A5)–(A7),  $\langle j_{m,z}(k,t) \rangle_{\text{ne}}$  is given by

$$\begin{aligned} \langle j_{m,z}(k,t) \rangle_{\text{ne}} &= \frac{k^2}{\langle |j_{m,z}(k)|^2 \rangle} \int_{-\infty}^t dt' \langle j_{m,z}^*(k) j_{m,z}(k,t-t') \rangle \\ &\times \int_{-\infty}^{t'} dt'' \Phi_{\text{ESA}}(k,t'-t'') \langle \phi(k,t'') \rangle_{\text{ne}}. \quad (\text{A8}) \end{aligned}$$

### APPENDIX B: SITE-CURRENT CORRELATION IN THE HYDRODYNAMIC LIMIT

We prove Eq. (44) in this Appendix. First, we assume that the sites  $\alpha, \alpha', \dots$  belong to the molecule  $A, \gamma, \gamma', \dots$  belong to  $\Gamma$ , and so on. According to the definition of  $\mathbf{J}(k)$ , Eq. (28), we can derive the following equation as

$$\begin{aligned} \sum_{\alpha} m_{\alpha} \mathbf{J}^{\alpha\gamma}(k=0) &= \sum_A \sum_{j \in \gamma} \frac{1}{V} \left\langle \left( \sum_{\alpha \in A} \sum_{i \in \alpha} m_{\alpha} v_{i,z} \right) v_{j,z} \right\rangle \\ &= \sum_A \sum_{i \in A} \sum_{j \in \gamma} \frac{1}{V} \langle M_A v_{i,z}^C v_{j,z} \rangle, \quad (\text{B1}) \end{aligned}$$

where  $M_A$  stands for the total mass of molecule  $A$ , and  $\mathbf{v}_i^C$  means the center-of-mass velocity of molecule  $i$ . Since the center-of-mass velocity and the angular velocity are independent, the innerpart of the angular brackets on the right-hand side is  $k_B T$  if  $\gamma$  belongs to  $A$ , and otherwise zero. Therefore, Eq. (B1) can be transformed as

$$\sum_{\alpha} m_{\alpha} \mathbf{J}^{\alpha\gamma}(k=0) = \frac{N_{\gamma} k_B T}{V} = \rho_{\gamma} k_B T, \quad (\text{B2})$$

which easily leads to Eq. (44).

### APPENDIX C: MEMORY FUNCTION IN THE HYDRODYNAMIC LIMIT

Equation (45) can be shown by proving the following relation:

$$\forall \gamma, \lim_{k \rightarrow 0} \sum_{\alpha} \rho_{\alpha} [\mathbf{J}^{-1}(k) \tilde{\mathbf{K}}(k,t)]_{\alpha\gamma} \rightarrow 0. \quad (\text{C1})$$

According to the definition of the memory function, Eq. (34), the left-hand side of Eq. (C1) is transformed as

$$\begin{aligned} \sum_{\alpha, \mu, \nu} \rho_{\alpha} \mathbf{J}^{-1, \alpha\mu}(k=0) [\tilde{\mathbf{K}}(k=0,t) \mathbf{J}(k=0)]_{\mu\nu} \mathbf{J}^{-1, \nu\gamma}(k=0) \\ = \frac{1}{k_B T V} \sum_{\nu} \left\langle \mathcal{Q} \frac{d}{dt} \left( \sum_{\mu} \sum_{i \in \mu} m_{\mu} v_{i,z} \right) \right. \\ \left. \times e^{i\mathcal{Q}\mathcal{L}\mathcal{Q}t} \mathcal{Q} j_{\nu,z}^{\dagger}(k=0) \right\rangle \mathbf{J}^{-1, \nu\gamma}(k=0), \quad (\text{C2}) \end{aligned}$$

where we used the relationship (44). The right-hand side of Eq. (C2) is zero, since (...) is the total momentum.

### APPENDIX D: PROOF OF EQ. (91)

According to the definition of  $\mathbf{B}(k)$ , the hydrodynamic limit of the left-hand side of Eq. (91) is described as

$$\begin{aligned} \sum_{\alpha\gamma} \rho_{\alpha} B^{\alpha\gamma}(0) \rho_{\gamma} &= \frac{1}{(k_B T)^2 V} \sum_{\alpha\gamma} m_{\alpha} m_{\gamma} \langle j_{\alpha,z}^*(0) j_{\gamma,z}(0) \rangle \\ &\times \langle |\rho_q(0)|^2 \rangle^{-1} \langle j_{q,z}^*(0) j_{\gamma,z}(0) \rangle. \quad (\text{D1}) \end{aligned}$$

We used here Eq. (44).

Here we introduce the chemical potential of *interaction sites*, denoted as  $\{\mu_{\alpha}\}$ , as was done by Imai *et al.*<sup>21</sup> The hydrodynamic limits of the correlation functions are then given by

$$\frac{1}{V} \langle \rho_{\epsilon}(k) \rangle \rightarrow \frac{k_B T^2}{V} \left( \frac{\partial U}{\partial T} \right)_{v, \mu T}, \quad (\text{D2})$$

$$\frac{1}{V} \langle \rho_{\epsilon}(k) \rho_{\gamma}^*(k) \rangle \rightarrow k_B T^2 \left( \frac{\partial \rho_{\gamma}}{\partial T} \right)_{v, \mu T}, \quad (\text{D3})$$

$$\chi^{\alpha\gamma}(k) \rightarrow -k_B T \left( \frac{\partial \rho_{\alpha}}{\partial \mu_{\gamma}} \right)_{T, v, \mu_{\nu} (v \neq \gamma)}, \quad (\text{D4})$$

$$\begin{aligned} \frac{1}{V} \sum_{\alpha} m_{\alpha} \langle j_{\alpha,z}^*(k) j_{\epsilon,z}(k) \rangle \\ = \frac{1}{V} \langle j_{m,z}^*(k) j_{\epsilon}(k) \rangle \\ = \frac{1}{V} \langle \sigma_{zz}^*(k) \rho_{\epsilon}(k) \rangle \rightarrow k_B T^2 \left( \frac{\partial P}{\partial T} \right)_{v, \mu T}. \quad (\text{D5}) \end{aligned}$$

From Eqs. (78)–(80) and (D2)–(D5), the first and the second factors of Eq. (D1) are, respectively, transformed as

$$\frac{1}{V} \sum_{\alpha} \langle j_{\alpha,z}^*(0) j_{q,z}(0) \rangle = k_B T^2 \left( \frac{\partial P}{\partial T} \right)_{v, \rho}, \quad (\text{D6})$$

$$\frac{1}{V} \langle |\rho_q(0)|^2 \rangle = \frac{k_B T^2}{V} \left( \frac{\partial U}{\partial T} \right)_{v, N}. \quad (\text{D7})$$

Substituting Eqs. (D6) and (D7) into Eq. (D1), we can obtain Eq. (91).

### APPENDIX E: PROOF OF THE SUM RULE OF $X_{\alpha}$

From Eqs. (98), (44) and (D5), the left-hand side of Eq. (98) is given by

$$\begin{aligned} \sum_{\alpha} \rho_{\alpha} X_{\alpha} &= \frac{1}{k_B T V} \langle j_{\epsilon,z}^*(0) j_{m,z}(0) \rangle \\ &= T \left( \frac{\partial P}{\partial T} \right)_{v, \mu} + \sum_{\gamma} \left( \frac{\partial P}{\partial \mu_{\gamma}} \right)_{T, v, \mu_{\nu} (v \neq \gamma)} \mu_{\gamma}. \quad (\text{E1}) \end{aligned}$$

Using Gibbs–Duhem relationship as

$$\left(\frac{\partial P}{\partial T}\right)_{V,\mu} = \frac{S}{V}, \quad (\text{E2})$$

$$\left(\frac{\partial P}{\partial \mu_\gamma}\right)_{T,V,\mu_\nu(\nu \neq \gamma)} = \frac{N_\gamma}{V}, \quad (\text{E3})$$

Eq. (E1) is transformed as

$$\sum_\alpha \rho_\alpha X_\alpha = \frac{TS}{V} + \sum_\alpha \frac{N_\alpha \mu_\alpha}{V} = \frac{H}{V}. \quad (\text{E4})$$

<sup>1</sup>P. Debye, J. Chem. Phys. **1**, 13 (1933).

<sup>2</sup>E. Yeager, J. Bugosh, F. Hovorka, and J. McCarthy, J. Chem. Phys. **17**, 411 (1949).

<sup>3</sup>R. Zana and E. Yeager, J. Phys. Chem. **71**, 521 (1967).

<sup>4</sup>R. Zana, G. A. Lage, and C. M. Criss, J. Solution Chem. **9**, 667 (1980).

<sup>5</sup>M. Dollet, J. Juillard, and R. Zana, J. Solution Chem. **9**, 827 (1980).

<sup>6</sup>R. Zana, J. Chem. Soc., Faraday Trans. 1 **78**, 1323 (1982).

<sup>7</sup>R. Zana, J. E. Desnoyers, G. Perron, R. L. Kay, and K. Lee, J. Phys. Chem. **86**, 3996 (1982).

<sup>8</sup>N. Takenaka and K. Arakawa, Bull. Chem. Soc. Jpn. **62**, 2880 (1989).

<sup>9</sup>T. Oja, G. L. Patersen, and D. W. Cannon, US. Patent No. 4497208 (1985).

<sup>10</sup>R. W. O'Brien, J. Fluid Mech. **190**, 71 (1988).

<sup>11</sup>R. W. O'Brien, J. Fluid Mech. **212**, 81 (1990).

<sup>12</sup>R. W. O'Brien, P. Garside, and R. J. Hunter, Langmuir **10**, 931 (1994).

<sup>13</sup>J. Hermans, Philos. Mag. **25**, 426 (1938).

<sup>14</sup>J. Hermans, Philos. Mag. **26**, 674 (1938).

<sup>15</sup>J. Bugosh, E. Yeager, and F. Hovorka, J. Chem. Phys. **15**, 592 (1947).

<sup>16</sup>S. D. Vidal, J. P. Simmonin, P. Turq, and O. Bernard, J. Phys. Chem. **99**, 6733 (1995).

<sup>17</sup>R. Kubo, J. Phys. Soc. Jpn. **12**, 570 (1957).

<sup>18</sup>F. O. Raineri, Y. Zhou, H. L. Friedman, and G. Stell, Chem. Phys. **152**, 201 (1991).

<sup>19</sup>S.-H. Chong and F. Hirata, Phys. Rev. E **57**, 1691 (1998).

<sup>20</sup>U. Balucani and M. Zoppi, *Dynamics of the Liquid State* (Clarendon, Oxford, 1994).

<sup>21</sup>T. Imai, M. Kinoshita, and F. Hirata, J. Chem. Phys. **112**, 9469 (2000).

<sup>22</sup>J.-P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, 2nd ed. (Academic, London, 1990).

<sup>23</sup>M. Ohba, F. Kawaizumi, and H. Nomura, J. Chem. Phys. **96**, 5129 (1992).

<sup>24</sup>A. N. Hunter, Proc. Phys. Soc. (London) **71**, 847 (1958).

<sup>25</sup>A. N. Hunter and T. B. Jones, Proc. Phys. Soc. London **80**, 795 (1962).

<sup>26</sup>A. Weinmann, Proc. Phys. Soc. London **73**, 345 (1959).

<sup>27</sup>A. Weinmann, Proc. Phys. Soc. London **75**, 102 (1960).

<sup>28</sup>J. P. Boon and S. Yip, *Molecular Hydrodynamics* (McGraw-Hill, New York, 1980).