Theory of the liquid-glass transition in water

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Abstract

A quantum field theory of the liquid-glass transition in water based on the two band model in the harmonic potential approximation is presented by taking into account of the hydrogen bonding effect and the polarization effect. The sound and diffusion associated with intra-band density fluctuations, and the phonons and viscosity associated with inter-band density fluctuations are calculated. The Kauzmann paradox on the Kauzmann’s entropy crisis and the Vogel-Tamman-Fulcher (VTF) law on the relaxation times and the transport coefficients are elucidated from the sound instability at a reciprocal particle distance corresponding a hydrogen bond length and at the sound instability temperature very close to the Kauzmann temperature. The gap of specific heat at the glass transition temperature and the boson peaks are also presented.

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1 Introduction

Water plays an essential role in a medium in which chemical and biological molecules operate and it influences their functions. Its properties are far from being fully understood. Experimental studies of the glassy behaviours of bulk water are extremely difficult, while hydration water particularly on the surface of proteins can provides an interesting alternative to study the slow dynamics of water, because the binding of water molecules to the surface can prevent crystallization. Experimental studies in hydration water certainly show the universal features in the liquid-glass transition \[1, 2, 3, 4\]. We intend to develop theory of the liquid-glass in hydration water. Here at the first stage we develop the glass transition in bulk water.

We have established quantum field theory of the liquid-glass transition in a one-component liquid in the framework of the two band model to elucidate the Kauzmann paradox, the VTF law, the gap of specific heat at the glass transition temperature and boson peaks \[5, 6\], which appear universally in the liquid-glass transition. We have also proposed a quantum field theory of phonons in a two-component liquid \[5, 7, 8\], and also proposed a quantum field theory of phonons and melting in compounds taking into account of the electric polarization in the rigid ion approximation, the Ewald method \[9, 10, 11\]. Here we extend the quantum field theory of the liquid-glass transition in a one-component liquid to that in water considering the quantum field theory of phonons in a multi-component liquid and the electric polarization in the rigid ion approximation \[9, 10, 11\]. The essential points of our theory are as follows \[5, 6\]:

(1) The two band model. A particle is temporarily in a randomly distributed harmonic potential made up by the surrounding particles, making up and down transitions between the ground state and the first excited states, and then hops to a surrounding vacancy. This picture constitutes the model Hamiltonian which consists of the random eigenfrequencies and random hopping magnitudes. The configurational averaged model Hamiltonian yields an unperturbed Hamiltonian. Due to hopping, instead of individual states of the local potentials, the system have energy bands having a width determined by the hopping magnitude.

(2) Intra-band and inter-band density fluctuations. Density fluctuations consist of intra-band density fluctuations related to the hopping to a neighbouring vacancy and inter-band density fluctuations associated to the up and down transitions between two bands. Intra-band and inter-band density fluctuations are associated with intra-band and inter-band elementary excitations, respectively. The collective excitations of intra-band and inter-band elementary excitations are sound and phonons, respectively. Sound is a density fluctuation wave. In the classical limit the particle energy dispersion associated to intra-band elementary excitations tends to a free particle one so that the sound reduces to a density fluctuation wave \[12\]. Phonons are elastic waves. In the classical limit coupling strengths between particles deviated from their assigned positions constitute spring constants so that the phonons reduce to elastic waves \[12\].

(3) Dissipation and relaxation times. Random scattering processes come from the random potentials which is described by subtracting the unperturbed Hamiltonian from the model Hamiltonian. Dissipative process comes from the simultaneous scattering processes of two particles by the same random potential. The sum of the configurationally
averaged simultaneous scattering processes over all sites yields the correlation functions
of random harmonic frequencies and random hopping magnitudes, which leads to the
relaxation times; the former and the latter correspond to the $\beta$ and $\alpha$-relaxations, respecti-
vately. When the relaxation times of sound and phonons are shorter than their respective
periods, diffusivity and viscosity appear, respectively.

(4) The Kauzmann entropy and the VTF law. Intra-band density fluctuation entropy
consists of sound entropy, fluctuation entropy due to intra-band elementary excitations
and dissipative entropy due to diffusion. In an equilibrium state the dissipative entropy
compensates the fluctuation entropy with a negative value and the system reaches a
local equilibrium. But since sound depends on temperature, a mixing between the sound
and fluctuation entropies occurs. The mixing entropy yields the Kauzmann entropy: a
Curie law with a minus sign, where the critical temperature corresponds to the sound
instability temperature which indicates fragility. The hopping amplitude relates to the
multi-dimensional configuration space of the Kauzmann entropy; the hopping amplitude
is proportional to the exponent of the Kauzmann entropy per particle. This hopping
amplitude explains the VTF law: the exponent of the Curie law with a minus sign per
particle. The hopping amplitude is the origin of the $\alpha$-relaxation.

(5) The glass transition temperature and the magnitude of the randomness of harmonic
frequencies. Inter-band density fluctuation entropy also consists of phonon entropy, fluctu-
ation entropy due to inter-band elementary excitations and dissipative entropy due to
viscosity. In an equilibrium state the dissipative entropy compensates the fluctuation
entropy with a negative value and the system reaches a local equilibrium. Since phonons
do not depend on temperature, mixing does not occur. The magnitude of randomness of
harmonic frequencies relates to the multi-dimensional configurational space of the fluctu-
ation entropy; the magnitude of randomness of harmonic frequencies is proportional to
the exponent of the fluctuation entropy per particle. The fluctuation entropy prevents
the Kauzmann entropy crisis at the glass transition temperature. The magnitude of the
randomness of harmonic frequencies is the origin of the $\beta$-relaxation.

In applying the two band model to the liquid-glass transition in water [13, 14, 15], we
should clarify the structure of water. The characteristic features of the structure of water
are as follows [16]: (i) Hydrogen bonds play an essential role in clustering water molecules
comparing with the common molecules. A water molecule consists of an oxygen and two
covalent bonded hydrogens so that the water molecule has the two protons and the lone
pairs. A proton of a water molecule is hydrogen bonded to a lone pair of the nearest
neighbour water molecule. (ii) Water has the proper geometric structure. Water is made
up of a strongly hydrogen bonded network and locally very similar to ice. But these
hydrogen bonds have very short lifetimes. (iii) A water molecule is electrically polarized,
which originates from the hydrogen covalent bonds.

In order to include the above characteristic features, first we determine the interac-
tion potentials $V_{\alpha\beta}$ with the corresponding pair distribution functions $g_{\alpha\beta}$, which predict
the structure of water, where $\alpha$, $\beta$ mean an oxygen atom O or a hydrogen atom H. (i)
The interaction potential between O-H, $V_{\text{OH}}$ consists of hydrogen covalent bonding, $V_{\text{OH}}^{\text{hc}}$
and hydrogen bonding, $V_{\text{OH}}^{\text{hb}}$. A strong hydrogen bonded network is constructed by the
couplings of $V_{\text{OH}}^{\text{hc}}V_{\text{OH}}^{\text{hb}}$ and $V_{\text{OH}}^{\text{hb}}V_{\text{OH}}^{\text{hc}}$, which comes from the fact that the configurational
average of the term $V_{\text{OH}}V_{\text{HO}}$ over the position of the hydrogen atoms yields the terms
V^{hcb}V^{hcb}_{OH}$ and $V^{hb}V^{hcb}_{OH}$, not the terms $V^{hcb}V^{hcb}_{OH}$ and $V^{hh}V^{hb}_{OH}$, because the former terms are favorable. The hydrogen bonding plays an essential role in clustering water. The first peak of $g_{OH}(R)$ corresponds to the hydrogen bond length [13]. Since hydrogen bonding plays an essential role in water, the sound instability occurs at a reciprocal particle distance corresponding to a hydrogen bond length. (ii) In the interaction potential $V_{HH}$ we take into account of the interaction between hydrogens in different water molecules. Hopping between protons and lone pairs reflects $V_{HH}$ and the hopping yields very short lifetimes of hydrogen bondings. (iii) There exists the electric polarization between O-H. The electric polarization relates to the $p$-state of particles. An excited state of a particle corresponds to a $p$-state, while a ground state to an $s$-state. Thus we need not take into account of the polarization in the interaction potentials between intra-band density fluctuations because the intra-band density fluctuations annihilate and create the same states. However we should take into account of the polarization between inter-band density fluctuations because the inter-band density fluctuations annihilate an $s$-state and create a $p$-state, and vice versa. We take into account of the electric polarization in the rigid ion approximation, the Ewald method [9, 10, 11].

We organize as follows: in section 2, we briefly survey the formulation. We obtain the model Hamiltonian with random harmonic frequencies and random hopping magnitudes. Taking the configurational average of the model Hamiltonian, We obtain the unpurterbed Hamiltonian. We construct the interaction Hamiltonian for intra-band and inter-band density fluctuations, which leads to the sound and the phonon modes. In section 3, we introduce the interaction Hamiltonian for the random scattering processes, which leads to the dissipative process. In section 4, the correlation functions of intra-band density fluctuations with the vertex corrected bubble diagrams of intra-band elementary excitations yield the sound and diffusivity. The sound instability occurs at a temperature $T_0$ and at a reciprocal particle distance corresponding to a hydrogen bond length. In section 5, taking into account of the electric polarization due to hydrogen covalent bond, we calculate the correlation functions of inter-band density fluctuations with the vertex corrected bubble diagrams, which yield phonons and viscosity modified by the polarization. We also show the boson peaks. In section 6, we obtain the Kauzmann entropy from the mixing of the sound and the intra-band fluctuation entropies in the sound instability regime. We show that a unique hopping amplitude corresponding to the Kauzmann entropy governs the velocities of individual particles, the sound and the hopping amplitudes of individual particles, while the magnitude of the randomness of the hamonic frequencies of particles depends on the individual particles. The glass transition occurs at the crossover temperature of the Kauzmann entropy and the inter-band fluctuation entropy. We derive the specific heat and show the VTF law for the relaxation times for sound and phonons, and the transport coefficients. Section 7 is devoted by some concluding remarks.

2 Formulation

Here we briefly survey the formulation. We start with the following Hamiltonian:

$$H = \sum_{\alpha} \int d^3x \psi_{\alpha}^\dagger(x) \hbar \epsilon_{\alpha}(-i\nabla)\psi_{\alpha}(x) + \frac{1}{2} \sum_{\alpha\beta} \int d^3x d^3y n_{\alpha}(x)V_{\alpha\beta}(x-y)n_{\beta}(y), \quad (2.1)$$
where $\hbar \epsilon^0_{\alpha}(-i\nabla)$ is the energy operator of a free $\alpha$-particle, $n_{\alpha}(x) = \psi_{\alpha}^+(x)\psi_{\alpha}(x)$. We write the operator $\psi_{\alpha}(x)$ by using the localized operators, which are rewritten by the extended operators.

$$\psi_{\alpha}(x) = \sum_{m\mu} \tilde{w}_{\alpha m\mu}(x - R_{\alpha m}) b_{\alpha m\mu}. \quad b_{\alpha m\mu} = \frac{1}{\sqrt{N_{\alpha}}} \sum_{p} e^{i p \cdot R_{\alpha m}} a_{\alpha m p}. \quad (2.2)$$

The Heisenberg equation for $b_{\alpha m\mu}$ is given by

$$-\hbar \frac{\partial}{\partial \tau} b_{\alpha m\mu} = \sum_{n\nu} \int d^3 x \tilde{w}_{\alpha m\mu}(x - R_{\alpha m}) \left[ \hbar \epsilon^0_{\alpha}(-i\nabla) + \Phi_{R_{\alpha n}}(x) \right] \tilde{w}_{\alpha n\nu}(x - R_{\alpha n}) b_{\alpha n\nu}, \quad (2.3)$$

$$\Phi_{R_{\alpha n}}(x) = \sum_{\beta} \int_{\{R_{\alpha n}\}} d^3 y V_{\alpha \beta}(x - y) n_{\beta}(y), \quad (2.4)$$

where $\{R_{\alpha n}\}$ means summing the surrounding sites of the particle at $R_{\alpha n}$ in $n_{\beta}(y)$. The term $\Phi_{R_{\alpha n}}$ means that a potential is determined by the surrounding particles of the site $R_{\alpha n}$. Thus we obtain the Schrödinger equation:

$$\left\{ \hbar \epsilon^0_{\alpha}(-i\nabla) + \Phi_{R_{\alpha n}}(x) \right\} \tilde{w}_{\alpha n\nu}(x - R_{\alpha n}) = \hbar \tilde{\omega}_{\alpha n\nu} \tilde{w}_{\alpha n\nu}(x - R_{\alpha n}), \quad (2.5)$$

where $\tilde{\omega}_{\alpha n\mu}$ and $\tilde{w}_{\alpha n\mu}$ are the eigenfrequency and the eigenfunction of the $\mu$th state at the site $R_{\alpha n}$ in a similar manner to a one-component liquid in the harmonic approximation. We consider the following relations:

$$w_{\alpha n\mu}(x) = -2\zeta_{\alpha n} \nabla_i w_{\alpha n0}(x); \quad w_{\alpha n0}(x) = 2\zeta_{\alpha n} \nabla_i w_{\alpha n0}(x); \quad \zeta_{\alpha n} = \sqrt{\frac{\hbar}{2M_{\alpha} \omega_{\alpha n}}}, \quad (2.6)$$

where $\zeta_{\alpha n}$ is the mean width of the zero point motion, $M_{\alpha}$ is the mass of the $\alpha$-particle and $\omega_{\alpha n}$ is the harmonic frequency; $\hbar \tilde{\omega}_{\alpha n0} = \frac{3}{2} \hbar \omega_{\alpha n}$ and $\hbar \tilde{\omega}_{\alpha n\mu} = \frac{5}{2} \hbar \omega_{\alpha n}$. At this stage, we can take the following model Hamiltonian in terms of localized operators:

$$H = \sum_{\alpha m\mu} \hbar \tilde{\omega}_{\alpha m\mu} b_{\alpha m\mu}^+ b_{\alpha m\mu} + \sum_{\alpha m\mu n\nu} \hbar J_{\alpha m\mu n\nu} b_{\alpha m\mu}^+ b_{\alpha n\nu}, \quad (2.7)$$

where the hopping matrix is given by

$$\hbar J_{\alpha m\mu n\nu} = \int d^3 x \tilde{w}_{\alpha m\mu}(x - R_{\alpha m}) \Phi_{R_{\alpha n}}(x) \tilde{w}_{\alpha n\nu}(x - R_{\alpha n}). \quad (2.8)$$

Note that the interaction Hamiltonian is nonlinear through the term $n_{\beta}(y)$ in $\Phi_{R_{\alpha n}}$ and the potential $\Phi_{R_{\alpha n}}$ permits a particle to hop only to a vacancy.

Now we start with the new unperturbed Hamiltonian which is the configurational average of the model Hamiltonian (2.7):

$$H_0 = \langle H \rangle = \sum_{\alpha m\mu} \hbar \tilde{\omega}_{\alpha m\mu} b_{\alpha m\mu}^+ b_{\alpha m\mu} + \sum_{\alpha m\mu n\nu} \hbar J_{\alpha m\mu n\nu} (R_{\alpha m} - R_{\alpha n}) b_{\alpha m\mu}^+ b_{\alpha n\nu}, \quad (2.9)$$
where $J_{\alpha\mu}$ is the hopping magnitude. < > means the configurational average. The configurationally averaged values do not include the indices of the positions. Here for simplicity we limit ourselves to the hopping between like atoms and the hopping to those between the same levels. Using Eq. (2.2), we obtain

$$H_0 = \sum_{\alpha p} \hbar \epsilon_{\alpha p} a^{\dagger}_{\alpha p} a_{\alpha p}, \quad \epsilon_{\alpha p} = \bar{\omega}_{\alpha p} + J_{\alpha p}(p), \quad J_{\alpha p}(p) \equiv \frac{1}{N_\alpha} \sum_m e^{ip\cdot R_{am}} J_{\alpha p}(R_{am}).$$

(2.10)

From Eq. (2.2), we obtain

$$n_{\alpha}(x) = \frac{1}{N_\alpha} \sum_{m q} e^{-iq\cdot R_{am}} [\sum_{\mu} \bar{w}_{\alpha\mu}^2(x - R_{am}) \rho_{\alpha p}^{\dagger} q - \sum_i \zeta_i \nabla_i \bar{w}_{\alpha 0}^2(x - R_{am}) \rho_{\alpha i}^{\dagger} q + \cdots],$$

(2.11)

where

$$\rho_{\alpha p} = \sum_p a^{\dagger}_{\alpha p} a_{\alpha p}, \quad \rho_{\alpha i} = \sum_p (a^{\dagger}_{\alpha i} a_{\alpha i} + q + a^{\dagger}_{\alpha 0} a_{\alpha 0} + q).$$

(2.12)

$\rho_{\alpha p}$ and $\rho_{\alpha i}$ are intra-band and inter-band density fluctuation operators, respectively. Substituting Eq. (2.11) into the interaction Hamiltonian in Eq. (2.1) we obtain the interaction Hamiltonian:

$$H_I = \frac{1}{2} \sum_{\alpha \beta \mu \nu} \sqrt{\frac{1}{N_\alpha N_\beta}} V_{\alpha \beta \mu \nu}^{d}(q) \rho_{\alpha p}^{\dagger} q \rho_{\beta q} + \frac{1}{2} \sum_{\alpha \beta \mu \nu q} \sqrt{\frac{1}{N_\alpha N_\beta}} V_{\alpha \beta q}^{d}(q) \rho_{\alpha i}^{\dagger} q \rho_{\beta j} q,$$

(2.13)

$$V_{\alpha \beta \mu \nu}^{d}(q) \equiv \sqrt{N_\alpha N_\beta} V_{\alpha \beta \mu \nu}, \quad V_{\alpha \beta q}^{d}(q) \equiv \sqrt{N_\alpha N_\beta} V_{\alpha \beta 0 q},$$

(2.14)

$$V_{\alpha \beta \mu' \nu'}(q) = \frac{1}{N_\alpha N_\beta} \sum_{m \neq n} e^{-iq(R_{am} - R_{bn})}$$

$$\times \int d^3 x d^3 y \bar{w}_{\alpha p}(x - R_{am}) \bar{w}_{\alpha'}(x - R_{an}) \bar{w}_{\beta\nu}(y - R_{bn}) \bar{w}_{\beta'\nu'}(y - R_{bn}).$$

(2.15)

where the prime on $\Sigma$ means $H_I$ excludes loop diagrams, which are taken into account in the potential $\Phi_{R_{am}}$.

3 Dissipative process

In randomly distributed particles, we have a model Hamiltonian, Eq. (2.7). Taking the configurationally averaged Hamiltonian of Eq. (2.7), we obtain the unperturbed Hamiltonian, Eq. (2.9) and (2.10), which constitutes the two bands. The intra-band and inter-band elementary excitations are excited around the two bands and they are associated with intra-band and inter-band density fluctuations, Eq. (2.12), which constitute the model Hamiltonian (2.13). We employ the model Hamiltonian (2.13) to describe the dynamical process. The collective excitations for the intra-band and inter-band elementary excitations are sound and phonons. The life times of sound and phonons appears when the
dispersion curves merge into the continuum of the intra-band and inter-band elementary excitations, respectively.

Here we investigate the dissipative process from the random scatterings due to the random harmonic frequencies and the random hopping magnitudes. The original model Hamiltonian, Eq.(2.7) reflects the randomly distributed particles, while the unperturbed Hamiltonian, Eqs.(2.9) and (2.10) reflect the free particle picture. The random scattering process is represented by the interaction Hamiltonian $H_I$:

$$H_I = \sum_{\alpha m} \hbar (\bar{\omega}_{\alpha m} - \bar{\omega}_{\alpha m}) b_{\alpha m}^\dagger b_{\alpha m} + \sum_{\alpha n m} \hbar \{ J_{\alpha m\alpha n -} - J_{\alpha m\alpha n} (R_{am} - R_{an}) \} b_{\alpha m}^\dagger b_{\alpha n}.$$ (3.1)

Note that since the term $J_{\alpha m\alpha n}$ involves operators $n(y)$, $H_I$ is essentially nonlinear. But at low temperatures an atom stays longer at the same site. Thus we make the approximation that the term $J_{\alpha m\alpha n}$ is a random c-number. Using Eq.(2.2), we rewrite Eq.(3.1) as

$$H_I = \frac{1}{N_\alpha} \sum_{\alpha m\nu} \left[ \sum_m \hbar (\bar{\omega}_{\alpha m} - \bar{\omega}_{\alpha m}) e^{-i(p - p') \cdot R_{am}} + \sum_{mn} \hbar \{ J_{\alpha m\alpha n} - J_{\alpha m} (R_{am} - R_{an}) \} e^{-i p \cdot R_{am} + i p' \cdot R_{an}} \right] a_{\alpha m}^\dagger a_{\alpha n}.$$ (3.2)

Dissipative process is constructed by elementary scattering processes due to simultaneously scattering processes of two particles in $\mu$ and $\nu$th bands by the same random potentials. Elementary scattering processes come from the scattering processes due to random harmonic frequencies and random hopping magnitudes, Eqs.(3.1) and (3.2). The sum of configurationally averaged elementary scattering process over all sites due to random harmonic frequencies yields a correlation functions of random harmonic frequencies, $U_{\omega}^{\alpha\mu\nu}$ and that due to random hopping magnitudes yields a correlation function of random hopping magnitudes, $U_{J}^{\alpha\mu\nu}$, which are given by

$$U_{\omega}^{\alpha\mu\nu} = \frac{1}{N_\alpha^2} \sum_m \langle \bar{\omega}_{\alpha m} \bar{\omega}_{\alpha m} \rangle e^{-i (p - p') \cdot R_{am}}.$$ (3.3)

$$U_{J}^{\alpha\mu\nu}(q) = \frac{1}{N_\alpha} \int d^3 R g(R) e^{-i q \cdot R} \{ \langle J_{\alpha m\alpha n} J_{\alpha m\alpha n} \rangle e^{-i (p - p') \cdot R_{am} + i p' \cdot R_{an}} \},$$ (3.4)

Eqs.(3.3, 3.4) yield the relaxation times; the $\beta$ and $\alpha$-relaxation, respectively. The elementary scattering processes, $U_{\omega,J}^{\alpha\mu\nu}$ correspond to that in the case of two electrons scattered simultaneously by the same random impurity in electric conductivity. The statistical average on a random system constrains the dynamical processes, which leads to dissipation.

4 Sound and diffusivity

We first investigate the sound Green’s function. In the low temperature regime, we confine ourselves to the lower band.

$$F_{\alpha\beta}(\tau_1 - \tau_2) \equiv -\frac{1}{\hbar \sqrt{N_\alpha N_\beta}} \langle T_{\tau_1} \rho_{\alpha q}(\tau_1) \rho_{\beta q}^\dagger(\tau_2) \rangle e^{-i \omega_\tau (\tau_1 - \tau_2)} F_{\alpha\beta}(q),$$ (4.1)
where we should not confuse the temperature $\beta = 1/k_BT$ and the suffices $\beta$; the temperature $\beta$ appears as an independent parameter with the inverse energy dimension, while the suffices $\beta$ stand for O or H. In the random phase approximation, we obtain

$$F_{\alpha\beta}(q) = P_{\alpha}(q)\delta_{\alpha\beta} + \sum_{\gamma} P_{\alpha}(q)V_{\alpha\gamma}(q)F_{\gamma\beta},$$

(4.2)

$$P_{\alpha}(q) \simeq \frac{\beta(\omega_{0\alpha})^2}{q_0(q_0 + \frac{1}{\tau_{0\alpha}}) - (\omega_{0\alpha})^2},$$

(4.3)

$$V_{\alpha\beta}(q) = \frac{1}{\sqrt{\mathcal{V}_\alpha N_\beta}} \sum_{m \neq n} e^{-iq(R_m-R_n)}V_{\alpha\beta}(R_m - R_n) >_c$$

$$= \sqrt{\frac{\mathcal{V}_\alpha}{\mathcal{V}_\beta}} \int d^3Rg_{\alpha\beta}(R)e^{iqR}V_{\alpha\beta}(R)$$

(4.4)

$$V_{\alpha\beta}(R_{am} - R_{\beta n}) = \int d^3x d^3y \tilde{w}_{am}(x - R_{am})V_{\alpha\beta}(x - y)\tilde{w}_{\beta n}(y - R_{\beta n}),$$

(4.5)

$$\frac{1}{2\tau_{0\alpha}} = \sqrt{\mathcal{V}_\alpha(U^{\alpha\alpha}_\omega + U^{\alpha\alpha}_J)}$$

(4.6)

$$\langle \omega_{0\alpha}^2 \rangle \simeq \frac{(v_{op})^2}{3}q^2, \quad v_{op} = \frac{1}{N} \sum_p \frac{\partial \epsilon_{opp}}{\partial p},$$

(4.7)

where we have analytically continued $i\nu_n \rightarrow q_0$ in Eq.(4.3). $\tau_{0\alpha}$ and $v_{op}$ are the relaxation time and the mean velocity of the $\alpha$-particle. Eq.(4.3) is presented in [5]. Hereafter, we omit the suffices $d$ and $0$ in $V_{\alpha\beta}^d$.

Applying Eq.(4.2) to water, we obtain the dynamical equation:

$$\begin{pmatrix} 1 - P_OV_{OO} & P_OV_{OH} \\ P_HV_{HO} & 1 - P_HV_{HH} \end{pmatrix} \begin{pmatrix} F_{OO} & F_{OH} \\ F_{HO} & F_{HH} \end{pmatrix} = \begin{pmatrix} P_O & 0 \\ 0 & P_H \end{pmatrix},$$

(4.8)

with the solution:

$$\begin{pmatrix} F_{OO} & F_{OH} \\ F_{HO} & F_{HH} \end{pmatrix} = \frac{1}{\det} \begin{pmatrix} \left(1 - P_HV_{HH}\right)P_O & P_OV_{OH}P_H \\ P_HV_{HO}P_H & \left(1 - P_OV_{OO}\right)P_H \end{pmatrix},$$

(4.9)

$$\det = \left(1 - P_OV_{OO}\right)\left(1 - P_HV_{HH}\right) - P_OV_{OH}P_HV_{HO}.$$  

(4.10)

Here in order to construct the hydrogen bonding network, we should consider that $V_{OH}(R)$ in Eq.(4.4) consists of hydrogen covalent bonding, $V_{OH}^{hc}(R)$ and hydrogen bonding, $V_{OH}^{hb}(R)$, the pair distribution functions of which are $g_{OH}^{hc}(R)$ and $g_{OH}^{hb}(R)$, respectively. Corresponding to this fact, we consider that $V_{OH}(q)$ consists of hydrogen covalent bonding $V_{OH}^{hc}(q)$ and hydrogen bonding $V_{OH}^{hb}(q)$. Thus we put

$$V_{OH}(q) = V_{OH}^{hc}(q), V_{OH}^{hb}(q).$$

(4.11)

But in deriving Eq.(4.8), we have used Eq.(4.4) under the nearest neighbour approximation so that the terms in Eqs.(4.9, 10) involves unphysical cross terms such as $V_{OH}^{hc}V_{HO}^{hc}$.
and $V_{OH}V_{HO}$. When we calculate Eq.(4.1), we should configurationally average all possible Feynmann diagrams over the position of particles $R_{am}$. If we configurationally average the term $< V_{OH}V_{HO} >$ over $R_{Hm}$ considering the pair distribution functions $g_{OH}^{hc}(R)$ and $g_{OH}^{hc}(R)$, the most dominant terms in $< V_{OH}V_{HO} >$ come from the terms $V_{OH}^{hc}(a_{OH}^{hc})V_{HO}^{hc}(a_{HO}^{hc})$ and $V_{OH}^{hc}(a_{OH}^{hc})V_{HO}^{hc}(a_{HO}^{hc})$, where $a_{OH}^{hb}$ are the mean distances of hydrogen covalent and hydrogen bond, respectively. Since in our calculation we concentrate ourselves to the hydrogen bonding network, we should take into account of both the terms $V_{OH}^{hc}V_{HO}^{hc}$ and $V_{OH}^{hc}V_{HO}^{hc}$ as pairs. Thus when the term $V_{OH}V_{HO}$ appears, $V_{OH}V_{HO}$ should be replaced by $V_{OH}^{hc}V_{HO}^{hc} + V_{OH}^{hc}V_{HO}^{hc}$.

We can obtain the modes by solving the secular equation of Eq. (4.8):
\[
\{1 - P_{O}(q)V_{OO}(q)\}\{1 - P_{H}(q)V_{HH}(q)\} - P_{O}(q)P_{H}(q)V_{OH}(q)V_{HO}(q) = 0. \tag{4.12}
\]

Before we solve Eq.(4.12), we investigate the secular equation for the sound in a system consist of only $\alpha$-type of particles:
\[
1 + P_{\alpha}(q)V_{\alpha\alpha}(q) = 0 \tag{4.13}
\]

We investigate Eq.(4.13) in the two limiting cases:

(i) $q_0\tau_{\alpha0} \gg 1$

Eq.(4.13) leads to the sound frequency for $\alpha$-particles:
\[
q^2 = \omega_{\alpha\alpha}(q) = (1 + \beta V_{\alpha\alpha}(q))\omega_{\alpha\alpha}^0 = \frac{(\omega_{\alpha\alpha}^0)^2}{S_{\alpha}(q)} = v_{\alpha\alpha}^2q^2, \tag{4.14}
\]

where $S_{\alpha}(q)$ and $v_{\alpha\alpha}$ are the static structure factor and the sound velocity of the $\alpha$-particle:
\[
S_{\alpha}(q) \equiv (1 + \beta V_{\alpha\alpha}(q))^{-1}, \tag{4.15}
\]

\[
v_{\alpha\alpha} = \frac{v_{\alpha\alpha}}{\sqrt{3S_{\alpha}(0)}}, \tag{4.16}
\]

Next we investigate the sound instability. In the first approximation, if we consider a first peak for a pair distribution function, we can put
\[
g_{\alpha\alpha}(R) = \rho_{\alpha}\delta(R - a_{\alpha\alpha}), \tag{4.17}
\]

where $a_{\alpha\alpha}$ is the mean distance between the $\alpha$- particles. Then we obtain
\[
V_{\alpha\alpha}(q) = 4\pi a_{\alpha\alpha}^2\rho_{\alpha}V_{\alpha\alpha}(a_{\alpha\alpha})\frac{\sin a_{\alpha\alpha}q}{a_{\alpha\alpha}q}, \tag{4.18}
\]

where $V_{\alpha\alpha}$ has the minimum negative value at a reciprocal particle distance $\tilde{K}_{\alpha\alpha} \approx 3\pi/2a_{\alpha\alpha}$. Since
\[
\lim_{q_0 \to 0} P_{\alpha}(q) \approx -\beta, \tag{4.19}
\]

and $V_{\alpha\alpha}$ has the minimum negative value at a reciprocal particle distance $\tilde{K}_{\alpha\alpha}$, the sound instability in the $\alpha$-liquid occurs at the temperature $T_{\alpha0}$ and the reciprocal particle distance $\tilde{K}_{\alpha\alpha}$ in Eq.(4.15):
\[
1 + \beta_{\alpha0}V_{\alpha\alpha}(\tilde{K}_{\alpha\alpha}) = 0. \tag{4.20}
\]
(ii) $q_0 \tau_{\alpha\gamma} \ll 1$

Eq. (4.13) leads to the diffusion mode

$$q_0 = i \tau_{\alpha\gamma} \nu_{\alpha\gamma}^2,$$

where the diffusion coefficient is given by

$$D_\alpha = \tau_{\alpha\gamma} \nu_{\alpha\gamma}^2.$$

Next we investigate the secular equation Eq. (4.12) for water in the two limiting cases:

(I) $q_0 \tau_{\alpha\gamma} \gg 1$

We obtain the sound modes:

$$q_0^2 = \omega_{s+}^2(q)$$

$$= \frac{1}{2} \left[ \omega_H^2(q) + \omega_M^2(q) \pm \sqrt{(\omega_H^2(q) - \omega_M^2(q))^2 + 4 \beta^2 (\omega_M^0)^2 \nu_{h\gamma}^2 V_{OH}(q) V_{HO}(q)} \right]$$

$$= v_{s+}^2 q^2,$$

where $v_{s+}$ are the sound velocities:

$$v_{s+} = \sqrt{\frac{1}{2} \left( \nu_{OS}^2 + \nu_{HS}^2 \pm \sqrt{(\nu_{OS}^2 - \nu_{HS}^2)^2 + 4 \beta^2 \nu_{OP}^2 \nu_{HP}^2 V_{OH}(q) V_{HO}(q)} \right)}.$$

If the term $V_{OH} V_{HO}$ dominates, $\omega_{s-}$ and $v_{s-}$ disappear. Next we investigate the sound instability. In the first approximation, if we consider a peak for the pair distribution function, we can put

$$g_{\alpha\beta}(R) = \rho_{\beta} \delta(R - a_{\alpha\beta}),$$

where $a_{\alpha\beta}$ is the mean distance between the $\alpha$ and $\beta$ particles. Then we obtain

$$V_{\alpha\beta}(q) = 4 \pi a_{\alpha\beta}^2 \rho_{\beta} V_{\alpha\beta}(a_{\alpha\beta}) \frac{\sin a_{\alpha\beta} q}{a_{\alpha\beta} q},$$

where $V_{\alpha\beta}$ has the minimum negative value at a reciprocal particle distance $K_{\alpha\beta} \approx 3\pi/2a_{\alpha\beta}$.

In water the interaction potential $V_{h\gamma}^{h\gamma}$ and the pair distribution function $g_{h\gamma}^{h\gamma}$ in $V_{h\gamma}$ are the most important. The peak of $g_{h\gamma}^{h\gamma}$ corresponds to the hydrogen bond, which constitute the cluster of hydrogen bonded molecules. If we denote the mean distance corresponding to the peak by $a_{h\gamma}^{h\gamma}$, the reciprocal particle distance is given by $K_{h\gamma}^{h\gamma}$. The sound instability occurs when the secular equation Eq. (4.12) with Eq. (4.19) becomes zero at a temperature $T_0$ and at a wave vector $K \approx K_{h\gamma}^{h\gamma}$:

$$\{1 + \beta_0 V_{OO}(K)\} \{1 + \beta_0 V_{HH}(K)\} - \beta_0^2 V_{OH}(K) V_{HO}(K) = 0.$$

$T_0$ is given by

$$T_0 = \frac{1}{2k_B} \{V_{OO}(K) + V_{HH}(K) + \sqrt{(V_{OO}(K) - V_{HH}(K))^2 + 4V_{OH}(K) V_{HO}(K)}\}.$$
equation \[1\]:

In the random phase approximation, we obtain the phonon Green’s functions and the gap

\[\pm \sqrt{(\tau_{00}\omega^2_0(q) - \tau_{H0}\omega^2_H(q))^2 + 4\beta^2\tau_{00}(\omega^0_{0q})^2\tau_{H0}(\omega^0_{Hq})^2V_{OH}(q)V_{HO}(q)}\] \(q^2\),

where \(D^{\pm}\) are diffusion coefficients:

\[D^{\pm} = \frac{1}{2}\left\{(\tau_{00}v^2_{0s} + \tau_{H0}v^2_{Rs}) \pm \sqrt{(\tau_{00}v^2_{0s} - \tau_{H0}v^2_{Rs})^2 + \frac{4}{9}\beta^2\tau_{00}v^2_{Op}\tau_{H0}v^2_{Hp}V_{OH}(q)V_{HO}(q)}\right\}
\]

\[= \frac{1}{2}\{(D_O + D_H) \pm \sqrt{(D_O - D_H)^2 + \frac{4}{9}\beta^2\tau_{00}v^2_{Op}\tau_{H0}v^2_{Hp}V_{OH}(q)V_{HO}(q)}\}.\]

If the term \(V_{OH}V_{HO}\) dominates, \(D^-\) disappears.

5 Phonons, boson peaks and viscosity

Next we investigate the phonon Green’s functions, which are defined by

\[D_{\alpha\beta\gamma\delta}(\tau_1\tau_2) \equiv \frac{-1}{\hbar\sqrt{N_{\alpha}N_{\beta}}} < T\rho_{\alpha\delta}(\tau_1)^\dagger \rho_{\beta\gamma}(\tau_2) >_c \equiv \frac{1}{\beta\hbar} \sum_{\nu_{\alpha}} e^{-iv\alpha(\tau_1-\tau_2)} D_{\alpha\beta\gamma\delta}(q),\]

In the random phase approximation, we obtain the phonon Green’s functions and the gap equation \[1\]:

\[D_{\alpha\beta\gamma\delta}(q) = Q_{\alpha}(q)\delta_{\alpha\beta}\delta_{\gamma\delta} + Q_{\alpha}(q) \sum_{\gamma l} < V^{\dagger}_{\alpha\dagger\gamma l}(q) >_c D_{\gamma l\beta\gamma}(q),\]

\[\frac{\bar{\Delta}_\alpha}{\sqrt{N_{\alpha}}} \delta_{ij} = Q_{\alpha}(0) < V^{\dagger}_{\alpha\dagger\beta j}(0) >_c \frac{\bar{\Delta}_\beta}{\sqrt{N_{\beta}}},\]

where

\[V^{\dagger}_{\alpha\dagger\beta j}(q) = \frac{\zeta_{\alpha}\zeta_{\beta}}{\sqrt{N_{\alpha}N_{\beta}}} \sum_{m \neq n} e^{-i\mathbf{q} \cdot (\mathbf{R}_m - \mathbf{R}_n)} V_{\alpha\dagger\beta j}(\mathbf{R}_m - \mathbf{R}_n),\]

\[V_{\alpha\dagger\beta j}(\mathbf{R}_m - \mathbf{R}_n) \equiv \int d^3x d^3y \nabla_i \tilde{u}^2_{\alpha m0}(\mathbf{x} - \mathbf{R}_m) V_{\alpha\beta}(\mathbf{x} - \mathbf{y}) \nabla_j \tilde{u}^2_{\beta 0}(\mathbf{y} - \mathbf{R}_n).\]

\[Q_{\alpha}(q) = \frac{2\omega_{\alpha}/\hbar}{(q_0 + i/2\tau_{aM})^2 - \omega^2_{\alpha}},\]

where \(\tau_{aM}\) is called the Maxwell relaxation time and

\[\frac{1}{2\tau_{aM}} \equiv \frac{1}{2\tau_{a0}} + \frac{1}{2\tau_{a1}} = \frac{1}{2\tau_{a0}} - \frac{1}{2\tau_{a1}}.\]
\( \tau_{0,1} \) are the relaxation times of the particles in the lower or upper bands, respectively. \( \tau_{0,1}^0 \) comes from the simultaneously scattering processes of particles between the lower and upper bands. This term corresponds to the cosine-function term with the scattering angle of an electron in the electric conductivity.

At low temperatures, since \( \tilde{\Delta}_\alpha = \frac{N_\alpha}{\zeta_\alpha} \), the gap equation (5.3) leads to

\[
1 = \zeta_\alpha^2 Q_\alpha(0) \sum_{\beta n} < V_{\alpha i\beta j}(R_{\beta n}) > c .
\]

Substituting \( \zeta_{\alpha} = < \zeta_{\alpha n} > c \) in Eqs. (2.6) and (5.6) into Eq. (5.8) under \( \omega_{\alpha} \tau_{\alpha M} \ll 1 \), we obtain

\[
M_{\alpha} \omega_{\alpha}^2 = - \sum_{\beta n} < V_{\alpha i\beta j}(R_{\beta n}) > c .
\]

Eq. (5.9) means that every \( \alpha \)-particle feels the same statistical averaged potential. From Eq. (5.4, 5) the matrix element of the dynamical equation (5.2) is written as

\[
\delta_{\alpha\beta} \delta_{ij} - Q_\alpha(q) < V_{\alpha i\beta j}(q) > c = -\zeta_\alpha^2 Q_\alpha(q)M_{\alpha}[q_0(q_0 + \frac{i}{\tau_{\alpha M}})\delta_{\alpha\beta}\delta_{ij} - M_{\alpha i\beta j}(q)],
\]

where \( M_{\alpha i\beta j} \) is the dynamical matrix for phonons. At low temperatures the dynamical matrix is given by

\[
M_{\alpha i\beta j}(q) = \frac{1}{M_{\alpha}} \sum_{\gamma} \int d^3 R g_{\alpha\gamma}(R) \{ \delta_{\gamma\alpha} \zeta_\gamma \sqrt{\frac{N_\alpha}{N_\gamma}} e^{i q \cdot R} - \delta_{\alpha\beta} \delta_{ij} \} V_{\alpha \gamma \beta j}(R).
\]

Here, as discussed on the term \( V_{OH}(q) \) in Eq. (4.11) in taking into account of the hydrogen bonding network, we should consider that the term \( M_{OHiJ}(q) \) consists of the term \( M_{OHiJ}^{rb}(q) \) corresponding to the hydrogen covalent bonding and the term \( M_{OHiJ}^{rb}(q) \) to the hydrogen bonding. Hereafter, in the same manner as the sound, if the cross term \( M_{OHiJ}(q)M_{HiOJ}(q) \) appears, \( M_{OHiJ}(q)M_{HiOJ}(q) \) should be replaced by \( M_{OHiJ}^{rb}(q)M_{HiOJ}^{rb}(q) + M_{OHiJ}^{rb}(q)M_{HiOJ}^{rb}(q) \).

Now we investigate Eq. (5.5). We separate the potential \( V \) into the short range one, \( V^N \), and the Coulombic one, \( V^C \):

\[
V_{\alpha i\beta j}(R_{\alpha m} - R_{\beta n}) = V_{\alpha i\beta j}^N(R_{\alpha m} - R_{\beta n}) + V_{\alpha i\beta j}^C(R_{\alpha m} - R_{\beta n}).
\]

When we take into account of the polarization of the hydrogen covalent bonds, we make the rigid ion approximation, the Ewald’s method [9, 10, 11]. In the rigid ion approximation; 
\( \omega_{\alpha 0}(R) \rightarrow \delta(R) \), we obtain

\[
V_{\alpha i\beta j}^C(R) = - \frac{\partial^2}{\partial x_i \partial x_j} \frac{\epsilon_\alpha \epsilon_{\beta}}{4 \pi \epsilon_0 R},
\]

where we have used the SI units, \( \epsilon_0 \) is the dielectric constant in vacuum and \( \epsilon_\alpha \) is the charge of an \( \alpha \)-particle; \( \epsilon_O = -2 \epsilon_H \). We define the Fourier transformed potential as

\[
\hat{V}_{\alpha i\beta j}(q) = < \sum_n e^{-iq(R_{\alpha m} - R_{\beta n})} V_{\alpha i\beta j}(R_{\alpha m} - R_{\beta n}) > c = \hat{V}_{\alpha i\beta j}^N(q) + \hat{V}_{\alpha i\beta j}^C(q).
\]
Next we investigate the Coulomb potential:

\[
\varphi_{\alpha\beta}^C(R) = \frac{e_\alpha e_\beta}{4\pi \epsilon_0 R}, \quad \hat{\varphi}_{\alpha\beta}^C(q) = \frac{e_\alpha e_\beta}{\epsilon_0 q^2},
\]

(5.15).

which satisfy

\[
\varphi_{\alpha\beta}^C(R) = \frac{1}{(2\pi)^3} \int d^3 q e^{i q \cdot R} \hat{\varphi}_{\alpha\beta}^C(q).
\]

(5.16)

In the Ewald method, we define a potential, \(\varphi_{\alpha\beta}^G(R)\), which is the potential energy of a point charge \(e_\alpha\) at a distance \(R\) from a three dimensional Gaussian distribution \(\rho_{\beta}^G(R)\) with the total charge \(e_\beta\):

\[
\rho_{\beta}^G(R) = e_\beta \left( \frac{P}{\pi} \right)^{3/2} e^{-PR^2}, \quad \hat{\rho}_{\beta}^G(q) = e_\beta e^{-q^2/4P},
\]

(5.17)

which satisfy

\[
\rho_{\beta}^G(R) = \frac{1}{(2\pi)^3} \int d^3 q \hat{\rho}_{\beta}^G(q) e^{i q \cdot R}.
\]

(5.18)

Thus we obtain

\[
\varphi_{\alpha\beta}^G(R) = \frac{e_\beta}{4\pi \epsilon_0} \frac{1}{R} \int_0^R \rho_{\beta}^G(R') d^3 R' + \int_R^\infty \frac{\rho_{\beta}^G(R')}{R'} d^3 R'.
\]

(5.19)

The Poisson equation:

\[
\nabla^2 \varphi_{\alpha\beta}^G(R) = \frac{1}{(2\pi)^3} \int d^3 q (-q^2 \hat{\varphi}_{\alpha\beta}^G(q)) e^{i q \cdot R} = -\frac{e_\alpha}{\epsilon_0} \rho_{\beta}^G(R),
\]

(5.20)

and Eq.(5.17) lead to

\[
\hat{\varphi}_{\alpha\beta}^G(q) = \frac{e_\alpha e_\beta}{\epsilon_0 q^2} e^{-q^2/4P}.
\]

(5.21)

Now we introduce

\[
\varphi_{\alpha\beta}^C(R) = \varphi_{\alpha\beta}^G(R) + \varphi_{\alpha\beta}^C(R) - \varphi_{\alpha\beta}^G(R) \equiv \varphi_{\alpha\beta}^G(R) + \varphi_{\alpha\beta}^H(R)
\]

(5.22)

Using Eqs.(5.15), (5.19) and \(\int_0^\infty d^3 R' \rho_{\beta}^G(R') = e_\beta\), we obtain

\[
\varphi_{\alpha\beta}^H(R) = \frac{e_\alpha e_\beta}{2\epsilon_0 \pi^{3/2}} \frac{1}{R} \int_0^\infty e^{-s^2} ds.
\]

(5.23)

Here we define

\[
\hat{V}_{\alpha\beta}^G(q) = -\sum_n e^{-i q \cdot (R_{am} - R_{an})} \frac{\partial^2}{\partial x_i \partial x_j} \{\varphi_{\alpha\beta}^G(R) + \varphi_{\alpha\beta}^H(R)\}|_{R = R_{am} - R_{an} > c}
\]

\[
\equiv \hat{V}_{\alpha\beta}^G(q) + \hat{V}_{\alpha\beta}^H(q).
\]

(5.24)
First we investigate the term \( \hat{V}^G \), which is written as

\[
\hat{V}^G_{\alpha i\beta j}(q) = -\sum_n e^{-iq\cdot(R_m-R_{\beta n})} \frac{\partial^2}{\partial x_i \partial x_j} \left\{ \frac{1}{(2\pi)^3} \int d^3q' e^{iq'\cdot \mathbf{R}} \varphi^G(q') \right\}|_{R=R_m-R_{\beta n}} > c \\
= -\sum_n e^{i(q'-q)\cdot(R_m-R_{\beta n})} \frac{e_\alpha e_\beta}{(2\pi)^3 \epsilon_0} \int q^3 q' \frac{q'_j q'_i}{q^2} e^{-q^2/4P} > c \\
= -\sum_n \int d^3q \left[ \frac{q'_j q'_i}{q^2} + \frac{q'_i q'_j}{q^2} (e^{-q^2/4P} - 1) \right] e^{i(q'-q)\cdot(R_m-R_{\beta n})} > c \\
= \frac{e_\alpha e_\beta}{(2\pi)^3 \epsilon_0 v_a} \int d^3R g_{\alpha \beta}(R) \int d^3q \left[ \frac{q'_j q'_i}{q^2} + \frac{q'_i q'_j}{q^2} (e^{-q^2/4P} - 1) \right] e^{i(q'-q)\cdot R} \\
\approx \frac{e_\alpha e_\beta \rho_\beta}{\epsilon_0 v_a} \left( \frac{q'_j q'_i}{q^2} + \frac{q'_i q'_j}{q^2} (e^{-q^2/4P} - 1) \right),
\]

where we have made the approximation; \( g_{\alpha \beta}(R) \approx \rho_\beta \) and \( v_a \) is a primitive unit cell. The term \( V^H \) is given by

\[
\hat{V}^H_{\alpha i\beta j}(q) = -\sum_n e^{-iq\cdot(R_m-R_{\beta n})} \frac{\partial^2}{\partial x_i \partial x_j} \left\{ \frac{1}{(2\pi)^3} \int d^3q' e^{iq'\cdot \mathbf{R}} \varphi^H(q') \right\}|_{R=R_m-R_{\beta n}} > c \\
= -\sum_n e^{-i(q)\cdot(R_m-R_{\beta n})} \frac{\partial^2}{\partial x_i \partial x_j} \frac{e_\alpha e_\beta}{(2\pi)^3 \epsilon_0} 1 \int_{\sqrt{PR}}^{\infty} ds e^{-s^2} |_{R=R_m-R_{\beta n}} > c \\
= \frac{e_\alpha e_\beta \rho_\beta}{(2\pi)^3 \epsilon_0 v_a} \int d^3R g_{\alpha \beta}(R) H_{ij}(\sqrt{PR}) e^{-iq\cdot R} \\
\approx \frac{e_\alpha e_\beta \rho_\beta}{(2\pi)^3 \epsilon_0 v_a} \int d^3R H_{ij}(\sqrt{PR}) e^{-iq\cdot R},
\]

\[
H_{ij}(x) \equiv \frac{\partial^2}{\partial x_i \partial x_j} \frac{2}{\sqrt{\pi}} \frac{1}{x} \int_x^{\infty} ds e^{-s^2}.
\]

It should be noted the function \( H_{ij}(x) \) is singular at \( x = 0 \). When we treat the crystalline state, \( H_{ij}(x) \) is replaced by \( H_{ij} = \frac{\partial^2}{\partial x_i \partial x_j} \frac{2}{\sqrt{\pi}} \frac{1}{x} \int_0^x ds e^{-s^2} \), because we should exclude the singularity, since the dynamical matrix includes \( R_m = R_n \). But in our case, taking into account of the spherical symmetry \( \sum_i H_{ii} = \frac{4}{\sqrt{\pi}} e^{-x^2} \) and the property of the argument of integration \( d^3R = 4\pi R^2dR \) yields the integration finite. Thus Eqs.(5.25) and (5.26) lead to

\[
V^C_{\alpha i\beta j}(q) = e_\alpha e_\beta \rho_\beta \left[ \frac{q'_j q'_i}{v_a \epsilon_0 q^2} - Q_{ij}(q) \right],
\]

\[
Q_{ij}(q) = -\frac{q'_j q'_i}{\epsilon_0 v_a} (e^{-\frac{q^2}{4P}} - 1) + \frac{p^{3/2}}{4\pi \epsilon_0 v_a} \int d^3R H_{ij}(\sqrt{PR}) e^{-iq\cdot R},
\]

where the first term and the second term in Eq.(5.28) relate to the macroscopic electric field and the Lorentz field, respectively. In the spherical symmetry, we obtain

\[
Q_{ij}(q) = \delta_{ij} Q(q) \equiv \delta_{ij} \frac{1}{3\epsilon_0 v_a}.
\]
There is the electrical charge neutrality:

$$\sum e_\alpha \rho_\alpha = 0. \quad (5.31)$$

Next we investigate the short range potential $V^N$. In order to do so, we introduce the couplings like the chemical bondings:

$$V_{\sigma\alpha\beta}(R) = - \int d^3x d^3y \nabla_{x_3} \bar{w}_{\alpha0}^2(x) V_{\alpha\beta}(x-y) \nabla_{y_3} \bar{w}_{\beta0}^2(y - Re_3), \quad (5.32)$$

$$V_{\pi\alpha\beta}(R) = - \int d^3x d^3y \nabla_{x_1} \bar{w}_{\alpha0}^2(x) V_{\alpha\beta}(x-y) \nabla_{y_3} \bar{w}_{\beta0}^2(y - Re_3). \quad (5.33)$$

Here we take $q = q e_z$ and $\xi = q R$. Since we are concerned with the spherical symmetry distribution of particles, we obtain

$$M_{\sigma\alpha\alpha}(q) = M_{\sigma\gamma\beta}(q) = - \frac{1}{M_\alpha} \int d^3R g_{\alpha\alpha}(R) \left[ V_{\sigma\alpha\alpha}(R) \left\{ - \frac{\cos \xi}{\xi^2} + \frac{\sin \xi}{\xi^3} \right\} ight]$$

$$+ \frac{1}{M_\alpha} \sum_\gamma \int d^3R g_{\alpha\gamma}(R) \left\{ \frac{V_{\sigma\alpha\gamma}(R)}{3} + \frac{2 V_{\pi\alpha\gamma}(R)}{3} \right\}, \quad (5.34)$$

$$M_{\pi\alpha\alpha}(q) = - \frac{1}{M_\alpha} \int d^3R g_{\alpha\alpha}(R) \left[ V_{\pi\alpha\alpha}(R) \left\{ \frac{\sin \xi}{\xi} + \frac{2 \cos \xi}{\xi^2} - \frac{2 \sin \xi}{\xi^3} \right\} \right]$$

$$+ \frac{1}{M_\alpha} \sum_\gamma \int d^3R g_{\alpha\gamma}(R) \left\{ \frac{V_{\sigma\alpha\gamma}(R)}{3} + \frac{2 V_{\pi\alpha\gamma}(R)}{3} \right\}, \quad (5.35)$$

$$M_{\sigma\beta\alpha}(q) = M_{\gamma\beta\gamma}(q) = - \frac{1}{M_\alpha} \frac{\zeta_\beta}{N_\alpha} \frac{\sqrt{N_\alpha}}{N_\beta} \int d^3R g_{\alpha\beta}(R)$$

$$\times \left\{ V_{\alpha\beta\alpha}(R) \left( - \frac{\cos \xi}{\xi^2} + \sin \xi \right) + V_{\alpha\beta\beta}(R) \left( \sin \xi + \frac{\cos \xi}{\xi^2} - \frac{\sin \xi}{\xi^3} \right) + \epsilon_\alpha e_\beta \rho_\beta \frac{2}{3 \epsilon_0 v_a} \right\}, \quad (5.36)$$

$$M_{\pi\beta\alpha}(q) = - \frac{1}{M_\alpha} \frac{\zeta_\beta}{N_\alpha} \frac{\sqrt{N_\alpha}}{N_\beta} \int d^3R g_{\alpha\beta}(R) \left\{ V_{\alpha\beta\alpha}(R) \left( \frac{\sin \xi}{\xi} + \frac{2 \cos \xi}{\xi^2} - \frac{2 \sin \xi}{\xi^3} \right) \right.$$

$$\left. + V_{\pi\alpha\beta}(R) \left( - \frac{2 \cos \xi}{\xi^2} + \frac{2 \sin \xi}{\xi^3} \right) \right\} - \epsilon_\alpha e_\beta \rho_\beta \frac{2}{3 \epsilon_0 v_a}, \quad (5.37)$$
where the other terms are zero. Since we have taken \( q = q e_3 \), the z-component of the dynamical matrix corresponds to the longitudinal mode and x and y-components to the transverse modes. It should be noted that the dynamical matrices have the effects of the electric polarization in the last term in the curly brackets. But because of the charge neutrality (5.31), the last terms in Eqs.(5.34) and (5.35) do not have the effect of the polarization.

The secular equation of Eq.(5.2) leads to

\[
\{q_0(q_0 + \frac{i}{\tau_{OM}}) - M_{OIOI}(q)\} \{q_0(q_0 + \frac{i}{\tau_{HM}}) - M_{HHHI}(q)\} - M_{OHII}(q)M_{HIOI}(q) = 0, \quad (5.38)
\]

where \( i = z \) corresponds to a longitudinal mode and \( i = x, y \) to two transverse modes.

Now we investigate the secular equation (5.38) in the two limiting cases:

(I) \( q_0\tau_\alpha \gg 1 \):

We obtain phonon modes

\[
q_0^2 = \omega^2_{i\pm}(q)
= \frac{1}{2} \left[ M_{OIOI}(q) + M_{HHHI}(q) \pm \sqrt{M_{OIOI}(q) - M_{HHHI}(q)}^2 + 4M_{OHII}(q)M_{HIOI}(q) \right].
\]

(5.39)

Note that the term \( M_{\alpha i \alpha i} \) consists of the \( \alpha \)th individual phonon frequency and the frequency shift due to the coupling of particles with different masses, whereas \( M_{\alpha i \beta i} \) plays a role in the mixing between the individual phonon frequencies.

Next we investigate the phonon frequencies in the two limiting cases: First we introduce

\[
v^{(n)}_{\sigma \alpha} \equiv \frac{1}{M_{\alpha}} \int d^3R g_{\alpha\alpha}(R) \frac{V_{\sigma\alpha\alpha}}{3} \zeta^n, \quad v^{(n)}_{\pi \alpha} \equiv \frac{1}{M_{\alpha}} \int d^3R g_{\alpha\beta}(R) \frac{2V_{\pi\alpha\beta}}{3} \zeta^n, \quad v^{(2)}_{\sigma \alpha} \equiv \frac{1}{M_{\alpha}} \int d^3R g_{\alpha\alpha}(R) \frac{2V_{\sigma\alpha\alpha}}{3} \zeta^n, \quad v^{(2)}_{\pi \alpha} \equiv \frac{1}{M_{\alpha}} \int d^3R g_{\alpha\beta}(R) \frac{2V_{\pi\alpha\beta}}{3} \zeta^n, \quad (5.40)
\]

\[
c_{\alpha} \equiv \frac{1}{M_{\alpha}} e^2 \rho_{\alpha} \frac{1}{3\epsilon_0 v_a}, \quad (5.41)
\]

(i) \( qR = \xi \ll 1 \)

If we define as

\[
A_{at} \equiv A_{ax} = A_{ay} \equiv v^{(0)}_{\sigma \alpha} + v^{(0)}_{\pi \alpha} - c_{\alpha} \equiv A_{\alpha} - c_{\alpha}, \quad B_{at} \equiv B_{ax} = B_{ay} \equiv \frac{v^{(2)}_{\sigma \alpha}}{10} + \frac{v^{(2)}_{\pi \alpha}}{5},
\]

\[
A_{al} \equiv A_{az} \equiv v^{(0)}_{\sigma \alpha} + v^{(0)}_{\pi \alpha} + 2c_{\alpha} \equiv A_{\alpha} + 2c_{\alpha}, \quad B_{al} \equiv B_{az} \equiv \frac{3v^{(2)}_{\sigma \alpha}}{10} + \frac{v^{(2)}_{\pi \alpha}}{10},
\]

\[
B'_{at} \equiv B'_{ax} = B'_{ay} \equiv \frac{v^{(2)}_{\sigma \alpha}}{10} + \frac{v^{(2)}_{\pi \alpha}}{5}, \quad B'_{al} \equiv B'_{az} \equiv \frac{3v^{(2)}_{\sigma \alpha}}{10} + \frac{v^{(2)}_{\pi \alpha}}{10}, \quad (5.42)
\]
we obtain

\[
M_{\alpha\alpha x} = M_{\alpha\alpha y} = A_{\alpha} + B_{\alpha} = A_{\alpha} + B_{\alpha} - c_{\alpha},
\]

\[
M_{\alpha\alpha x} = A_{\alpha} + B_{\alpha} = A_{\alpha} + B_{\alpha} + 2c_{\alpha},
\]

\[
M_{\alpha\alpha x} = M_{\alpha\alpha y} = \frac{\zeta_{\beta}}{\zeta_{\alpha}} \sqrt{\frac{N_{\alpha}}{N_{\beta}}} \{-A_{\alpha} + B'_{\alpha}\} = \frac{\zeta_{\beta}}{\zeta_{\alpha}} \sqrt{\frac{N_{\alpha}}{N_{\beta}}} \{-A_{\alpha} + B'_{\alpha} + c_{\alpha}\},
\]

\[
M_{\alpha\alpha z} = \frac{\zeta_{\beta}}{\zeta_{\alpha}} \sqrt{\frac{N_{\alpha}}{N_{\beta}}} \{-A_{\alpha} + B'_{\alpha}\} = \frac{\zeta_{\beta}}{\zeta_{\alpha}} \sqrt{\frac{N_{\alpha}}{N_{\beta}}} \{-A_{\alpha} + B'_{\alpha} - 2c_{\alpha}\}. \tag{5.43}
\]

In the long wavelength limit, we obtain the phonon frequencies:

\[
q_{0}^{2} = \omega_{l_{\pm}}^{2}(q)
\]

\[
= \left\{ \begin{array}{l}
A_{O} + A_{H} - c_{O} - c_{H} + \frac{2A_{O} - 2c_{O}}{A_{O} + A_{H} - c_{O} - c_{H}}(B_{01} - B'_{01}) + \frac{2A_{H} - 2c_{H}}{A_{O} + A_{H} - c_{O} - c_{H}}(B_{01} - B'_{01}),
\frac{2A_{O} - 2c_{O}}{A_{O} + A_{H} - c_{O} - c_{H}}(B_{01} + B'_{01}) + \frac{2A_{H} - 2c_{H}}{A_{O} + A_{H} - c_{O} - c_{H}}(B_{01} + B'_{01}).
\end{array} \right.
\tag{5.44}
\]

\[
q_{0}^{2} = \omega_{l_{\pm}}^{2}(q)
\]

\[
= \left\{ \begin{array}{l}
A_{O} + A_{H} + 2c_{O} + 2c_{H} + \frac{2A_{O} + 4c_{O}}{A_{O} + A_{H} + 2c_{O} + 2c_{H}}(B_{01} - B'_{01}) + \frac{2A_{H} + 4c_{H}}{A_{O} + A_{H} + 2c_{O} + 2c_{H}}(B_{01} - B'_{01}),
\frac{2A_{O} + 4c_{O}}{A_{O} + A_{H} + 2c_{O} + 2c_{H}}(B_{01} + B'_{01}) + \frac{2A_{H} + 4c_{H}}{A_{O} + A_{H} + 2c_{O} + 2c_{H}}(B_{01} + B'_{01}).
\end{array} \right.
\tag{5.45}
\]

\(\omega_{q+}\) are the optical modes and \(\omega_{q-}\) the acoustic modes. The velocities of the acoustic phonons are given by

\[
v_{l} = \sqrt{\frac{2A_{O} - 2c_{O}}{A_{O} + A_{H} - c_{O} - c_{H}}(B_{01} + B'_{01}) + \frac{2A_{H} - 2c_{H}}{A_{O} + A_{H} - c_{O} - c_{H}}(B_{01} + B'_{01}) \frac{1}{q}} \tag{5.46}
\]

\[
v_{l} = \sqrt{\frac{2A_{O} + 4c_{O}}{A_{O} + A_{H} + 2c_{O} + 2c_{H}}(B_{01} + B'_{01}) + \frac{2A_{H} + 4c_{H}}{A_{O} + A_{H} + 2c_{O} + 2c_{H}}(B_{01} + B'_{01}) \frac{1}{q}} \tag{5.47}
\]

(ii) \(qR \gg 1\):

In the short wavelength limit, we obtain

\[
M_{\alpha\alpha x} = M_{\alpha\alpha y} = v_{(0)}^{(0)} + v_{(0)}^{(0)} + v_{(0)}^{(0)} + v_{(0)}^{(0)} - c_{\alpha} \equiv S_{\alpha} - c_{\alpha},
\]

\[
M_{\alpha\alpha z} = v_{(0)}^{(0)} + v_{(0)}^{(0)} + v_{(0)}^{(0)} + v_{(0)}^{(0)} + 2c_{\alpha} \equiv S_{\alpha} + 2c_{\alpha}
\]

\[
M_{\alpha\beta x} = M_{\alpha\beta y} = \frac{\zeta_{\beta}}{\zeta_{\alpha}} \sqrt{\frac{N_{\alpha}}{N_{\beta}}} c_{\alpha}
\]

\[
M_{\alpha\beta z} = \frac{\zeta_{\beta}}{\zeta_{\alpha}} \sqrt{\frac{N_{\alpha}}{N_{\beta}}} (-2c_{\alpha}), \tag{5.48}
\]

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Then we obtain
\[ q_0^2 = \omega_{\pm}(q) = \frac{1}{2}\{S_O + S_H - c_O - c_H \pm \sqrt{(S_O - S_H - c_O + c_H)^2 + 4c_O c_H}\}, \quad (5.49) \]
\[ q_0^2 = \omega_0(q) = \frac{1}{2}\{S_O + S_H + 2c_O + 2c_H \pm \sqrt{(S_O - S_H + 2c_O - 2c_H)^2 + 16c_O c_H}\}, \quad (5.50) \]
These modes correspond to the boson peaks, where the density of states has peaks. In nonpolarized liquids, because of \(c_o = 0\) the corresponding logitudinal and transverse frequencies and the boson peaks are of the same.

Next we investigate the secular equation (5.38) in the low frequency regime:

(II) \(\eta\alphaM \ll 1\)

Eq.(5.38) leads to
\[ (q_0 + i\tau_\alpha M_{\alpha i})(q_0 + i\tau_\beta M_{\beta j}) - i\tau_\alpha M_{\alpha i} i\tau_\beta M_{\beta j} = 0. \quad (5.51) \]
Thus we obtain the dissipative modes due to viscosity
\[ q_0 = \frac{i}{2}[\tau_\alpha M_{\alpha O i} + \tau_\beta M_{\beta H i} - \sqrt{(\tau_\alpha M_{\alpha O i} - \tau_\beta M_{\beta H i})^2 + 4\tau_\alpha M_{\alpha O i} \tau_\beta M_{\beta H i} \tau_\alpha M_{\alpha H i} \tau_\beta M_{\beta O i}}] \approx i\frac{2\tau_\alpha M_{\alpha O i}}{\tau_\alpha M_{\alpha O i} + \tau_\beta M_{\beta H i}} \tau_{\alpha O M} (B_{\alpha i} + B'_{\alpha i}) + i\frac{2\tau_\beta M_{\beta H i}}{\tau_\alpha M_{\alpha O i} + \tau_\beta M_{\beta H i}} \tau_{\beta O M} (B_{\beta i} + B'_{\beta i}), \quad (5.52) \]
where the modes corresponding to the optical modes disappear because of the large imaginary value. We should not confuse the imaginary number \(i\) and the suffices \(i\); the \(i\) in front of the terms means the imaginary number, but \(i\) in the suffices means the component of the coordinates. Thus viscosities are given by
\[ \eta_{\alpha} = \sqrt{\frac{2\tau_\alpha M_{\alpha O i} - \tau_\beta M_{\beta H i}}{\tau_\alpha M_{\alpha O i} + \tau_\beta M_{\beta H i}} \tau_{\alpha O M} (B_{\alpha i} + B'_{\alpha i})}, \quad (5.53) \]
\[ \eta_{\beta} = \sqrt{\frac{2\tau_\beta M_{\beta O i} - \tau_\alpha M_{\alpha H i}}{\tau_\alpha M_{\alpha O i} + \tau_\beta M_{\beta H i}} \tau_{\beta O M} (B_{\beta i} + B'_{\beta i})}, \quad (5.54) \]
where \(\eta_{\alpha}\) and \(\eta_{\beta}\) correspond to longitudinal and transverse acoustic phonons, respectively.

6 The Kauzmann paradox and the VTF law; specific heat, relaxation times and transport coefficients

First, we investigate the entropy due to intra-band density fluctuations. Since sound depends on the temperature, we must start with the interaction Hamiltonian. Here we consider the thermodynamical function. We introduce the Hamiltonian with a parameter \(\lambda\) [57][L8]:
\[ H(\lambda) = H_0 + \lambda H_I. \quad (6.1) \]
The thermodynamical function \(\Omega_\lambda\) for the above Hamiltonian is given by
\[ \Omega_\lambda = -\frac{1}{\beta} \ln\{\text{Tr}e^{-\beta(H_0 - \mu N + \lambda H_I)}\}. \quad (6.2) \]
Here we calculate the thermodynamical function due to intra-band density fluctuations denoted by $\Omega_{\text{ intra} \lambda}$. From Eq.(2.13), we obtain
\[
\frac{\partial \Omega_{\text{ intra} \lambda}}{\partial \lambda} = \frac{1}{\lambda} < \lambda H_\lambda >_\lambda \approx \frac{1}{2} \sum_q \frac{1}{\sqrt{N_\alpha N_\beta}} V_{\alpha \beta}(q) < \rho_{\alpha 0 q}^* \rho_{\beta 0 q} >_\lambda, \\
= -\frac{1}{2\beta} \sum_{\alpha \beta q} V_{\alpha \beta}(q) F_{\beta \alpha}^\lambda(q),
\tag{6.3}
\]
where $< \cdots >_\lambda$ and $F_{\gamma \lambda}(q)$ are calculated by $H_\gamma$ replaced by $\lambda H_\gamma$ in $< \cdots >_\epsilon$ and $F(q)$. Replacing $V_{\alpha \beta}(q)$ by $\lambda V_{\alpha \beta}(q)$ into Eq.(6.3), neglecting the $\lambda$-dependence of $P_\alpha(q)$ because of the condition $\beta \hbar |J_\mu| \ll 1$ in Eq.(4.3), we obtain
\[
\sum_{\gamma} \{\delta_{\alpha \gamma} - P_\alpha(q)\lambda V_{\alpha \gamma}(q)\} F_{\gamma \beta}^\lambda(q) = P_\alpha(q)\delta_{\alpha \beta}.
\tag{6.4}
\]
Eq.(6.4) leads to
\[
\begin{pmatrix}
F_{\alpha 0}^\lambda \\
F_{\beta 0}^\lambda \\
F_{\gamma \alpha}^\lambda
\end{pmatrix} = \frac{1}{\det \mid |} \begin{pmatrix}
(1 - \lambda P_H V_{HH}) P_O & \lambda P_O V_{OH} P_H \\
\lambda P_H V_{HO} P_H & (1 - \lambda P_O V_{OO}) P_H
\end{pmatrix},
\tag{6.5}
\]
\[
\det \mid | = (1 - \lambda P_O V_{OO})(1 - \lambda P_H V_{HH}) - \lambda^2 P_O V_{OH} P_H V_{HO}.
\tag{6.6}
\]
Thus Eq.(6.3) yields
\[
\frac{\partial \Omega_{\text{ intra} \lambda}}{\partial \lambda} = -\frac{1}{2\beta} \sum_q \frac{(1 - \lambda P_H V_{HH}) P_O V_{OO} + (1 - \lambda P_O V_{OO}) P_H V_{HH} + 2\lambda P_O P_H V_{OH} V_{HO}}{(1 - \lambda P_O V_{OO})(1 - \lambda P_H V_{HH}) - \lambda^2 P_O P_H V_{OH} V_{HO}}
\]
\[
= \sum_q \frac{\partial}{\partial \lambda} \ln\{1 - \lambda P_O V_{OO})(1 - \lambda P_H V_{HH}) - \lambda^2 P_O P_H V_{OH} V_{HO}\}
\tag{6.7}
\]
Integrating Eq.(6.7) in $\lambda$ and putting $\lambda \to 1$, we obtain the thermodynamical function due to the intra-band density fluctuations, $\Omega_{\text{ intra}}$:
\[
\Omega_{\text{ intra}} = \sum_{\nu_{\alpha q}} \ln\{1 - P_O V_{OO})(1 - P_H V_{HH}) - P_O P_H V_{OH} V_{HO}\} + \Omega_{\text{ intra} 0},
\tag{6.8}
\]
where the term $\Omega_{\text{ intra} 0}$ comes from the initial condition. In order to calculate the entropy we neglect $1/\tau_0$ terms under the condition $\beta \hbar /\tau_0 \ll 1$ and we put $q_0 \to i v_n$. From Eq.(4.3), $P_\alpha(q) = \beta (\omega_n^0)^2/(iv_n^2 - (\omega_{0 q}^0)^2)$, we obtain
\[
\Omega_{\text{ intra}} = \sum_q \ln\{1 - (iv_n^2 - \omega_0^2(q))(iv_n^2 - \omega_0^2(q) - \beta^2(\omega_{0 q}^0)^2(\omega_{0 q}^0)^2 V_{OH} V_{HO}) + \Omega_{\text{ intra} 0}
\]
\[
= \sum_q \ln\{1 - (iv_n^2 - \omega_0^2(q))(iv_n^2 - \omega_0^2(q) - \beta^2(\omega_{0 q}^0)^2(\omega_{0 q}^0)^2 V_{OH} V_{HO}) + \Omega_{\text{ intra} 0}
\tag{6.9}
\]
The Contour integration of Eq.(6.9) gives
\[ \Omega_{\text{intra}} = \frac{1}{\beta} \sum_{\mathbf{q}} \left[ \ln(1 - e^{-\beta \hbar \omega_+ (q)}) (1 - e^{-\beta \hbar \omega_- (q)}) - \ln(1 - e^{-\beta \hbar \omega^0_{\mathbf{q}}}) (1 - e^{-\beta \hbar \omega^0_{\mathbf{q}}}) \right] + \Omega_{\text{intra}0}. \] (6.10)
\[ \Omega_{\text{intra}0} = \frac{1}{\beta} \sum_{\mathbf{q}} \ln(1 - e^{-\beta \hbar \omega^0_{\mathbf{q}}}), \] (6.11)
where we have neglected the term \( \frac{1}{2} \sum_{\mathbf{q}} (\hbar \omega_{\mathbf{q}} - \hbar \omega^0_{\mathbf{q}}). \) The first, the second and the third terms in Eq.(6.10) correspond to the thermodynamical function for the sound, the fluctuations due to the bubbles of the intra-band elementary excitations and the dissipation due to the diffusion, respectively. The third term compensates the second term and the system becomes a local equilibrium. From the instability of sound, Eq.(4.27), the dominant contribution of the temperature dependence to the thermodynamical function in the first and the second terms comes from the regions \( q \sim \tilde{K}. \) We separate the region of wavevector \( q \) into the number of states \( N_0 \) near \( \tilde{K} \) and the remaining part. Using \( \beta \hbar \omega_{\pm} (q), \beta \hbar \omega^0_{\mathbf{q}} \ll 1 \) under the condition \( \beta \hbar |J_\mu| \ll 1, \) we obtain
\[ \Omega_{\text{intra}} \approx \frac{N_0}{\beta} \ln \frac{\omega_+ (\tilde{K}) \omega_- (\tilde{K})}{\omega^0_{\mathbf{q}} \omega^0_{\mathbf{q}}} + \Omega'_{\text{sound}} \]
\[ \Omega_{\text{intra}} = \frac{N_0}{\beta} \ln \sqrt{\frac{\omega_0 (\tilde{K})^2 \omega_H (\tilde{K})^2 - \beta^2 (\omega^0_{\mathbf{q}})^2 \omega^0_{\mathbf{q}}^2 V_{\text{OH}} (\tilde{K}) V_{\text{HO}} (\tilde{K})}{(\omega^0_{\mathbf{q}})^2 \omega^0_{\mathbf{q}}^2}} + \Omega'_{\text{sound}} \]
\[ \Omega'_{\text{sound}} = \frac{1}{\beta} \sum_{\mathbf{q}}' \ln(1 - e^{-\beta \hbar \omega_+ (q)}) + \ln(1 - e^{-\beta \hbar \omega_- (q)}), \] (6.12)
where the prime on \( \Omega_{\text{sound}} \) and \( \Sigma \) means that the region of the wavevector \( \mathbf{q} \) is limited in the remaining region with the number of states \( N - N_0 \) excluding the region with the number of states \( N_0 \) near \( \tilde{K} \). Now we investigate the first term of Eq.(6.12) using Eq.(4.27).
\[ (1 + \beta V_{\text{OO}} (\tilde{K}))(1 + \beta V_{\text{HH}} (\tilde{K})) - \beta^2 V_{\text{OH}} (\tilde{K}) V_{\text{HO}} (\tilde{K}) \]
\[ = \{1 - \frac{T_0}{T}\} \{1 + \frac{T_0 - (V_{\text{OO}} (\tilde{K}) + V_{\text{HH}} (\tilde{K}))}{T}\} \]
\[ \approx (1 - \frac{T_0}{T})(2 - \frac{V_{\text{OO}} (\tilde{K}) + V_{\text{HH}} (\tilde{K})}{T_0}) \] (6.14)
Thus we obtain
\[ \Omega_{\text{intra}} \approx \frac{N_0}{2\beta} \ln\{1 - \frac{T_0}{T}\} + \Omega'_{\text{sound}}, \] (6.15)
where we have neglected the constant term, which does not contribute to entropy. Note that the dissipation compensates the fluctuation entropy in the remaining region with the
number of states $N - N_0$. The entropy due to the intra-band density fluctuations, $S_{\text{intra}}$, is given by

$$S_{\text{intra}} = S_K + S'_{\text{sound}},$$

$$S_K \approx -\frac{N_0 k_B}{2} \frac{T_0}{T - T_0},$$

$$S'_{\text{sound}} \approx -k_B \sum_q \left\{ \ln(1 - e^{-\beta \omega_{\pm+}(q)}) + \ln(1 - e^{-\beta \omega_{\pm-}(q)}) \right\} + \frac{1}{T} \sum_q \left\{ \frac{\hbar \omega_{\pm+}(q)}{e^{\beta \omega_{\pm+}(q)} - 1} + \frac{\hbar \omega_{\pm-}(q)}{e^{\beta \omega_{\pm-}(q)} - 1} \right\}. \tag{6.18}$$

$S_K$ manifests the Kauzmann crisis. We call $S_K$ the Kauzmann entropy.

A state of $N$-particles distributed randomly in space corresponds to a minimum of $N$-particle potential in a configuration space. A hopping of a particle from a site to a vacancy corresponds to a jump from a deep valley to another deep valley in the multi-dimensional configuration space in the energy landscape model (ELM) as the $\alpha$-relaxation process. The successive hoppings constitute a configuration space. A hopping also generates intra-band elementary excitations and the successive hoppings yield the fluctuation entropy $S_K$ due to the intra-band density fluctuations. The hopping probability is proportional to the configuration number, which is $e^{S_K/k_B}$ from the Einstein relation. The hopping probability of a particle is given uniquely by the hopping amplitude:

$$J = e^{i S_K} = e^{\frac{i E}{N k_B}}, \tag{6.19}$$

where $E = z N_0 T_0 / 2N$ and $z$ is of the order of the number of the surrounding H$_2$O molecules. This equation manifests the Vogel-Tamman-Fulcher (VTF) law. The sound $\omega_{\pm}$ consists of the individual sound frequencies $\omega_0(q)$ and $\omega_H(q)$. As seen in the first terms on the right hand side of the first line in Eq.(6.12), the mixing between the entropy of sound $\omega_{\pm}$ and the fluctuation entropy due to the intra-band elementary excitations $\omega^0_{\Omega q}$ and $\omega^0_{H q}$ yields a unique hopping amplitude $J$. This fact originates from the temperature-dependent sound. Thus $J$ governs all individual quantities $v_{\alpha}$ and $J_{\alpha \mu}$. Then we can put

$$|J_{\alpha \mu}| \propto J, \tag{6.20}$$

$$\sqrt{U_{\alpha \mu}^{\text{Rab}}} \propto J. \tag{6.21}$$

Since all $J_{\alpha \mu}$ are governed by a unique $J$, we can regard $z$ as the order of the number of the surrounding H$_2$O molecules. It should be noted that the hopping $J$ generates the intra-band elementary excitations, the sound $\omega_{\pm}(q)$ and the Kauzmann entropy $S_K$, while $S_K$ determines $J$ in Eq.(6.19). Thus $\omega_{\pm}(q)$ in Eq.(4.23) is self-consistently determined.

Next we investigate the entropy due to inter-band density fluctuations. The thermodynamical function due to the inter-band density fluctuations is given in a similar manner to the sound:

$$\Omega_{\text{inter}} = \frac{1}{2 \beta} \sum_{\lambda q} \ln \left\{ \frac{(i \nu_n^2 - \omega_{\lambda+}^2(q))(i \nu_n^2 - \omega_{\lambda-}^2(q))}{(i \nu_n^2 - \omega_0^2)(i \nu_n^2 - \omega_H^2)} \right\} + \Omega_{\text{inter0}},$$

$$= \frac{1}{\beta} \sum_{\lambda q} \left\{ \ln(1 - e^{-\beta \omega_{\lambda+}(q)})(1 - e^{-\beta \omega_{\lambda-}(q)}) - \ln(1 - e^{-\beta \omega_0})(1 - e^{-\beta \omega_H}) \right\} + \Omega_{\text{inter0}}, \tag{6.22}$$
\[ \Omega_{\text{inter0}} = \frac{1}{\beta} \sum_{\lambda q} \ln(1 - e^{-\beta \hbar \omega_{\lambda}})(1 - e^{-\beta \hbar \omega_{\nu}}) \]  

(6.23)

where we have neglected the term \( \frac{1}{2} \sum_{\lambda q} (\hbar \omega_{\lambda} - \hbar \omega) \). The entropy due to the inter-band density fluctuations is given by

\[ S_{\text{inter}} = S_{\text{phonon}} + S_{\Omega} - S_{\Omega}, \quad S_{\Omega} = S_{\Omega_\alpha} + S_{\Omega_H}, \]  

(6.24)

\[ S_{\text{phonon}} = -k_B \sum_{\lambda q} [\ln(1 - e^{-\beta \hbar \omega_{\lambda+}(q)}) + \ln(1 - e^{-\beta \hbar \omega_{\lambda-}(q)})] + \frac{1}{T} \sum_{\lambda q} \left[ \frac{\hbar \omega_{\lambda+}(q)}{e^{\beta \hbar \omega_{\lambda+}(q)} - 1} + \frac{\hbar \omega_{\lambda-}(q)}{e^{\beta \hbar \omega_{\lambda-}(q)} - 1} \right]. \]  

(6.25)

\[ S_{\Omega_\alpha} = k_B \sum_{\lambda q} \ln(1 - e^{-\beta \hbar \omega_{\alpha}}) - \frac{1}{T} \sum_{\lambda q} \frac{\hbar \omega_{\alpha}}{e^{\beta \hbar \omega_{\alpha}} - 1}. \]  

(6.26)

In Eq. (6.24), the first, the second and the third terms correspond to the entropies for the phonons, the fluctuations due to the bubbles of inter-band elementary fluctuations and the dissipation due to the viscosity, respectively. In this case compared with the Kauzmann entropy, the phonon entropy and the fluctuation entropy do not mix. This fact originates from the temperature-independent phonons. The fluctuation entropy lowers the equilibrium entropy, but the dissipative entropy compensates the fluctuation entropy and the system becomes to a local equilibrium.

A propagation of an up and down transition at a site to a surrounding site corresponds to a jump of a shallow valley to another shallow valley in the multi-dimensional configuration space in the ELM as the \( \beta \)-relaxation process. The successive propagations constitute another configuration space different from hoppings. The probability of the magnitude of the randomness of harmonic frequencies of \( \alpha \)-particles is proportional to the configuration number \( e^{S_{\Omega_\alpha}/k_B} \). The probability of the magnitude of randomness of the harmonic frequency of an \( \alpha \)-particle is proportional to

\[ \Omega_{\alpha} = e^{z_{\alpha} S_{\Omega_\alpha}/Nk_B} = \exp\{-3z_{\alpha}\beta \hbar \omega_{\alpha}/(e^{\beta \hbar \omega_{\alpha}} - 1)\}, \]  

(6.27)

where \( z_{\alpha} \) is of the order of the \( \alpha \)-surrounding particles of an \( \alpha \)-particles. Thus we obtain

\[ \sqrt{U_\alpha^\mu \nu} \propto \Omega_{\alpha}. \]  

(6.28)

The Kauzmann entropy \( S_K \) diverges negatively at \( T_0 \) so that the system seems to occur the entropy crisis. But the inter-band fluctuation entropy \( S_\Omega \) crosses \( S_K \) above \( T_0 \) and prevents the crisis. The Kauzmann entropy \( S_K \) dominates above the crossover temperature, but the fluctuation entropy \( S_\Omega \) dominates below the crossover temperature. But below the crossover temperature, the dissipative entropy compensates the \( S_\Omega \) completely. We can identify the crossover temperature with the liquid-glass transition temperature \( T_g \):

\[ S_K = S_{\Omega}|_{T=T_g}. \]  

(6.29)

Sound is a collision wave essential in a fluid, while phonons are elastic waves essential in a solid. The glass transition is a sort of dynamical transition.
Next we investigate the specific heat. First, we calculate the specific heat due to the entropy of the intra-band density fluctuations, which consists of the Kauzmann entropy $S_K$ and the entropy due to the conventional sound, $S_{\text{sound}}'$. The specific heat due to $S_K$, $C_K$ is given by

$$C_K = \begin{cases} \frac{N k_B T}{T_0} & \text{for } T_g < T \\ 0 & \text{for } T < T_g \end{cases}$$

(6.30)

The specific heat due to the sound, $C_{\text{sound}}'$ is given by

$$C_{\text{sound}}' = \frac{k_B}{4} \sum_q \left[ \frac{\langle (\beta \hbar \omega_\alpha(q))^2 \rangle}{\sinh^2 \frac{\beta \hbar \omega_\alpha(q)}{2}} + \frac{\langle (\beta \hbar \omega_\beta(q))^2 \rangle}{\sinh^2 \frac{\beta \hbar \omega_\beta(q)}{2}} \right] \approx k_B (N - N_0),$$

(6.31)

where we have used the relation $\beta \hbar \omega_{\pm}(q) \ll 1$. $C_{\text{sound}}'$ remains $k_B (N - N_0)$: constant around the liquid-glass transition $T_g$. Eqs.(6.30,31) shows the gap of specific heat at $T_g$.

Next we investigate the specific heat due to the inter-band density fluctuations. In this case, since the inter-band fluctuation entropy cancels with the dissipative entropy, there remains only the specific heat of phonons. This is because the structure of the phonons does change little above and below the glass transition, while the structure of the sound essentially depends on the temperature. We obtain the conventional specific heat of phonons, $C_{\text{phonon}}$ as

$$C_{\text{phonon}} = \frac{k_B}{4} \sum_{\lambda q} \left[ \frac{\langle (\beta \hbar \omega_\lambda^+(q))^2 \rangle}{\sinh^2 \frac{\beta \hbar \omega_\lambda^+(q)}{2}} + \frac{\langle (\beta \hbar \omega_\lambda^-(q))^2 \rangle}{\sinh^2 \frac{\beta \hbar \omega_\lambda^-(q)}{2}} \right].$$

(6.32)

At low temperatures, $C_{\text{phonon}} \propto T^3$.

Now, we investigate the VTF law on the transport coefficients, the relaxation times and the velocities of the modes.

(i) $T_0 < T$:

The velocities of the particles and the sound only depend on $J_{\alpha_0}$, so we obtain

$$v_{\alpha_0}, v_{s_\pm} \propto J, \quad v_{\lambda_\pm} \approx \text{constant}.$$  

(6.33)

Here it should be noted the phonon velocities $v_{\lambda_\pm}$ is constant.

(ii) $T_0 < T_g < T$:

The term $\sqrt{U_{\alpha_\mu}} \propto J_{\alpha_\mu}$ dominates; the $\alpha$-relaxation. We obtain

$$\tau_{\alpha_0}^{-1}, \tau_{\alpha M}^{-1} \propto J.$$ 

(6.34)

If we consider Eqs.(6.33), (6.34) and diffusivity in (4.30) and viscosity $\eta_{\lambda}$ in Eqs.(5.53) and (5.54), we obtain

$$D^\pm, \eta_{\lambda}^{-1} \propto J.$$ 

(6.35)

It should be noted that the sound velocity $v_{s_\pm} \propto J$ in Eq.(6.33) plays an essential role in the diffusivity $D^\pm$. Eq.(6.35) satisfies the Stokes law.

(iii) $T_0 < T < T_g$:

The term $\sqrt{U_{\omega_\mu}} \propto \Omega_\alpha$ dominates; the $\beta$-relaxation. Thus we obtain

$$\tau_{\alpha_0}^{-1}, \tau_{\alpha M}^{-1} \propto \Omega,$$

$$D^\pm \propto J^2, \quad \eta_{\lambda} \propto \Omega^{-1}.$$ 

(6.36)

(6.37)

In this regime there remains little diffusion.
7 Concluding Remarks

We have calculated the sound and the diffusion from intra-band density fluctuations, and the phonons and the viscosity from inter-band density fluctuations in water taking into account of the interaction potentials $V_{OO}$, $V_{HH}$ and $V_{OH}$, where we have included the pair distribution functions $g_{OO}$, $g_{HH}$, and $g_{OH}$. The terms $V_{OH}$ consists of $V_{OH}^{hcb}$ and $V_{OH}^{hb}$, where the pair distribution function of which are given by $g_{hcb}^{OH}$ and $g_{hb}^{OH}$, respectively.

In water the hydrogen bonding plays an essential role in constructing the hydrogen bonding network. But in the nearest neighbour approximation the $\langle V_{OH}V_{HO} \rangle_c$ includes the unphysical terms such as $V_{hcb}^{hcb}$ and $V_{hb}^{hb}$. Since we concentrate ourselves to the hydrogen bonding network, we have taken into account of only the physical terms, $V_{hcb}^{hcb}$ and $V_{hb}^{hb}$, having confirmed that when the term $V_{OH}V_{HO}$ appears, $V_{OH}V_{HO}$ should be replaced by $V_{hcb}^{hcb}V_{HC} + V_{hb}^{hb}V_{HC}$.

In water the interaction potential $V_{OH}^{hb}$ and the pair distribution function $g_{hb}^{OH}$ are the most important. The peak of $g_{hb}^{OH}$ relates to the hydrogen bonding, which clusters water molecules. Thus the sound instability occurs at a reciprocal particle distance corresponding to a hydrogen bond length $\tilde{K} \approx \tilde{K}_{hb}^{OH}$. If the magnitude of $V_{OH}^{hb}(a_{OH})$ is large enough compared with the magnitude $V_{OO}(a_{OO})$ and $V_{HH}(a_{HH})$, the $\omega_{s-}(q)$ and $v_{s-}$ in Eqs.(4.23), (4.24), and the diffusion coefficient $D^-$ in Eq.(4.30) disappear.

In the term $V_{HH}$ we have taken into account of the interaction between hydrogens in different water molecules so that the term relates to the hopping of hydrogens. Since we neglect the interaction between hydrogens in the same water molecule counting the number of hydrogens, $2N$, in phonons we obtain the 3-acoustic modes, and the 3-optical modes which are doubly degenerate. Since the number of hydrogens in a water molecules is 2, if we include the interaction between hydrogens in the same water molecule, the degenerate 3-optical phonon modes split into 6-optical ones.

We have elucidated the Kauzmann paradox on the entropy crisis which originates from the sound instability at a reciprocal particle distance $\tilde{K} \approx \tilde{K}_{hb}^{OH}$ corresponding to a hydrogen bond length and at an instability temperature $T_0$. The Kauzmann entropy $S_K$ originates from the mixing between the sound and the intra-band fluctuation entropies which determine a unique hopping amplitude $J$. $J$ governs the velocities $v_\alpha$ and the hopping amplitudes $J_{\mu\alpha}$ for the individual particles and sound velocity. But the relative magnitude of the individual particle velocities are determined by the coupling strength in Eq.(2.8). On the other hand, since the mixing between the phonon and inter-band fluctuation entropies does not occur, the inter-band fluctuation entropies for the individual particles $S_{\Omega_{\alpha}}$ are independent. Thus the inter-band fluctuation entropy $S_{\Omega} = S_{\Omega_{\alpha}} + S_{\Omega_{hv}}$ prevents the Kauzmann entropy crisis at $T_g$. Below $T_g$ the remaining intra-band fluctuation entropy free from the mixing and the inter-band fluctuation entropy are compensated by the dissipative entropy due to diffusion and viscosity, respectively; there remain the sound entropy only with the remaining number of states $N - N_0$ free from the mixing, and the complete phonon entropy.

We have elucidated the VTF law on the relaxation times and the transport coefficients taking into account of the random scattering processes due to the random hopping amplitudes and the random harmonic frequencies. The random hopping amplitudes determine the VTF law and the $\alpha$-relaxation, while the random harmonic frequencies determine the
\(\beta\)-relaxation.

We have calculated phonons and viscosity taking into account of the electric polarization. Since the electric polarization relates to the p-states of particles, the electric polarization connects the inter-band density fluctuations and does not connects the intra-band density fluctuations. The effect of the electric polarization on phonon modes is to separate the longitudinal and transverse modes constant values according to the parameters \(c_\alpha\) in Eq.(5.41). We have also elucidated the boson peaks Eqs.(5.49, 50).

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