Vibrational Contribution to Density and Current Autocorrelations in a Monatomic Liquid

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(Dated: January 19, 2022)

Abstract

We consider for a monatomic liquid the density and current autocorrelation functions from the point of view of the Vibration-Transit (V-T) theory of liquid dynamics. We also consider their Fourier transforms, one of which is measured by X-ray and neutron scattering. In this description, the motion of atoms in the liquid is divided into vibrations in a single characteristic potential valley, called a random valley, and nearly-instantaneous transitions called transits between valleys. The theory proposes a Hamiltonian for the vibrational motion, to be corrected to take transits into account; this Hamiltonian is used to calculate the autocorrelation functions, giving what we call their vibrational contributions. We discuss the multimode expansions of the autocorrelation functions, which provide a physically helpful picture of the decay of fluctuations in terms of n-mode scattering processes; we also note that the calculation and Fourier transform of the multimode series are numerically problematic, as successive terms require larger sums and carry higher powers of the temperature, which is a concern for the liquid whose temperature is bounded from below by melt. We suggest that these problems are avoided by directly computing the autocorrelation functions, for which we provide straightforward formulas, and Fourier transforming them numerically.

PACS numbers: 05.20.Jj, 63.50.+x, 61.20.Lc, 61.12.Bt
I. INTRODUCTION

V-T theory is being developed specifically to describe atomic motion in real monatomic liquids. This theory adopts a point of view different from, and in a certain way complementary to, the more traditional formulations. The theory most successful for equilibrium thermodynamic properties is based on the interatomic pair potential and the pair distribution function \([1, 2]\). This theory can be made exact by including \(n\)-body potentials for \(n \geq 3\). On the other hand, the most widely studied formulation of nonequilibrium properties, as expressed through time correlation functions, is generalized hydrodynamics \([3, 4, 5]\). The memory function analysis is formally exact, but has not yet proved amenable to first-principles evaluation. V-T theory is based on an approximate but tractable zeroth order Hamiltonian, which in principle can be systematically improved to include corrections beyond zeroth order. It complements traditional theory in that both equilibrium and nonequilibrium properties can be calculated from the same zeroth order theory, without adjustable parameters \([6]\).

V-T theory is based on a symmetry classification of the potential energy valleys among which the liquid atoms move \([6, 7, 8]\). Specifically, the amorphous (noncrystalline) valleys are classified as (a) symmetric valleys, with e.g. microcrystalline structures, which have significant variations in their potential energy and vibrational frequencies but are relatively few in number, and (b) random valleys, with approximately random close-packed structures, which all have the same potential energy and vibrational frequencies in the thermodynamic limit, and which are of overwhelming numerical superiority. As a zeroth order model for the potential energy surface, we neglect the symmetric valleys, and construct an “extended random valley” as the harmonic extension to infinity of one (any) random valley. The partition function is then the extended random valley partition function, times the number of such valleys. This is a universal number, calibrated from the constant density melting entropy of the elements \([9]\). The zeroth order theory gives a good account of the experimental thermodynamic properties of the elemental liquids at melt, indicating that the corrections are small at melt \([6]\).

In a real monatomic liquid the motion consists of two parts: vibrational motion in a random valley, and transit motion, wherein the system crosses valley-valley intersections. In applying V-T theory to a physical process, we evaluate the vibrational contribution in zeroth
order, exactly and without adjustable parameters, and then model the effect of transits. Thus in the liquid partition function the major contribution is vibrational, while the role of transits is to allow the system to access the multitude of random valleys, and hence to possess the extra entropy associated with melting. In the dynamic response function we have found that both the location and area of the Brillouin peak are given by the vibrational contribution, while transits are responsible only for a partial broadening of this peak. Hence an a priori calculation of the vibrational contribution to the Brillouin peak dispersion curve for pseudopotential sodium agrees within experimental error with the measured results of inelastic x-ray scattering for real liquid sodium [10]. In addition, the vibrational contribution can be modified to account for transits, and this model provides an excellent fit to the entire Brillouin peak [11].

The purpose of the present paper is to study the vibrational contributions to density and current correlations in a monatomic liquid. The density autocorrelation function \( F(q, t) \) and its Fourier transform \( S(q, \omega) \) are the basis for inelastic neutron scattering theory. This theory was originally developed for crystals, and expansions of \( S(q, \omega) \) in powers of nuclear displacements were analyzed in detail by Maradudin and Fein [12], Ambegaokar, Conway, and Baym [13], Cowley [14], Lovesey [15], and Glyde [16]. A comparison of different expansions may be found in Glyde [16]. (Physically motivated approximations for the glassy state are discussed by Egelstaff [17].) Liquid theory has important similarities to, and differences from, the crystal theory. First, in liquid and crystal alike, the multimode expansion converges more slowly as the momentum transfer \( q \) increases, and as the temperature \( T \) increases. While the range of \( q \) is approximately the same for inelastic scattering from a given material in crystal and liquid form, the temperature is quite the opposite, being below \( T_m \) for the crystal and above \( T_m \) for the liquid. Second, vibrational dynamics is more complicated for a random valley, because every site is inequivalent, as opposed to inequivalence of only the crystal sites in one unit cell. As a result, the dynamical matrix is \( 3N \times 3N \) for a random valley, but is block diagonal in \( N \times 3 \times 3 \) matrices for a primitive lattice crystal. We will show how to overcome convergence problems resulting from the high temperatures of the liquid, and how to address computability problems resulting from the large dynamical matrix. On the other hand, we will not address anharmonic corrections here, as it is first necessary to formulate and test the harmonic theory. Further, since the atomic motion is classical in most monatomic liquids, we work with classical statistical mechanics, which allows us to
freely commute atomic positions and momenta.

The longitudinal and transverse current autocorrelation functions $C_{L,T}(q,t)$ are discussed by March [2], Hansen and McDonald [4], and Balucani and Zoppi [5]. The relation of these functions via Green-Kubo theory to the longitudinal and transverse viscosities is described, as well as their treatment within the framework of generalized hydrodynamics. We notice that $C_L(q,\omega) = (\omega^2/q^2)S(q,\omega)$, while $C_T(q,\omega)$ is an independent function [4, 5]. For the liquid alkali metals, dispersion curves associated with $C_L(q,\omega)$ have been attributed to sound-like collective modes of the atomic motion (5, Fig. 6.6). These authors also argue for the existence of distinct fast and slow decay mechanisms in $C_L(q,\omega)$ for monatomic liquids (5, Sec. 6.2). In V-T theory, these would result from vibrations and transits respectively. Dispersion curves associated with $C_T(q,\omega)$ have also been studied [18]. For the transverse current correlation function in liquid rubidium, it has been shown that the usual phenomenological relaxation time approximations for the memory functions are not capable of fitting the MD data [19].

Currently there is no theory, short of computer simulations, that will account for these dispersion curves without adjustable parameters. Since the vibrational contribution alone does this for the Brillouin peak dispersion curve [10], it is possible that it will do so as well for the dispersion curves associated with $C_L(q,\omega)$ and $C_T(q,\omega)$. This possibility motivates the present work. In addition, the computational problems mentioned above for $S(q,\omega)$ need to be addressed also for $C_{L,T}(q,\omega)$; these are the poor convergence of the multimode expansions at high temperatures, and the difficulty of evaluating nested $3N$-fold sums for moderately large $N$.

In Sec. II we briefly summarize the vibrational normal mode theory for an extended random valley, and obtain the pair correlation functions involving atomic positions and velocities. In Sec. III we write the formulas for vibrational contributions to the dynamic response functions, $F(q,t)$ and $S(q,\omega)$; we compare these with the formulas derived by Carpenter and Pelizzari [20]; and we show how to circumvent practical limitations posed by convergence and computability problems. The vibrational contributions to $C_{L,T}(q,t)$ are derived in closed form in Sec. IV and are shown to consist of decoupled velocity-position terms and velocity-position interference terms. The one- and two-mode contributions to $C_{L,T}(q,\omega)$ are derived, and accurate but practical evaluation procedures are described for all the current correlation functions. A brief summary is presented in Sec. V.
II. RANDOM VALLEY VIBRATIONAL MODES

This topic has been discussed previously [21], so a brief outline will suffice here and will establish our notation. Our mechanical system consists of \( N \) atoms in a cubical box, with the atomic motion governed by periodic boundary conditions at the box surface. The atomic positions and momenta at time \( t \) are respectively \( \mathbf{r}_K(t) \) and \( \mathbf{p}_K(t) \) for \( K = 1, \ldots, N \). For motion in a single random valley we follow the lattice dynamics tradition of Born and Huang [22] and write

\[
\mathbf{r}_K(t) = \mathbf{R}_K + \mathbf{u}_K(t),
\]

where \( \mathbf{R}_K \) is the equilibrium position and \( \mathbf{u}_K(t) \) is the displacement. The system potential is \( \Phi(\{\mathbf{r}_K\}) \) and the potential at the equilibrium structure is \( \Phi_0 = \Phi(\{\mathbf{R}_K\}) \). The extended random valley is by definition harmonic, and has the Hamiltonian

\[
\mathcal{H}_{\text{vib}} = \Phi_0 + \sum_{K_i} \frac{p_{K_i}^2}{2M} + \frac{1}{2} \sum_{KL} \sum_{ij} \Phi_{Ki,Lj} u_{Ki} u_{Lj},
\]

where \( i, j \) represent Cartesian directions and \( M \) is the atomic mass. The potential energy coefficients \( \Phi_{Ki,Lj} \) form a real symmetric \( 3N \times 3N \) matrix, which is the dynamical matrix [22] for the random valley. The vibrational normal modes have coordinates and momenta respectively \( q_\lambda(t) \) and \( p_\lambda(t) \), for \( \lambda = 1, \ldots, 3N \). The transformation from displacements is defined by

\[
q_\lambda = \sum_{Ki} w_{Ki,\lambda} u_{Ki},
\]

\[
p_\lambda = \sum_{Ki} w_{Ki,\lambda} p_{Ki},
\]

where the eigenvector components \( w_{Ki,\lambda} \) are real and diagonalize the dynamical matrix. It follows that

\[
\mathcal{H}_{\text{vib}} = \Phi_0 + \sum_\lambda \left[ \frac{p_\lambda^2}{2M} + \frac{1}{2} M \omega_\lambda^2 q_\lambda^2 \right],
\]

where \( \omega_\lambda \) are the mode frequencies, from which it also follows that

\[
q_\lambda(t) = q_\lambda(0) \cos \omega_\lambda t + \frac{p_\lambda(0)}{M \omega_\lambda} \sin \omega_\lambda t
\]

\[
p_\lambda(t) = p_\lambda(0) \cos \omega_\lambda t - M \omega_\lambda q_\lambda(0) \sin \omega_\lambda t.
\]
The eigenvector components also satisfy orthonormality and completeness relations \[21\], respectively given by
\[
\sum_{K_i} w_{Ki,\lambda} w_{Ki,\lambda'} = \delta_{\lambda\lambda'}, \tag{6}
\]
\[
\sum_{\lambda} w_{Ki,\lambda} w_{Lj,\lambda} = \delta_{KL}\delta_{ij}. \tag{7}
\]

The basic ingredients of vibrational time correlation functions are the mode-mode functions such as \(\langle q_\lambda(t) q_{\lambda'}(0) \rangle\). These can be calculated from Eqs. (4) and (5), in classical or quantum mechanics, where the classical limit of the quantum result is the leading term in the expansion for \(kT/\hbar \omega_\lambda > 1\). For \(-\infty < t < \infty\), the classical expressions are
\[
\langle q_\lambda(t) q_{\lambda'}(0) \rangle = \frac{kT}{M \omega_\lambda^2} \delta_{\lambda\lambda'} \cos \omega_\lambda t, \tag{8}
\]
\[
\langle p_\lambda(t) p_{\lambda'}(0) \rangle = M kT \delta_{\lambda\lambda'} \cos \omega_\lambda t, \tag{9}
\]
\[
\langle p_\lambda(t) q_{\lambda'}(0) \rangle = -\frac{kT}{\omega_\lambda} \delta_{\lambda\lambda'} \sin \omega_\lambda t. \tag{10}
\]

Correlation functions involving the atomic positions and momenta follow from these and the normal mode transformation, Eqs. (3). It will be convenient to use velocity \(\dot{\mathbf{u}}_K\) instead of \(\mathbf{p}_K = M \dot{\mathbf{u}}_K\), and to eliminate the Cartesian components in favor of vector dot products. Then with \(\mathbf{a}\) and \(\mathbf{b}\) arbitrary vectors,
\[
\langle \mathbf{a} \cdot \dot{\mathbf{u}}_K(t) \mathbf{b} \cdot \dot{\mathbf{u}}_L(0) \rangle = \frac{kT}{M} \sum_\lambda \mathbf{a} \cdot \mathbf{w}_{K\lambda} \mathbf{b} \cdot \mathbf{w}_{L\lambda} \cos \omega_\lambda t, \tag{11}
\]
\[
\langle \mathbf{a} \cdot \dot{\mathbf{u}}_K(t) \mathbf{b} \cdot \mathbf{u}_L(0) \rangle = -\frac{kT}{M} \sum_\lambda \mathbf{a} \cdot \mathbf{w}_{K\lambda} \mathbf{b} \cdot \mathbf{w}_{L\lambda} \frac{\sin \omega_\lambda t}{\omega_\lambda}, \tag{12}
\]
\[
\langle \mathbf{a} \cdot \mathbf{u}_K(t) \mathbf{b} \cdot \mathbf{u}_L(0) \rangle = \frac{kT}{M} \sum_\lambda \mathbf{a} \cdot \mathbf{w}_{K\lambda} \mathbf{b} \cdot \mathbf{w}_{L\lambda} \frac{\cos \omega_\lambda t}{\omega_\lambda^2}. \tag{13}
\]

The fluctuation results are obtained by setting \(t = 0\). Notice Eq. (12), the velocity-displacement correlation function, is odd in \(t\), and the fluctuation vanishes. Eq. (12) satisfies
\[
\langle \mathbf{a} \cdot \mathbf{u}_K(t) \mathbf{b} \cdot \dot{\mathbf{u}}_L(0) \rangle = -\langle \mathbf{a} \cdot \dot{\mathbf{u}}_K(t) \mathbf{b} \cdot \mathbf{u}_L(0) \rangle, \tag{14}
\]
which is valid for any motion as a consequence of time translation invariance. Eq. (12) also satisfies
\[
\langle \mathbf{a} \cdot \mathbf{u}_K(0) \mathbf{b} \cdot \dot{\mathbf{u}}_L(t) \rangle = \langle \mathbf{a} \cdot \dot{\mathbf{u}}_K(t) \mathbf{b} \cdot \mathbf{u}_L(0) \rangle, \tag{15}
\]
but this relation follows from the specific form of Eq. (12) and is not true for general motions. The above equations are valid at all temperatures for which the atomic motion is classical. Hence these equations are appropriate for comparison with ordinary (classical) MD calculations at all $T \geq 0$.

### III. DYNAMIC STRUCTURE FACTOR

Because the system motion is constrained by periodic boundary conditions, Fourier components are defined only at a discrete set of $q$. To reflect the isotropic nature of a real liquid, a macroscopic average can include an average over the star of $q$ for each $|q|$, this average being denoted $\langle \cdots \rangle_{q^*}$. The density autocorrelation function, also called the van Hove function, is then written

$$F(q, t) = \frac{1}{N} \left\langle \left\langle \sum_K e^{-iq \cdot r_K(t)} \sum_L e^{iq \cdot r_L(0)} \right\rangle \right\rangle_{q^*}. \quad (16)$$

Here each sum is a $q$-component of the system density, and the inner average is over the vibrational motion, as in Eqs. (8-15). Notice the $q^*$ average makes $F(q, t)$ a function only of the magnitude $q = |q|$. We have previously used notation such as $F_{\text{vib}}(q, t)$ and $\langle \cdots \rangle_{\text{vib}}$, but here the vibrational subscript will be omitted. Then inserting Eq. (1) for $r_K(t)$,

$$F(q, t) = \frac{1}{N} \left\langle \left\langle \sum_{KL} e^{-iq \cdot R_{KL}} e^{-\frac{1}{2} \langle q \cdot (u_K(t) - u_L(0)) \rangle^2} \right\rangle \right\rangle_{q^*}. \quad (17)$$

where $R_{KL} = R_K - R_L$. The vibrational average is evaluated by Bloch’s identity (e.g. [15]), which is derived via the normal mode transformation, to write

$$F(q, t) = \frac{1}{N} \left\langle \left\langle \sum_{KL} e^{-iq \cdot R_{KL}} e^{-\frac{1}{2} \langle q \cdot (u_K(t) - u_L(0)) \rangle^2} \right\rangle \right\rangle_{q^*}. \quad (18)$$

Finally we separate the fluctuation terms to find

$$F(q, t) = \frac{1}{N} \left\langle \left\langle \sum_{KL} e^{-iq \cdot R_{KL}} e^{-W_K(q)} e^{-W_L(q)} e^{iq \cdot u_K(t) - q \cdot u_L(0)} \right\rangle \right\rangle_{q^*}. \quad (19)$$

where $e^{-W_K(q)}$ is the Debye-Waller factor for atom $K$, which can be expressed with the aid of Eq. (13) as

$$W_K(q) = \frac{kT}{2M} \sum_{\lambda} \frac{(q \cdot w_{K\lambda})^2}{\omega^2_{\lambda}}. \quad (20)$$
The function in the exponential may also be evaluated using Eq. (13).

The time dependence of \( F(q, t) \) is contained in the time correlation functions \( \langle q \cdot u_K(t) q \cdot u_L(0) \rangle \) in Eq. (19). The multimode expansion is obtained by expanding in powers of these functions, according to

\[
e^{(q \cdot u_K(t) q \cdot u_L(0))} = 1 + \langle q \cdot u_K(t) q \cdot u_L(0) \rangle + \frac{1}{2} \langle q \cdot u_K(t) q \cdot u_L(0) \rangle^2 + \cdots. \tag{21}
\]

This is a useful procedure, because each term can be Fourier transformed analytically, to give an explicit picture of the scattering process in each order. For a random valley, \( \langle q \cdot u_K(t) q \cdot u_L(0) \rangle \to 0 \) as \( t \to \infty \), so that \( F(q, \infty) \) is positive and is given by

\[
F(q, \infty) = \frac{1}{N} \left\langle \left| \sum_K e^{-iq R_K} e^{-W_K(q)} \right|^2 \right\rangle_q^*. \tag{22}
\]

Then the series for \( S(q, \omega) \) is

\[
S(q, \omega) = F(q, \infty) \delta(\omega) + S^{(1)}(q, \omega) + S^{(2)}(q, \omega) + \cdots. \tag{23}
\]

The leading term expresses elastic scattering. \( S^{(1)}(q, \omega) \) arises from the linear term in Eq. (21), and with Eq. (13) the expression can be organized into

\[
S^{(1)}(q, \omega) = \frac{kT}{M} \frac{1}{N} \sum_{\lambda} \langle \left| f_\lambda(q) \right|^2 \rangle_q \frac{1}{2} \left[ \delta(\omega + \omega_\lambda) + \delta(\omega - \omega_\lambda) \right], \tag{24}
\]

where

\[
f_\lambda(q) = \frac{1}{\omega_\lambda} \sum_K e^{-iq R_K} e^{-W_K(q)} q \cdot w_{K\lambda}. \tag{25}
\]

(Note that this \( f_\lambda(q) \) differs from our definition in [10, 11], although \( S^{(1)}(q, \omega) \) is the same.) Hence \( S^{(1)}(q, \omega) \) is the sum over all vibrational modes of single-mode scattering at momentum transfer \( hq \), in which energy \( h\omega_\lambda \) is either created in mode \( \lambda \) (the \( \delta(\omega + \omega_\lambda) \) term), or is annihilated in mode \( \lambda \) (the \( \delta(\omega - \omega_\lambda) \) term).

In a similar way, \( S^{(2)}(q, \omega) \) can be written

\[
S^{(2)}(q, \omega) = \left( \frac{kT}{M} \right)^2 \frac{1}{2N} \sum_{\lambda \lambda'} \langle \left| f_{\lambda\lambda'}(q) \right|^2 \rangle_q \langle \delta(\omega \pm \omega_\lambda \pm \omega_{\lambda'}) \rangle_S, \tag{26}
\]

where

\[
f_{\lambda\lambda'}(q) = \frac{1}{\omega_\lambda \omega_{\lambda'}} \sum_K e^{-iq R_K} e^{-W_K(q)} q \cdot w_{K\lambda} q \cdot w_{K\lambda'}, \tag{27}
\]
and \( \langle \delta(\omega \pm \omega_\lambda \pm \omega_\lambda') \rangle_S \) is the symmetric average of four \( \delta \)-functions,

\[
\langle \delta(\omega \pm \omega_\lambda \pm \omega_\lambda') \rangle_S = \frac{1}{4} \left[ \delta(\omega + \omega_\lambda + \omega_\lambda') + \delta(\omega - \omega_\lambda - \omega_\lambda') + \delta(\omega + \omega_\lambda - \omega_\lambda') + \delta(\omega - \omega_\lambda + \omega_\lambda') \right].
\]

(28)

\( S^{(2)} \) is therefore the sum over all pairs of vibrational modes of the cross section for scattering at momentum transfer \( \hbar q \), in which two excitations are created (the \( \delta(\omega + \omega_\lambda + \omega_\lambda') \) term) or annihilated (the \( \delta(\omega - \omega_\lambda - \omega_\lambda') \) term), or in which one excitation is created and another is annihilated (the \( \delta(\omega \pm (\omega_\lambda - \omega_\lambda')) \) terms).

In the multimode expansion of \( S(q, \omega) \) we see from Eqs. (24) and (26) that \( S^{(n)}(q, \omega) \) is proportional to \( T^n \). Therefore any finite termination of the series diverges with increasing \( T \) even though \( S(q, \omega) \) does not. We also see from the above equations that \( S^{(n)}(q, \omega) \) requires evaluation of \( n + 1 \) nested sums, each over atoms or over normal modes, so that each sum contains of order of \( N \) terms. To characterize the magnitude of the computation, we consider a system of \( N = 1000 \) atoms, for which the data \( \{ \mathbf{R}_K; \omega_\lambda; w_{K\lambda} \} \) are available. Then single, double, and triple sums are readily computed, while a quadruple sum challenges current computer facilities. On the other hand, problems related to both convergence and computability of the multimode expansion are eliminated by writing

\[
F(q, t) = [F(q, t) - F(q, \infty)] + F(q, \infty)
\]

(29)

where \( F(q, \infty) \) is given in Eq. (22); the first term can be Fourier transformed numerically, and the transform of the second term is just \( F(q, \infty)\delta(\omega) \) (see Eq. (23)). Since the time correlation functions in Eq. (19) are proportional to \( T \), \( F(q, t) \) is well behaved as a function of \( T \). Further, \( F(q, t) \) can be computed exactly as a triple sum, as can any term in the multimode expansion of \( F(q, t) \).

The quantum expressions for \( S^{(1)}(q, \omega) \) and \( S^{(2)}(q, \omega) \) for a polyatomic amorphous solid were derived by Carpenter and Pelizzari [20]. When their results are applied to a monatomic system and the classical limit is taken, our Eqs. (24-28) are obtained with the following minor differences. Our eigenvectors are real (not complex) and are normalized to 1 (not \( N \)); our \( \lambda' = \lambda \) term in Eq. (26) contains the two inelastic terms of Carpenter and Pelizzari, plus two additional elastic terms in \( \delta(\omega) \); and by writing the \( \sum_{K \lambda} \) in Eq. (19) as \( | \sum_{K \lambda} |^2 \) in Eqs. (24-27), our multimode terms have one lower order of nested sums than those of Carpenter and Pelizzari.
IV. CURRENT AUTOCORRELATION FUNCTIONS

Fourier components of the particle current are denoted \( j(q,t) \), where

\[
j(q,t) = \sum_K \dot{r}_K(t) \, e^{-i q \cdot r_K(t)}.
\]

(30)

Let us define for each \( q \) the orthogonal set of unit vectors \( \hat{q}, \hat{s}_1 \) and \( \hat{s}_2 \). Then the longitudinal and transverse currents are

\[
\begin{align*}
j_L(q,t) &= \hat{q} \cdot j(q,t), \\
j_T(q,t) &= \hat{s}_1 \cdot j(q,t) + \hat{s}_2 \cdot j(q,t).
\end{align*}
\]

(31)

The corresponding current autocorrelation functions are defined by

\[
\begin{align*}
C_L(q,t) &= \frac{1}{N} \langle \langle j_L(q,t) \cdot j_L^*(-q,0) \rangle \rangle_{q^*}, \\
C_T(q,t) &= \frac{1}{2N} \langle \langle j_T(q,t) \cdot j_T^*(-q,0) \rangle \rangle_{q^*}.
\end{align*}
\]

(32)

In these defining equations the inner averages are over the complete atomic motion for a macroscopic system. In what follows we shall limit ourselves to the vibrational motion in a finite system with periodic boundary conditions.

Let \( \hat{a} \) represent any one of \( \hat{q}, \hat{s}_1, \hat{s}_2 \), and define the autocorrelation function

\[
D(\hat{a}, q, t) = \frac{1}{N} \left\langle \left\langle \sum_K \hat{a} \cdot \dot{r}_K(t) \, e^{-i q \cdot r_K(t)} \sum_L \hat{a} \cdot \dot{r}_L(0) \, e^{i q \cdot r_L(0)} \right\rangle \right\rangle_{q^*},
\]

(33)

where the inner average is over vibrations in an extended random valley. Then both \( C_L \) and \( C_T \) are represented by \( D \), since

\[
\begin{align*}
C_L(q,t) &= D(\hat{q}, q, t) \\
C_T(q,t) &= \frac{1}{2} [D(\hat{s}_1, q, t) + D(\hat{s}_2, q, t)] = D(\hat{s}_1, q, t).
\end{align*}
\]

(34)

The last equality reflects the isotropic symmetry of a real liquid.

With Eq. (11) for \( r_K(t) \), Eq. (33) becomes

\[
D(\hat{a}, q, t) = \frac{1}{N} \left\langle \left\langle \sum_{KL} \hat{a} \cdot \dot{r}_{KL}(t) \, e^{-i q \cdot r_{KL}(t)} \sum_L \hat{a} \cdot \dot{u}_L(0) \, e^{i q \cdot u_L(0)} \right\rangle \right\rangle_{q^*},
\]

(35)

The average is quadratic in velocities, and contains terms of all positive powers in displacements. The odd powers are imaginary, and harmonic averages involving them vanish. Hence
the nonzero averages are quadratic in velocities and of all even powers in displacements. To evaluate the thermal average in Eq. (35), we first use the normal mode expansion from Eq. (3), with the result

$$\langle \hat{a} \cdot \dot{\mathbf{u}}_K(t) \hat{a} \cdot \dot{\mathbf{u}}_L(0) e^{-i\mathbf{q} \cdot [\mathbf{u}_K(t) - \mathbf{u}_L(0)]} \rangle = \sum_{\lambda,\lambda'} \hat{a} \cdot \mathbf{w}_K \hat{a} \cdot \mathbf{w}_L \exp \left( \sum_{\mu} -i\mathbf{q} \cdot \mathbf{w}_{K\mu} + i\mathbf{q} \cdot \mathbf{w}_{L\mu} \right) \langle \dot{q}_\lambda(0) \dot{q}_{\lambda'}(0) \exp \left( \sum_{\mu} A_{\mu} q_\mu + B_{\mu} p_\mu \right) \rangle \text{ (36)}$$

where the vectors $\mathbf{w}_K \lambda$ have components $w_{Ki,\lambda}$. Eliminating $q_\lambda(t)$ and $\dot{q}_\lambda(0)$ using Eqs. (5) and replacing $q_\lambda(0)$ and $p_\lambda(0)$ by $q_\lambda$ and $p_\lambda$ respectively yields

$$\sum_{\lambda,\lambda'} \hat{a} \cdot \mathbf{w}_K \hat{a} \cdot \mathbf{w}_L \exp \left( \frac{\cos \omega_\lambda t}{M} p_\lambda p_{\lambda'} - \frac{\omega_\lambda \sin \omega_\lambda t}{M} q_\lambda q_{\lambda'} \right) \exp \left( \sum_{\mu} A_{\mu} q_\mu + B_{\mu} p_\mu \right) \text{ (37)}$$

where the coefficients $A_{\mu}$ and $B_{\mu}$ can easily be calculated, but their exact values are unneeded. The first term in brackets is proportional to

$$\langle p_\lambda p_{\lambda'} \exp \left( \sum_{\mu} A_{\mu} q_\mu + B_{\mu} p_\mu \right) \rangle = \frac{\partial}{\partial B_\lambda} \frac{\partial}{\partial B_{\lambda'}} \langle \exp \left( \sum_{\mu} A_{\mu} q_\mu + B_{\mu} p_\mu \right) \rangle \text{ (38)}$$

In passing to the second line we used Bloch’s identity,

$$\langle p_\lambda p_{\lambda'} \rangle = \frac{1}{2} \left\langle \left( \sum_{\mu} A_{\mu} q_\mu + B_{\mu} p_\mu \right)^2 \right\rangle \text{ (39)}$$

(Lovesey’s proof [15] is for the quantum mechanical single-mode case; the generalization to multiple modes is trivial. The result can also be proved very simply in the classical case by completing the squares in the integrals.) In the third line we relabelled dummy indices, and
in the final line we returned the quantity in the exponential to its original form. A similar
calculation shows that the other term can be expressed
\[
\left< q_{\lambda} p_{\lambda'} \exp \left( \sum_{\mu} A_{\mu} q_{\mu} + B_{\mu} p_{\mu} \right) \right> = \frac{\partial}{\partial A_{\lambda}} \frac{\partial}{\partial B_{\lambda'}} \exp \left[ \sum_{\mu} \frac{1}{2} \left( (A_{\mu} q_{\mu} + B_{\mu} p_{\mu})^2 \right) \right]
\]
\[
= \left[ \left< q_{\lambda} p_{\lambda'} \right> - \left< q \cdot [u_K(t) - u_L(0)] q_{\lambda} \right> \right] \left< q \cdot [u_K(t) - u_L(0)] p_{\lambda'} \right>
\times \exp \left[ -\frac{1}{2} \left< (q \cdot [u_K(t) - u_L(0)])^2 \right> \right].
\] (40)

Putting this back together and rearranging, we get
\[
\left< \hat{a} \cdot \hat{u}_K(t) \hat{a} \cdot \hat{u}_L(0) e^{-iq[u_K(t)-u_L(0)]} \right>
\]
\[
= \left\{ \sum_{\lambda,\lambda'} \hat{a} \cdot w_{K \lambda} \hat{a} \cdot w_{L \lambda'} \left[ \left< \hat{q}_{\lambda}(t) \hat{q}_{\lambda'}(0) \right> - \left< q \cdot [u_K(t) - u_L(0)] \hat{q}_{\lambda}(t) \right> \right.
\times \left. \left< q \cdot [u_K(t) - u_L(0)] \hat{q}_{\lambda'}(0) \right> \right] \exp \left[ -\frac{1}{2} \left< (q \cdot [u_K(t) - u_L(0)])^2 \right> \right].
\] (42)

Next, we change \( q_{\lambda} \) and \( p_{\lambda} \) back to \( q_{\lambda}(0) \) and \( p_{\lambda}(0) \) and use Eq. (5) to simplify the time-
dependent factors, reducing the expression to
\[
\left\{ \sum_{\lambda,\lambda'} \hat{a} \cdot w_{K \lambda} \hat{a} \cdot w_{L \lambda'} \left[ \left< \hat{q}_{\lambda}(t) \hat{q}_{\lambda'}(0) \right> - \left< q \cdot [u_K(t) - u_L(0)] \hat{q}_{\lambda}(t) \right> \right.
\times \left. \left< q \cdot [u_K(t) - u_L(0)] \hat{q}_{\lambda'}(0) \right> \right] \exp \left[ -\frac{1}{2} \left< (q \cdot [u_K(t) - u_L(0)])^2 \right> \right].
\] (42)

When this is summed over \( \lambda \) and \( \lambda' \) using Eq. (3), the expression becomes
\[
\left[ \left< \hat{a} \cdot \hat{u}_K(t) \hat{a} \cdot \hat{u}_L(0) \right> - \left< q \cdot [u_K(t) - u_L(0)] \hat{a} \cdot \hat{u}_K(t) \right> \left< q \cdot [u_K(t) - u_L(0)] \hat{a} \cdot \hat{u}_L(0) \right> \right]
\times \exp \left[ -\frac{1}{2} \left< (q \cdot [u_K(t) - u_L(0)])^2 \right> \right].
\] (43)

The second term, involving products of displacements and velocities, can be simplified some-
what. Terms such as \( \left< q \cdot u_K(t) \hat{a} \cdot \hat{u}_K(t) \right> \) are invariant under time translation, so they can be evaluated at \( t = 0 \). In this case, the expression is a linear combination of terms of the
form \( \left< q_{\lambda} p_{\lambda'} \right> \), all of which vanish. Thus the two equal-time terms drop out, so
\[
\left< \hat{a} \cdot \hat{u}_K(t) \hat{a} \cdot \hat{u}_L(0) e^{-iq[u_K(t)-u_L(0)]]} \right>
\]
\[
= \left[ \left< \hat{a} \cdot \hat{u}_K(t) \hat{a} \cdot \hat{u}_L(0) \right> + \left< q \cdot u_L(0) \hat{a} \cdot \hat{u}_K(t) \right> \left< q \cdot u_K(t) \hat{a} \cdot \hat{u}_L(0) \right> \right]
\times \exp \left[ -\frac{1}{2} \left< (q \cdot [u_K(t) - u_L(0)])^2 \right> \right].
\] (44)
The exponential is the same term that appears in Eq. (18), so it may be transformed the same way. Putting all this together, Eq. (35) becomes

\[
D(\hat{a}, q, t) = \frac{1}{N} \left\langle \sum_{KL} e^{-iq \cdot R_{KL}} e^{-W_K(q)} e^{-W_L(q)} \langle \hat{q} \cdot u_K(t) \rangle q \cdot u_L(0) \right\rangle_{q^*},
\]

and all of the correlation functions may be evaluated with the aid of Eqs. (11–13). Comparison with Eq. (19) verifies the well known relation for the longitudinal correlation function

\[
D(\hat{q}, q, t) = -\frac{1}{q^2} \ddot{F}(q, t).
\]

Just as with \( F(q, t) \), expansion of the time-dependent exponential in Eq. (45) produces a series which can be Fourier transformed analytically, term by term. We express this transformed series as

\[
D(\hat{a}, q, \omega) = D^{(1)}(\hat{a}, q, \omega) + D^{(2)}(\hat{a}, q, \omega) + \cdots,
\]

where the superscript reveals the number of normal modes coupled in the correlation. \( D^{(1)} \) is the pure velocity term, given by

\[
D^{(1)}(\hat{a}, q, \omega) = \frac{kT}{M} \frac{1}{N} \sum_{\lambda} \langle |h_\lambda(\hat{a}, q)|^2 \rangle_{q^*} \frac{1}{2} \left[ \delta(\omega + \omega_\lambda) + \delta(\omega - \omega_\lambda) \right],
\]

where

\[
h_\lambda(\hat{a}, q) = \sum_K e^{-iq \cdot R_K} e^{-W_K(q)} \hat{a} \cdot w_{K\lambda}.
\]

The similarity with one mode scattering as described by Eqs. (24) and (25) is apparent. The disappearance here of the \( \omega_\lambda^{-1} \) factor in Eq. (25) arises from velocities replacing displacements.

The two-mode contribution takes the form

\[
D^{(2)}(\hat{a}, q, \omega) = \left( \frac{kT}{M} \right)^2 \frac{1}{N} \sum_{\lambda\lambda'} \frac{1}{\omega_{\lambda'}} \langle h_{\lambda\lambda'}(\hat{a}, q) h^*_{\lambda\lambda'}(\hat{a}, q) \rangle_{q^*} \langle \delta(\omega \pm \omega_\lambda \pm \omega_{\lambda'}) \rangle_S
\]

\[
+ \left( \frac{kT}{M} \right)^2 \frac{1}{N} \sum_{\lambda\lambda'} \frac{1}{\omega_\lambda \omega_{\lambda'}} \langle h_{\lambda\lambda'}(\hat{a}, q) h^*_{\lambda\lambda'}(\hat{a}, q) \rangle_{q^*} \langle \delta(\omega \pm \omega_\lambda \pm \omega_{\lambda'}) \rangle_A,
\]

where

\[
h_{\lambda\lambda'}(\hat{a}, q) = \sum_K e^{-iq \cdot R_K} e^{-W_K(q)} \hat{a} \cdot w_{K\lambda} q \cdot w_{K\lambda'},
\]
and where \( \langle \delta(\omega \pm \omega_\lambda \pm \omega_\lambda') \rangle_A \) is the antisymmetric combination of four \( \delta \)-functions,

\[
\langle \delta(\omega \pm \omega_\lambda \pm \omega_\lambda') \rangle_A = \frac{1}{4} \left[ \delta(\omega + \omega_\lambda + \omega_\lambda') + \delta(\omega - \omega_\lambda - \omega_\lambda') - \delta(\omega + \omega_\lambda - \omega_\lambda') - \delta(\omega - \omega_\lambda + \omega_\lambda') \right].
\]

The first line of Eq. (50) is the velocity-decoupled term, and contains \( \langle \sum_K \cdots \rangle_{q^*} \), similar to \( S^{(2)}(q, \omega) \) in Eqs. (26) and (27). The second line of Eq. (50) is the velocity-interference term, and does not contain an absolute square, because of the interchange of \( \lambda \) and \( \lambda' \) in \( h_{\lambda\lambda'}^* \).

It is still possible to show that the velocity-interference term is overall real, even without the \( q^* \) average. A more prominent difference from the velocity-decoupled term is the change in sign of two of the \( \delta \)-functions in the velocity-interference term. This will give the two terms a strongly different \( \omega \)-dependence, since \( \delta(\omega \pm (\omega_\lambda + \omega_\lambda')) \) is spread broadly over \( \omega \), while \( \delta(\omega \pm (\omega_\lambda - \omega_\lambda')) \) is concentrated at smaller frequencies.

V. SUMMARY

In V-T theory of monatomic liquid dynamics, the vibrational contribution to a statistical average can be evaluated exactly from the vibrational eigenvalues and eigenvectors of a single random valley. The transit contribution consists of small but not negligible corrections to the vibrational contribution, and has so far been accounted for by parametrized models. In the thermodynamic properties of the elemental liquids, the transit correction accounts for the constant density entropy of melting [6, 9] and for the contribution to thermal energy from valley-valley intersections [23]. In nonequilibrium properties, as expressed by time correlation functions, the transits cause decay of correlations in addition to that already present in the vibrational contribution [10, 11, 24]. Continuing in this line of theoretical development, we have two goals in the present paper: (a) to derive the equations for the vibrational contribution to the current autocorrelation functions, and (b) to address difficulties present in the liquid state in computing these functions and the related density autocorrelation functions.

The current autocorrelation functions are denoted \( D(\hat{a}, q, t) \), where \( \hat{a} = \hat{q} \) for the longitudinal current, and \( \hat{a} \) is transverse to \( \hat{q} \) for the transverse current. A closed form expression for \( D(\hat{a}, q, t) \) is derived in Eq. (45). This expression contains two classes of terms: (a) velocity-decoupled terms, containing one velocity-velocity correlation function, and (b)
velocity-interference terms, containing a product of two velocity-displacement correlation functions. The one- and two-mode contributions to the Fourier transform \( D(\hat{a}, q, \omega) \) are written in Eqs. (48-52): \( D^{(1)}(\hat{a}, q, \omega) \) expresses decay of current fluctuations through processes involving one vibrational mode, and \( D^{(2)}(\hat{a}, q, \omega) \) expresses the same decay through processes involving two vibrational modes (including one mode twice).

The density autocorrelation function \( F(q, t) \), and its Fourier transform \( S(q, \omega) \), are the basis of inelastic neutron scattering theory for condensed matter. With notable exceptions, the point of view in crystal theory \([12, 13, 14, 15]\), and in amorphous solid theory \([20]\), is that the multimode expansions of these functions converge well. The exceptions include the quantum crystals \([16]\), and soft phonons associated with the hcp-bcc transition in Ti \([25, 26]\) and Zr \([27, 28]\). However, this viewpoint is precarious for the liquid, because the characteristic liquid state persists to temperatures of several times \( T_m \) \([29]\), while the multimode expansions in question diverge in \( T \) at any finite order. The same convergence issue is present in the current correlations, and the following conclusions apply to density and current correlation functions alike.

(a) The multimode series for the vibrational contribution to the Fourier transforms \( S(q, \omega) \) and \( D(\hat{a}, q, \omega) \) are very informative, as they resolve the decay of fluctuations into one-mode processes, two-mode processes, and so on. In classical statistical mechanics, the one-mode processes go as \( T \) and are computable as a double \( N \)-fold sum; the two-mode processes go as \( T^2 \) and are computable as a triple \( N \)-fold sum, and so on. In general we expect the series to converge at about the same rate for liquid and crystal phases at \( T_m \). Then, as \( T \) increases above \( T_m \), higher order terms which are more difficult to compute become more important.

(b) These convergence and computability problems are circumvented by computing the vibrational contributions to the time correlation functions, \( F(q, t) \) and \( D(\hat{a}, q, t) \), and by numerically transforming these. (We suggest subtracting off \( F(q, \infty) \) and transforming that term analytically, which is not necessary for \( D(\hat{a}, q, t) \) because \( D(\hat{a}, q, \infty) = 0 \).) The real exponential function in Eq. (19) for \( F(q, t) \) appears also in Eq. (45) for \( D(\hat{a}, q, t) \), and this function is well behaved at all \( T \). Eqs. (19) and (45) for the time correlation functions are computable as triple \( N \)-fold sums.
Acknowledgments

We would like to thank Renzo Vallauri for suggesting that it would be useful to study the current correlation functions in terms of V-T theory. This work was supported by the US DOE through contract DE-AC52-06NA25396.

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