Application of vibration-transit theory to distinct dynamic response for a monatomic liquid

Duane C. Wallace, Eric D. Chisolm, and Giulia De Lorenzi-Venneri

Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

(Dated: May 20, 2013)

The purpose of this research is to apply vibration-transit (V-T) theory of monatomic liquid dynamics to the distinct part of the density autocorrelation function, $F^d(q,t)$. A similar study has been reported for the self part [G. De Lorenzi-Venneri, E. D. Chisolm, and D. C. Wallace, Phys. Rev. E 78, 041205 (2008)], and it is necessary to study the self and distinct parts separately because their damping processes are not simply related. The theory is minimally calibrated, then tested, by means of Molecular Dynamics (MD) calculations for liquid Na at 395 K. Our formulation begins with the perfect vibrational system, which provides precise definitions of the liquid correlations, and provides the vibrational approximation $F^d_{\text{vib}}(q,t)$ at all $q,t$. Two independent liquid correlations are defined, motional and structural, and these are decorrelated sequentially, with a crossover time $t_c(q)$. Two independent decorrelation processes then complete the theory: vibrational dephasing is automatically present in $F^d_{\text{vib}}(q,t)$ and operates to damp the motional correlation; transit decorrelation is invoked to enhance the damping of motional correlation, and then to damp the structural correlation. A microscopic model is made for the “transit drift,” the averaged transit motion that damps motional correlation on $0 \leq t \leq t_c(q)$. Following the previously developed self-decorrelation theory, a microscopic model is also made for the “transit random walk,” which damps the structural correlation on $t \geq t_c(q)$. The complete model explains the common MD property in both self and distinct decorrelation: simple exponential decay following a delay period, where the delay is $t_c(q)$, the time required for the random walk to emerge from the drift. The theory developed here provides an accurate account of $F^d(q,t)$ for all $q$ through the first peak in $S^d(q)$, but a modification will be required at $q$ where $S^d(q)$ converges to zero. We note that V-T theory provides a unification of equilibrium and nonequilibrium statistical mechanics theories, unprecedented in liquid dynamics.

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

I. INTRODUCTION

Our goal in developing V-T theory is to apply the established techniques of many body physics to the mechanical problem of the motion of atoms in a monatomic liquid. The many body formulation begins with an approximate Hamiltonian $H_0$ composed of a complete orthogonal set of excitations, bosons or fermions, whose exact statistical mechanics is known. $H_0$ is complemented with an interaction Hamiltonian $H_I$, expressing the key effect missing from $H_0$, and often but not always treated as a perturbation. The approach was developed to treat the wide variety of physical behaviors observed in condensed matter, and is well illustrated in the monographs of Pines and Kittel. The principles are evident in Boltzmann’s theory for a gas of freely moving atoms which interact via collisions and in the theory of Born and coworkers for a crystal of harmonic phonons interacting via anharmonicity.

In the absence of such a many body formulation, liquid dynamics theory has been advanced by a series of conceptual developments. An important early step was learning how to construct physically realistic interatomic potentials for nearly-free-electron metals from pseudopotential perturbation theory. It was shown that MD calculations using these potentials give an excellent account of experimental data for elemental condensed systems, for example: for thermodynamic properties of crystals and liquids and for the liquid structure factor $S(q)$ and dynamic structure factor $S(q,\omega)$. The same technique was used to assess the validity of anharmonic theory in $S(q,\omega)$ for bcc K. Ab initio MD was introduced and has since become the method of choice for reliable calculations on many liquid types. Exemplary applications of ab initio MD are the calculations of structural and dynamic properties of liquid Fe under earth’s core conditions pair distribution functions for group IIIIB-VIB elements $S(q)$ and $S(q,\omega)$ for liquid Ge and electronic structure changes in liquid Na under high compression. The last study was in response to the earlier prediction by Neaton and Ashcroft of specific electronic structure changes in compressed crystalline Na. The resulting physical picture of liquids as nuclei moving on the ground state adiabatic potential, and subject to conventional statistical mechanical averaging, is the basis of our theoretical work. Formal derivation of the corresponding condensed matter Hamiltonian is reviewed in Ch. 1 of Ref. 21.

In V-T theory, the intersecting potential energy valleys that constitute the many-atom potential surface are classified as random or symmetric. Originally by hypothesis, and now with numerical verification, the random valleys all have the same statistical mechanical averages, and together they dominate the potential surface, in the thermodynamic limit. The atomic motion is vibrations in one (any) random valley, interspersed by transits, which carry the system between random valleys. Accordingly, we define the extended random valley as the
harmonic extension to infinity of any random valley, and take the Hamiltonian $H_{vib}$ for motion in one extended random valley as our zeroth order liquid Hamiltonian.

Transits have been observed in MD calculations for liquid Na and Ar, at very low temperatures where single transits are well resolved. These transits occur in the highly correlated motion of a small local group of atoms. At $T > T_m$, transits proceed at a high rate throughout the liquid. In its initial formulation, V-T theory incorporated an empirical melting-entropy constant to represent the transit contribution to the entropy of elemental liquids. This formulation requires extension in two ways: in order to treat all thermodynamic properties, the transit entropy theory must be replaced by a free energy theory; and in order to make a purely liquid theory, all sensitivity to the nature of the crystal or the melting process must be removed. These extensions were carried out through an analysis of the temperature dependence of experimental entropy for elemental liquids plus a statistical mechanics free energy model calibrated to the entropy results. A priori DFT calculations then verified the theory to high accuracy for thermodynamic properties of liquid Na and Cu.

In nonequilibrium problems, V-T theory has achieved success in two applications to dynamic response. First, it was found that an a priori calculation of the Brillouin peak dispersion curve, based on the vibrational motion alone, is in essentially perfect agreement with MD calculations and with experimental inelastic scattering data for liquid Na. Second, a simple theory for the self part of the density autocorrelation function was shown analytically to have the correct small-time behavior to exponential accuracy, and to have the correct free particle limit at large $q$, and was shown numerically to be in accurate agreement with MD data for liquid Na at all $q$ and $t$. The purpose of the present work is to test the viability of V-T theory for the distinct part of the density autocorrelation function.

Hansen and McDonald define time correlation functions related to self and distinct contributions to dynamic response, and discuss the self dynamic structure factor, including its Gaussian approximation. These authors also point out it is possible in principle to measure separately the self and distinct parts. We have not found studies dedicated to the distinct part, presumably because the self part and the total function cover the entire theoretical problem. However, the distinct part must be studied separately, because the strong difference between self and distinct correlations implies a similar difference in their decorrelation processes.

Formulation of dynamic response theory is a quintessential quantum mechanics problem, analyzed for crystals by Maradudin and Fein, Ambegaokar, Conway and Baym, Cowley, and Ashcroft and Mermin, and for crystals and liquids by Lovesey and Glyde. However, our focus is the elemental liquids in general, so we omit the few quantum liquids and work in classical statistical mechanics. We study the density autocorrelation function $F(q,t)$ for all $q$ and $t$. Expansions in powers of scattering events are inefficient, and we must work with the full theory, correct to all powers of $q$ (see Appendix N of Ref. [44]). We apply the primitive-lattice harmonic crystal analysis from the above references to a system moving in an extended random valley, then extract the classical limit to obtain the zeroth order liquid function $F_{vib}(q,t)$ (details may be found in Ref. [47]). In the present paper we begin with the distinct part $F_{vd}(q,t)$, and introduce the decorrelating effects of transits to damp $F_{vd}(q,t)$ to the function representing V-T theory, $F_{VT}(q,t)$.

Our computational system represents liquid Na at 395K, a bit above the melting temperature $T_m = 371$ K. The system is a cube containing $N = 500$ atoms, with periodic boundary conditions, and with theory and MD evaluated for the same system. The MD time step is 7 fs. The interatomic potential is based on pseudopotential theory, and has produced excellent agreement with a wide range of experimental data.

Sec. II sets out the “standard plan” for constructing the theoretical function $F_{VT}(q,t)$. The perfect vibrational system provides equations for $F_{vd}(q,t)$ and for the motional and structural correlations. Transits are responsible for all damping beyond the dephasing already contained in $F_{vd}(q,t)$. The transit contribution to $F_{VT}(q,t)$ is assigned to the structural correlation and is calibrated from MD. A crossover time $t_c(q)$ is defined, such that motional correlation is to be damped to zero on $0 \leq t \leq t_c$, and structural correlation is to be damped to zero on $t \geq t_c$.

In Sec. III, an empirical scaling of the transit-induced motional decorrelation is analyzed. In Sec. IV, the massively averaged motion due specifically to transits on $0 \leq t \leq t_c$ is modeled as the transit drift, and a microscopic theory is made for its contribution to motional decorrelation. In Sec. V, the transit random walk theory from self dynamic response is extended to the structural decorrelation. The agreement of theory with MD is at the remarkable level of 0.01$|F_{vd}(q,0)|$, for all $t$, and all $q$ for which the standard plan applies. Sec. VI examines the validity of the standard decorrelation plan as function of $q$. Our primary conclusions, Sec. VII, concern the viability of V-T theory for distinct dynamic response; the unifying character of V-T theory in its application to both equilibrium and nonequilibrium statistical mechanics; and the theoretical status of transit dynamics as currently modeled.

II. OUTLINE OF THE THEORY

A. Perfect vibrational system

We study the distinct autocorrelation function, defined by

$$F^{d}(q,t) = \frac{1}{N} \sum_{KL} \langle e^{-iQ(\mathbf{r}_K(t)-\mathbf{r}_L(0))} \rangle ,$$

(1)
for a system of atoms \( K = 1, ..., N \), located at \( \mathbf{r}_K(t) \) at time \( t \). The average may be evaluated for a single MD system, on an equilibrium trajectory, and includes an average over the star of \( q \) when periodic boundary conditions are used. The function measures static pair configurational correlations in terms of the structure factor \( S^d(q) = F^d(q, 0) \), and measures their statistical average time decay at \( t > 0 \).

To evaluate Eq. (1) for the vibrational system, we write

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

where \( \mathbf{R}_K \) is the random valley equilibrium position (structural site) and \( \mathbf{u}_K(t) \) is the motional displacement. The vibrational average is then

\[
F^d_{vib}(q, t) = \frac{1}{N} \sum_{KL} e^{-i\mathbf{q} \cdot \mathbf{R}_{KL}} e^{-W_K(q)} e^{-W_L(q)} \sum_i e^{i\mathbf{q} \cdot \mathbf{u}_K(t)} e^{i\mathbf{q} \cdot \mathbf{u}_L(0)},
\]

where \( \mathbf{R}_{KL} = \mathbf{R}_K - \mathbf{R}_L, W_K(q) \) is the Debye-Waller factor,

\[
W_K(q) = \frac{1}{2} \langle (\mathbf{q} \cdot \mathbf{u}_K)^2 \rangle_{vib},
\]

and the motional-time-correlation functions are given by

\[
\langle \mathbf{q} \cdot \mathbf{u}_K(t) \rangle \mathbf{q} \cdot \mathbf{u}_L(0) = \frac{kT}{M} \sum_{\lambda} \frac{\cos \omega_{\lambda}t}{\omega_{\lambda}^2}.
\]

The normal modes are labeled \( \lambda = 1, ..., 3N-3 \), the three zero-frequency modes being omitted, mode \( \lambda \) has frequency \( \omega_{\lambda} \), and eigenvector \( \lambda \) has Cartesian vector \( \mathbf{w}_{\lambda K} \) at atom \( K \). The right side of Eq. (3) is also averaged over each \( q \) star.

Equation (3) for \( F^d_{vib}(q, t) \) makes use of three data sets, the structural positions \( \mathbf{R}_K \), the Debye-Waller factors in Eq. (4), and the motional time correlation functions in Eq. (5). These data sets are all strongly coupled inside the sums in Eq. (3), and that equation admits of no acceptable decoupling approximation. The key to analysis is in the time dependence.

\( F^d_{vib}(q, t) \) is subject to natural vibrational decorrelation, or vibrational dephasing, of the \( \cos \omega_{\lambda}t \) factors in Eq. (5), as \( t \) increases from zero. This process is always present, and has the effect of reducing the time correlation functions to zero as \( t \to \infty \). What remains of \( F^d_{vib}(q, t) \) as \( t \to \infty \) is therefore \( F^d_{vib}(q, \infty) \), given by

\[
F^d_{vib}(q, \infty) = \frac{1}{N} \sum_{KL} e^{-i\mathbf{q} \cdot \mathbf{R}_{KL}} e^{-W_K(q)} e^{-W_L(q)}.
\]

Because the Debye-Waller factors are positive and increasing with \( q \), Eq. (4), \( F^d_{vib}(q, \infty) \) \( \to 0 \) as \( q \) increases.

\( F^d_{vib}(q, t) \) accounts for all correlations in a perfect vibrational system. These correlations can be classified as motional and structural. We shall follow this intuitive notation, in a modification designed for V-T theory.

a) Motional correlation is that contained in the time correlation functions with \( K \neq L \) in Eq. (3). Motional correlation is in the normal mode motion and resides in the eigenvectors, Eq. (5).

b) For vibrational motion in a single random valley, each atom \( K \) remains within a small volume around its equilibrium position \( \mathbf{R}_K \). This constraint describes the structural correlation, as the term is used here, and it is contained in Eq. (6).

B. Transit contribution to the structure factor

Fig. 1 compares the distinct functions \( F^d_{vib}(q, 0) \) and \( F^d_{MD}(q, 0) \) for all the allowed \( q \) in our system. Fluctuations are larger in the vibrational curve because it is calculated for a single random valley while the MD data averages over random valleys. The difference \( F^d_{MD}(q, 0) - F^d_{vib}(q, 0) \) is formally identified in V-T theory as the transit contribution. However, the structure factor and the density autocorrelation function pose essentially different problems. Given a very large system, the fluctuation \( F^d_{MD}(q, 0) \) can be calculated from a single configuration, while the regression \( F^d_{MD}(q, t) \) depends only on the evolution of a configuration relative to its initial state. Since we are interested in the regression, we shall not invoke a theory for the fluctuation, but shall instead calibrate it from MD data, and remove it as a source of error. For this purpose, we define the transit contribution \( A(q) \) by

\[
F^d_{vib}(q, 0) + A(q) = F^d_{MD}(q, 0).
\]

FIG. 1. Circles are \( F^d_{vib}(q, 0) \) at allowed \( q \), fluctuating line is \( F^d_{MD}(q, 0) \) at the same \( q \) (unsmeothed), and large opaque circles show the test \( q \) (Table I). The MD-vibrational difference is the transit contribution \( A(q) \).
We shall now determine the role of \( A(q) \) in the decorrelation process. For this discussion, useful reference orders of magnitude are \( |F^d_{MD}(q, 0)| \sim 1 \), and our ultimate level of theoretical error is \( \sim 0.01 \). At all \( q \) except the first peak tip, \( |A(q)| \lesssim 0.1 \), a small correction. A detailed interpretation of \( A(q) \) will not be required where it is this small. In severe contrast, \( A(q) \) at the first peak tip is large and negative, being around \( -1.0 \) (see Fig. 2). This large excess of correlation in \( F^d_{vib}(q, 0) \) is precisely at the nearest neighbor distance, hence is structural and is contained in \( F^d_{vib}(q, \infty) \). Accordingly we write

\[
A(q) = C(q)F^d_{vib}(q, \infty),
\]  

where \( C(q) \) has no dependence on \( \{R_K\} \).

C. Standard decorrelation plan

We chose a representative set of \( q \) values to use in developing the present theory. These \( q \) are listed in Table I along with the theoretically important parameters for each \( q \). The nine \( q \) in Table I are among the 17 \( q \) for which self-decorrelation calculations were done.

The vibrational density autocorrelation function, normalized to MD data at \( t = 0 \), is \( F^d_{vib}(q, t) + A(q) \). Our object is to construct a theory for the transit-induced decorrelation of this function.

Fig. 2 shows curves of \( F^d_{MD}(q, t) \) and \( F^d_{vib}(q, t) + A(q) \) for \( q = 1.09 \), at the tip of the first peak. The curves agree at \( t = 0 \), but the MD curve damps faster, and falls increasingly below the vibrational curve as \( t \) increases. Recall the vibrational curve contains natural vibrational decorrelation, which makes the curve converge eventually to the constant \( F^d_{vib}(q, \infty) + A(q) \). Through the convergence process, from around 0.4 ps to around 5 ps, the vibrational curve displays the vibrational excess, an oscillatory variation about its \( t \to \infty \) limit. The feature is due to very-slowly-damped lowest frequency normal modes. The same vibrational excess is present in all the \( F^d_{vib}(q, t) \) curves, and in the curves of \( F^s_{vib}(q, t) \) as well. Its appearance in the self autocorrelation function was noted previously.\(^{38}\) Exceptionally, we note that the vibrational excess does not appear at sufficiently large \( q \), in \( F^d_{vib}(q, t) \) nor in \( F^d_{vib}(q, t) \), because the functions converge to zero before the excess develops.

In fact, the vibrational excess cannot be present in the liquid state, because the long-time normal-mode correlation cannot survive in the presence of transits. The vibrational excess must therefore be damped out of \( F^d_{vib}(q, t) \) by transit-induced motional decorrelation. The situation is shown graphically in Fig. 2. The constant \( F^d_{vib}(q, \infty) + A(q) \) is the value of the normalized vibrational autocorrelation function with all motional correlation damped and all structural correlation present. The figure suggests, and we shall adopt, a simplifying approximation for the complete decorrelation process: make the motional and structural decorrelations sequential, the first ending and the second beginning at the same (crossover) point. That point must lie on the horizontal line in Fig. 2. Then with the crossover time denoted \( t_c(q) \), the theory must satisfy

\[
F^d_{vib}(q, t_c(q)) = F^d_{vib}(q, \infty) + A(q).
\]

As for \( t_c(q) \) itself, we shall calibrate it with the help of MD data by

\[
F^d_{vib}(q, t_c(q)) = F^d_{vib}(q, \infty) + A(q).
\]

The standard decorrelation plan is then described as follows.

- Introduce transit-induced motional decorrelation to damp the vibrational curve toward the MD curve on \( 0 \leq t \leq t_c(q) \).
TABLE I. MD and vibrational data for nine $q$ chosen as test cases in the present study. All parameters are defined in text and equations.

| $q$ ($a_0^{-1}$) | $F_{MD}^d(q,0)$ | $F_{vib}^d(q,0)$ | $A(q)$ | $F_{vib}^d(q,\infty)$ | $t_c(q)$ (ps) | $s(q,t_c)(a_0)$ | $B(q)$ | $q$-regime |
|----------------|----------------|----------------|-------|----------------|--------------|---------------|-------|-----------|
| 0.29711       | -0.9730        | -0.9747        | 0.0017 | -0.9388        | 0.2937       | 0.761         | 1.286 | Brillouin peak |
| 0.70726       | -0.8943        | -0.8878        | -0.0065 | -0.7118        | 0.2595       | 0.774         | 1.265 | Brillouin peak |
| 1.01482       | 0.9423         | 0.8787         | 0.0636 | 0.4921         | 0.3547       | 0.658         | 1.111 | first peak  |
| 1.09165       | 1.6037         | 2.1415         | -0.4478 | 1.6819         | 0.3336       | 0.613         | 1.405 | first peak  |
| 1.10505       | 1.5504         | 2.6187         | -1.0683 | 2.1902         | 0.3222       | 0.528         | 1.436 | first peak  |
| 1.14429       | 1.0201         | 0.9820         | 0.0381 | 0.6619         | 0.2787       | 0.844         | 1.564 | first peak  |
| 1.150523      | -0.3540        | -0.3929        | 0.0389 | -0.1791        | 0.2790       | 0.583         | 1.134 | large $q$  |
| 2.0041        | 0.2055         | 0.1227         | 0.0828 | -0.0021        | 0.198        | 0.153         | large $q$ |
| 2.5064        | -0.1042        | -0.0725        | -0.0317 | -0.0134        | 0.153        | 0.153         | large $q$ |

- Introduce transit-induced structural decorrelation to damp the line ($F_{vib}^d(q,\infty) + A(q)$) toward the MD curve on $t \geq t_c(q)$.

In the process of this study we shall find those $q$ for which the standard plan applies, and shall summarize the results in Sec. VI. While such a qualitative conclusion can be drawn with some reliability, quantitative behavior differs with $q$. In this work, one should be mindful that every $q$ measures a different correlation.

III. MOTIONAL DECORRELATION VIA SCALING

![FIG. 3. The motional decorrelation period: decrease in the vibrational curve is due to vibrational dephasing. Transit-induced decorrelation is supposed to damp the vibrational curve to the MD curve.](image)

Schematic curves of $F_{MD}^d(q,t)$ and $F_{vib}^d(q,t) + A(q)$ on $0 \leq t \leq t_c(q)$ are shown in Fig. 3, where their endpoint values are also noted. Our decorrelation theory will consist of introducing transits into the equation for $F_{vib}^d(q,t)$, thereby modifying that equation to include the additional damping. The process is subject to three constraints from V-T theory, that $F_{vib}^d(q,t)$ retains its natural vibrational decorrelation, that the transit-induced decorrelation damps away the vibrational excess, and that the structural quantity $A(q)$ remains constant.

More immediately, however, a glance at Fig. 3 suggests the possibility of merely scaling $F_{vib}^d(q,t)$ to fit $F_{MD}^d(q,t)$. Linear scaling is expressed by the following equation, a proposition to be tested:

$$\frac{F_{MD}^d(q,t) - F_{MD}^d(q,t_c)}{F_{MD}^d(q,0) - F_{MD}^d(q,t_c)} = \frac{F_{vib}^d(q,t) - F_{vib}^d(q,t_c)}{F_{vib}^d(q,0) - F_{vib}^d(q,t_c)}$$  (11)

On the right side, the functions are initially $F_{vib}^d(q,t) + A(q)$ in all terms, and the $A(q)$ cancel.

In the system we study, Eq. (11) is found to be accurate for all $q$ where the standard plan applies, and equally accurate for different random structures at a given $q$. Let us therefore rewrite Eq. (11) as a scaling theory, and present its results in that format. The left side is rewritten with the definitions of $t_c(q)$, Eq. (11), and of $A(q)$, Eq. (7); the equation is then solved for $F_{MD}^d(q,t)$ and the result is identified as $F_{sc}^d(q,t)$, the scaling theory for $F_{MD}^d(q,t)$. Then for $0 \leq t \leq t_c(q)$,

$$F_{sc}^d(q,t) = [F_{vib}^d(q,\infty) + A(q)] + B(q) [F_{vib}^d(q,t) - F_{vib}^d(q,t_c)]$$  (12)

where

$$B(q) = \frac{F_{vib}^d(q,0) - F_{vib}^d(q,\infty)}{F_{vib}^d(q,0) - F_{vib}^d(q,t_c)}.$$  (13)

The right side of Eq. (12) is given entirely in terms of the theoretical function $F_{vib}^d(q,t)$, plus the two parameters $A(q)$ and $t_c(q)$, which are determined a priori from their definitions. Eq. (12) satisfies the three theoretical constraints mentioned in the first paragraph of this Section.

Fig. 3b compares $F_{sc}^d(q,t)$ with $F_{MD}^d(q,t)$ for $q = 1.09$ and $0 \leq t \leq 2t_c(q)$. On the meaningful scaling range $0 \leq t \leq t_c(q)$, the maximum deviation between the curves is 0.01, very small compared to their magnitude (see also Fig. 2a, before scaling). The extension beyond $t_c$ shows the theoretical slope has only a small error at $t_c$, but
FIG. 4. For $F^d(q,t)$: Comparison of scaling theory (dash line) and microscopic theory (solid line) with MD (circles) on $0 \leq t \leq 2t_c$. Theory is intended to apply on $0 \leq t \leq t_c$. a) is representative of all $q$ in the first peak regime; b) and c) are characteristic of the Brillouin peak regime.

the curves diverge in a short time after $t_c$. The same graphs for $q = 1.01, 1.11$ and 1.14, the other three $q$ in Table II which are in the first peak, are very similar to Fig. 4a, with maximum discrepancy being $\lesssim 0.01$ in all cases. This is a significant result, as it shows the scaling property is practically identical across the extreme variation of $A(q)$ from 0.06 to $-1.07$ (see also Fig. 1).

Figs. 4b and 4c compare $F^d_{sc}(q,t)$ with $F^d_{MD}(q,t)$ for $q = 0.30$ and 0.71 respectively, in the Brillouin peak regime. The Brillouin peak oscillation is apparent at $t > t_c$, undamped in $F^d_{sc}(q,t)$ and damped in $F^d_{MD}(q,t)$. The standard decorrelation plan does not address the special problem of damping the Brillouin peak oscillation; this will not be a relevant issue until structural decorrelation is studied in Sec. V. For $q = 0.30$, Fig. 4b, the two curves are virtually identical to well past $t_c$, with maximum discrepancy of 0.0005 on $0 \leq t \leq t_c(q)$. For $q = 0.71$, Fig. 4c, the maximum discrepancy of 0.01 on $0 \leq t \leq t_c(q)$ is much larger. This disparity of behavior is what we have come to expect at different $q$. Nevertheless, scaling theory remains accurate to $\lesssim 0.01$ for all $q$ where the standard plan applies.

IV. MICROSCOPIC THEORY FOR MOTIONAL DECORRELATION

A. Transit drift

For the present construction, we start with a perfect vibrational system, for which the equilibrium trajectory has perfect vibrational configurations. Vibrational dephasing operates in $F^d_{vib}(q,t)$, and transits will contribute additional damping of the motional correlations. The decorrelation must begin from zero at any time chosen for the start of the calculation. This condition is satisfied by the vibrational dephasing, but it must be made an initial condition for the transit-induced decorrelation. While the transits observed in MD calculations occur in correlated groups, the present statistical mechanics theory, Eq. (1), requires only the separate motion of one atom at a time. In the MD transits, the single atom motion shows a simple uniform behavior in graphs of the atomic Cartesian coordinates as functions of time. A schematic representation of one such graph is shown in Fig. 5a. A model representation of the same motion in the $x - y$ plane is shown in Fig. 5b. The motion in 3-d is minimally described as follows.

a) Before transit, the atom is in motion on the vibrational surface, approximately a sphere, about equilibrium position $\mathbf{R}$.

b) After transit, the atom is in motion on the vibrational surface, approximately the same sphere, about equilibrium position $\mathbf{R} + \delta \mathbf{R}$.

c) The transit itself is merely the crossing of the boundary between two potential energy valleys, and is essentially instantaneous.

Because the transit is instantaneous, the complete motion as described is consistent with every equilibrium configuration being a perfect vibrational configuration.
from the transit. The transit location is the midpoint
sit similar to that depicted in Fig. 5, in three dimensions.

0

are

fusion coefficient.

fitting a transit random walk to MD data for the self dif-

the mean transit rate for one atom, and is evaluated by

in the equilibrium position of one atom in one transit,

δR

uid Na at 395 K, are needed.

in the nearest-neighbor
atoms that move together in a single transit (from Ref. 33).

FIG. 5. Representation of Cartesian coordinates for a tran-

0 ps.

Consider a single atom trajectory containing one tran-

Two transit parameters, previously calibrated for liq-

liquid Na at 395 K, are needed. δR is the mean change
in the equilibrium position of one atom in one transit, and is evaluated from the transits observed in MD,ν is the
mean transit rate for one atom, and is evaluated from the transits observed in MD. The results, in the form needed here,
are

\[ \frac{1}{2} \delta R = 0.88 \ a_0, \]

\[ \nu^{-1} = 0.26 \ \text{ps}, \] (14)

where \( \nu^{-1} \) is the mean period between successive tran-
sits for one atom. For comparison, the nearest-neighbor
distance is 7.0 \( a_0 \) and the mean vibrational period is
0.40 ps.49

Consider a single atom trajectory containing one tran-
sit similar to that depicted in Fig. 5 in three dimensions.
We ask for the motion contribution resulting specifically
from the transit. The transit location is the midpoint
of \( \delta \mathbf{R} \), and for all transits with a given \( \delta \mathbf{R} \) the col-
clective motion has cylindrical symmetry about \( \delta \mathbf{R} \). Hence
the mean transit-induced motion, \( \mathbf{s}(t) \), is along \( \delta \mathbf{R} \), from
the transit location, to the ultimate mean position \( \frac{1}{2} \delta \mathbf{R} \)
away.

Consider now the entire system. The motions \( \mathbf{s}(t) \)
are proceeding throughout the system at a constant rate.
For each spatial direction, the \( \mathbf{s}(t) \) collectively produce
a steady state motion characterized in the mean per atom by a constant velocity. At any time, these motions
are uniformly distributed over angles. The total motion,
measured per atom, is referred to as the transit drift.

The last theoretical issue is the state of the transit drift
at the endpoint \( t_c \) of the motional decorrelation period.
We expect a single transit per atom, operating along with
the natural dephasing, to damp the motional correlation
to zero. This takes a time \( \nu^{-1} \), hence provides a theo-
retical prediction for \( t_c(q) \). The drift magnitude \( s(t_c) \)
achieved in time \( t_c \) is close to \( \frac{1}{2} \delta R \). The theory there-
fore makes three qualitative predictions about the micro-
scopic process:

\[ t_c(q) \approx \nu^{-1}, \]

\[ s(t_c) \approx \frac{1}{2} \delta R, \] (15)

\[ s(t) \ll t. \]

For the microscopic theory of transit-induced motional
decorrelation, we write

\[ F_{VT}^d(q, t) = F_{vib}^d(q, t) + A(q), \quad 0 \leq t \leq t_c(q), \] (16)

where \( F_{vib}^d(q, t) \) is \( F_{vib}(q, t) \), Eq. (8), modified to include
the transit-induced motion:

\[ F_{vib}^d(q, t) = \frac{1}{N} \sum_{K, L} e^{-i\mathbf{q} \cdot \mathbf{R}_{KL}} \times \]

\[ \left< \left< e^{-i\mathbf{q} \cdot (\mathbf{s}_K(t) + \mathbf{u}_K(t) - \mathbf{u}_L(0))} \right> \right>_tr \times \] (17)

where subscript \( tr \) denotes a transit property. Here
the displacements \( \mathbf{u}_K(t) \) and \( \mathbf{u}_L(0) \) express normal-mode
motion, while \( \mathbf{s}_K(t) \) represents the additional motion due
to transits. We now decouple the \( \mathbf{s}_K(t) \), by evaluating
them as the steady-state average \( \mathbf{s}(t) \), with the initial
condition \( s(0) = 0 \). Then the factor \( e^{-i\mathbf{q} \cdot \mathbf{s}(t)} \) can be se-
parately averaged over angles and removed from the sums.
The remaining factor is just \( F_{vib}^d(q, t) \), so that

\[ F_{vib}^d(q, t) = F_{vib}^d(q, t) \chi_{tr}^d(q, t), \] (18)

where the decorrelation factor (damping factor) is

\[ \chi_{tr}^d(q, t) = \frac{\sin q s(t)}{q s(t)}, \quad 0 \leq t \leq t_c(q). \] (19)

From Eqs. (18) and (19), the two motional decorrelation
processes, natural and transit-induced, operate independ-
ently, and they satisfy the condition of zero decorrela-
tion at \( t = 0 \).
From Eqs. (16) and (18), the final microscopic theory is
\[
F_{VT}^d(q, t) = F_{vib}^d(q, t) \chi^d_{tr}(q, t) + A(q), \quad 0 \leq t \leq t_c(q).
\]
(20)
We have \( \chi^d_{tr}(q, 0) = 1 \), and the endpoint magnitude is calibrated by comparing Eq. (20) with Eq. (9), to find
\[
\chi^d_{tr}(q, t_c) = \frac{F_{vib}^d(q, \infty)}{F_{vib}^d(q, t_c)}.
\]
(21)
Then with Eq. (15), \( \chi^d_{tr}(q, t_c) \) can be solved for \( s(t_c) \), and Eq. (15) prescribes
\[
s(t) = \frac{t}{t_c}s(t_c).
\]
(22)

B. Comparison of theory with MD

Comparison of \( F_{VT}^d(q, t) \) with \( F_{MD}^d(q, t) \) is shown in Fig. 4a for \( q = 1.09 \) and \( 0 \leq t \leq 2t_c \). On the intended theoretical range, \( 0 \leq t \leq t_c \), the agreement of V-T with MD is excellent. The time extension shows the theory is accurate to well beyond \( t_c \). At the same time, the drift has no effect on structural correlation, because it does not noticeably alter the structure.

At \( t_c \leq t \leq 2t_c \), each atom undergoes its second transit after \( t = 0 \). Here and at all later times, the mean transit effect is still the drift, which persists as the same steady flow, while the motional correlation remains zero. But the net drift of each atom accumulates, surpassing the time and distance scales of the normal mode motion, at which point the drift constitutes motion of the atomic equilibrium positions. This motion will damp the system structural correlation.

The analysis now is specifically for \( t \geq t_c \). When structural decorrelation begins, at \( t_c \), Eqs. (8) and (9) combine to yield
\[
F_{VT}^d(q, t_c) = [1 + C(q)]F_{vib}^d(q, \infty).
\]
(23)
The structural information is explicit in the set \( \{R_K\} \) contained in \( F_{vib}^d(q, \infty) \). When the equilibrium positions begin to move, \( R_K \) becomes \( R_K(t) \), with \( R_K(t_c) = R_K(0) \). The theoretical time dependence is then
\[
F_{VT}^d(q, t) = \frac{1}{N} \sum_{K} \left\langle e^{-iq(R_K(t-\delta R_L(0)))} \right\rangle_{tr} e^{-W_K(q)}e^{-W_L(q)},
\]
(24)
Denote the average \( \langle \cdot \rangle_{tr} \) by \( D_{KL}(t) \), suppressing the \( q \) dependence. Consider a time interval \( \delta t \) so small that atom \( K \) is very unlikely to transit more than once in \( \delta t \). Then in \( \delta t \), \( D_{KL}(t) \) changes by
\[
\delta D_{KL}(t) = \left\langle e^{-iq \delta R_K} - 1 \right\rangle_{tr} e^{iq \delta R_L(0)} \nu \delta t.
\]
(25)
In \( \delta t \), atom \( K \) does not transit, or atom \( K \) transits once with probability \( \nu \delta t \). If atom \( K \) does not transit, \( R_K(t+\delta t) = R_K(t) \). If atom \( K \) does transit, \( R_K(t+\delta t) = R_K(t) + \delta R_K \), where \( \delta R_K \) has no time dependence. Then Eq. (25) becomes
\[
\delta D_{KL}(t) \approx \gamma(q)D_{KL}(t),
\]
(27)
where
\[
\gamma(q) = \nu \left[ 1 - \sin\left(\frac{q\delta R}{\delta R}\right) \right].
\]
(28)
The above derivation was presented in our self decorrelation study where $\gamma(q)$ is found to provide accurate structural damping. Here, however, Eq. (27) contains an error due to the neglect of directional correlation in Eq. (26) between the vectors $\delta \mathbf{R}_K$ and $\mathbf{R}_K(t) - \mathbf{R}_L(0)$. This correlation is especially strong for the first transit and for atoms $K, L$ being nearest neighbors at $t = 0$. The result is an anisotropic contribution to the random walk. The corresponding damping coefficient is $G(q)$, which we write in the form

$$G(q) = \gamma(q) + \delta G(q),$$

where $\delta G(q)$ represents the anisotropic contribution to the random walk decorrelation. Then Eq. (27) becomes

$$\frac{\delta D_{KL}(t)}{\delta t} = -G(q)D_{KL}(t), \quad t \geq t_c.$$ (30)

The equation integrates to

$$D_{KL}(t) = e^{-G(q)(t-t_c)}D_{KL}(t_c).$$ (31)

Putting this into Eq. (24) gives the structural decorrelation theory,

$$F_{VT}(q, t) = [1 + C(q)]F_{vib}(q, \infty) e^{-G(q)(t-t_c(q))}. $$ (32)

B. Comparison of theory with MD

Here we shall compare the complete microscopic decorrelation theory with MD, for $t \geq 0$. The parameters needed to calibrate $F_{VT}(q, t)$ are listed in Tables I and II. $G(q)$ is determined by fitting a straight line to log $F_{MT}(q, t)$ vs $t$ on $t > t_c$, where Eq. (32) is supposed to be valid. $\gamma(q)$ is from Table I of Ref. 38. For all test $q$ for which the standard plan applies, the deviations $\Delta F^d(q, t)$ are graphed in Fig. 6 where

$$\Delta F^d(q, t) = F_{VT}(q, t) - F_{MD}(q, t).$$ (33)

Consider the first peak regime. The challenge here is the parameter $A(q)$, which is very large (and negative) at the tip of the first peak, $q = 1.09$ and 1.11, while it has the character of a small systematic correction at all other $q$, including the two additional $q$ in the first peak regime (see Table I, also Fig. 1). The significant result is that the theory accounts uniformly well for the entire decorrelation process for all four test $q$ in the first peak regime. The example of $q = 1.09$ is shown in Fig. 7. For the other three $q$, the overall shape is similar to Fig. 7 and the comparison of theory with MD is qualitatively the same (Fig. 8). Two details are specific to the first peak regime. First, $\delta G/\gamma$ is small and negative at the tip of the first peak ($q = 1.09$ and 1.11), $\delta G/\gamma$ is small and positive on the leading edge ($q = 1.01$), and $\delta G/\gamma$ is negligible on the trailing edge ($q = 1.14$). The physical implication will be discussed in Sec. VI. Second, while

the slope of theory is not controlled at $t_c$, so that a slope discontinuity is to be expected, there is no significant discontinuity in the first peak regime (Fig. 7). Note the
The regime is shown in Fig. 8a and 8b for $q$ generally less than our theoretical error. It is significant that we can set $\delta G/\gamma = 0$ for this $q$.

Success of the standard plan in the first peak regime encourages application of the same procedure to the Brillouin peak regime. The challenge here is the Brillouin peak oscillation. The oscillation itself is present in both $F^d_{MD}(q, t)$ and $F^d_{vib}(q, t)$, but it requires an additional damping in the vibrational function to agree with the MD function at $t > t_c$. However, in the standard plan, the oscillation is completely removed in $F^d_{VT}(q, t)$, via Eq. (32), so the entire oscillation in $F^d_{MD}(q, t)$ appears as an error in $F^d_{VT}(q, t)$ at $t > t_c$. This is not a problem for the standard plan, since the oscillation amplitude is generally less than our theoretical error.

Comparison of theory with MD in the Brillouin peak regime is shown in Fig. 8a and 8b for $q = 0.30$ and 0.71, respectively. The oscillation is much too small to be seen in these two graphs, and the standard plan remains accurate to $\lesssim 0.01$ in the Brillouin peak regime (Fig. 8a). It is significant that we can set $\delta G(q) = 0$ for both test $q$ in the Brillouin peak regime (see Table II).

The $F^d_{MD}(q, t)$ data exhibit a feature not related to decorrelation, a long-time irregular behavior in which the MD function breaks from its smooth decay curve, and avoids further damping for an extended period. In the present study, the irregular behavior ranges in magnitude from 0 to 0.02, the maximal example being at $q = 1.11$, shown in Fig. 9. We suspect this is an artifact of periodic boundary conditions. Fig. 9 also shows the good agreement of theory with MD as the curves approach zero, before the irregular behavior begins.

In the large $q$ regime, at $q$ beyond the first peak, three $q$ were chosen for study, located respectively at the first minimum, second maximum, and second minimum of $F^d_{MD}(q, 0)$ (see Fig. 1 and Table I). At $q = 1.51$, shown in Fig. 10 it is perhaps surprising that the standard plan still works well. Both motional and structural decorrelation are accurately accounted for, the theoretical slope discontinuity at $t_c$ is insignificant, and we are able to set $\delta G(q) = 0$ in the structural damping. The deviation $\Delta F^d(q, t)$ in Fig. 10 is well below 0.01.

As $q$ increases further, two important changes occur. First, $F^d_{vib}(q, \infty)$ goes to zero, as noted following Eq. (30), and as seen in the last three entries of Table I. Second, the decorrelation process becomes faster, with $t_c(q)$ falling below the first-transit period of $\nu^{-1}$, again as seen in Table I. These changes mark the ultimate convergence of the distinct autocorrelation function toward zero as $q$ increases. Both trends are also found in the self autocorrelation function as $q$ increases toward the free particle limit. As a result, at $q = 2.00$ and 2.51, the total process resembles a single motional decorrelation of an unusual shape. The indication is that $q \gtrsim 2.00$ does not measure structural correlation, and measures motional correlation in a way different from what we have seen at smaller $q$.

### Table II. Data required for the structural decorrelation, at $t \geq t_c(q)$. $\gamma(q)$ is from Table I of Ref. 38.

| $q$ ($a^{-1}$) | $1 + C(q)$ | $\gamma(q)$ (ps$^{-1}$) | $\delta G(q)/\gamma(q)$ |
|---------------|-----------|----------------|--------------------------|
| 0.29711       | 0.9982    | 0.1733         | -0.009$^a$               |
| 0.70726       | 1.0091    | 0.9222         | -0.036$^a$               |
| 1.01482       | 1.1292    | 1.7500         | 0.173                    |
| 1.09165       | 0.7338    | 1.9753         | -0.273                   |
| 1.10505       | 0.5122    | 2.0146         | -0.258                   |
| 1.14429       | 1.0576    | 2.1312         | -0.004$^a$               |
| 1.50523       | 0.7828    | 3.1805         | -0.075$^a$               |

$^a$ In applying the theory, we set $\delta G/\gamma = 0$ for this $q$. 

![FIG. 8. For $F^d(q, t)$: Comparison of the complete microscopic V-T theory (line) with MD (circles), for two $q$ in the Brillouin peak regime.](image)

![FIG. 9. For $F^d(q, t)$: Long-time data showing the MD irregular behavior at $t/t_c > 8$ (circles), not addressed in V-T theory (line).](image)
VI. RANGE OF APPLICABILITY OF THE STANDARD PLAN

A. Exclusion band

There are several q-segments where $F_{MD}^d(q,0)$ and/or $F_{vib}^d(q,0)$ are of small magnitude, say $\lesssim 0.1$, where analysis is difficult for two reasons. First, the values of the MD and vibrational autocorrelation functions are small enough to be compromised by finite-$N$ error, at our present $N = 500$. Second, the MD and vibrational functions cross zero at different $q$-values, a phase shift not treated in the standard plan. It makes sense to leave these effects until the dominant part of the theory is developed.

B. First-peak regime

This is where $F_{MD}^d(q,0)$ and $F_{vib}^d(q,0)$ are positive in the first peak. This regime provided the test case from which the standard plan was developed. Here the $F_{MD}^d(q,t)$ curves have uniform character across the $q$-range, and so do the $F_{vib}^d(q,t)$ curves. Since distinct and self contributions are both positive, no cancellation complications arise.

C. Brillouin-peak regime

This is where the Brillouin peak oscillation is apparent in $F_{MD}^d(q,t)$; in our system it runs from $q = 0.13$, the smallest allowed $q$, to somewhat beyond $q = 0.80$. Here, $F_{MD}^d(q,0)$ and $F_{vib}^d(q,0)$ are around $-1$; on this scale the standard plan is accurate, as shown in Fig. 5 and may be applied.

In this regime, the self and distinct autocorrelation functions nearly cancel for MD data, and also for vibrational data. The Brillouin peak oscillation appears entirely in the distinct function, and contains important physics not addressed in the standard plan, namely the inelastic scattering cross section as function of $q$ and $\omega$. For our system, the Brillouin peak oscillation appears in $F_{vib}^d(q,t)$ with the same frequency as it appears in $F_{MD}^d(q,t)$, for all $q$ in the regime. Hence $F_{vib}^d(q,t)$ already contains the Brillouin peak dispersion curve, a priori and to very high accuracy. What is still required for a complete theory of dynamic response is an extremely accurate decorrelation theory for the Brillouin peak oscillation.

D. Large-$q$ regime

Beyond the first peak, near the first and second minima and the second maximum, where $|F_{MD}^d(q,0)|$ is large enough to justify an exploratory investigation, the character of the decorrelation process changes under two influences: The motional decorrelation becomes faster, and $F_{vib}^d(q,\infty)$ goes to zero (see Table I). At $q = 1.51$, the standard plan still applies and is still accurate, but a practiced eye will see the beginning of change. At $q = 2.00$ and 2.51, the entire process has the appearance of a single motional decorrelation, an appearance we expect to remain as $q$ increases further, and the MD and vibrational autocorrelation functions converge to zero (see the discussion at the end of Sec. V). The standard plan does not apply at these $q$.

VII. CONCLUSION

A. Physical nature of the theory

This work is an investigation into the validity of V-T theory for the distinct density autocorrelation function of a monatomic liquid. The simple conclusion is that the theory is valid, indeed accurate, over the broad range of $q$ for which the standard decorrelation plan applies. That question answered, the primary interest shifts to the physical nature of the theory, which is unique in this study.

At the outset, the two classes of configurational correlation, motional and structural, are precisely defined by the perfect vibrational system. The motional correlation is measured by the time correlation functions in Eq. (5), and the motional decorrelation carries these functions from their values at $t = 0$ to zero. In the process, $F_{vib}^d(q,t)$ goes from $F_{vib}^d(q,0)$ to $F_{vib}^d(q,\infty)$ according to Eqs. (3) and (4). The structural correlation is measured by the set of equilibrium positions $\{R_K\}$, and the Debye-Waller factors $\{W_K(q)\}$, in Eq. (1) for $F_{vib}^d(q,\infty)$. The $R_K$ remain fixed during the motional damping, then the $R_K$ begin to move and proceed to damp $F_{vib}^d(q,\infty)$ to zero. This outline of the process is defined entirely in terms of the theoretical function $F_{vib}^d(q,t)$, the definition applying to all monatomic liquids.

The three $q$-dependent parameters that enable calculation of the detailed time dependence are transit properties. They are theoretically defined and hence in prin-
ciple amenable to theoretical determination. In physical meaning, $A(q)$ is the transit contribution to the static structure factor. $A(q)$ is supposed to be mainly structural, hence is modeled as a multiple of $F_{\text{eq}}^c(q, \infty)$. The crossover time $t_c(q)$ is the time required to damp the motional correlation to zero, under the simultaneous actions of natural dephasing and transit-induced decorrelation.

The physical key to $t_c(q)$ is the condition that long-time motional correlation due to low-lying normal modes is damped out by transits in the liquid. Finally, the structural damping coefficient $G(q)$ expresses the transit random walk, and an a priori zeroth-order theory for $G(q)$ is already in place. All these properties are attributed to the same transits in every monatomic liquid.

With the present study, and our previous one on self density autocorrelation [3], it is clear that V-T theory provides a formal unification of equilibrium and nonequilibrium statistical mechanics. Now, statistical mechanics of the vibrational motion is based on exact normal-mode theory, numerically evaluated from the same eigenvector data sets, for equilibrium and non-equilibrium properties alike. Moreover, there is consistency between the transit models in the equilibrium and nonequilibrium formulations. This unification is unprecedented in liquid dynamics theory, and is conceptually equivalent to that in lattice dynamics, with interacting harmonic phonons and that in gas dynamics, with interacting free particles.

**B. Predictions of the transit model**

The transit drift is the massively averaged motion resulting specifically from transits in the liquid state, and present in addition to the normal mode motion. In Sec. IV, in constructing a model equation for the drift-induced motional decorrelation, in the period $0 \leq t \leq t_c(q)$, three predictions are made about characteristic properties of the drift. The predictions are expressed in terms of the transit parameters $\nu$ and $\delta R$, previously calibrated independently of density autocorrelation theory, with values given in Eq. (14). The predictions are listed in Eq. (15).

a) The first prediction is $t_c(q) \approx \nu^{-1}$. This is qualitatively correct. Specifically, $\nu^{-1} = 0.26$ ps, while from Table I the average $t_c(q)$ for seven $q$ in the standard plan is $0.30 \pm 0.10$ ps.

b) The second prediction is $s(q, t_c) \approx \frac{1}{2} \delta R$. This is qualitatively correct. Specifically, $\frac{1}{2} \delta R = 0.88$ $a_0$, while from Table I the average $s(q, t_c)$ for seven $q$ in the standard plan is $0.70 \pm 0.10$ $a_0$.

c) The third prediction is $s(q, t) \propto t$ for $0 \leq t \leq t_c(q)$. The linear $t$ dependence is used in evaluating the motional decorrelation, Eq. (22), and agreement of theory with MD in Fig. 3 verifies the $t$ dependence within the observed errors.

The level of agreement cited is excellent for nonequilibrium data. The three-point rationalization can be considered an approximate transit theory, capable of providing a priori estimates of the quantities compared. Finally, the systematic character of the V-T theory errors, shown in Fig. 5, indicates that the motional decorrelation theory of Eqs. (19) and (20) can still be improved.

As an independent exercise, it was found that a linear scaling approximation accurately accounts for the damping of $F_{\text{eq}}^c(q, t)$ to $F_{MD}^c(q, t)$ on $0 \leq t \leq t_c(q)$. The physical implication is that the transit-induced motional decorrelation is proportional to the vibrational dephasing.

The transit drift is a steady state motion, hence is always present in the liquid. However, in order to address the structural decorrelation at $t > t_c$, it is necessary to resolve the drift into its effective motion of the equilibrium positions. This resolution yields the transit random walk. Indeed, the time required after $t = 0$ for the random walk to come into effect provides the physical explanation for the delay to $t_c(q)$ of the onset of structural decorrelation, as it appears in Eq. (12).

Simple exponential decay, beginning after a delay period, is a hallmark of MD data for self and distinct density autocorrelation functions. In self decorrelation, the theoretical damping coefficient $\gamma(q)$ is in excellent agreement with MD data for all $q$. The result constitutes another unification within V-T theory: One cannot calculate the density autocorrelation damping coefficient $\gamma(q)$ from the self diffusion coefficient $D_{\text{MD}}$, but one can calculate both $\gamma(q)$ and $D$ from the same random walk of the equilibrium positions.

Finally, we shall make a highly approximate model for the anisotropic damping coefficient $\delta G(q)$. Consider a representative pair of atoms $K$, $L$ which are nearest neighbors at $t = 0$. Because the atomic dynamics enforces a minimum distance between atoms, the first-transit drift of atom $K$ will not be isotropically distributed about $\mathbf{R}_K(0)$, but will move preferentially away from $\mathbf{R}_L(0)$. The transit random walk will not develop about $\mathbf{R}_K(0)$, but about $\mathbf{R}_K(0) + \delta \mathbf{s}_K$, where $\delta \mathbf{s}_K$ is a small displacement in the direction of $\mathbf{R}_KL(0)$. The picture can be developed from Eq. (17). The resulting $\delta G(q)$ will be positive for $q$ on the first-peak leading edge, and negative at the first-peak tip. This is what we see in Sec. V. Moreover, since the effect appears only for nearest neighbors, $\delta G/\gamma$ will be significant only for $q$ in the first peak regime. Even for $q$ in the first peak, $\delta G/\gamma$ is small because the correlation is weak after the first transit. All these details of $\delta G/\gamma$ are confirmed by the last column of Table II. The theoretical challenge now is a more quantitative understanding of $\delta G/\gamma$.

**ACKNOWLEDGMENTS**

We are pleased to thank Brad Clements and Renzo Vallauri for helpful comments on the manuscript.
