Atomic motion from the mean square displacement in a monatomic liquid

Duane C Wallace¹, Giulia De Lorenzi-Venneri¹ and Eric D Chisolm²

¹ Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM 87545, USA
² Descartes Labs, Los Alamos, NM 87544, USA

E-mail: gvenneri@lanl.gov

Received 28 December 2015, revised 10 February 2016
Accepted for publication 14 March 2016
Published 8 April 2016

Abstract
V-T theory is constructed in the many-body Hamiltonian formulation, and is being developed as a novel approach to liquid dynamics theory. In this theory the liquid atomic motion consists of two contributions, normal mode vibrations in a single representative potential energy valley, and transits, which carry the system across boundaries between valleys. The mean square displacement time correlation function (the MSD) is a direct measure of the atomic motion, and our goal is to determine if the V-T formalism can produce a physically sensible account of this motion. We employ molecular dynamics (MD) data for a system representing liquid Na, and find the motion evolves in three successive time intervals: on the first ‘vibrational’ interval, the vibrational motion alone gives a highly accurate account of the MD data; on the second ‘crossover’ interval, the vibrational MSD saturates to a constant while the transit motion builds up from zero; on the third ‘random walk’ interval, the transit motion produces a purely diffusive random walk of the vibrational equilibrium positions. This motional evolution agrees with, and adds refinement to, the MSD atomic motion as described by current liquid dynamics theories.

Keywords: liquid theory, Hamiltonian, atomic motion in liquids, statistical mechanics, dynamic response

(Some figures may appear in colour only in the online journal)
case, and they provide us with the following motional description of the liquid MD data for the MSD [6]: Ballistic motion at short times, with $X_{\text{MD}}(t) \propto t^2$, and diffusive motion at long times, with $X_{\text{MD}}(t) \propto t$. This behavior is common in a broad range of liquid types, for example in binary LJ and silica systems (figure 3 of [6]), complex hard sphere systems [7], a one-component LJ system [8], and in first-principles MD simulations for Al [9]. We shall compare our present results for the atomic motion with this established description in the conclusion.

The theory presented here, which we call V-T (vibration-transit) theory, follows the classic many body Hamiltonian formulation; this is an interesting option for liquid dynamics, because that formulation already encodes in a common language much of our understanding of condensed matter physics [10–17]. We start with the tractable Hamiltonian for harmonic vibrational motion within a single many atom potential energy valley of the class of valleys the system visits in the liquid state. To account for the liquid diffusive properties, we add transit motion, where each transit is the correlated motion of a small local group of atoms that carries the system across the boundary between two potential energy valleys. Such transits have been observed in low temperature equilibrium MD trajectories [18]. The vibrational Hamiltonian is calculated from first principles, transits are modeled in terms of adjustable parameters, and a time correlation function is calculated directly from the combined motions.

2. Liquid potential energy surface

Many years ago, Frenkel argued that the motion of a liquid atom consists of vibrations about a temporary equilibrium position, interspersed by jumps of that equilibrium position [19, 20]. Zwanzig considered the liquid motion to consist of normal-mode vibrations interrupted by positional jumps that destroy the vibrational coherence, and proceeded to derive an approximate formula for the Stokes–Einstein relation [21]. Zwanzig’s motional description is modified here to produce additive, instead of multiplicative, vibrational and transit contributions (equations (9)–(11)). Stillinger and Weber found the potential energy minima that underlie the liquid system, the ‘inherent structures’, and suggested that liquid properties result from vibrational excitations within, and shifting equilibria between, these structures [22]. These authors also found a wide range of inherent structure energies, which is included in their free energy [23]. As described below, our formulation includes only the statistically dominant structures. For a binary Lennard-Jones system, Büchner and Heuer found complex dynamical behaviors related to the glass transition that were not present at liquid temperatures [24]. Angelani et al observed a change in the character of the motion at the mode-coupling temperature $T_{\text{MCT}}$, from motion within the basin of an inherent structure below $T_{\text{MCT}}$, to motion within the basin of a saddle above $T_{\text{MCT}}$ [25]. The picture developed of a ‘rugged potential energy landscape’, with a wide distribution of structural energies, separated by saddles also having a wide distribution of energies. Keyes and Chowdhary made an extremely detailed investigation of the temperature ($T$) dependent diffusion process, with emphasis on the crossover from high- to low-$T$ dynamics as $T$ decreases to $T_{\text{MCT}}$ [26]. Among other new observations, they find a temperature range where the motion is diffusive within a single basin because of the roughness of the upper reaches of the basin. A possible projection of this effect is seen here in the saturation of the vibrational contribution (figure 1).

We also studied the potential energy surface, with the goal of better understanding the atomic motion in monatomic liquids at $T \gtrsim T_\text{m}$, the melting temperature. We studied $N$-atom MD equilibrium trajectories, and quenches from them, for Na and Lennard-Jones Ar. The following properties were established [27–31].

The 3$N$-dimensional potential surface is composed of intersecting nearly harmonic valleys which we classify as random, being maximally disordered, and symmetric, having a measure of crystalline symmetry. Random and symmetric structures are unambiguously identified by their energy distributions, pair distribution functions, Voronoi neighbor symmetries and other properties. The structural potentials lie in three distinct distributions, the crystal at the lowest energy, a narrow random distribution at the highest energy, and a scatter of symmetries ranging from crystal to random. Upon increasing $N$, the random distribution approaches zero width at constant mean, and the randoms become so vastly more numerous that symmetries vanish from the structural energy distribution. These results provide two conclusions upon which V-T theory is based, both subject to finite-$N$ error. (a) The random valleys dominate the statistical mechanics at $T \gtrsim T_\text{m}$. (b) The random valley distribution of a macroscopic statistical mechanical function has negligible variance, so that a single such valley suffices for vibrational theory.

At this point we have a reliable, accurate, and ab initio procedure for evaluating liquid vibrational properties. It begins.
3. Evolution of the atomic motion

In this first application of V-T theory to the MSD, our goal is to determine if the many-body formulation can produce a physically sensible account of the atomic motion underlying the MSD. Our system represents liquid Na at 395 K, in terms of a well tested interatomic potential from pseudopotential perturbation theory (figures 1.1, 17.3 19.1–19.3, 20.1 of [17]).

\( X_{\text{MD}}(t) \) is calculated directly from the theoretical expression for the MSD,

\[
X_{\text{MD}}(t) = \frac{1}{N} \sum_{K} (|\mathbf{r}_{K}(t) - \mathbf{r}_{K}(0)|^{2})_{\text{MD}},
\]

where \( \mathbf{r}_{K}(t) \) is the position of atom \( K \) for \( K = 1, \ldots, N \), and \( < \cdot >_{\text{MD}} \) is the average over \( t = 0 \) start times. The V-T theory expression, \( X_{\text{VT}}(t) \), has vibrational and transit terms plus an interaction, written as

\[
X_{\text{VT}}(t) = X_{\text{vib}}(t) + X_{\text{d}}(t) + X_{\text{int}}(t).
\]

Our premise is that all significant contributions are contained in \( X_{\text{vib}}(t) \) or \( X_{\text{d}}(t) \), while \( X_{\text{int}}(t) \) expresses residual errors that can be neglected or trivially approximated. Two interaction examples are discussed in this report.

Figure 1 presents a comparative graph of \( X_{\text{MD}}(t) \) and \( X_{\text{vib}}(t) \), from which \( X_{\text{d}}(t) \) can be visualized. The figure is divided into three time intervals, which correspond to distinct atomic motions that underlie the MSD. The vibrational interval recognizes the remarkable property that \( X_{\text{MD}}(t) \) is in near perfect agreement with \( X_{\text{vib}}(t) \) up to time \( \tau_{D} \), the delay time. \( \tau_{D} \) is defined as the time when \( X_{\text{MD}}(t) \) moves away from \( X_{\text{vib}}(t) \), hence \( \tau_{D} \) is qualitative and may be chosen with some leeway. Our calibration of \( \tau_{D} \) and the remaining parameters is listed in table 1. \( \tau_{\text{RW}} \) is defined as the time when \( X_{\text{MD}}(t) \) reaches its ultimate straight line behavior, and will be calibrated below.

To derive \( X_{\text{vib}}(t) \) we 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 vibrational displacement. Following equation (1) we have

| \( \nu \) | \( \delta R \) | \( S \) | \( \tau_{D} \) | \( \tau_{\text{RW}} \) |
|---|---|---|---|---|
| 3.9 ps\(^{-1} \) | 1.75 a\(_{0}\) | 1.46 a\(_{0}\) | 28 \( \delta t \) | 60 \( \delta t \) |

*Note:* The MD time step is \( \delta t = 7.002 \) 88 fs.

with calculation of the vibrational Hamiltonian for a single random valley, via known interatomic potentials or DFT. The DFT case is described in sections 2 and 4 of [32]. With the valley formally extended to infinity, exact statistical mechanical formulas may be derived for all thermodynamic functions.

Corrections for the inter-valley intersections is made part of the ballistic contribution, which is accurate only to \( \tau_{\text{RW}} = 9 \delta t \).

\[
X_{\text{vib}}(t) = \frac{1}{M} \sum_{K} \left( |\mathbf{u}_{K}(t) - \mathbf{u}_{K}(0)|^{2} \right)_{\text{vib}}.
\]

Equation (4) is evaluated by transforming to normal modes, as shown in section 5.1 of [35], to obtain

\[
X_{\text{vib}}(t) = \frac{6k_{B}T}{M} \sum_{\lambda} \frac{1 - \cos \omega_{\lambda}t}{\omega_{\lambda}^{2}} \sum_{\lambda} \frac{1 - \cos \omega_{\lambda}t}{\omega_{\lambda}^{2}}
\]

where \( M \) is the atomic mass, and \( \omega_{\lambda} \) are the frequencies of the normal modes \( \lambda = 1, \ldots, 3N - 3 \), having omitted the three modes for which \( \omega_{\lambda} = 0 \). Equation (5) is explicit and tractable; it depends on the frequency spectrum but not on the mode eigenvectors.

Ballistic motion satisfies \( \mathbf{u}_{K}(t) - \mathbf{u}_{K}(0) = \mathbf{v}_{K}(0)t \), where \( \mathbf{v}_{K} \) is the velocity of atom \( K \), so the ballistic contribution to the MSD is \( (3k_{B}T/M)\tau_{\text{RW}}^{2} \). This is precisely the leading term in the small-\( t \) expansion of equation (5); the vibrational motion automatically produces the correct ballistic contribution in \( X_{\text{vib}}(t) \). As shown in figure 2, the ballistic contribution is accurate for only a small part of the vibrational interval, namely to a time around \( \frac{1}{3} \tau_{D} \) and a magnitude around \( \frac{1}{3} X_{\text{vib}}(\tau_{D}) \). Following the ballistic regime, the terms in \( \cos(\omega_{\lambda}t) \) take over and change the curvature of \( X_{\text{vib}}(t) \) from positive to negative in figure 2. Moreover, the set of \( \cos(\omega_{\lambda}t) \) begins to dephase, and this dephasing causes the leveling of \( X_{\text{vib}}(t) \) until it becomes constant at \( \tau_{\text{RW}} \) in figure 1.

In figure 1, \( X_{\text{vib}}(t) \) shows a small slope discontinuity at \( \tau_{\text{RW}} \), arising as follows. The actual \( X_{\text{vib}}(t) \) curve weakly overshoots \( X_{\text{vib}}(\tau_{\text{RW}}) \) and rises to a low maximum around 150 \( \delta t \), where \( \delta t \) is the MD time step, then falls back to \( X_{\text{vib}}(\tau_{\text{RW}}) \) at 300 \( \delta t \), where it remains. The overshoot is the final dephasing of the lowest frequency vibrational modes. However, we are not able to discern a remnant of this overshoot in \( X_{\text{MD}}(t) \); the slope of \( X_{\text{MD}}(t) \) is strictly constant where the vibrational overshoot is

![Figure 2](https://example.com/image2.png)
We attribute this effect to an extra damping of the vibrational motion by the strong transit activity in the MD system at $\tau/\geq \tau_{RW}$. This damping is a vibration transit interaction, which we account for by setting $\tau_{vib}^{vib}$ to $\tau_{vib}^{RW}$ at $\tau_{RW}$, causing the slope discontinuity in figure 1.

The question now is, how can the MD system measure nothing but pure vibrational motion for $\tau$ up to $\tau_D$? As illustrated in equation (1), the MSD measures the motion of one atom at a time on the system trajectory. This single-atom motion can be decomposed into continuous vibration about its fixed equilibrium position $R_K$, plus the mean transit-induced motion of its equilibrium position, abbreviated ‘transit motion’. With each transit, this mean motion starts from zero and covers a distance denoted $\delta R$. The MSD cannot resolve this motion, hence cannot measure it, until it has reached a sufficient magnitude. This requires a certain time which we identify as $\tau_D$.

For the collective liquid system, transits are occurring throughout the volume uniformly in space and time, with mean transit rate $\nu$ per atom. Eventually, $X_{MD}(t)$ is able to fully measure every transit, from start to completion, and the measured collective transit motion becomes a steady process: its effect is to move the equilibrium position of every atom a distance $\delta R$, uniformly distributed over directions, in each time period $\nu^{-1}$. This motion is a random walk, whose contribution to the MSD starts at $\tau_{RW}$ and thereafter is

$$X_{RW}(t) = \nu(\delta R)^2(t - \tau_{RW}), \quad t \geq \tau_{RW}. \quad (6)$$

This random walk was initially derived as a damping factor for the self intermediate scattering function [36] and was calibrated to the Einstein relation $\nu(\delta R)^2 = 6D$, which of course is the correct calibration here as well. Moreover, $\delta R$ was also calibrated independently [36], from our observed transits [18], so we have values for both $\nu$ and $\delta R$, which are listed in table 1.

Finally we can define $\tau_{RW}$ in the context of V-T theory: it is the time when $X_{vib}(t)$ has saturated to a constant and the transit random walk has become a steady process. As a practical way to calibrate $\tau_{RW}$, the slope of $X_{MD}(t)$ should reach $6D$ at $\tau_{RW}$ and should remain there as $t$ increases. Graphical application of this technique is shown in figure 3 and gives the value $\tau_{RW} = 60 \delta t$. This evaluation is confirmed below.
To study the transit contribution to the MSD at $t \geq \tau_{RW}$, we graph $X_{MD}(t) - X_{vb}(t)$ as the dotted curve in figure 4. The Figure confirms the accuracy of $X_{vb}(t)$ for the ballistic motion. The dotted curve shows a very small negative dip in the vibrational interval, the curve then turns sharply upward, but the dominant time dependence is linear in $t$ from $\tau_{D}$ to $\tau_{RW}$. All this allows a simple mean-transit approximation for $X_{e}(t)$ on $0 \leq t \leq \tau_{RW}$:

$$X_{e}(t) = 0,$$

$$X_{e}(t) = \nu(t - \tau_{D})S^{2}, \quad \tau_{D} \leq t \leq \tau_{RW}.$$  

(7)

(8)

In equation (8), $\nu(t - \tau_{D})$ is the number of transits per atom in $t - \tau_{D}$, and $S^{2}$ is the mean single-transit contribution over the crossover interval. $S^{2}$ is calibrated by setting $X_{e}(\tau_{RW})$ to $X_{MD}(\tau_{RW}) - X_{vb}(\tau_{RW})$, which expresses the endpoint at $\tau_{RW}$ of the second line segment in figure 4. The error of equations (7) and (8) is seen in figure 4 and is assigned to $X_{e}(t)$ and neglected. We find $S = 1.46 a_{0}$, a bit less than $bR$ in table 1 because some of the transit contribution is lost in the delay.

The approximation equation (8) is specifically in terms of the atomic motion, and is tractable.

To test the stability of the fit provided by equations (6)–(8), we systematically varied $\tau_{D}$ and $\tau_{RW}$ away from their values in figure 4, and found the overall error increases but remains acceptable for $\tau_{D} = (27 \pm 29) \delta t$ and $\tau_{RW} = (56 \pm 66) \delta t$. The theory does not ask for accurate calibration of these characteristic times.

4. Summary and conclusion

The potential energy surface employed by V-T theory is not the rugged landscape that is well-studied in the literature; it is only the statistically dominant class of random valleys whose structures form the high energy plateau of that landscape.

The equations for $X_{VT}(t)$ on the three time intervals of figure 1 are summarized as follows.

1. Vibrational interval: $0 \leq t \leq \tau_{D}$
   $$X_{VT}(t) = X_{vb}(t)$$

2. Crossover interval: $\tau_{D} \leq t \leq \tau_{RW}$
   $$X_{VT}(t) = X_{vb}(t) + \nu(t - \tau_{D})S^{2}$$

3. Transit random walk interval: $t \geq \tau_{RW}$
   $$X_{VT}(t) = X_{VT}(\tau_{RW}) + \nu(t - \tau_{RW})(\delta R)^{2}$$

The following summary of the motion compares directly with the established description cited in the Introduction.

The vibrational motion contributes to the MSD on $t \geq 0$ (figure 1). This motion is ballistic for a very short time, then goes over to vibrational dephasing until its completion at $\tau_{RW}$, when $X_{vb}(t)$ becomes constant. $X_{vb}(t)$ accurately agrees with $X_{MD}(t)$ on $0 \leq t \leq \tau_{D}$, therefore $X_{vb}(t)$ constitutes the complete theory until $\tau_{D}$.

Transit motion contributes to the MSD on $t \geq \tau_{D}$ (figure 1), and $X_{d}(t)$ builds up from zero at $\tau_{D}$ to the ultimate random walk $X_{MD}(t)$ (figure 4). This build up is accurately accounted for: figure 5 compares $X_{VT}(t)$ and $X_{MD}(t)$ for all $t$, and shows the maximum error magnitude of 2.5% near the center of the crossover interval.

At $t \geq \tau_{RW}$, the transit motion constitutes a random walk of the atomic equilibrium positions, which is calibrated from the self-diffusion coefficient $D$, making the theory agree with $X_{MD}(t)$.

We conclude that this account of the atomic motion is physically sensible because it agrees with the established description, and the account also adds significant information to that description. The equations for the atomic motion can be implemented more generally in liquid dynamics research. We are currently applying precisely the same atomic motion to the self intermediate scattering function at all $q$ and $t$.

Acknowledgments

We are pleased to thank B Clements, L Collins, J Kress and A Votier for helpful and encouraging discussions. This research is supported by the Department of Energy under Contract No. DE-AC52-06NA25396.

References

[1] Einstein A 1905 Ann. Phys. 17 549
[2] Hansen J-P and McDonald I R 2007 Theory of Simple Liquids 3rd edn (New York: Academic)
[3] Boon J P and Yip S 1991 Molecular Hydrodynamics (New York: Dover)
[4] Güttel W 2009 Complex Dynamics of Glass Forming Liquids: a Mode-Coupling Theory (Oxford: Oxford University Press)
[5] Binder K and Kob W 2005 Glassy Materials and Disordered Solids: An Introduction to their Statistical Mechanics (Singapore: World Scientific)
[6] Kob W 1999 J. Phys.: Condens. Matter 11 R85
[7] Tokuyama M 2008 Physica A 387 5003
[8] Voang V 2013 Phil. Mag. 91 3443
[9] Jakse N and Pasturel A 2013 J. Phys.: Condens. Matter 25 285103
[10] Pines D 1997 The Many-Body Problem (Reading, MA: Addison-Wesley)
[11] Pines D 1997 Elementary Excitations in Solids (Reading, MA: Addison-Wesley)
[12] Kittel C 1963 Quantum Theory of Solids (New York: Wiley)
[13] Harrison W A 1966 Pseudopotentials in the Theory of Metals (New York: Benjamin)
[14] Ashcroft N W and Mermin N D 1976 Solid State Physics (Orlando: Harcourt Brace)
[15] Lovesey L W 1984 Theory of Neutron Scattering from Condensed Matter vol 1 (Oxford: Clarendon)
[16] Glyde H R 1994 Excitations in Liquid and Solid Helium (Oxford: Clarendon)
[17] Wallace D C 2002 Statistical Physics of Crystals and Liquids (New Jersey: World Scientific)
[18] Wallace D C, Chiselin E D and Clements B E 2001 Phys. Rev. E 64 011205
[19] Frenkel J 1926 Z. Phys. 35 652
[20] Frenkel J 1946 Kinetic Theory of Liquids (Oxford: Clarendon) chapter 3, section 1
[21] Zwanzig R 1983 *J. Chem. Phys.* **79** 4507
[22] Stillinger F H and Weber T A 1983 *Phys. Rev. A* **28** 2408
[23] Stillinger F H and Weber T A 1984 *Science* **225** 983
[24] Büchner S and Heuer A 2000 *Phys. Rev. Lett.* **84** 2168
[25] Angelani L, Di Leonardo R, Ruocco G, Scala A and Sciortino F 2000 *Phys. Rev. Lett.* **85** 5356
[26] Keyes T and Chowdhary J 2002 *Phys. Rev. E* **65** 041106
[27] Wallace D C and Clements B E 1999 *Phys. Rev. E* **59** 2942
[28] Clements B E and Wallace D C 1999 *Phys. Rev. E* **59** 2955
[29] De Lorenzi-Venneri G and Wallace D C 2007 *Phys. Rev. E* **76** 041203
[30] Holmström E, Bock N, Peery T B, Lizárraga R, De Lorenzi-Venneri G, Chisolm E D and Wallace D C 2009 *Phys. Rev. E* **80** 051111
[31] Holmström E, Bock N, Peery T, Chisolm E, Lizárraga R, De Lorenzi-Venneri G and Wallace D 2010 *Phys. Rev. B* **82** 024203
[32] Rudin S P, Bock N and Wallace D C 2014 *Phys. Rev. B* **90** 174109
[33] Wallace D C, Chisolm E D, Bock N and De Lorenzi-Venneri G 2010 *Phys. Rev. E* **81** 041201
[34] Bock N, Holmström E, Peery T B, Lizárraga R, Chisolm E D, De Lorenzi-Venneri G and Wallace D C 2010 *Phys. Rev. B* **82** 144101
[35] Chisolm E D and Wallace D C 2001 *J. Phys.: Condens. Matter* **13** R739
[36] De Lorenzi-Venneri G, Chisolm E D and Wallace D C 2008 *Phys. Rev. E* **78** 041205