New theoretical description of neutron scattering in a monatomic liquid

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In a recently developed theory of the atomic motion in monatomic liquids, the motion is comprised of normal mode vibrations in any of the large number of equivalent random valleys, interspersed with nearly instantaneous transits which carry the system between neighboring valleys. The consequences for $S(q,\omega)$ are presented here: when the system moves in a single random valley, the inelastic part of $S(q,\omega)$ is a sum over all vibrational modes of the inelastic cross section of each single mode; in the liquid state the system undergoes transits at a rapid rate, causing the Rayleigh and Brillouin peaks to broaden but not to shift; over the entire $q$ range where the Brillouin peak is distinguishable, its location in the liquid is the same as it is in a single random valley. These properties are verified by comparison between theory and MD calculations. We believe our theory provides a physically realistic approach for the study of liquid dynamics.

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A theory of the motion of atoms in a monatomic liquid has been developed, strongly motivated by the measured thermodynamic properties of elemental liquids. The potential energy surface underlying the motion is supposed to consist of a very large number of intersecting nearly harmonic many particle valleys. Valleys whose structure (the configuration of atoms at the bottom of the valley) has crystalline or microcrystalline symmetry are relatively few in number, while valleys with the maximally disordered random structures are of overwhelming numerical superiority, and consequently dominate the statistical mechanics of the liquid. The identification of random valleys is an important step, since they all have identical macroscopic properties in the thermodynamic limit, hence have the same structural potential energy and the same distribution of normal vibrational modes. The corresponding atomic motion is comprised of two parts: normal mode vibrational motion within a single random valley, interspersed with motions across valley intersections, called transits. Further, the valley intersections are supposed to be sharp, and the transits nearly instantaneous, so that the equilibrium thermodynamic properties result from motion within a single random valley, while the transits are responsible for diffusion. The presence of inherent structures in the liquid was demonstrated by Stillinger and Weber [1,2], while the remaining details regarding the potential energy surface and the nature of the vibrational and transit motion were postulated in [3]. The theory has been confirmed by comparison with thermodynamic properties of elemental liquids [3,4], by computer studies of random valleys and their normal vibrational modes [3,4], by observation of single transits in molecular dynamics (MD) calculations [5] and by a study of the velocity autocorrelation function and self-diffusion [5]. A review has been presented [9].

Here we apply our theory to the analysis of inelastic neutron scattering in a monatomic liquid. We work with a small system, having $N = 500$ atoms in a cubic box with periodic boundary conditions, and with density and interatomic potential representing liquid sodium at melt. Fourier components are evaluated at $q$ consistent with periodic boundary conditions. Statistical averages are denoted $\langle \ldots \rangle$, and consist of an average over the atomic motion, in classical statistical mechanics, followed by an average over $q$ in a star, denoted $\langle \ldots \rangle_q^*$. Under these conditions it is appropriate to compare theoretical calculations directly with MD, since finite-$N$ effects are the same in both, and the MD ensemble correction vanishes for fluctuations considered here [10]. The same approach of comparing theory with MD was successfully used to evaluate the contribution of anharmonicity to the dynamic structure factor of crystalline potassium [11].

The intermediate scattering function is $F(q,t)$,

$$F(q,t) = \frac{1}{N} \langle \rho(q,t)\rho(-q,0) \rangle \quad (1)$$

where $\rho(q,t)$ is the Fourier transform of the density operator,

$$\rho(q,t) = \sum_K e^{-iq\cdot r_K(t)} \quad (2)$$

and the atomic positions are $r_K(t)$ for $K = 1,\ldots,N$. When the system moves in a single random valley, each particle has fixed equilibrium position $R_K$ and displacement $u_K(t)$, so that

$$r_K(t) = R_K + u_K(t) \quad (3)$$

When the displacements undergo harmonic vibrations, the average over the atomic motion is denoted $\langle \ldots \rangle_h$, and the average in Eq. (1) is $\langle \ldots \rangle_{q^*}$. Then for harmonic motion, $F(q,t)$ becomes
where $R_{KL} = R_K - R_L$, and where $W_K(q)$ is the Debye-Waller factor. Notice the functions $(q \cdot u_K(t) \cdot q \cdot u_L(0))_h$ vanish as $t \to \infty$.

The dynamic structure factor $S(q, \omega)$ is the Fourier transform of $F(q, t)$. This can be evaluated analytically in the one-mode approximation, obtained by expanding $e^{\langle \cdots \rangle - 1}$ to linear order in Eq. (4). The transformation from $u_{K_i}$, where $i = x, y, z$, to the normal mode amplitudes $q_i(t)$, where $\lambda = 1, \ldots, 3N$, is real orthogonal, with eigenvector components $w_{K,\lambda}$ and normal mode frequencies $\omega_\lambda$. Then in the harmonic one-mode approximation, where the inelastic part of $S(q, \omega)$ is denoted $S_1(q, \omega)$, one has in classical statistics

$$S(q, \omega) = F(q, \infty)\delta(\omega) + S_1(q, \omega),$$

where

$$S_1(q, \omega) = \frac{3kT}{2M} \frac{1}{3N} \sum_\lambda f_\lambda(q)[\delta(\omega + \omega_\lambda) + \delta(\omega - \omega_\lambda)],$$

and the key function in $S_1(q, \omega)$ is

$$f_\lambda(q) = \frac{1}{\omega_\lambda} \left\langle \left| \sum_K e^{-i q \cdot R_K} e^{-W_K(q) q \cdot w_{K,\lambda}} \right|^2 \right\rangle_{q^*}.$$

Apart from the thermal factor $3kT/2M$ and the normalization $1/3N$, $f_\lambda(\omega + \omega_\lambda)$ is the cross section for neutron scattering at momentum transfer $h\omega_\lambda$ with annihilation of energy $h\omega_\lambda$ in mode $\lambda$, and $f_\lambda(\omega - \omega_\lambda)$ is the cross section for neutron scattering at momentum transfer $h\omega_\lambda$ with creation of energy $h\omega_\lambda$ in mode $\lambda$. The normal mode resolution of the Debye-Waller factor is

$$W_K(q) = \sum_\lambda \frac{kT(q \cdot w_{K,\lambda})^2}{2M\omega_\lambda^2}.$$
395 K, some 24 K above melting, is shown in Fig. 4. The theoretical \( S(q, \omega) \) still represents motion in a single random valley, so the Rayleigh peak is \( F(q, \infty)\delta(\omega) \) at 395 K, and the Brillouin peak has nearly the same location and width as in Fig. 1. On the other hand, the MD system at 395 K transits between random valleys at a very high rate, producing two net effects in the Rayleigh and Brillouin peaks relative to their shapes in a single random valley: (a) the peaks are not shifted, and (b) each peak retains approximately the same area but is broadened. Point (a) needs to be understood first, so we shall address it here.

First, when transits are present, \( R_{KL} = R_K - R_L \) in Eqs. (4) and (5) becomes \( R_K(t) - R_L(0) \). If now atom \( K \) is involved in a transit from valley \( a \) to valley \( b \) at time \( t_1 \), its motion in first approximation is as follows: \( a \): the atom is in vibrational motion in valley \( a \) before \( t_1 \) and in valley \( b \) after \( t_1 \); its position and velocity are continuous at \( t_1 \) but its equilibrium position \( R_K \) and its displacement \( u_K \) are discontinuous at \( t_1 \). According to Eqs. (4) and (5), the discontinuities in \( R_K \) will disrupt correlations inside the \( \sum_{KL} \), and so will broaden the Rayleigh and Brillouin peaks; the discontinuities in \( u_K \) will hasten the decay of \( (q \cdot u_K(t) q \cdot u_L(0))_h \) to zero, and so will broaden the Brillouin peak; but none of the discontinuities will cause the peaks to shift. The fact that the presence of transits does not cause the peaks to shift in the MD system, according to Fig. 4, is evidence that transits are indeed nearly instantaneous in the liquid.

It is well known that the Brillouin peak varies with \( q \), and its maximum frequency \( \Omega(q) \) follows a characteristic curve. The question is, does the agreement shown in Fig. 4 hold for all \( q \)? That it does is shown in Fig. 4 for the complete range of \( q \), from the smallest allowed \( q \) for our system up to 0.8 \( \text{a}_0^{-1} \), where the Brillouin peak disappears. Analysis of our data for \( \Omega(q) \) from theory for a single random valley, and from MD calculations, reveals that the theory and MD agree within errors at 24 K and at 395 K, with an overall rms relative difference of 0.02 (negligible), and that the shift from 24 K to 395 K is zero within errors for theory and for MD, with an overall rms relative shift of 0.02 (negligible).

Our theory provides an interpretation of the \( \Omega(q) \) dispersion curve which, as far as we know, is new: the maximum frequency in the dispersion curve is near the maximum frequency of the normal mode distribution. The maximum \( \Omega \) in Fig. 4 is around 23 ps\(^{-1} \), while the distribution of \( q_\omega \) has very few modes beyond this frequency. Hence liquid experiments can provide information on the random valley vibrational mode distribution. We note Fig. 4 is in good agreement with experiments for liquid sodium at 390 K.

In the past twenty years or so, the dynamic structure factor has been extensively studied by means of mode coupling theory. Recently, highly accurate inelastic x-ray scattering measurements have been done for a wide range of \( q \) (e.g. [20]). These data, and MD data as well, have been analyzed by using an ansatz for the memory function in the generalized Langevin equation for \( F(q, t) \), in which the memory function possesses two (or sometimes three) decay channels for density fluctuations, with each decay process represented by adjustable \( q \)-dependent parameters for the decay strength and relaxation time. Though the fits to \( S(q, \omega) \) data are excellent, it remains to interpret their meaning.
by identifying the physical process responsible for each decay channel \[21, 22, 23\].

In comparison, our theory is based on well defined physical processes from the outset, namely nearly harmonic motion in a single random valley, plus nearly instantaneous transits. Harmonic motion in a single random valley has been shown to account for the thermodynamic properties of elemental liquids, with small corrections from transits \[3, 4\]. Here this harmonic motion accurately reproduces MD for \(S(q, \omega)\) in the glass state, Fig. 1, and this motion also accounts for the Brillouin peak dispersion curve in the liquid, where the system moves rapidly among a host of random valleys, as shown in Fig. 4. Moreover, the interpretation of the vibrational contribution to the Brillouin peak is clear from Eq. (7): the peak at a fixed \(q\) is the sum of cross sections from a band of normal modes which scatter efficiently at that \(q\). Transits, on the other hand, are the liquid counterpart of binary collisions in a gas: a transit is the highly correlated motion of a small local group of atoms that carries the system across the boundary between two random valleys. Single transits have been resolved in MD calculations at low temperatures \[5\], and a model for transits gives a good account of the velocity autocorrelation function from the glass state to the very hot liquid \[6\]. While much study of the transit process remains, transits are nevertheless well defined, and their role of broadening the peaks of \(S(q, \omega)\) in the liquid state is expressed through Eqs. \[4\] and \[5\] for \(F(q, t)\) as discussed in the text. In summary, we believe the case has been made that our representation of the atomic motion provides a physically realistic theory of liquid dynamics.

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