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Analysis of the velocity autocorrelation function of water

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Abstract. The centre-of-mass velocity autocorrelation function of liquid water under room conditions is examined through a mode-coupling approach developed to study monatomic liquids. The wavevector-dependent current correlations relevant to the theory are evaluated by computer simulations using a recently developed interaction potential, which accounts for the polarizability of the molecule. The theory is found to reproduce all the relevant dynamical features of water. Moreover, the analysis in terms of longitudinal and transverse contributions clarifies the origin of some peculiarities in the dynamics of this single-molecule correlation. A discussion of the corresponding spectra is also given.

1. Introduction

The understanding of the single-particle velocity autocorrelation function (VACF) in simple monatomic liquids has been the subject of considerable effort [1–3]. In particular, the introduction of a *microscopic velocity field* has been successful for the interpretation of the VACF data obtained by computer simulations of Lennard-Jones (LJ) and alkali-metal liquids [4]. The resulting theory can be considered as one of the simplest applications of mode-coupling concepts to liquid-state dynamics [2, 3].

In the case of molecular liquids modelled by a site–site potential (which usually includes LJ interactions), the essential features of the centre-of-mass VACF are quite similar to those of monatomic LJ systems. Namely, after some time, the VACF becomes negative because of the ‘rebound’ of the molecule from the shell of its neighbours, and subsequently shows a slow decay without any oscillations. However, liquid water appears to be rather peculiar since an evident positive bump appears in the time interval immediately before the one in which the VACF becomes negative. This feature is clearly relevant for the magnitude of the diffusion coefficient (proportional to the area under the VACF), and seems to be largely independent of the particular potential model used in the simulations. In this context we recall that starting from the early attempt of Rahman and Stillinger [5] all the potentials proposed for water have at least one LJ interaction (the centres generally being the oxygen atoms), plus a number of Coulomb interactions between fractional charges located at different places over the molecule (e.g. SPC/E [6], TIP4P [7] and MCY [8] models).

Quite recently a potential model which accounts even for the polarizability of the molecule has been implemented [9]. As in the previous non-polarizable models, an LJ centre is positioned on the oxygen. Three charges are then suitably placed (two of them on the hydrogens, and a third one on the molecular symmetry axis), and their magnitudes scaled

in order to reproduce the dipole moment of the molecule in the gas phase. The position of the third charged site as well as the LJ parameters are adjusted in order to reproduce the internal energy and the pressure of liquid water under ambient conditions. The molecule is polarizable, with the induced dipole moment placed at the molecular centre of mass. Details of the implementation of this potential and of the ‘best’ values of the parameters are reported in [9], where it is also shown that the model reproduces quite satisfactorily both the structural properties (i.e. the partial radial distribution functions) and the diffusion coefficient D of real water under ambient conditions. At the level of the centre of mass, the VACF is expected to exhibit features similar to those present in other non-polarizable models, such as the SPC/E one (which also reproduces the correct value of D). Our simulation results in fact confirm this expectation (see figure 1).

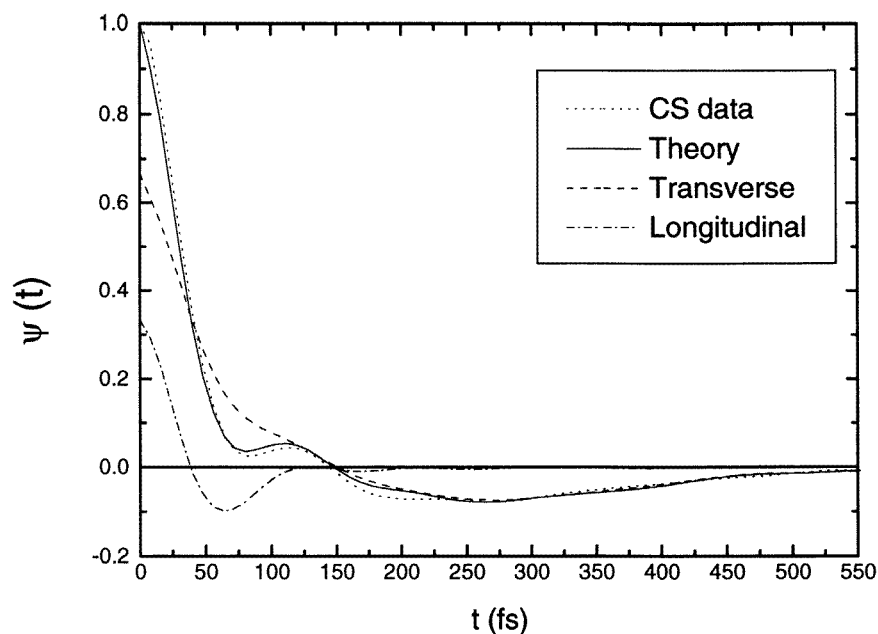


Figure 1. Normalized velocity autocorrelation function of the centre of mass of water at a temperature $T = 298$ K and mass density $\rho = 1$ g cm $^{-3}$. Dots: computer simulation (CS) data; full line: theoretical results from (5). The chain and dashed lines represent the longitudinal and transverse current contributions, respectively.

The aim of the present work is to understand these ‘universal’ features of the VACF of water. For this purpose, we have performed an analysis using the above-mentioned velocity field approach [4]. As the latter was originally developed for monatomic systems, the first point to ascertain is its applicability in a complex molecular system. To check this in a way free from approximations other than those intrinsic to the theory, all the quantities needed for the theoretical evaluation of the VACF have been obtained by computer simulation. As we shall see in the following, the velocity field approach is found not only to yield remarkably good results in the case of water, but also provides a deeper insight into the physical origin of several peculiar features present in the microdynamics of this liquid. In particular, the aforementioned ‘bump’ in the VACF is shown to be closely related to the presence of damped sound-like longitudinal modes with unusually high frequencies.

2. The velocity field approach

In this section we briefly summarize the main outcomes of the theory. As a result of the introduction of the velocity field, the normalized VACF $\psi(t)$ can approximately be expressed as [4]

$$\psi(t) \approx (1/24\pi^3) \int d\mathbf{q} f(q) [C_L(q, t) + 2C_T(q, t)] F_s(q, t). \quad (1)$$

Here $C_L(q, t)$ and $C_T(q, t)$ are the Fourier components (normalized to their $t = 0$ values) of the longitudinal and transverse current correlation functions, respectively. $F_s(q, t)$ is the self-intermediate scattering function, and $f(q)$ is the Fourier transform of the quantity $f(r)$ entering the definition of the microscopic velocity field

$$\mathbf{v}(\mathbf{r}, t) \equiv \sum_j f(|\mathbf{r} - \mathbf{r}_j(t)|) \mathbf{v}_j(t) \quad (2)$$

with $\mathbf{r}_j(t)$ and $\mathbf{v}_j(t)$ being the position and the velocity of the j th particle, respectively. The form factor $f(r)$ is chosen to be unity across a suitable particle size a :

$$f(r) = \vartheta(a - r). \quad (3)$$

Here $\vartheta(x)$ is the usual step function, and the ‘radius’ a is determined by means of a macroscopic requirement which leads to the relation $(4/3)\pi n a^3 = 1$, where $n = N/V$ is the number density of the liquid. Then one finds that

$$f(q) = \frac{3}{n} \frac{j_1(qa)}{qa} \quad (4)$$

where $j_1(x) = [\sin(x)/x^2 - \cos(x)/x]$ is the spherical Bessel function of order one. In isotropic systems all the quantities entering (1) depend only on the magnitude of the wavevector \mathbf{q} , thus allowing a straightforward integration over the angles. Moreover, (1) can be further simplified by noting that at liquid density there is a rather well-defined separation of time scales between the slow diffusive motion (which basically rules the time decay of F_s) and that of the current correlations C_L and C_T associated with momentum transfer. Consequently, it is reasonable to neglect the time dependence of $F_s(q, t)$ in (1), which can be written as

$$\psi(t) \approx \frac{2}{3\pi} \int_0^\infty \left[\frac{\sin(qa)}{qa} - \cos(qa) \right] [C_L(q, t) + 2C_T(q, t)] d(qa). \quad (5)$$

3. Results for liquid water and discussion

Equation (5) does not seem to represent substantial progress because the determination of the VACF is traced back to the knowledge of other dynamical quantities, i.e. the collective current correlations C_L and C_T . However, previous works on simple liquids indicate that an extremely accurate knowledge of all the features of $C_L(q, t)$ and $C_T(q, t)$ is not required. In other words, well-known approximations for the current correlations (such as, for example, those deduced from a viscoelastic model [1–3]) often suffice to yield a remarkably good reproduction of all the features of the VACF. As already pointed out in the Introduction, in the case of water, where a peculiar behaviour is found to be present, we have preferred to check the validity of the approach by inserting in (5) results free of any approximation, namely the direct simulation data obtained for these quantities. Therefore, the q -dependent correlation functions have been evaluated over a trajectory of 40 ps obtained by molecular dynamics. Specifically, our simulation has been performed in a system of 256 water

molecules interacting through the aforementioned polarizable potential model [9]. The range of q goes from 0.32 \AA^{-1} (the minimum accessible wavevector) to 5.32 \AA^{-1} , where a good convergence of the integral is found. The result of this numerical integration of (5) is reported in figure 1, and compared with the 'exact' VACF $\psi(t)$ directly obtained by molecular dynamics. As is apparent, the agreement is quite good, indicating that the velocity field approach has a range of applicability much broader than that expected from its original formulation.

In order to get more insight into the detailed dynamical behaviour of $\psi(t)$, we have reported the separate contributions to the integral (5) coming from the longitudinal and transverse components. Besides the excellent capability of the theory to reproduce the features of the VACF in the overall time domain, several observations can now be made by this detailed analysis. To begin with, from figure 1 it is apparent that the positive bump of the VACF stems from the fast decay of the longitudinal component, which after a negative minimum at a rather short time (≈ 0.06 ps) decreases rapidly to zero. This fact, together with the comparatively slower decay of the transverse component, is ultimately responsible for the appearance of the bump at ≈ 0.12 ps. Remarkably enough, at later times the dynamics of the VACF appears to be entirely ruled by the behaviour of the transverse component.

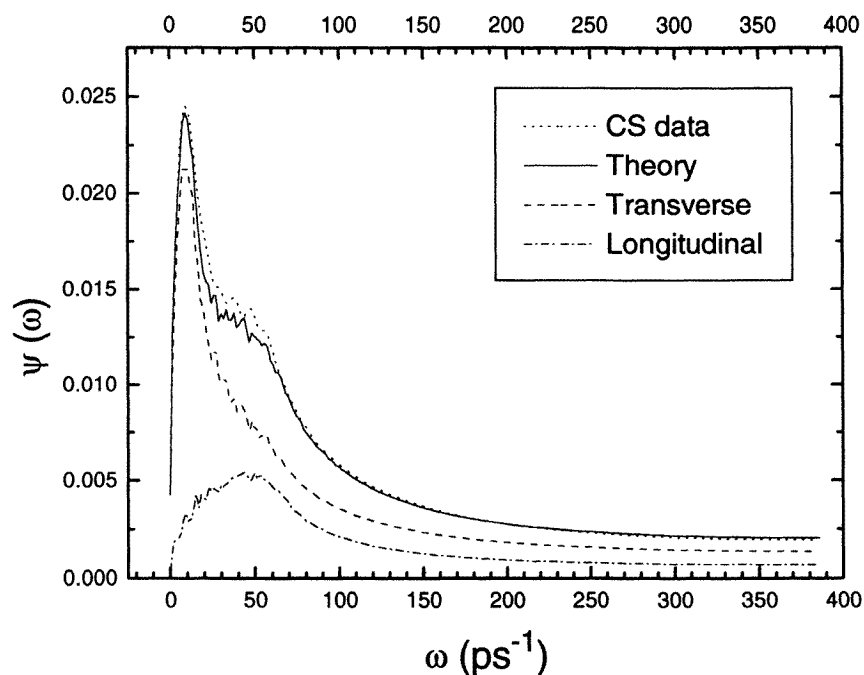


Figure 2. Spectra of the velocity autocorrelation function and of its contributions. The notation is the same as in figure 1. The Einstein frequency is located at $\omega \approx 35 \text{ ps}^{-1}$.

A comparison with the situation met in simple monatomic liquids (as reported in [4]) is helpful in clarifying the peculiar behaviour of water. In the case of *LJ liquids*, the longitudinal component is found to contribute over a wider time interval: as a result, the crossing through zero of $\psi(t)$ is determined by a balance between the negative longitudinal and the positive transverse components, and the VACF minimum is affected by both of them. In contrast, in *molten alkali metals* the oscillations of the VACF around zero are

entirely determined by the longitudinal component (and hence by the well-known presence in these liquids of definite sound modes up to relatively high q). In *water* the situation is quite different. As the longitudinal component decays much more rapidly than the transverse one, it affects the VACF only in the short-time regime. The large damping of the longitudinal current has already been discussed in connection with the presence of a strong positive dispersion of the modes associated with the propagation of density fluctuations at wavevectors outside the hydrodynamic regime [10]. As shown in [10], this behaviour can be traced back to the high value of the Einstein frequency in water (in turn caused by the peculiar structural properties of this hydrogen-bond fluid). In a simple viscoelastic model, all these features imply that the peaks associated with the corresponding density modes are not well-defined. This large damping is immediately reflected on the VACF dynamics as shown in figure 1.

In figure 2 we report the spectrum of the VACF and those of the longitudinal and transverse current contributions. As is evident, the low-frequency part of the spectrum is dominated by the transverse contribution with a first sharp peak at $\omega \approx 10 \text{ ps}^{-1}$, whereas the shoulder at $\omega \approx 40 \text{ ps}^{-1}$ occurs at the position where the longitudinal component has a maximum. These values are in quantitative agreement with those expected from the times where the longitudinal and transverse components cross zero (see figure 1). The amplitude of the transverse peak is considerably larger than that of the longitudinal one. Again, a comparison with the situation present in simple liquids is interesting. In the LJ case, the peak of the transverse component appears to be much broader than the longitudinal one, and the latter is considerably sharper than in water [4]. Furthermore, in LJ fluids the frequencies and the amplitudes of the two peaks are found to be much closer. Coming back to water, the leading current contributions to the VACF as given by (5) are found to come from a q region beyond the hydrodynamic one (in the latter range, the integrand is vanishingly small). At these finite wavevectors, *both* the longitudinal and the transverse current correlation functions exhibit damped oscillations. The ascertainment of the precise nature of these modes will undoubtedly shed additional light on the interpretation of the experimental spectra obtained by inelastic scattering both of neutrons and x-rays [11]; however, this analysis goes beyond the scope of the present work, and deserves to be the subject of future investigations.

4. Conclusion

To summarize, we have shown that the dynamics of the centre-of-mass VACF in liquid water can profitably be understood by a theoretical approach which exploits the projection over the collective currents. When compared with monatomic liquids such as LJ and alkali metals, the main feature peculiar to the VACF of water (a bump before the function becomes negative) is explained by the fast decay of the longitudinal component. In contrast to what happens in simple fluids, the subsequent behaviour of the VACF is found to be dominated only by the transverse contribution. These peculiarities are reflected, at low frequencies, in a sharp peak in the VACF spectrum followed by a broad shoulder at higher frequencies.

Acknowledgments

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