Neutron study of non-Gaussian self dynamics in liquid parahydrogen

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Abstract. A time-honoured approach to single-molecule, or self, dynamics of liquids is based on the so-called Gaussian approximation (GA), where it is assumed that, in the whole dynamical range between hydrodynamic diffusion and free-particle streaming, the motion of a particle is fully determined by a unique function of time directly related to the velocity autocorrelation function. An evident support to the GA is offered by the fact that the approximation becomes exact in both above limit conditions. Yet, experimental inquiries into the presence of non-Gaussian dynamics are very scarce, particularly in liquid parahydrogen in spite of its importance as the prototype of a “quantum Boltzmann liquid” which has also served as a benchmark for the development of quantum dynamics simulation algorithms. Though experimental evidence of the breakdown of the GA was obtained by some of the authors a few years ago, the localization in $Q$ space of non-Gaussian behaviour was still undetermined, and no quantitative assessment of the effect was ever obtained. These issues have been tackled and solved by a new neutron investigation, which provides the first determination of non-Gaussian behaviour in the framework of the well-known theoretical approach by Rahman, Singwi and Sjölander.

Single-particle microscopic dynamics has always been a major research subject in the physics of fluid matter [1], and a huge amount of work has been devoted to its understanding both theoretically and experimentally, while an ever-growing role has been played by computer simulations. In the standard formulation of statistical mechanics, where the dynamical properties of a system composed of $N$ identical particles are expressed through time-dependent correlation functions, the relevant quantity is the self intermediate scattering function which for an isotropic fluid is written as [2]

$$F_s(Q,t) = \frac{1}{N} \sum_{j=1}^{N} \left\langle \exp \left[ -iQ \cdot r_j(0) \right] \exp \left[ iQ \cdot r_j(t) \right] \right\rangle = \left\langle \exp \left[ -iQ \cdot r(0) \right] \exp \left[ iQ \cdot r(t) \right] \right\rangle$$

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and represents the time autocorrelation of the spatial Fourier components, with wave vector \( \mathbf{Q} \), of microscopic density fluctuations. Here \( \langle \ldots \rangle \) indicates a quantum statistical average, \( Q = |\mathbf{Q}| \), and \( \mathbf{r}_j(t) \) is the Heisenberg position operator for the \( j \)-th particle at time \( t \), while the absence of a subscript indicates that one tagged, but arbitrary, particle is referred to.

One of the most important approaches to self dynamics is surely the one based on the so-called Gaussian approximation (GA) [3], expressed by

\[
F_s(Q,t) = \exp[-Q^2\gamma(t)],
\]

which consists in the assumption that, in the whole dynamical range between hydrodynamic diffusion (\( Q \to 0 \) and long times) and free-particle motion (\( Q \to \infty \) and short times), the motion of a particle is completely determined by a function of time only, \( \gamma(t) \), while the exponential dependence on \( Q^2 \) is what justifies the name of GA.

Equation (2) is valid in both the above limit conditions. If the simpler case of classical fluids is considered, one has [4] \( \gamma(t) = t^2/(2M\beta) \) for a free gas and \( \gamma(t) = Dt \) for a system where self diffusion dominates, where \( M \) is the mass of the particles, \( D \) is the diffusion coefficient, \( \beta = 1/(k_B T) \), \( k_B \) is the Boltzmann constant, and \( T \) is the temperature. Moreover, equation (2) also applies to the case of a perfect solid with harmonic vibrations. Therefore, the GA is a good starting point to approach the problem of self dynamics in a liquid because, even if shown to disagree in detail with real dynamical data, still the discrepancy is probably not too large in any specific range of \( Q \) and \( t \), including those most interesting for the study of molecular motions, at the nanometer-picosecond time and length scales.

Turning to the more general, but relevant here, case of quantum systems, where \( F_s(Q,t) \) becomes a complex quantity, it was shown by Rahman et al. [5] that in an isotropic system one can rigorously write

\[
F_s(Q,t) = \exp \left[ \sum_{p=1}^{\infty} (iQ)^{2p} \gamma_p(t) \right],
\]

where the \( \gamma_p \)'s are functions related to increasing-order correlation functions of different-time velocities of one particle. The \( p = 1 \) term, which also includes the recoil effect, is given by

\[
\gamma_1(t) = -\frac{\hbar t}{2M} + \frac{1}{3} \int_0^t dt_1(t-t_1)u(t_1)
\]

where \( \hbar \) is the Planck constant and \( u(t) = \langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle \) is the velocity auto-correlation function (VACF). If only the first term of (3) is retained, one immediately recovers the GA with \( \gamma(t) = \gamma_1(t) \). The following \( \gamma_p \)'s describe then the non-Gaussian behaviour, and most important of them, \( \gamma_2(t) \), is related to a multiple time integral of a four-velocity correlation function of the type \( \langle v_Q(t_1)v_Q(t_2)v_Q(t_3)v_Q(t_4) \rangle \), with \( v_Q = \mathbf{v} \cdot \mathbf{Q} \) denoting the projection of the tagged-particle velocity along the wave vector direction.

If the GA is assumed to be valid, \( F_s(Q,t) \) can be directly computed from the knowledge of \( u(t) \) alone without any further approximation. We recall here only a few important formulas and definitions, referring the interested reader to the more detailed treatments in Refs. [5, 6].

The VACF obeys the relationships \( u(-t) = u^*(t) = u(t + i\beta \hbar) \) with the asterisk denoting complex conjugation. As a consequence, its power spectrum

\[
p(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \ e^{-i\omega t} u(t)
\]

is a real but in general not an even function of \( \omega \) that can be split into the sum of its symmetric part \( p_S(\omega) = [p(\omega) + p(-\omega)]/2 \) and its asymmetric part \( p_A(\omega) = [p(\omega) - p(-\omega)]/2 \), related to
each other by virtue of the fluctuation-dissipation theorem [7]. Following Ref. [5] we define the spectral function

\[ f(\omega) = \frac{4M}{3\hbar} p_3(\omega) \omega, \]

which is symmetric and obeys \( \int_0^\infty d\omega \ f(\omega) = 1 \) and \( f(0) = 2MD\beta/\pi \). \( f(\omega) \) is the quantity of interest, since it can be shown [5] that

\[ \gamma_1(t) = \frac{\hbar}{2M} \int_0^\infty d\omega \ \frac{f(\omega)}{\omega} \left[ (1 - \cos \omega t) \coth \left( \frac{\beta \hbar \omega}{2} \right) - i \sin \omega t \right]. \]

Within the GA, the self intermediate scattering function is then immediately calculated as

\[ F_s(Q,t) = \exp[-Q^2 \gamma_1(t)] \]

and, from this, a Fourier transformation leads to the self dynamic structure factor

\[ S_s(Q,\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \ e^{-i\omega t} F_s(Q,t), \]

which is the suitable quantity to make contact with the results of spectroscopic experiments.

Despite its fundamental significance, the VACF itself is not directly accessible experimentally, and is a typical dynamical property to be studied through molecular dynamics (MD) simulation. However, while MD has proven effective and reliable in determining the microscopic dynamics of classical fluids [8], the situation is far less settled, and thus far more interesting, for systems belonging to what has often been termed the class of quantum Boltzmann liquids (QBLs), where the denomination summarizes a peculiar situation in which the fluid can still be thought of as made of distinguishable particles obeying Boltzmann statistics, with negligible quantum exchange effects, while quantum delocalization may be relevant, as evidenced by the structural properties [9].

Intense research activity has been carried out in the last two decades in order to come to a satisfactory understanding of QBL dynamics, driven by both a per se theoretical interest [10, 11, 12, 13] and, even more, by the need of developing still missing algorithms for a quantum dynamics simulation, for which various approaches have been devised [10, 11, 14, 15, 16].

Molecular hydrogen in its liquid state is the system most often studied, for a number of reasons. An obvious interest exists in extending to the dynamical side the investigation of the microscopic properties of such a fundamental substance, for which only recently a full account of the static structure was obtained by the joint use of Path Integral Monte Carlo computations and neutron diffraction experiments [17]. It has to be remarked that the molecular nature of hydrogen does not constitute a problem, as it is known that, even in the condensed phases, the rotovibrational degrees of freedom of \( \text{H}_2 \) molecules can be considered as decoupled from the translational motion [18], and the same concepts and formalism used for a monatomic system apply to hydrogen as well provided that the dynamical variables such as position and velocity are referred to the molecular centre of mass and \( M \) is taken to be the total mass of the molecule. Hydrogen is also considered as a prototype QBL featuring evident quantum effects while still remaining composed of distinguishable particles. Moreover, from the experimental point of view, \( \text{H}_2 \) is by far the best sample for experimental studies of the self dynamics due to its very large cross section for incoherent neutron scattering, which is the most important probe of single-particle microscopic dynamics. The possibility of experimental checks, together with the other reasons mentioned above, has therefore made liquid hydrogen a default benchmark for quantum simulation techniques [13, 15, 16, 19].
In talking of H\textsubscript{2} one should be more specific by mentioning that, at the liquid temperature (typically in the range between 15 and 20 K), the equilibrium species is practically 100% parahydrogen, i.e. the one having zero total nuclear spin and only the even-\textit{J} rotational states populated. Actually, the temperature is such that all molecules find themselves in the \textit{J} = 0 level.

A critical assessment of GA is still lacking, mainly because experimental studies have been rare. As far as classical fluids are concerned, only very few results were obtained a long time ago through neutron scattering [20] and MD simulation [21] on liquid argon, which showed the existence of regions of the (\textit{Q}, \textit{t}) space where the GA does not hold precisely. Non-Gaussian dynamics was also found in the simulation of a much more complex system such as a glass-forming polymer [22]. In contrast, no advance was to be recorded until recently on the question whether the GA can be more than a working hypothesis in the field of QBL in general, and of H\textsubscript{2} in particular, where it still kept the status of a conjecture to be either validated or disproved. In any case, most of the experimental studies of QBLs have so far concerned liquid parahydrogen [6, 23].

A first important result came a few years ago from a neutron scattering experiment [24] carried out on the TOSCA spectrometer at the pulsed neutron source ISIS. The validity of GA was questioned without resorting to calculations based on a quantum-simulated VACF. Rather, a consistency check was performed with the following procedure. The centre-of-mass \textit{S}_{\text{cm}}(\textit{Q}, \textit{\omega}) was computed within GA with an adjustable model of \textit{f}(\textit{\omega}), written in the form suggested by Levesque and Verlet [25] with free parameters that could be fitted so as to give good agreement with the neutron data in a \textit{Q} range around 20 nm\textsuperscript{-1}. This \textit{f}(\textit{\omega}) was then employed in the computation, again within GA, of the spectrum in a higher-\textit{Q} range (∼40 nm\textsuperscript{-1}), where a clear discrepancy appeared with the measured one. This result evidenced a breakdown of GA in liquid para-H\textsubscript{2}, since it was not possible to find a unique \textit{f}(\textit{\omega}) reproducing the experimental data in both investigated regions of \textit{Q}. In other words, one was forced to conclude that, besides the explicit quadratic dependence on \textit{Q}\textsuperscript{2}, a residual \textit{Q} dependence was to be allowed for in the exponential function of equation (2).

A different question, however, is whether the actual \textit{S}_{\text{cm}}(\textit{Q}, \textit{\omega}) at a given \textit{Q} can be obtained on the basis of the GA, i.e. from (7), (8), and (9), with the \textit{f}(\textit{\omega}) corresponding to an independently determined VACF. The experiment reported on in Refs. [24] could not provide an answer. Actually, the above described analysis might induce one to think that the GA is a less exact representation of the real spectrum at the higher \textit{Q}'s, at least in the explored range, while, as indeed shown below, the opposite conclusion is true.

The above situation motivated a further effort towards the experimental assessment of this still unsolved issue, by combining a new neutron study carried out on a wider (\textit{Q}, \textit{\omega}) region in constant-\textit{Q} conditions with a GA analysis of data computed using a reliable simulated VACF. For the latter, the Path Integral Centroid Molecular Dynamics (PICMD) method was applied [10, 14, 15]. In this paper we report on the results of this investigation as far as the validity of GA is concerned.

The inelastic scattering of neutrons from a liquid para-H\textsubscript{2} sample, at temperature \textit{T} = 15.7 K and a molecular number density of 22.53 nm\textsuperscript{-3} [26], was recorded with two thermal-neutron time-of-flight spectrometers at the Institut Laue-Langevin (ILL) in Grenoble in order to cover different \textit{Q} ranges. The small-angle BRISP spectrometer was used for \textit{Q} values not exceeding 10 nm\textsuperscript{-1}, while for 20 ≤ \textit{Q}/nm\textsuperscript{-1} ≤ 45 the experiment was carried out on IN4C. The incident neutron energies were \textit{E}_{0} = 50 and 65.2 meV, respectively.

The already mentioned separability of the internal motions from the translation of the molecule as a whole is effectively exploited in the Young-Koppel modelling of neutron spectra from fluid hydrogen [27] as those of a system of harmonically vibrating free rotors. Taking into account that only the ground rotational and vibrational levels are thermally populated at the
temperature of the liquid, and that no vibrational excitations are possible with the available neutron energy, the double-differential cross section for neutron scattering consists of replicas of $S_s(Q, \omega)$ shifted by the rotational energies of the $J \to J'$ transitions with odd $J'$ [28]. Due to the small moment of inertia of the molecule, these lines are well separated and only the most intense of them, the $J = 0 \to 1$ transition corresponding to a shift $\hbar \omega_{0 \to 1} = 14.69$ meV [29], is probed in the energy window of the experiment. The very small contribution of coherent scattering is, instead, located around the quasielastic line and plays no role at all. Then, to an extremely good approximation, the studied sample scatters neutrons according to

$$\frac{d^2 \sigma}{d \Omega d\omega} = \frac{k'}{k} a(Q)_{0 \to 1} S_s(Q, \omega - \omega_{0 \to 1})$$

(10)

where $k$ and $k'$ are the neutron wave vectors before and after scattering. Here the factor $a(Q)$ is a known, transition-specific, form factor [28]. Equation (10) allows for the extraction of $S_s(Q, \omega)$ from an experimental set of constant-$Q$ spectral intensity data, eliminating the rotational frequency shift, although the result remains broadened by the instrumental energy resolution function $R(\omega)$. This was measured from the scattering of a vanadium sample to be a Gaussian line with a half width at half maximum (HWHM) of 0.62 and 1.39 meV for BRISP and IN4C, respectively. An absolute normalization of the dynamic structure factor was not attempted at this stage.

As far as the simulation is concerned, we note that the PICMD method is well suited to the computation of the so-called canonical (or Kubo-transformed [30]) VACF

$$u_c(t) = \frac{1}{\beta} \int_0^\beta d\lambda \left\langle e^{\lambda \mathcal{H}} \mathbf{v}(0) \cdot e^{-\lambda \mathcal{H}} \mathbf{v}(t) \right\rangle$$

(11)

where $\mathcal{H}$ is the Hamiltonian operator of the system. $u_c(t)$ is a real, even function of $t$, whose power spectrum

$$p_c(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \ e^{-i\omega t} u_c(t)$$

(12)

is related to that of the complex $u(t)$ through

$$p(\omega) = p_c(\omega) \frac{\beta \hbar \omega}{1 - \exp(-\beta \hbar \omega)}$$

(13)

and is directly proportional to $f(\omega)$, since

$$p_c(\omega) = \frac{3}{2M\beta} f(\omega).$$

(14)

We have applied the PICMD algorithm to a system of 256 molecules interacting with the Silvera-Goldman potential [31] in a cubic box. The Trotter number (i.e. the number of beads on the classical ring polymers replacing the quantum mechanical particles) was $P = 64$. Our implementation of PICMD consisted in a combination of alternating MD and Monte Carlo phases. At each time step of the centroid MD, i.e while keeping the centroid positions fixed, a short PIMC simulation of 160 passes was performed in the space of bead coordinates relative to the centroid, and then the centroid positions and velocities were moved forward in time with the leapfrog integrator in the isokinetic ensemble. The important point is that, in contrast to the usual implementation, where the sampling of “intramolecular” bead coordinates is performed on the fly by molecular dynamics, we have done it by Monte Carlo, thus avoiding the ergodicity problems [32] affecting the intramolecular modes in MD. Due to this splitting between MD and
Figure 1. Short-time behavior of the real (left) and imaginary (right) parts of $\gamma_1(t)$ as calculated by PICMD (blue dots). The red straight line in the left frame shows the large-time linear behaviour fitted to the data in the time interval between 0.6 and 1.0 ps. In the right frame the large-time limit is calculated from $\gamma''_1(t) \approx -(\hbar \beta/2)D_1$ where $D_1 = 4.94 \cdot 10^{-5}$ cm$^2$s$^{-1}$ is the fitted real-part asymptotic slope, in excellent agreement with the diffusion coefficient $D = 4.95 \cdot 10^{-5}$ cm$^2$s$^{-1}$ [33].

PIMC a large time step of $5 \cdot 10^{-3}$ ps could be used, and the results obtained after $2 \cdot 10^5$ steps (i.e. 1 ns) are expected to be statistically accurate.

Once $u_c(t)$ is determined from the PICMD simulations, the above equations together with (7) can be used to evaluate $\gamma_1(t)$, which is shown in figure 1. Employing prime and double prime notation for the real and imaginary parts of complex quantities, the theory of Ref. [5] predicts large-time asymptotic linear behaviours of $\gamma_p(t)$ given by $\gamma'_p(t) \approx D_p t - C_p$ and $\gamma''_p(t) \approx -(\hbar \beta/2)D_p$ for all values of $p$, with, in particular, $D_1 = D$. The PICMD calculations agree with this theoretical prescription.

At all $Q$ values of the experiments, the spectra resulting from the use of (8) and (9), convoluted with $R(\omega)$, can be compared with the measured ones, once the latter have been normalized by a scale factor determined at the highest $Q$ values, where they have the same shape as the computed ones (see below).

We first consider the case $Q = 10$ nm$^{-1}$ using BRISP data. As shown in the first panel of figure 2, the agreement is good, implying the validity of the GA. This statement has to be taken with caution, since the resolution broadening strongly affects the shape of the spectrum which consists of a narrow line. It cannot be rigorously excluded that the calculated $S_s(Q, \omega)$ actually differs from the true one. If so, however, one should admit that the resolution broadening is such as to exactly mask the non-Gaussian contributions, a result which seems rather unlikely. A different result is found, instead, at the $Q$ values explored in the IN4C experiment, as displayed in the other panels of figure 2. A substantial agreement observed at the highest $Q$ changes into an emerging discrepancy with decreasing $Q$.

Thus, while confirming the already found overall breakdown of the GA, the present study provides interesting new results. First, non-Gaussian effects in the self dynamics are confined in the $Q$ range between 10 and 40 nm$^{-1}$, approximately. Second, the maximum deviation from GA is located somewhere between 10 and 20 nm$^{-1}$, where its detection could probably be made difficult by resolution limitations of the available spectrometers.

The above results suggest to try to get insight into the time dependence of non-Gaussian
Figure 2. Self dynamic structure factor obtained from neutron data (blue dots) and calculated within the GA using the quantum simulated VACF (red line) at various $Q$ values indicated in each frame. The top left frame refers to data from the BRISP experiment, all other frames show results of the IN4C experiment. All spectra are broadened by the respective instrumental resolution. The right shift of the peak position with increasing $Q$ is due to the molecular recoil.

contributions to $F_s(Q, t)$. In this respect the present BRISP data do not provide useful information, covering a $Q$ range where self dynamics shows an essentially Gaussian behaviour. Using the convolution theorem to express the resolution broadening in $t$ space as the product with the Fourier transform of $R(\omega)$, the IN4C experimental spectra are seen to correspond to the function

$$\tilde{F}(Q, t) = R(t)F_s(Q, t) = R(t) \exp[-Q^2\gamma(Q, t)]$$

where equation (2) is now replaced by a more general expression allowing for non-Gaussian dynamical behaviour through an explicitly indicated $Q$ dependence of $\gamma$. Making the assumption that most of the non-gaussianity is contained in the $p = 2$ term of equation (3), we set up a simplified model of $\gamma(Q, t)$, written as

$$\gamma(Q, t) = \gamma_1(t) - Q^2\gamma_2(t) + Q^4x(t), \quad (15)$$

where $\gamma_2(t)$ is retained, but all possible contributions beyond the $Q^2$ term are, somewhat roughly, included in a remainder denoted $x(t)$, whose characterization is likely beyond feasibility and is not attempted, since the object of our present analysis was the determination of $\gamma_2(t)$ at least at a semi-quantitative level.

To this aim, we Fourier-transformed the experimental spectra into the time domain to obtain $\tilde{F}(Q, t)$ and, from this, $\gamma(Q, t)$. Then, $\gamma'(Q, t)$ and $\gamma''(Q, t)$ have been separately analysed by performing at each value of $t$ parabolic fits of the real and imaginary part of equation (15) as functions of $Q^2$. In the fits, the PICMD simulated $\gamma'_1(t)$ and $\gamma''_1(t)$ have been used, while $\gamma'_2(t)$
Figure 3. Short-time behavior of the real (left) and imaginary (right) parts of $\gamma_2(t)$ as derived by means of the procedure described in the text (blue dots). The red straight line in the left frame shows the large-time linear behavior fitted to the data in the time interval between 0.6 and 1.0 ps. In the right frame the large-time limit is calculated from $\gamma''_2(t) \approx -(\hbar \beta/2)D_2$ where $D_2$ is the fitted real-part asymptotic slope.

and $\gamma''_2(t)$ are obtained as fitted free parameters, displayed in figure 3. It can be observed that $\gamma_2(t)$ is nearly three orders of magnitude smaller than $\gamma_1(t)$, while the remainder $x(t)$ turns out to be of the order of $10^6$ times smaller, supporting the assumption that its contribution is fully negligible.

With the present data, $\gamma_2(t)$ can only be studied at short times. In fact, the extraction of $\gamma(Q,t)$ requires to divide $\tilde{F}(Q,t)$ by $R(t)$, which is a Gaussian function with a HWHM of $\sim 0.6$ ps. The fast decaying tails of $R(t)$ produce unreliable data at times larger than about 1 ps, since the main effect of the division is to magnify the unavoidable noise. This limitation is, therefore, related to the fact that the $J = 0 \rightarrow 1$ rotational line, located at $\sim 15$ meV, requires for its excitation a neutron energy of tens of meV, which, with the currently available spectrometers, does not allow for a higher resolution power.

Nevertheless, the time range $t \lesssim 1$ ps is shown in figure 1 to be sufficient for $\gamma_1(t)$ to reach its asymptotic behaviour, and the same seems likely to be case for $\gamma_2(t)$. It has to be noted that, in addition to the limitation mentioned above, the extraction of $\gamma''_2(t)$ as the argument of an oscillatory function (the complex exponential of equation (15)) is a further difficulty, so that we have to consider our determination of $\gamma''_2(t)$ as probably not much more than a semi-quantitative estimate. However, it shows the right order of magnitude and most of its non-trivial time dependence seems confined to the explorable time range.

In summary, a careful neutron study of the self dynamics of liquid parahydrogen, besides confirming the presence of non-Gaussian dynamics, has provided as a new result the so-far missing knowledge about the $Q$ ranges that can or cannot be properly accounted for by GA calculations. The comparison of neutron data with GA spectra computed from the PICMD-simulated VACF reveals non-Gaussian behaviour below $Q \sim 40$ nm$^{-1}$ and a smooth approach to the expected high-$Q$ recovery of Gaussian dynamics. On the other hand, a detailed study of the onset of non-gaussianity at low $Q$, where parahydrogen spectra consist of an intrinsically narrow line, still remains an experimental technical challenge given the resolution performances of present neutron spectrometers. The data collected in the experiments here reported have also provided the first determination of non-Gaussian effects in the $\gamma_p(t)$ expansion of equation (3) for a quantum liquid, at least in the very important subpicosecond regime.
In perspective, the efforts currently being made in the field of quantum dynamics simulation will hopefully lead to effective and reliable algorithms for the calculations not only of the VACF, but also, directly, of the dynamic structure factor, a goal which is presently within reach only for classical fluids. Once the simulation results can be matched directly with the experimental data, independently of any underlying approximation, studies on the GA will be possible with a higher degree of confidence.

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References
[1] Boon J P and Yip S 1980 Molecular Hydrodynamics (New York: McGraw-Hill)
Balucani U and Zoppi M 1994 Dynamics of the Liquid State (Oxford: Clarendon)
[2] Van Hove L 1954 Phys. Rev. 95 249
[3] Vineyard G H 1958 Phys. Rev. 110 999
[4] Squires G L 1996 Introduction to the Theory of Thermal Neutron Scattering (New York: Dover)
[5] Rahman A, Singwi K S and Sjölander A 1962 Phys. Rev. 126 986
[6] Celli M, Colognesi D and Zoppi M 2002 Phys. Rev. E 66 021202
[7] Schofield P 1960 Phys. Rev. Lett. 4 239
[8] Allen M P and Tildesley D J 1987 Computer Simulation of Liquids (Oxford: University Press)
[9] Zoppi M 2003 J. Phys.: Condens. Matter 15 R1
[10] Cao J and Voth G A 1994 J. Chem. Phys. 100 5106
[11] Martyna G J 1996 J. Chem. Phys. 104 2018
Cao J and Martyna G J 1996 J. Chem. Phys. 104 2028
[12] Rabani E and Reichman D R 2002 J. Chem. Phys. 116 6271
Makri N 1999 Annu. Rev. Phys. Chem. 50 167
[13] Reichman D R and Rabani E 2002 J. Chem. Phys. 116 6279
[14] Cao J and Voth G A 1994 J. Chem. Phys. 101 6168
Hone T D and Voth G A 2004 J. Chem. Phys. 121 6412
[15] Calhoun A, Pavese M and Voth G A 1996 Chem. Phys. Lett. 262 415
Pavese M and Voth G A 1996 Chem. Phys. Lett. 249 231
Kinugawa K 1998 Chem. Phys. Lett. 292 454
Yonetani Y and Kinugawa K 2003 J. Chem. Phys. 119 9651
[16] Georgescu I, Deckman J, Fredrickson L J and Mandelshtam V A 2011 J. Chem. Phys. 134 174109
[17] Zoppi M, Celli M and Soper A K 1998 Phys. Rev. B 58 11905
Bermejo F J, Kinugawa K, Cabrillo C, Bennington S M, Fäk B, Fernández-Díaz M T, Verkerk P, Dawidowski J and Fernández-Perea R 2000 Phys. Rev. Lett. 84 5359
Zoppi M, Neumann M and Celli M 2002 Phys. Rev. B 65 092204
Cunsolo A, Pratesi G, Colognesi D, Verbeni R, Sampoli M, Sette F, Ruocco G, Senesi R, Krisch M H and Nardone M 2002 J. Low Temp. Phys. 129 117
Dawidowski J, Bermejo F J, Ristig M L, Fäk B, Cabrillo C, Fernández-Perea R, Kinugawa K and Campo J 2004 Phys. Rev. B 69 14207
Celli M, Baille U, Cuello G J, Formisano F, Guarnier E, Magli R, Neumann M and Zoppi M 2005 Phys. Rev. B 71 014205
[18] Van Kranendonk J 1983 Solid Hydrogen (New York: Plenum)
[19] Craig I R and Manolopoulos D 2004 J. Chem. Phys. 121 3368
Liu J and Miller W H 2008 J. Chem. Phys. 128 144511
[20] Sköld K, Rowe J M, Ostrowski G and Randolph P D 1972 Phys. Rev. A 6 1107
[21] Desai R C 1978 J. Chem. Phys. 44 77
Tsang T 1978 Phys. Rev. A 17 393
[22] Colmenero J, Alvarez F and Arbe A 2002 Phys. Rev. E 65 041804
[23] Zoppi M, Colognesi D and Celli M 2001 Europhys. Lett. 53 34
Celli M, Colognesi D and Zoppi M 2002 J. Low Temp. Phys. 126 585
[24] Zoppi M 2003 J. Phys.: Condens. Matter 15 R1
Colognesi D, Celli M, Neumann M and Zoppi M 2004 Phys. Rev. E 70 061202
Celli M, Colognesi D, Ramirez-Cuesta A J and Zoppi M 2004 Physica B 350 e1083
[25] Levesque D and Verlet L 1970 Phys. Rev. A 2 2514
[26] Roder H M, Childs G E, McCarty R D and Angerhofer P E 1973 National Bureau of Standards Technical Note n. 641
[27] Young J A and Koppel J U 1964 Phys. Rev. A 135 603
[28] Guarini E 2003 J. Phys.: Condens. Matter 15 R775
[29] Huber K P and Herzberg G 1979 Constants of Diatomic Molecules (New York: Van Nostrand)
[30] Kubo R 1966 Rep. Prog. Phys. 29 255
[31] Silvera I F and Goldman V V 1978 J. Chem. Phys. 69 4209
[32] Pérez A, Tuckerman M E and Müser M H 2009 J. Chem. Phys. 130 184105
[33] O’Reilly D E and Peterson E M 1977 J. Chem. Phys. 66 934