Short time expansion of the relative motion of molecular pairs. Application to water

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Abstract. A detailed analysis of the short time expansion of the relative mean square displacement and mean square distance of pairs is performed for molecular fluids. A theoretical expression which relates the t^2 coefficient of the expansion to the local structure of the fluid is obtained. Good agreement between theoretical predictions and simulated data is found in the case of supercooled water.

1. Introduction

In monatomic fluids, many authors have devoted attention to the relative velocity correlation functions and to the relative mean square displacements [1]. The atomic pair dynamics is governed by the generalized time-dependent pair distribution function $G_2(r_0, r_t; t)$; this function is proportional to the joint probability of finding two particles separated by r_t at the time t if their separation was r_0 at $t = 0$. At the initial time one has $G_2(r_0, r_t; 0) = ng(r_0)\delta(r_t - r_0)$, where n is the number density, $g(r)$ is the pair distribution function and δ stands for the delta function. Some approximated forms of $G_2(r_0, r_t; t)$ have been proposed and their time evolution investigated via simulated experiments [1]. It turns out that $G_2(r_0, r_t; t)$ strongly depends on the initial pair separation r_0; at long times, this implies that the relative mean square displacement is proportional to $2Dt$, D being the self diffusion coefficient, only for pairs with a large initial separation [2]. In the short time regime, the series expansion of $G_2(r_0, r_t; t)$ has been calculated exactly up to the second term. It turns out that [3]

$$G_2(r_0, r_t; t) = G_2(r_0, r_t; 0) - \frac{KT}{\mu}n\nabla_{r_0}\nabla_{r_t}[g(r_0)\delta(r_0 - r_t)]\frac{t^2}{2} + \cdots \quad (1)$$

where μ and T are the reduced mass and the temperature, respectively. From equation (1), one can see that dynamical properties, based on the relative motion of pairs, could strongly depend on the local structure that the particles initially probe. In supercooled water, we have recently studied the relative motion of pairs which are in the first coordination shell at the initial time [4]. It has been shown that the anomalies of the relative diffusion in the intermediate time region are strongly related to the initial molecular orientations. Moreover, the mean square distance of some specific pairs does not increase with the usual free flight short time behaviour. This

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has polarized our attention on the short time expansion of equation (1) and on its applicability to molecular systems.

In molecular fluids, the local structure depends on the orientational pair correlation function $g(r, \omega_1, \omega_2)$ and can be properly investigated via the restricted angular averages, $g^\Gamma(r)$, of $g(r, \omega_1, \omega_2)$. To select the relative pair orientations, the set of eulerian angles in the local reference frame, $\omega = \{\theta, \psi, \phi\}$ has been used and the total angular space of a pair, $\Omega = \{(\omega_1, \omega_2)\}$, has been divided in subspaces Ω^Γ which collect a set of distorted dimer geometries; each set is referred to as a configuration state Γ (or simply configuration or state). So, the total $g(r)$ has been divided into partial contributions, $g^\Gamma(r)$; obviously, it must be $g(r) = \sum_\Gamma g^\Gamma(r)$. In [5] and [6], this kind of structural study is described in detail for the case of liquid water and the results are useful to study the extension of equation (1) to molecular fluids. Here, we will consider only the hydrogen-bond (HB) and non hydrogen-bond (NHB) states of water. The angular values, which limit the HB configuration, are reported in [5]. In figure 1, the total $g(r)$ and the partial contributions $g^{HB}(r)$ and $g^{NHB}(r)$ are shown. It is worth noting that the usual concept of hydrogen bond coincides with the HB configuration of pairs in the first coordination shell ($r < 3.5$ Å).
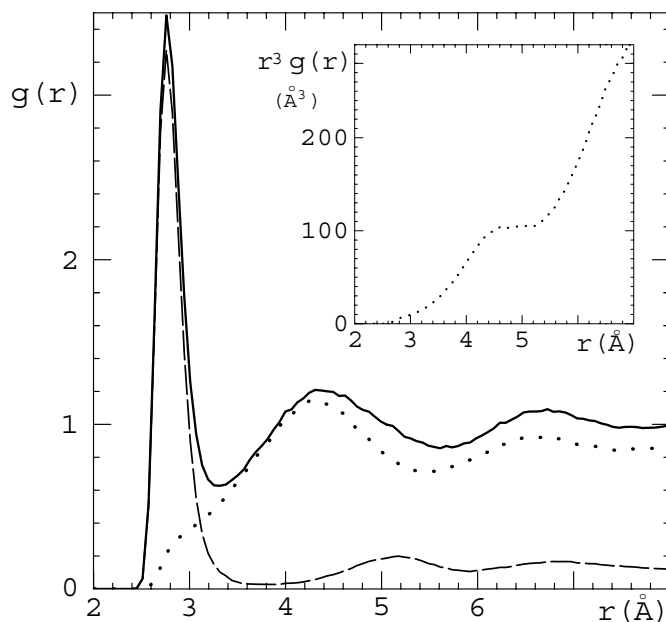

Figure 1. Centre of mass pair distribution functions of water at $T = 254$ K [5]: the total $g(r)$ (——), the partial $g^{HB}(r)$ (– – –) and $g^{NHB}(r)$ (· · · · ·) for HB and NHB pairs, respectively. $g^\Gamma(r)$ is computed as $(1/\Omega) \int \int_\Gamma d\omega_1 \, d\omega_2 \, g(r, \omega_1, \omega_2)$. The inset shows $r^3 g(r)$ for NHB states.

2. Theory

The translational dynamics can be investigated by using the functions

$$R^2(r_0, \Omega^\Gamma; t) = \langle r_{12}^2(t) \rangle_{0,\Gamma} - \langle r_{12}^2(0) \rangle_{0,\Gamma} \tag{2}$$

$$S^2(r_0, \Omega^\Gamma; t) = \langle (\boldsymbol{r}_{12}(t) - \boldsymbol{r}_{12}(0))^2 \rangle_{0,\Gamma} \tag{3}$$

where $\boldsymbol{r}_{12}$ is the intermolecular centre of mass (c.o.m.) separation vector and $\langle \ \rangle_{0,\Gamma}$ stands for averages over tagged pairs of molecules which, at the time $t = 0$, are in the region of the

configuration space characterized by the distance $r_0 = r_{12}(0)$ and by orientations belonging to the subspace Ω^Γ. The functions of equations (2) and (3) represent the extension to molecular fluids of the functions used to investigate the relative motion in monatomic fluids [1, 7]. To calculate the short time expansion of equations (2) and (3), we introduce $G_2(r_0, \Omega^\Gamma, r_t; t)$; with respect to $G_2(r_0, r_t; t)$, where $r_t = r_{12}(t)$, it adds to the pair the constraint to belong to the configuration Γ at $t = 0$. By definition, it must be

$$G_2(r_0, \Omega^\Gamma, r_t; 0) = ng^\Gamma(r_0)\delta(r_t - r_0) \tag{4}$$

where $g^\Gamma(r)$ stands for a restricted angular average of $g(r, \omega_1, \omega_2)$.

Then, equation (1) becomes

$$G_2(r_0, \Omega^\Gamma, r_t; t) = G_2(r_0, \Omega^\Gamma, r_t; 0) - \frac{KT}{\mu}n\nabla_{r_0}\nabla_{r_t}[g^\Gamma(r_0)\delta(r_0 - r_t)]\frac{t^2}{2} + \cdots. \tag{5}$$

The short time expansion of $\langle r_{12}^2(t)\rangle_{0,\Gamma}$ is

$$\langle r_{12}^2(t)\rangle_{0,\Gamma} = \langle r_{12}^2(0)\rangle_{0,\Gamma} - \frac{KT}{\mu}n\frac{\int_a^b \mathrm{d}r_0 \int_0^\infty r_t^2\nabla_{r_0}\nabla_{r_t}[g^\Gamma(r_0)\delta(r_0 - r_t)]\,\mathrm{d}r_t}{\int_a^b \mathrm{d}r_0 \int_0^\infty G_2(r_0, \Omega^\Gamma, r_t; 0)\,\mathrm{d}r_t}\frac{t^2}{2} + \cdots \tag{6}$$

where a and b are the limits defining the shell that the tagged pairs initially occupy, i.e. the initial separation r_0 varies between a and b.

It is worthwhile to write

$$\nabla_{r_0}\nabla_{r_t}[g^\Gamma(r_0)\delta(r_0 - r_t)] = g^\Gamma(r_0)\nabla_{r_0}\nabla_{r_t}\delta(r_0 - r_t) + \nabla_{r_0}[g^\Gamma(r_0)]\nabla_{r_t}[\delta(r_0 - r_t)] \tag{7}$$

and to write the numerator of the second term of the expansion (6) as.

$$\int_a^b g^\Gamma(r_0)\,\mathrm{d}r_0\nabla_{r_0}\int_0^\infty r_t^2\nabla_{r_t}[\delta(r_0 - r_t)]\,\mathrm{d}r_t$$
$$+ \int_a^b [\nabla_{r_0}g^\Gamma(r_0)]\,\mathrm{d}r_0\int_0^\infty r_t^2[\nabla_{r_t}\delta(r_0 - r_t)]\,\mathrm{d}r_t. \tag{8}$$

By exploiting the property of the Dirac δ function derivative,

$$\int f(r_t)\nabla_{r_t}\delta(r_0 - r_t)\,\mathrm{d}r_t = -\nabla_{r_0}f(r_0) \tag{9}$$

the expression (8) reduces to

$$-8\pi[b^3 g^\Gamma(b) - a^3 g^\Gamma(a)] \tag{10}$$

and equation (6) becomes

$$\langle r_{12}^2(t)\rangle_{0,\Gamma} = \langle r_{12}^2(0)\rangle_{0,\Gamma} + \frac{8\pi KT}{\mu}n\frac{[b^3 g^\Gamma(b) - a^3 g^\Gamma(a)]}{\int_a^b \mathrm{d}r_0 \int_0^\infty G_2(r_0, \Omega^\Gamma, r_t; 0)\,\mathrm{d}r_t}\frac{t^2}{2} + \cdots. \tag{11}$$

Finally, from the zero time condition of $G_2(r_0, \Omega^\Gamma, r_t; t)$, given by equation (4), and the definition of $R^2(r_0, \Omega^\Gamma; t)$, given by equation (2), one obtains

$$R^2(r_0, \Omega^\Gamma; t) = \frac{6KT}{\mu}\frac{\Delta g^\Gamma}{N_0^\Gamma}\frac{t^2}{2} + \cdots \tag{12}$$

where

$$\frac{\Delta g^\Gamma}{N_0^\Gamma} = \frac{\frac{4}{3}\pi n[b^3 g^\Gamma(b) - a^3 g^\Gamma(a)]}{4\pi n \int_a^b r^2 g^\Gamma(r)\,\mathrm{d}r}. \tag{13}$$

Equations (12) and (13) show that the curvature of $R^2(r_0, \Omega^\Gamma; t)$ depends on the selected range r_0 as well as on the pair configuration, and it can be positive, negative or vanishing; they

also state the relation between the local structure, given by restricted angular averages $g^\Gamma(r)$ of $g(r, \omega_1, \omega_2)$ and the microscopic dynamics of the system. If one applies equation (5) to calculate the statistical averages in the function $S^2(r_0, \Omega^\Gamma; t)$ of equation (3), one obtains the trivial result

$$S^2(r_0, \Omega^\Gamma; t) = \frac{6KT}{\mu} \frac{t^2}{2} + \cdots \tag{14}$$

which shows that the starting steps described by the mean square displacements of equation (3) are insensitive to the local structure. The regime described by equation (14) is usually known as the ballistic or free flight regime of motion. So, while $S^2(r_0, \Omega^\Gamma; t)$ always shows the free flight behaviour whatever the choices of the initial range r_0 or configuration Γ are, the short time behaviour of $R^2(r_0, \Omega^\Gamma; t)$ depends not only on r_0, as in monatomic systems, but also on the relative pair orientation determined by the configuration Γ. In what follows, we apply the results to liquid water owing to the strong orientational character of its molecular interactions which should make the $R^2(r_0, \Omega^\Gamma; t)$ dependence on Γ particularly relevant.

3. Results

The derived expressions have been applied to liquid water and compared with the simulated results. Molecular dynamics runs were performed by exploiting the TIP4P potential [8] at constant N, V, E conditions and using a time step of 1 fs. The particle configurations were stored every ten time steps and runs of 15 ps were used. A system of 864 particles in a cubic box of half length of 14.8 Å was chosen. The temperature fluctuated within 245 ± 5 K. Checks on the short time motions have been performed by running the particle system with a time step of 0.1 fs and storing the configurations every 1 fs.

The simplest way of applying equations (12) and (14) is to select $r_0 < 3.5$ Å, i.e. to choose molecules that at initial time are in the first coordination shell (see figure 1). In this case, equation (13) simplifies and becomes

$$\frac{\Delta g^\Gamma}{N_0^\Gamma} = \frac{\frac{4}{3}\pi n b^3}{4\pi n \int_0^b r^2 g^\Gamma(r)\,\mathrm{d}r} g^\Gamma(b) \tag{15}$$

where the ratio multiplying $g^\Gamma(b)$ is between the numbers of molecules present in two spheres of radius b which have the average density n and the local density of the configuration Γ, respectively. Figure 2 shows the functions $D_R^\Gamma(r_0; t) = R^2(r_0, \Omega^\Gamma; t)/12t$ and $D_S^\Gamma(r_0; t) = S^2(r_0, \Omega^\Gamma; t)/12t$ for pairs that initially are H-bonded or non H-bonded in a sphere of radius $b = 3.5$ Å. At short times, $0.015 < t < 0.04$ ps, all the functions show the free flight motion with exception of $D_R^{HB}(r_0; t)$ which has a time dependence t^α with α clearly greater than 1. Equations (12)–(14), with the help of the $g^\Gamma(r)$ of figure 1, allow us to explain these behaviours. From equation (14), one expects no dependence of $S^2(r_0, \Omega^\Gamma; t)$ from the initial configuration Γ. This agrees with the trends of figure 2 which show that $D_S^{HB}(r_0; t)$ and $D_S^{NHB}(r_0; t)$ (small dotted and dashed–dotted lines, respectively) coincide for $t < 0.04$ ps. By contrast the trends of $D_R(r_0; t)$ are very different: for NHB pairs (large dots), the t dependence holds and $D_R(r_0; t)$ is also greater than $D_S(r_0; t)$; for HB pairs, the linear time dependence fails. Equations (12) and (14) show that the short time expansion of $R^2(r_0, \Omega^\Gamma; t)$ and $S^2(r_0, \Omega^\Gamma; t)$ are equal when $\Delta g^\Gamma/N_0^\Gamma = 1$. For HB states, $g^{HB}(r)$ nearly vanishes around $b = 3.5$ Å (see figure 1) so that, from equation (15), $\Delta g^{HB}/N_0^{HB} \cong 0$ and the t^2-coefficient in equation (12) tends to vanish. Consequently, $D_S^{HB}(r_0; t)$ increases as t^α with $\alpha > 1$. For NHB pairs, since $N_0^\Gamma \cong 0.8$ [5], from equation (15) it turns out that $\Delta g^{NHB}/N_0^{NHB} \cong 4$. The t^2 dependence of
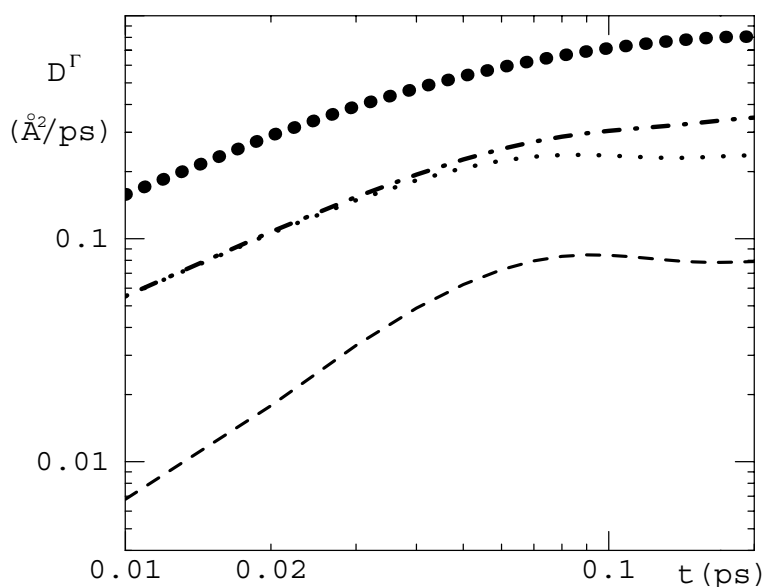
Figure 2. The functions $D_R^\Gamma(r_0; t) = R^2(r_0, \Omega^\Gamma; t)/12t$ and $D_S^\Gamma(r_0; t) = S^2(r_0, \Omega^\Gamma; t)/12t$ (logarithmic scales) for $r_0 < 3.5$ Å: $D_R^{NHB}(r_0; t)$ ($\bullet \bullet \bullet \bullet$), $D_R^{HB}(r_0; t)$ ($---$), $D_S^{NHB}(r_0; t)$ ($- \cdot -$) and $D_S^{HB}(r_0; t)$ ($\cdots$).

$R^2(r_0, \Omega^{NHB}; t)$ still holds; $D_S^{NHB}(r_0; t)$ increases linearly with time and the intensity is four times enhanced as is clearly shown in figure 2.

These results demonstrate the strong dependence of $R^2(r_0, \Omega^\Gamma; t)$ on the initial microscopic pair configuration Γ. It is now interesting to study its dependence on the initial r_0-range, in particular in the case of NHB configurations of the first coordination shell where the ballistic component of the radial motion is very strong. We search an initial separation range of r_0, for which $R^2(r_0, \Omega^{NHB}; t)$ should have a vanishing contribution of the quadratic term in the short time expansion. By analogy with the case of HB pairs, this would indicate the existence of a stable microscopic configuration around which the pair tends to stay before diffusing. Equation (13) indicates that this is possible for every r_0-interval where the function $r_0^3 g^\Gamma(r_0)$ ceases an increasing or decreasing trend. The inset of figure 1 suggests that, for $4.6 < r_0 < 5.1$ Å, $\Delta g^{NHB}/N_0^{NHB} \cong 0$. Figure 3 shows $R^2(r_0, \Omega^{NHB}; t)$ for this choice of the initial r_0 range; as expected the initial curvature tends to vanish. This means that around this zone the NHB pairs realize their more stable microscopic arrangement; in terms of local structure the distance of 4.8 Å roughly corresponds to the distance of peripheral molecules of a tetrahedral cluster.

From the short time dynamics of HB and NHB pairs, we can derive some information on the way the particles follow to overcome the first neighbour barrier and start the diffusion process. For $r_0 < 3.5$ Å, the lack of the t^2 dependence in the $R^2(r_0, \Omega^{HB}; t)$ function can be interpreted as the consequence of a hindered motion along the radial r_{12} direction (i.e. the H-bond direction); the HB pairs practically conserve their relative average distance for $t < 0.02$ ps, i.e. for the time in which the other functions start the characteristic free flight motion. The behaviour of NHB pairs is different for the particles in the first coordination shell (interstitial particles) and those around 4.5 Å which are peripheral molecules of a tetrahedral cluster [5]. The enhanced short time t^2 dependence of $R^2(r_0, \Omega^{NHB}; t)$ for $r_0 < 3.5$ Å,
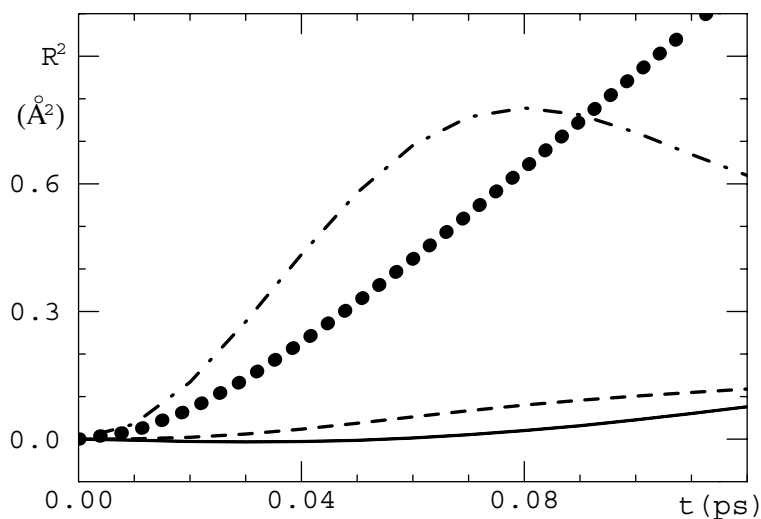
Figure 3. The functions $R^2(r_0, \Omega^{HB}; t)$ (— · —) for $r_0 < 2.8$ Å, $R^2(r_0, \Omega^{HB}; t)$ (– – –) for $r_0 < 3.5$ Å, $R^2(r_0, \Omega^{NHB}; t)$ (● ● ● ●) for $r_0 < 3.5$ Å and $R^2(r_0, \Omega^{NHB}; t)$ (———) for $4.6 < r_0 < 5.1$ Å.

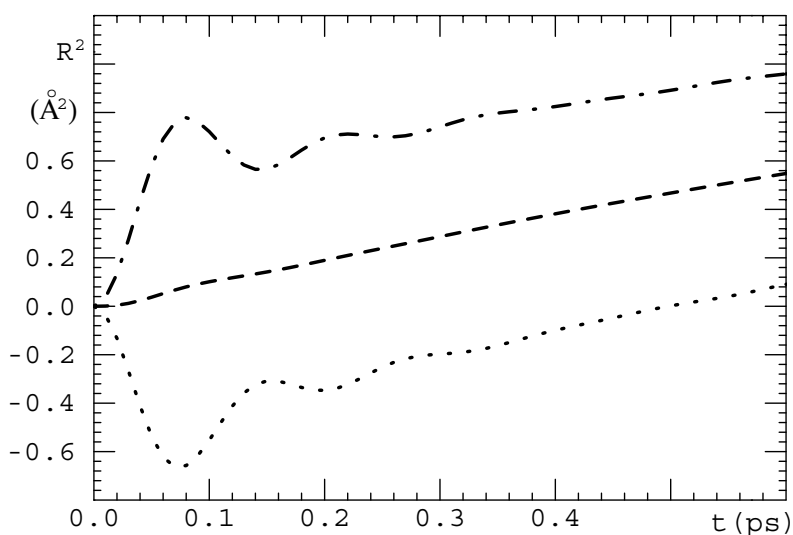**Figure 4.** The functions $R^2(r_0, \Omega^{HB}; t)$ (– – –) for $r_0 < 3.5$ Å (first coordination shell), $R^2(r_0, \Omega^{HB}; t)$ (— · —) for $r_0 < 2.8$ Å (first subshell), $R^2(r_0, \Omega^{HB}; t)$ (· · · · · ·) for $2.8 < r_0 < 3.5$ Å (second subshell).

indicates that the NHB particles behave as network defects: they are expelled from the first coordination shell towards the region around 4.5 Å. In this region, the NHB configurations of supercooled water are stable and a vanishing initial curvature of the function $R^2(r_0, \Omega^{NHB}; t)$ can be obtained. It is worthwhile to stress that the t^2 coefficient of $R^2(r_0, \Omega^\Gamma; t)$ vanishes only for particular choices of the a–b range. For HB pairs, for example, equation (13) and figure 1 suggest that for $a < 2.4$ Å and $b = 2.8$ Å one would obtain a fast increase of

$R^2(r_0, \Omega^{HB}; t)$ with time, since $\Delta g^{HB}/N_0^{HB} \cong 6$ (in this case $N_0^{HB} \cong 2$, i.e. one half of the HB molecules of the first coordination shell). Figure 3 shows that this prediction is confirmed by the results of the MD simulation: the nearest pairs are 'expelled' towards the stable position of 2.8 Å of the HB pairs. Moreover, the function $R^2(r_0 < 2.8 \text{ Å}, \Omega^{HB}; t)$ has a maximum around 0.07 ps that should indicate the presence of the HB vibrations already detected in the short-time behaviour of specific correlation functions [9, 10]. To confirm this argument, figure 4 shows the behaviours of $R^2(r_0, \Omega^{HB}; t)$ for $r_0 < 3.5$ Å (first shell), $r_0 < 2.8$ Å (first subshell) and $2.8 < r_0 < 3.5$ Å (second subshell). As is seen, the pairs in the first and second subshell seem to behave as damped oscillators with opposite phase relationship. An average non-oscillating trend results for all the pairs of the first coordination shell. A more refined explanation, based on an instantaneous normal mode approach, is reported in [11]. Here, we would stress that the function $R^2(r_0, \Omega^\Gamma; t)$ is very sensitive to the local structure that the molecules probe in the first time steps of motion. By contrast, the function $S^2(r_0, \Omega^\Gamma; t)$ is insensitive to the local structure and its short time behaviour (not shown) is independent of both the configuration and the r_0-range.

4. Conclusions

By introducing the time-dependent pair distribution function $G_2(r_0, \Omega^\Gamma, r_t; t)$, a relationship between the short time dynamics and the local structure has been obtained. Consequently, the short time pair dynamics joined to the structural properties turns into a powerful tool to achieve a reliable picture of the microscopic properties of molecular liquids. In the specific case of water, a crude description is gained by considering HB and NHB pairs. The starting time-steps of HB pairs appear mainly due to a re-orientation of the r_{12} vector since the average radial motions are rather hindered; the process is accompanied by the expulsion, from the first coordination shell, of NHB molecules (the defects of the tetrahedral network), in agreement with the structural analysis [5, 6] and previous dynamical studies [12, 13]. However, as indicated by the asymptotic trends of the $g(r)$ of figure 1, the NHB states represent about 90% of the pair angular space and have some structure in the first coordination shell visible as a shoulder around 3 Å in $g^{NHB}(r)$. A more refined dynamical description requires us to consider the microscopic configurations Γ which compose the NHB states [5] as well as to explore different initial ranges of r_0. For HB states, the choice of $r_0 < 2.8$ Å has revealed the presence of oscillating motions which confirm the strong sensitivity of the $R^2(r_0, \Omega^\Gamma; t)$ function to the local structure.

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