

## On the anomalous behaviour of microscopic diffusion of liquid water

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2007 J. Phys.: Condens. Matter 19 415118

(<http://iopscience.iop.org/0953-8984/19/41/415118>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

### Download details:

IP Address: 129.252.86.83

The article was downloaded on 29/05/2010 at 06:12

Please note that [terms and conditions apply](#).

## On the anomalous behaviour of microscopic diffusion of liquid water

A Cunsolo<sup>1,2</sup>, A Orecchini<sup>1,3</sup>, C Petrillo<sup>1,3</sup> and F Sacchetti<sup>1,3</sup>

<sup>1</sup> CNR-INFM, Centro di Ricerca e Sviluppo SOFT, I-00185 Roma, Italy

<sup>2</sup> OGG, Operative Group in Grenoble, 6 rue J. Horowitz, F-38042 Grenoble Cedex 9, France

<sup>3</sup> Dipartimento di Fisica, Università di Perugia, I-06123 Perugia, Italy

Received 30 April 2007, in final form 14 June 2007

Published 27 September 2007

Online at [stacks.iop.org/JPhysCM/19/415118](http://stacks.iop.org/JPhysCM/19/415118)

### Abstract

We propose here a new interpretation of recent quasi-elastic neutron scattering (QENS) measurements on water. A line-shape analysis based on a stretched exponential ansatz for the time decay of density fluctuations enabled us to observe an anomalous dependence on the exchanged momentum of relevant relaxation parameters. We discuss this effect and relate it to an *a priori* uncorrelated anomaly, previously evidenced by diffraction measurements.

Despite increasing efforts, the understanding of the physical properties of water still represents a scientific challenge for the near future, made more urgent by the continuous discovery of new anomalies in both static and dynamic properties [1, 2]. Among the former, a prominent interest was attracted by the divergence of static density correlations upon approaching the nucleation temperature,  $T_H = -45^\circ\text{C}$  [3, 4]. A divergence around  $T_H$  also characterizes the temperature evolution of dynamic (transport) parameters, even if the connection of such an effect with a critical phenomenon still seems controversial [1]. Various models were developed in an attempt to account for this intriguing behaviour [2]. Although each of them individually succeeds in explaining a single effect, a comprehensive explanation is still lacking [2]; on the other hand, a firm experiment allowing an unambiguous choice between the different models can hardly be envisaged at present. An anomalous connectivity of overcooled water was evidenced by compressibility [3, 4], neutron [5, 6] and x-ray [7–9] measurements, which experimentally demonstrated the occurrence of an intensity increase in the static structure factor  $S(Q)$  at low momentum transfers ( $Q$ ). This effect was ascribed to the influence of cooperatively arranging regions on density fluctuations [2]. However, its physical link with a critical phenomenon raised some controversy in the past, being first suggested by Bosio *et al* [6, 9], and then conclusively ruled out by Xie *et al* [8] on the basis of the fairly temperature-independent value of the correlation length ( $\lambda_C = 3.6\text{--}3.8 \text{ \AA}$ ). In contrast, the systematic enhancement of such an effect on decreasing temperature, likely due to the increasing number of cooperatively arranging domains, seems to be rather well assessed.

Another intriguing effect was observed in the pressure ( $P$ ) dependence of some transport parameters, such as viscosity (or diffusion coefficients), mainly appearing as a maximum

(or a minimum) at about 2 kbar [11]. Such behaviour has a rather simple explanation based on the assumption of two competing effects of pressure. On the one hand, increasing pressure causes a weakening of intermolecular attractions, owing to the increased overlap between close-contact electron orbitals, thus favouring diffusion. On the other hand, it reduces the free volume available for diffusive jumps [2], thus conversely increasing the resistance to diffusive flow, which typically occurs in simple, non-associated fluids. Therefore the minimum (maximum) of viscosity (diffusion coefficients) represents a crossover between a low- $P$  region where the non-trivial effect dominates, and a high- $P$  regime where the ‘normal’ behaviour is instead restored. According to some interpretation schemes [12], the viscosity minimum would likewise be reminiscent of a structural liquid–liquid transition between a low-pressure *open* arrangement and a high-pressure more *packed* one [1].

A deeper insight into both the  $P$ - and  $Q$ -dependences of microscopic diffusion of water was achieved in a recent quasi-elastic neutron scattering (QENS) experiment [13]. The relevant data analysis shows that the incoherent response of liquid water can be consistently described assuming a stretched exponential time-decay of density fluctuations [14], in which both the average relaxation frequency and the stretching parameter  $\beta$  follow a rather unexpected  $Q$ -dependence.

In order to get a more unified picture of the microscopic properties of water, the results of [13] are here compared with the independent and *a priori* uncorrelated diffraction measurements performed by Xie *et al* [8]. Such comparison allows to infer a  $1/S(Q)$ -dependence of the diffusion coefficient  $1/(\tau_{av} Q^2)$ , which turns out to be a rather unexpected result. Indeed, for the first time, an empirical link between an incoherent property such as the relaxation time and a truly coherent one such as the static structure factor is experimentally evidenced. Despite its novelty, such a result could not be fully unexpected, since the hypothesis of some entanglement between single-particle diffusion and structural arrangements seems somehow inherent to the ‘relaxing-cage’ approach. In fact such a model, derived in the frame of the ‘mode coupling’ theory, relies on the hypothesis that diffusive jumps of a single molecule are allowed only after the relaxation of the first-neighbour cage is accomplished.

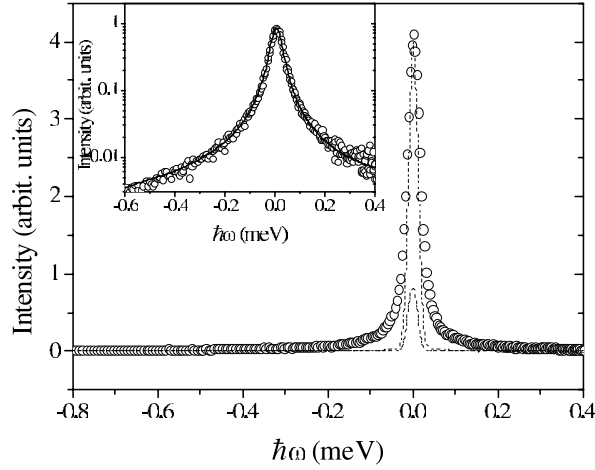
The experiment was carried out using the time-of-flight spectrometer IN5, which operates at the high-flux reactor of the Institut Laue-Langevin in Grenoble (France). Data were collected along the  $T = 268$  K isotherm, with pressures spanning the 80.9–350.4 MPa range. The instrumental resolution function, provided by the measurement of a vanadium standard, had the expected Gaussian profile with a full width at half maximum of 28  $\mu\text{eV}$ . Further details of the experiment are given elsewhere [13].

As an example, the quasi-elastic spectrum of water collected at  $P = 80.9$  MPa and  $35^\circ$  scattering angle is reported in figure 1, as it appears after all background and multiple scattering corrections. The corresponding empty cell contribution and the proper instrumental resolution function are also shown.

The spectral intensity reads

$$I^{\text{exp}}(Q, \varepsilon) = \frac{1}{2\pi\hbar} \int_{-\infty}^{+\infty} dt \exp\left[\frac{i\varepsilon t}{\hbar}\right] F^{\text{mod}}(Q, t) \mathfrak{R}(t) \quad (1)$$

where  $Q$  and  $\varepsilon = \hbar\omega$  are respectively the wavevector and energy transfers,  $F^{\text{mod}}(Q, t)$  is the intermediate scattering function (ISF) and  $\mathfrak{R}(t)$  the Fourier transform of the instrumental resolution function. The line-shape model used relies on the assumption of a mutual decoupling between vibrational, translational and rotational motions. This approximation has been successfully employed in a large number of  $T$ -dependent QENS studies of supercooled [17], supercritical [18] and confined [19] water. On such a basis, the ISF can be written as the product



**Figure 1.** Spectrum of the water sample at  $P = 80.9$  MPa and  $35^\circ$  scattering angle (O) compared with both the empty cell scattering (dash-dotted line) and instrumental resolution function as measured with vanadium standard (dashed line). Inset: logarithmic plot of the spectrum of water at  $P = 80.9$  MPa and  $Q = 0.44 \text{ \AA}^{-1}$  (O) compared with the corresponding best-fit curve (solid line) (see text).

of three uncoupled terms:

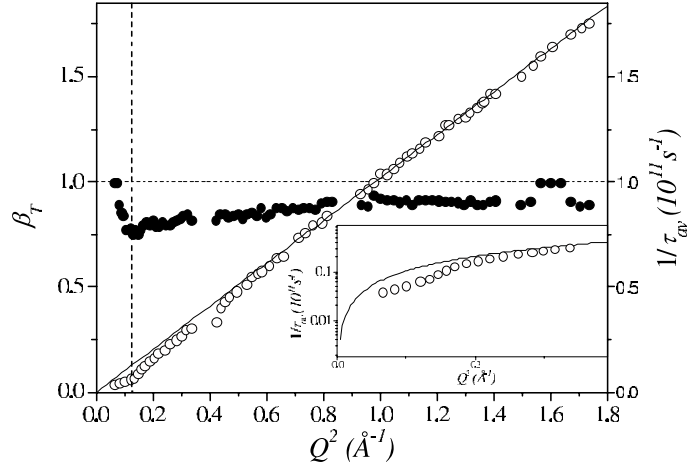
$$F^{\text{mod}}(Q, t) = A(Q) \exp \left[ - \left( \frac{t}{\tau_T} \right)^{\beta_T} \right] \left\{ \sum_{l=0}^{l_{\text{max}}} (2l+1) j_l^2(Qd) \exp \left[ - \frac{l(l+1)}{2} \left( \frac{t}{\tau_R} \right)^{\beta_R} \right] \right\}. \quad (2)$$

In equation (2),  $A(Q)$  represents a Debye–Waller-like scaling factor accounting for proton vibrations. The stretched exponential labelled by the suffix T describes the translational ISF according to the relaxing-cage model [14]. Finally the summation involving products of  $l$  th order spherical Bessel functions  $j_l(Qd)$  and stretched exponentials labelled by the suffix R describes the rotational ISF. The parameter  $d$  is indeed the rotation radius, here approximated by the O–H distance, namely  $0.98 \text{ \AA}$ . According to [20] (see equations (17) and (18)), the rotational contribution was truncated to the term  $l = 1$ . In fact, owing to the low- $Q$  range covered by the present experiment, higher-order rotational terms are not expected to contribute significantly to the spectral line-shapes. We recall that in the  $\beta_T \rightarrow 1$  limit the multi-exponential time-decay model [21] is retrieved.

In the adopted model, equation (2) is inserted in equation (1) while approximating  $\Re(t)$  with the Fourier transform of the Gaussian best fit of the instrumental resolution.

The spectral line-shapes were fitted within the  $-0.6 \text{ meV} \leq \hbar\omega \leq 0.6 \text{ meV}$  energy transfer window. The parameters  $A(Q)$ ,  $\tau_T(Q)$ ,  $\tau_R(Q)$ ,  $\beta_T(Q)$  and  $\beta_R(Q)$  were left free to vary without any constraint to both their  $P$ - and  $Q$ -dependences.

The agreement between model and experimental line-shapes can be easily judged even from a first inspection of the inset of figure 1, where a typical corrected spectrum is compared with the corresponding best fit, obtained as the Fourier transform of the optimized ISF model of equation (2). The logarithmic scale emphasizes the overall agreement even in the extreme portion of spectral tails. Various preliminary tests allowed us to conclude that the translational term alone accurately approximates the spectral shape, the agreement being not significantly improved by the inclusion of the rotational term, which was therefore discarded.



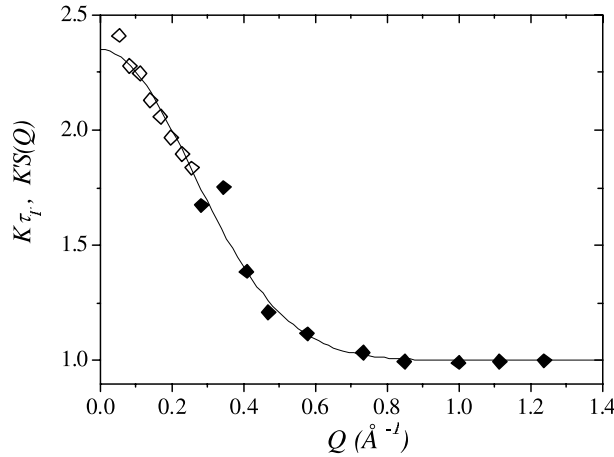
**Figure 2.** Best-fit values of  $1/\tau_{av}$  (open circles) reported as a function of  $Q^2$  at the lowest pressure investigated ( $P = 80.9$  MPa). The full line represents the parabolic trend as inferred from NMR measurements of [15]. Best-fit values of the stretching parameter  $\beta_T$  are also reported as dots and compared with the simple exponential result  $\beta_T = 1$ . The vertical line shows both the position of the minimum and the region where the  $1/\tau_{av}$  exhibits an anomalous behaviour (see text). In the inset the comparison between  $1/\tau_{av}$ -values and the NMR curve is reported in a semi-logarithmic plot and within a more restricted window.

Once a good consistency between experimental and model line-shapes is assessed, further physical insight can be derived from the analysis of the two relevant outputs of the best-fit routine: the stretching parameter  $\beta_T$ , and the average relaxation frequency  $1/\tau_{av}$ , defined as

$$\tau_{av} = \int_0^{\infty} \exp \left[ - \left( \frac{t}{\tau_T} \right)^{\beta_T} \right] dt. \quad (3)$$

In figure 2, the best-fit values of  $1/\tau_{av}$  and  $\beta_T$  referring to the lowest  $P$  investigated (80.9 MPa) are reported as a function of  $Q^2$ . We notice that, for  $Q \geq 0.5 \text{ \AA}^{-1}$ , the  $Q$ -behaviour of  $1/\tau_{av}$  is rather well approximated by the  $DQ^2$  law (solid line) obtained by nuclear magnetic resonance (NMR) measurements of  $D$  [15]. At variance, systematic deviations show up for  $Q \leq 0.5 \text{ \AA}^{-1}$ , as emphasized by the logarithmic plot reported in the inset, in which the comparison is displayed within a more restricted window. It clearly appears that the present data definitely lie below NMR ones, thus suggesting an unpredicted slowing down of diffusion at relatively low  $Q$ . At this preliminary stage, we can tentatively ascribe such behaviour to the occurrence of some coupling of diffusion processes with some internal degree of freedom; this also seems to be suggested by the inspection of the values of  $\beta_T$  reported in the same plot. In fact the latter shows a clear minimum around  $Q_m \sim 0.32 \text{ \AA}^{-1}$ , i.e. close to the low- $Q$  anomaly of  $1/\tau_{av}$  (both positions being shown by a vertical line). Such a minimum reveals a broadening of the relaxation time distribution, likely reminiscent of some coupling with an internal mode having a typical size of the order of  $\lambda_C \approx Q_m^{-1}$ .

The physical interpretation of such an effect is far from being trivial, since none of the existing models predict it and no simulation result provides data accurate enough to allow its observation [22]. It should be also remarked that previous experimental investigations of the self-dynamics of water only proposed multi-exponential line-shape modelling. In addition, the effect under investigation is scarcely perceptible on a linear scale, and is also circumscribed within a limited  $Q$ -range. However, the quality of the present data, as well as the reproducibility



**Figure 3.**  $Q$ -dependence of  $K\tau_T$  (◆), where  $K = D_f Q^2$  represents the parabolic best fit of the high- $Q$  trend of  $1/\tau_T(Q)$  (see text). The curve is compared with  $K'S(Q)$  (◇), where  $S(Q)$  is determined by diffraction techniques [8] and its normal component ( $K'^{-1}$ ) is derived from [23] (see text). The profile (equation (4)) best fitting both measurements is also reported as a solid line for comparison.

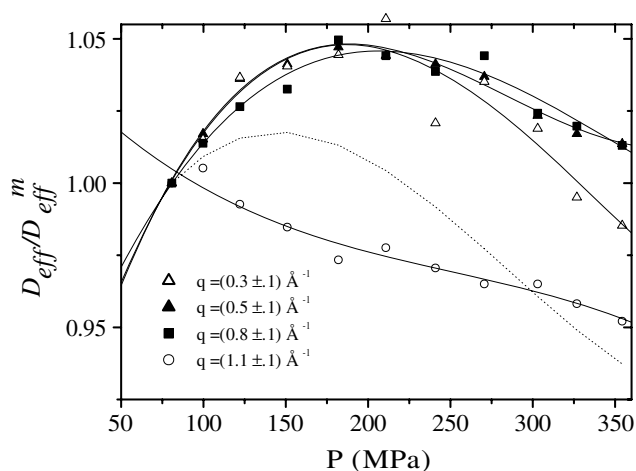
of the result all over the pressures investigated (see [13]), makes us confident that the observed behaviour is a real physical effect.

In this framework, a comparison between such intriguing  $Q$ -dependence and the anomalous low- $Q$  trend of the static structure factor, already studied in literature [5–9], would be rather appealing. In order to check if a more stringent connection exists, the best-fit values of  $\tau_T$  at  $P = 80.9$  MPa were multiplied by the parabola  $K = D_f Q^2$  best fitting the  $Q$ -dependence of  $1/\tau_T$  for  $Q \geq 0.7 \text{ \AA}^{-1}$ . In such a fitting routine the diffusion coefficient  $D_f$  was taken as the only free parameter. In figure 3 the  $Q$ -dependence of  $K\tau_T$  is compared with the closest- $T$  diffraction pattern reported in [8] multiplied by the scaling factor  $K' = 1/[nK_B T \chi''_T]$ , where  $n$ ,  $K_B$  and  $\chi''_T$  are the density, the Boltzmann constant and the normal component of isothermal compressibility (from [23]) respectively. More specifically, the coefficient  $K'$  coincides with the inverse of the normal, non-diverging component of  $S(Q)$  [23]. Although no adjustable scaling factor was used, the two independent curves— $K\tau_T$  and  $K'S(Q)$ —agree remarkably well, thus suggesting that  $\tau_T = \frac{K}{K'S(Q)}$ . Finally, the two independent sets of data were fitted by a single model consisting of the sum of a Lorentzian and a parabolic  $Q$ -profile:

$$I(Q) = I/(Q^2 + \lambda_C^{-2}) + B + C \times Q^2. \quad (4)$$

Here  $I$ ,  $B$ ,  $C$  and the correlation length,  $\lambda_C$ , are best-fit parameters. It is worthwhile noticing that the actual best-fit value of  $\lambda_C$  (2.79 Å) agrees fairly well with the independent determination reported in [8, 10]. This represents a rather interesting result, suggesting that dynamical and statical properties exhibit similar anomalies.

To the best of our knowledge, for the first time a direct link is unambiguously established here between an incoherent property such as  $1/\tau_T$  and a truly coherent one such as  $S(Q)$ . Despite the undoubted novelty, such a result appears somehow consistent with the ‘relaxing-cage’ framework, predicting a strong entanglement between single-particle jumps and the structural arrangement of the surrounding cage. We believe these findings deserve further experimental investigations, covering a wider  $Q$ -range, thus allowing one to approach the position of the first diffraction peak, and possibly exploring the supercooled region where a drastic enhancement is expected.



**Figure 4.** Pressure dependence of the diffusion coefficient  $D_{\text{eff}} = 1/(\tau_T(Q)Q^2)$  averaged within different  $Q$ -windows indicated in the plot and normalized to the lowest-pressure ( $P_{\text{min}} = 80.9$  MPa) datum,  $D_{\text{eff}}^m$ . The pressure dependence of the diffusion coefficient obtained by NMR measurements is also reported as a dashed line for comparison. Full lines are polynomial fits to the various curves and mainly serve as guides to the eye.

In order to shed more light on the phenomenology associated to molecular self-diffusion in water, a detailed analysis of the  $P$ - and  $Q$ -dependences of the effective diffusion coefficient  $D_{\text{eff}} = 1/(\tau_T Q^2)$  can be carried out. To improve the statistical accuracy of the results, best-fit values of  $1/(\tau_T Q^2)$  were averaged over different  $Q$ -windows centred at the  $Q$ -values indicated in the plot, with all of them having  $\pm 0.1 \text{ \AA}^{-1}$  spread. We readily notice that for  $Q \leq 0.8 \text{ \AA}^{-1}$  all the curves follow the same  $P$ -trend, mainly consisting in a maximum at  $200 \pm 10$  MPa. This behaviour parallels the  $P$ -evolution of the macroscopic self-diffusion coefficient, also reported in figure 4 as derived from NMR measurements [15]. It is worthwhile noticing that the maximum disappears in the highest- $Q$  datum ( $1.1 \text{ \AA}^{-1}$ ). This evidence is *per se* interesting and worth further comments.

In fact, the reported curves suggest that the general features of the macroscopic diffusion coefficient (displayed for example by the NMR datum) are observable also at mesoscopic scales, i.e. at least for  $Q \leq 0.8 \text{ \AA}^{-1}$ , in spite of the disparate time range covered by each measurement. However, when  $Q$  overcomes the  $\lambda_C^{-1}$ -range, changes in the diffusive behaviour show up abruptly, likely revealing once again some entanglement with internal degrees of freedom. This evidence appears, in turn, rather intriguing, since it suggests that the macroscopic anomaly characterizing the  $P$ -behaviour of the diffusion coefficient disappears on approaching truly microscopic distances. At these length-scales, the dynamic behaviour of water becomes more normal and similar to that of non-associated fluids (monotonic  $P$ -decrease). In this regime the pressure-induced weakening of hydrogen bonds, responsible for the diffusion anomaly, becomes quite less effective.

In summary, all presented results provide a rich and physically informative picture of the microscopic diffusion of liquid water. We observe that a stretched exponential ansatz for the time decay of density fluctuation allows one to find evidence of an anomalous  $Q$ -dependence of relaxation parameters, suggestive of a strong coupling between diffusive motions and some internal degrees of freedom. Moreover, the comparison with independent diffraction measurements points to a strict link between such an effect and the anomalies of the

large-distance structure of water that have been thoroughly reported in the literature. In view of the relevant physical interest of these findings, we believe that this subject is worth future investigative efforts, hopefully combining experimental and computational techniques.

### Acknowledgments

The authors acknowledge the Institut Laue-Langevin, Grenoble (France) for providing the beam time enabling the accomplishment of the present experiment. Mr L Melesi is also very warmly acknowledged for his valuable help during the assembly of the high-pressure apparatus.

### References

- [1] For an overview of the main experimental results see Angell C A 1972 *Water: a Comprehensive Treatise* vol 1, ed F Franks (New York: Plenum) chapter 1
- [2] Debenedetti P G 1997 *Metastable Liquids* (Princeton, NJ: Princeton University Press)
- [3] Speedy R J and Angell C A 1976 *J. Chem. Phys.* **65** 851
- [4] Angell C A and Kanno H 1976 *Science* **193** 1121
- [5] Hendricks R W, Mardon P G and Shaffer L B 1974 *J. Chem. Phys.* **61** 319
- [6] Bosio L, Teixeira J and Bellissent-Funel M C 1989 *Phys. Rev. A* **39** 6612
- [7] Michielsen J C F, Bot A and van der Elsken J 1988 *Phys. Rev. A* **38** 6439  
Dings J, Michielsen J C F and van der Elsken J 1992 *Phys. Rev. A* **45** 5731
- [8] Xie Y, Ludwig K F, Morales G, Hare D E and Sorensen C M 1993 *Phys. Rev. Lett.* **71** 2050
- [9] Bosio L, Teixeira J and Stanley H E 1981 *Phys. Rev. Lett.* **46** 597
- [10] Dings J, Michielsen J C F and van der Elsken J 1992 *Phys. Rev. A* **45** 5731
- [11] Bett K E and Cappi J B 1965 *Nature* **207** 620
- [12] DeFries T and Jonas J 1977 *J. Chem. Phys.* **66** 896
- [13] Cunsolo A, Orecchini A, Petrillo C and Sacchetti F 2006 *J. Chem. Phys.* **124** 084503
- [14] Chen S-H, Gallo P, Sciortino F and Tartaglia P 1997 *Phys. Rev. E* **56** 4231
- [15] Harris K R and Newitt P J 1977 *J. Chem. Eng. Data* **42** 346
- [16] Petrillo C and Sacchetti F 1990 *Acta Crystallogr.* **44** 440  
Petrillo C and Sacchetti F 1992 *Acta Crystallogr.* **44** 508
- [17] Chen S H, Teixeira J and Nicklow R 1982 *Phys. Rev. A* **26** 3477  
Teixeira J, Bellissent-Funel M-C, Chen S H and Dianoux A J 1985 *Phys. Rev. A* **31** 1913
- [18] Tassaing T and Bellissent-Funel M-C 2000 *J. Chem. Phys.* **113** 3332
- [19] Zanotti J M, Bellissent-Funel M C and Chen S H 1999 *Phys. Rev. E* **59** 3084  
Dellerue S and Bellissent-Funel M-C 2000 *Chem. Phys.* **258** 315
- [20] Liu L, Faraone A and Chen S H 2002 *Phys. Rev. E* **65** 041506
- [21] Sears V F 1966 *Can. J. Phys.* **44** 1299  
Sears V F 1966 *Can. J. Phys.* **45** 237
- [22] Starr F W, Harrington S, Sciortino F and Stanley H E 1999 *Phys. Rev. Lett.* **82** 3629  
Starr F W, Sciortino F and Stanley H E 1999 *Phys. Rev. E* **60** 6757
- [23] D'Arrigo G and Paparelli A 1987 *J. Chem. Phys.* **88** 405