IL NUOVO CIMENTO **39 C** (2016) 302
DOI 10.1393/ncc/i2016-16302-2

Colloquia: SWGM 2015

Fragile-to-strong crossover in supercooled water: A comparison between TIP4P and TIP4P/2005 models

M. De Marzio([1]), G. Camisasca([1]), M. Rovere([1]) and P. Gallo([1])([2])(*)

([1]) *Dipartimento di Matematica e Fisica, Università Roma Tre - Roma, Italy*
([2]) *INFN, Sezione di Roma Tre - Roma, Italy*

received 19 July 2016

Summary. — We present recent simulation results on the dynamics of supercooled water with the TIP4P/2005 potential. We find that the dynamical behaviour of the translational motion of the molecules is well interpreted in terms of the Mode Coupling Theory, as it was found for supercooled TIP4P water. We compare the results of the two models and in particular we find also in TIP4P/2005 a crossover from a fragile to a strong regime. We connect this crossover to the crossing of the Widom line emanating from the liquid-liquid critical point.

1. – Introduction

The hypothesis of a liquid-liquid critical point (LLCP) in supercooled water was formulated for the first time on the basis of numerical simulations of the phase diagram of the ST2 water model [1]. The presence of the LLCP provides a thermodynamically consistent interpretation of the anomalies in thermodynamic response functions found in experiments. In approaching $-39\,°C$, in fact, the constant pressure specific heat and the isothermal compressibility show a strong increase similar to the singularities observed close to a critical point [2]. The LLCP was considered as the end point of the coexistence curve between a low density liquid (LDL) and a high density liquid (HDL) that would continue the two glassy states of water, the low density amorphous (LDA) and high density amorphous (HDA) ice [3-6]. The search for the LLCP stimulated a great deal of experimental and computer simulation studies in the field. Evidences of the existence of a LLCP were found in a number of computer simulations performed with different models for water [1, 7-12] and they were confirmed by extensive free energy calculations [13-24].

The experimental study in the supercooled region of water however is made rather difficult for the tendency of water to form the ice crystal phase below the temperature of

(*) Corresponding author. E-mail: gallop@fis.uniroma3.it

homogeneous nucleation [25]. A great debate is still present in the literature about the possibility of observing the LLCP in real water.

In this framework the concept of Widom line has been introduced [26, 27]. Critical phenomena in fluids are characterized by the divergence of the density correlation length at the critical point and, as a consequence, a power law divergence of the thermodynamic response functions, like the specific heat and the compressibility, is found. Moving from the critical point into the one phase region, those functions show maxima along a line, defined as the Widom line. In the studies of the supercooled water the Widom line is considered a very relevant signature of the presence of the LLCP. Importantly it connects the thermodynamics also to the dynamical behaviour of the supercooled liquid.

Besides the thermodynamic calculations, in fact, also studies of the dynamical properties of supercooled water were performed starting from a computer simulation of SPC/E water [28, 29], where it was shown that the structural relaxation upon supercooling is in agreement with the Mode Coupling Theory (MCT) [30]. Experimental confirmations of this finding were found [31, 32]. In more recent years it was found that in a regime of deep supercooling the structural relaxation deviates from the MCT ideal behaviour and it is driven by activated processes. So, water approaching the LLCP shows a crossover from a fragile to a strong liquid behaviour [33, 26, 34-36]. This is in agreement with experimental findings [37, 38] and computer simulation results [39-41] on confined water. From all those previous studies a relation between the thermodynamics and the dynamical behaviour has been found and it has been demonstrated that the fragile-to-strong crossover (FSC) takes place in crossing the Widom line.

The FSC crossover can be interpreted in the framework of MCT as the transition from an ideal cage hopping free regime to a hopping-dominated regime upon deeply supercooling [40]. In this respect the Widom line signs the switching on of hopping processes upon supercooling. In a recent paper of our group it was shown that this interpretation is confirmed in TIP4P water [34]. The TIP4P water model is known to give a good qualitative agreement with the phase diagram of water as soon as a rigid shift of $-73\,\mathrm{MPa}$ in pressure and $+31\,\mathrm{K}$ in temperature is performed [11]. TIP4P water shows a dynamical behaviour upon supercooling that can be interpreted in terms of the MCT with the presence of the FSC. The line of the FSC is coincident with the Widom line, defined by the maxima of the specific heat in approaching the LLCP [34]. We now consider water with the TIP4P/2005 potential [42]. TIP4P/2005 reproduces very well the experimental temperature of maximum density and the different ice phases, moreover the existence of a LLCP with the associated Widom line defined from the line of the maxima of the isothermal compressibility that emanates from the critical point was recently found [12].

In this paper we present the results obtained from computer simulations of the dynamical properties of supercooled water with the use of the TIP4P/2005 potential [43] to compare the outcome of this model with the results of the TIP4P potential. The two models, in fact, are similar, since they are based on the same geometry but with a different parametrization of the potential.

2. – Simulation methods

In the following sections we present results obtained by computer simulation of water with two potentials, TIP4P and TIP4P/2005. In both the models the water molecule is described as a four-site system. Two charged positive hydrogen sites are connected with rigid bonds to a neutral site representing the oxygen. The negative charge of the

oxygen is shifted and carried by a fourth massless site placed along the bisector of the H-O-H angle and coplanar with the oxygen and hydrogens. The hydrogens have charges $q_{\rm H} = 0.520e$ for TIP4P $q_{\rm H} = 0.5564e$ for TIP4P/2005 and the neutral oxygen interacts only through a single Lennard-Jones force with $\sigma = 3.154\,$Å and $\epsilon/k_B = 78\,$K in TIP4P and $\sigma = 3.1589\,$Å and $\epsilon/k_B = 93.2\,$K in TIP4P/2005. The distance between the oxygen and the negative charged site is $0.150\,$Å in TIP4P and $0.1546\,$Å in TIP4P/2005.

3. – Dynamics upon supercooling

In fig. 1 we show the TMD as predicted by TIP4P and TIP4P/2005. It is evident that TIP4P/2005 is in very good agreement with the experimental findings. As it was already noted, TIP4P shows a TMD in qualitative agreement, but shifted to higher pressure and lower temperature with respect to experiments.

The phase diagram of TIP4P/2005 appears to be shifted at higher temperatures with respect to TIP4P, as a consequence the melting temperature is higher for TIP4P/2005, $T_m = 252\,$K, while for TIP4P $T_m = 232\,$K. We explored the dynamical properties of TIP4P/2005 upon supercooling. It was already found that the structural relaxation of TIP4P water shows in the mild supercooled regime an agreement with the Mode Coupling Theory (MCT) [34].

We calculated the self-intermediate scattering functions (SISF) of the oxygens of TIP4P/2005 at the peak of the static structure factor $Q_0 = 2.25\,$Å^{-1}, where MCT features can be more evident. As an example of our analysis, we present in this section the results for the density $\rho = 1.00\,$g/cm^3. The SISF are reported in fig. 2 for three

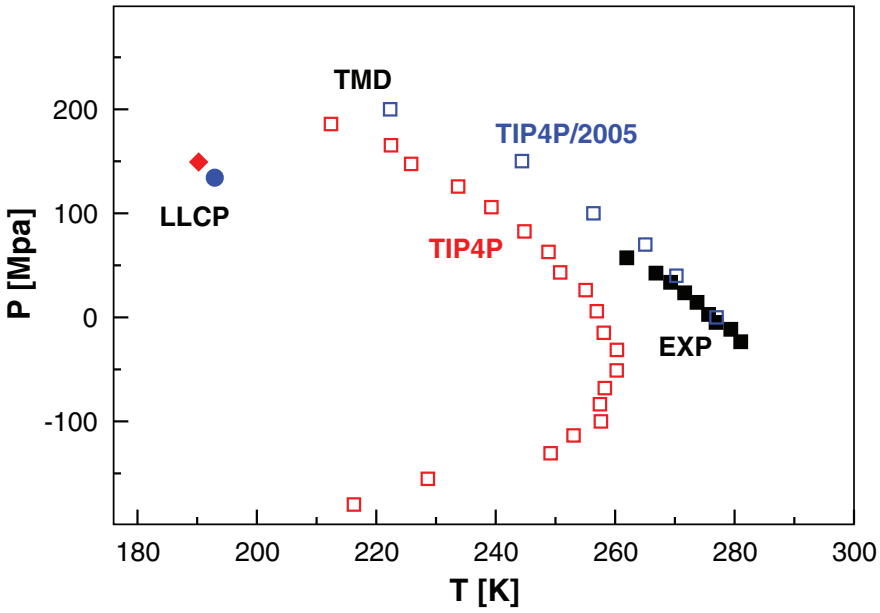

Fig. 1. – Portion of the phase diagram of TIP4P/2005 [42] and TIP4P [11] water. The open squares are the TMD lines predicted by simulations. The full squares are the experimental TMD. Also the locations of the LLCP for the two models are shown. Blue and red symbols refer to TIP4P/2005 and TIP4P, respectively.

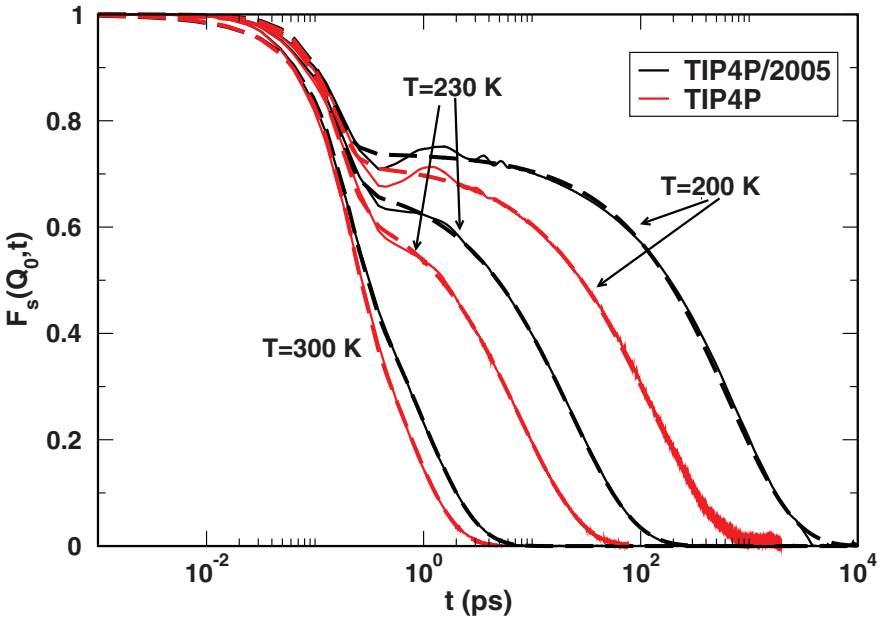

Fig. 2. – Oxygen self-intermediate scattering functions calculated at the maximum of the static structure factor for the density $\rho = 1.00\,\mathrm{g/cm^3}$ and for three different temperatures: 300 K, 230 K and 200 K. The black lines are for TIP4P/2005 while the red lines refer to TIP4P. In both cases the solid lines are the MD results and the dashed lines are the fits to eq. (1).

decreasing temperatures and they are compared with the analogous SISF of the TIP4P model.

The SISF of TIP4P/2005 shows a behaviour in agreement with the MCT predictions as the SISF of TIP4P. After the early time region, characterized by the initial ballistic regime for the $T < 300\,\mathrm{K}$ a two-step relaxation behaviour is observed. In the intermediate regime, the β relaxation regime, the particle is trapped in the cage of the nearest neighbors and in the SISF a constant plateau appears, it persists for a longer time at decreasing T. After the plateau the cage relaxes and the SISF enters in the so-called α relaxation region described by a stretched exponential decay. It is evident that, due to the higher value of the melting temperature, TIP4P/2005 shows a slower decay since it reaches at equal temperature a region of major supercooling with respect to TIP4P. The SISF of both models can be fitted with the formula used in previous studies of supercooled water [28, 29]

$$f_s(Q,t) = (1 - A(Q)) \exp[-(t/\tau_s)^2] + A(Q) \exp[-(t/\tau)^\beta], \tag{1}$$

where τ_s represents the short time fast relaxation, τ is the α relaxation time and β is the so-called Kohlrausch exponent of the long time stretched exponential decay. The Lamb-Mossbauer factor [30] $A(Q)$ measures the height of the plateau and it is related to the size of the cage.

The agreement with the MCT is preserved at the densities $\rho = 0.95\,\mathrm{g/cm^3}$ and $\rho = 0.98\,\mathrm{g/cm^3}$ [43].

4. – Fragile-to-strong crossover and the connection with the Widom line

From the fit with eq. (1) the values of τ as a function of temperature can be extracted for each density. In fig. 3 we show the results obtained from the SISF at $\rho = 1.00\,\mathrm{g/cm^3}$. We plot $1/\tau$ as a function of the inverse temperature on a semi-logarithmic scale. According to MCT the α relaxation time would diverge with a power law behaviour

$$\tau \sim (T - T_C)^{-\gamma}, \tag{2}$$

where T_C is the MCT asymptotic temperature of the ideal transition from an ergodic to a non-ergodic regime. In this limit the dynamics of the system would be frozen. The fit to eq. (2) is reported in fig. 3 as a red curve for both the models.

As it was already observed in TIP4P, also for TIP4P/2005 a deviation is found from the MCT prediction going to the lowest temperatures explored. This deviation is due to hopping phenomena that start to take place in the deep supercooled region. These phenomena are neglected in the ideal formulation of the MCT, they restore ergodicity without relaxing the cages. The particle at finite temperature can diffuse through activated processes induced by temperature fluctuations. The behaviour of τ crosses from

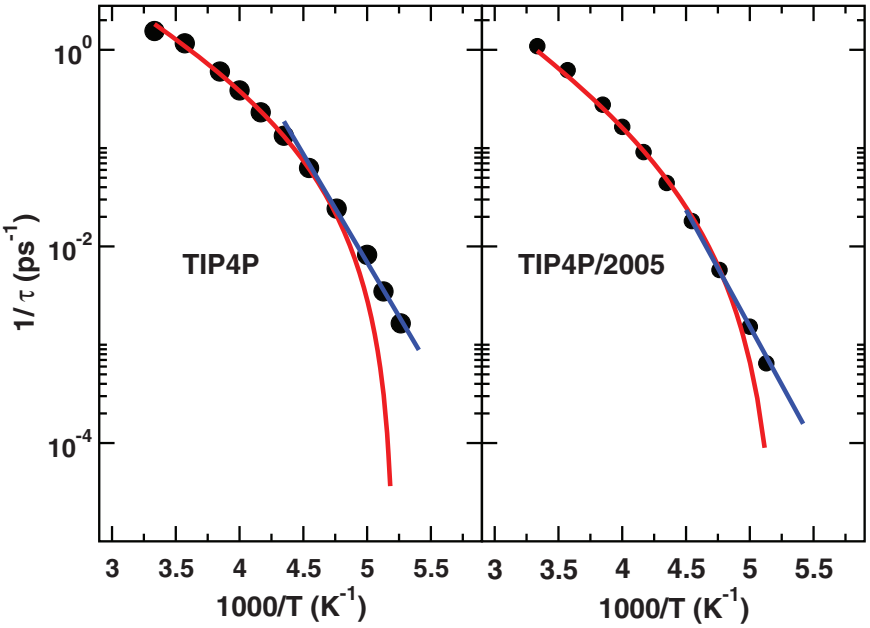

Fig. 3. – Inverse of the α relaxation time τ *versus* the inverse of the temperature for the density $\rho = 1.00\,\mathrm{g/cm^3}$. TIP4P and TIP4P/2005 are on the left and the right panel, respectively. The red curves are the fit to the fragile behaviour with the MCT power law, eq. (2), the fit gives $T_C = 191.5\,\mathrm{K}$ for TIP4P [34] and $T_C = 190.8\,\mathrm{K}$ for TIP4P/2005. The blue lines are the fit to the strong behaviour with Arrhenius formula eq. (3), the fit gives $E_A = 42.1\,\mathrm{kJ/mol}$ for TIP4P [34] and $E_A = 45.3\,\mathrm{kJ/mol}$ for TIP4P/2005.

the *fragile* MCT power law to the *strong* Arrhenius function

$$\tau = \tau_0 e^{E_A/k_B T}, \tag{3}$$

where E_A is the activation energy for the hopping.

This transition from the hopping free dynamics to the hopping dominated diffusion can be characterized in terms of a fragile-to-strong crossover (FSC).

We repeated the analysis we have shown for the density $\rho = 1.00\,\mathrm{g/cm^3}$ for the other two densities $\rho = 0.95\,\mathrm{g/cm^3}$ and $\rho = 0.98\,\mathrm{g/cm^3}$ and we found a FSC at the temperatures reported in fig. 4.

As said above, in TIP4P/2005 water a LLCP was found in recent computer simulation of the phase diagram upon supercooling [12]. The LLCP is located at $T = 193\,\mathrm{K}$, $P = 135\,\mathrm{MPa}$, $\rho = 1.012\,\mathrm{g/cm^3}$ to be compared with the corresponding LLCP in TIP4P at $T = 190\,\mathrm{K}$, $P = 150\,\mathrm{MPa}$, $\rho = 1.06\,\mathrm{g/cm^3}$. Both the LLCP are shown in fig. 1. In spite of the differences in the phase diagram of the two models, the liquid-liquid coexistence region of TIP4P/2005 appears to be very close to that of TIP4P model. The Widom line in TIP4P/2005 was obtained from the maxima of the isothermal compressibility in the original paper [12], we calculated from our MD the specific heat at constant volume and we derived the Widom line from the maxima of c_V. This is the same procedure we adopted for TIP4P. The Widom line is reported in fig. 4 and it is in close agreement with the Widom line of ref. [12].

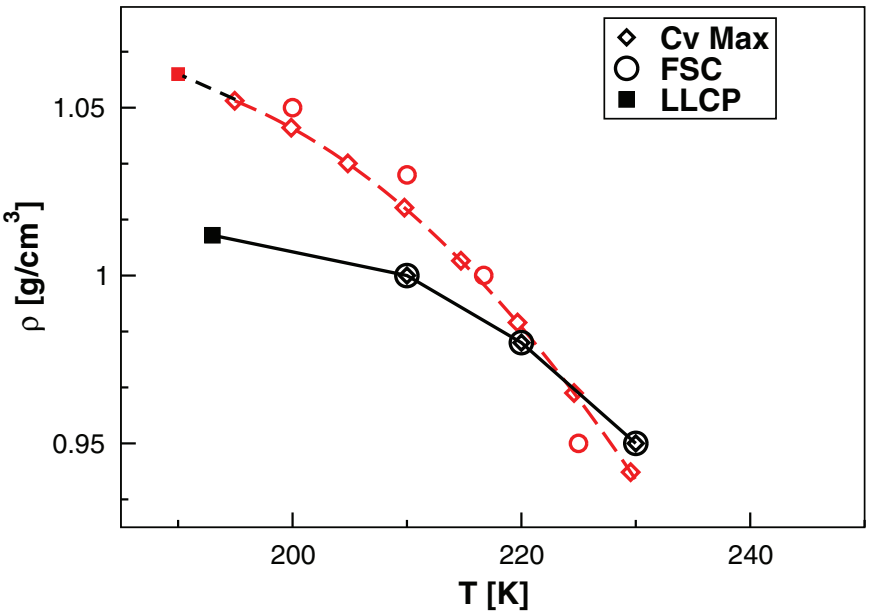

Fig. 4. – In the ρ *vs.* T plane for TIP4P/2005 (black symbols and line) and TIP4P (red symbols and line) the FSC points (circles), the points of the Widom line (diamonds) and the LLCP (full square) are reported. In the case of TIP4P the broken line is the fit to the diamond points, in the case of TIP4P/2005 the line connecting the diamonds is only a guide for the eyes.

5. – Conclusions

We considered the dynamical properties of TIP4P/2005 supercooled water. We have found strict analogies with the results already known for TIP4P water in spite of the differences between the phase diagrams of the two models. As TIP4P, also the structural relaxation of TIP4P/2005 can be described in terms of MCT in the region of mild supercooling. A fragile-to-strong crossover is found in the deep supercooled region. This crossover is related to the presence of the Widom line and to the LLCP and this shows a strict connection between dynamical and thermodynamic properties [43]. More detailed studies of the relation of the fragile-to-strong transition with the hopping phenomena will be the subject of a future paper [44].

* * *

PG wishes to acknowledge the longstanding and fruitful collaboration with Prof. Sow-Hsin Chen in the occasion of his 80th birthday. His ideas and findings are a continuous source of inspiration for research.

REFERENCES

[1] Poole P. H., Sciortino F., Essmann U. and Stanley H. E., *Nature*, **360** (1992) 324.
[2] Holten V., Bertrand C. E., Anisimov M. A. and Sengers J. V., *J. Chem. Phys.*, **136** (2012) 094507.
[3] Mishima O., Calvert L. D. and Whalley E., *Nature*, **314** (1985) 76.
[4] Winkel K., Elsaesser M. S., Mayer E. and Loerting T., *J. Chem. Phys.*, **128** (2008) 044510.
[5] Kim C. U., Barstow B., Tate M. V. and Gruner S. M., *Proc. Natl. Acad. Sci. U.S.A.*, **106** (2009) 4596.
[6] Winkel K., Mayer E. and Loerting T., *J. Phys. Chem. B*, **115** (2011) 14141.
[7] Harrington Stephen, Poole Peter H., Sciortino Francesco and Stanley H. Eugene, *J. Chem. Phys.*, **107** (1997) 7443.
[8] Yamada M., Mossa S., Stanley H. and Sciortino F., *Phys. Rev. Lett.*, **88** (2002) 195701.
[9] Poole P. H., Saika-Voivod I. and Sciortino F., *J. Phys.: Condens. Matter*, **17** (2005) L431.
[10] Paschek D., *Phys. Rev. Lett.*, **94** (2005) 217802.
[11] Corradini D., Rovere M. and Gallo P., *J. Chem. Phys.*, **132** (2010) 134508.
[12] Abascal J. L. F. and Vega C., *J. Chem. Phys.*, **133** (2010) 234502.
[13] Palmer J. C., Martelli F., Liu Y., Car R., Panagiotopoulos A. Z. and Debenedetti P. G., *Nature*, **510** (2014) 385.
[14] Smallenburg F., Poole P. H. and Sciortino F., *Mol. Phys.*, **113** (2015) 2791.
[15] Smallenburg F., Filion L. and Sciortino F., *Nat. Phys.*, **10** (2014) 653.
[16] Poole P. H., Bowles R. K., Saika-Voivod I. and Sciortino F., *J. Chem. Phys.*, **138** (2013) 034505.
[17] Palmer J. C., Car R. and Debenedetti P. G., *Faraday Discuss.*, **167** (2013) 77.
[18] Gallo P. and Sciortino F., *Phys. Rev. Lett.*, **109** (2012) 177801.
[19] Kesselring T. A., Franzese G., Buldyrev S. V., Herrmann H. J. and Stanley H. E., *Sci. Rep.*, **2** (2012) 474.
[20] Liu Yang, Palmer Jeremy C., Panagiotopoulos Athanassios Z. and Debenedetti Pablo G., *J. Chem. Phys.*, **137** (2012) 214505.
[21] Sciortino F., Saika-Voivod I. and Poole P. H., *Phys. Chem. Chem. Phys.*, **13** (2011) 19759.

[22] Poole P. H., Becker S. R., Sciortino F. and Starr F. W., *J. Phys. Chem. B*, **115** (2011) 14176.
[23] Liu Y., Panagiotopoulos A. Z. and Debenedetti P. G., *J. Chem. Phys.*, **131** (2009) 104508.
[24] Buhariwalla C. R. C., Bowles R. K., Saika-Voivod I., Sciortino F. and Poole P. H., *Eur. Phys. J. E*, **38** (2015) 39.
[25] Stanley H. Eugene, *MRS bulletin*, **24** (1999) 22.
[26] Xu L., Kumar P., Buldyrev S. V., Chen S. H., Poole P. H., Sciortino F. and Stanley H. E., *Proc. Natl. Acad. Sci. U.S.A.*, **102** (2005) 16558.
[27] Franzese G. and Stanley H. E., *J. Phys.: Condens. Matter*, **19** (2007) 205126.
[28] Gallo P., Sciortino F., Tartaglia P. and Chen S.-H., *Phys. Rev. Lett.*, **76** (1996) 2730.
[29] Sciortino F., Gallo P., Tartaglia P. and Chen S.-H., *Phys. Rev. E*, **54** (1996) 6331.
[30] Götze W., *Complex Dynamics of Glass-Forming Liquids: A Mode-Coupling Theory* (Oxford University Press, Oxford) 2009.
[31] Torre Renato, Bartolini Paolo and Righini Roberto, *Nature*, **428** (2004) 296.
[32] Sokolov A. P., Hurst J. and Quitmann D., *Phys. Rev. B*, **51** (1995) 12865.
[33] Starr F. W., Sciortino F. and Stanley H. E., *Phys. Rev. E*, **60** (1999) 6757.
[34] Gallo P. and Rovere M., *J. Chem. Phys.*, **137** (2012) 164503.
[35] Gallo P., Corradini D. and Rovere M., *J. Chem. Phys.*, **139** (2013) 204503.
[36] Corradini D., Gallo P., Buldyrev S. V. and Stanley H. E., *Phys. Rev. E*, **85** (2012) 051503.
[37] Faraone A., Liu L., Mou C.-Y., Yen C.-W. and Chen S.-H., *J. Chem. Phys.*, **121** (2004) 10843.
[38] Liu L., Chen S.-H., Faraone A., Yen C.-W. and Mou C.-Y., *Phys. Rev. Lett.*, **95** (2005) 117802.
[39] Gallo P., Rovere M. and Chen S.-H., *J. Phys. Chem. Lett.*, **1** (2010) 729.
[40] Gallo P., Rovere M. and Chen S.-H., *J. Phys.: Condens. Matter*, **24** (2012) 064109.
[41] Gallo P., Rovere M. and Chen S.-H., *J. Phys.: Condens. Matter*, **22** (2010) 284102.
[42] Abascal J. L. F. and Vega C., *J. Chem. Phys.*, **123** (2005) 234505.
[43] De Marzio M., Camisasca G., Rovere M. and Gallo P., *J. Chem. Phys.*, **144** (2016) 74503.
[44] De Marzio M., Camisasca G., Rovere M. and Gallo P., submitted (2016).