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Slow dynamics in supercooled water

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Abstract

This article reviews some recent results on the dynamics of water in deeply supercooled states, extracted from the analysis of a series of long molecular dynamics simulations. It shows that mode-coupling theory (MCT) offers a reference framework for the understanding of the dynamics in simulated supercooled water above a dynamical critical temperature. Interestingly enough, the temperature region where supercooled water exists coincides with the region where the ideal MCT holds. Finally, it briefly discusses the implication of such findings on the interpretation of the thermodynamic behavior of supercooled water. © 2000 Published by Elsevier Science B.V. All rights reserved.

1. Introduction

One of the most intriguing phenomena in condensed matter is the slowing down of the dynamics in liquids for which the formation of a crystalline phase can be bypassed. The slowing down manifests itself in the decrease of the molecular mobility by more than 15 orders of magnitude over a limited temperature range. The T dependence of the viscosity shows a similar increase. On lowering the temperature, the characteristic relaxation times of the liquid become comparable to the experimental observation time and the liquid behaves as a disordered solid, i.e. a glass. In the same temperature interval, the entropy of the liquid decreases significantly and it appears to approach the entropy of the crystalline phase [1].

Recent novel theoretical and numerical results have prompted a renewed interest in the physics of the glass formation. From a theoretical point of view, several important developments are taking place. For example, the know-how developed in the field of disordered spin systems is exported to structural glasses [2–4]. At the same time, the first principle ideal mode-coupling theory (MCT) [5,6] is generalized to the case of molecular liquids [7–11]. From a computational point of view, numerical simulations for liquids of different complexities, encompassing hard spheres, soft spheres, Lennard-Jones [12,13] as well as molecular liquids [14–17] are enlarging the available time window from the ps to the hundreds of ns time scale. It becomes possible to follow the change in the structure and in the dynamics of the system (in equilibrium) over a T range where the diffusivity changes more than five order of magnitudes. The availability of trajectories in phase space for times up to 100 ns offers an outstanding possibility for studying the origin of the slowing down of the dynamics and calls for a careful comparison between theories and exact numerical results. Numerical analysis of simulated liquid configurations are also starting to provide a detailed picture of the structure of the potential

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energy surface landscape probed in supercooled states [18–23].

In this article, we review one of the cases where this project of analysis and comparison has been started and it is currently under development [11,16,17,24–27]. We have chosen to study the widely used SPC/E model for water [28], which has been selected for its simplicity. Indeed SPC/E models a water molecule as a rigid three-site system, with an electrostatic charge on each site plus a Lennard-Jones term. Understanding the dynamics of supercooled SPC/E may also have a deep impact on the long-standing scientific debate on the thermodynamic behavior of liquid water [29–31] and on the origin of the anomalous increases of thermodynamic quantities and apparent divergences of dynamic quantities on approaching a singular but experimentally unreachable temperature of about 227 K at ambient pressure. Recent detailed review of such debate can be found in Refs. [31,32].

2. Dynamics of supercooled water

The T-dependence of the diffusion coefficient in supercooled water shows, rather clearly, a strongly non-Arrhenius behavior. Still, the relation $D\eta \sim T$ is rather well fulfilled [33]. NMR rotational relaxation times, τ_{NMR}, have also been measured with great care [34] and it has been shown that the T dependence of τ_{NMR} is well represented by power laws in $T - T_c(P)$, even if a Vogel–Fulcher law is not inconsistent. Recently, diffusivity measurements in extremely deep supercooled states have been performed [35,36], but results need to be validated with different techniques.

In supercooled bulk water, the viscosity increases about two decades on cooling before homogeneous nucleation drives the transformation to ice. Thus, compared to standard glass-forming liquids, in bulk water only the early supercooled region can be studied experimentally. Interestingly enough, this is exactly the region where the predictions of the MCT for the long time dynamics are supposed to hold. Since MCT predicts both the T independence of $D\eta/T$ and the power-law behavior of characteristic times, it is worth scrutinizing if MCT is indeed able to describe the dynamics of water, as it was suggested in Ref. [37].

3. Mode-coupling theory for supercooled liquids

The reader interested in the theoretical frame on which MCT is based and on the detailed derivation of the MCT predictions for the dynamics of supercooled liquids should see Ref. [38] or some of the more recent reviews [5,6]. For our purposes, it is relevant to note that MCT was first in identifying the existence of a novel (cross-over) temperature T_x, different from the melting and the calorimetric temperatures, which separates two different dynamical regions. Above T_x, the slowing down of the dynamics can be associated to a non-linear coupling between density fluctuations. This non-linear coupling models in a formal way the caging effect, i.e. the confinement of molecules due to the interactions with neighboring molecules. Recent work has provided convincing evidence that the two different dynamical regions are related to differences in the local properties of the sampled potential energy surface [23,39]. Above T_x, all points in configuration space sampled by the equilibrium liquid are characterized by several directions leading to different local minima (the so-called basins, in the inherent structure formalism [40,41]). At T_x, the system populates points in configuration space whose number of directions leading to different minima goes to zero. Below T_x, only rarely the system populates points in configuration space which are connecting different basins. On cooling, the system spends a larger and larger fraction of time inside the same basin of the potential energy surface. In this situation, activated processes become essential to dynamics. Thus, the MCT critical temperature signals the change from free exploration of configuration space to activated exploration. This change in the configuration space properties manifests itself-in a change of the molecular dynamics.

The ideal MCT [5,6,38] for supercooled liquids has been subjected to extensive tests in the latest years, both from experimental [42–46] and numerical work [12–15,47]. As a result, there is now growing consensus in the scientific community that the theory can successfully describe the slow dynamics of liquids in the early supercooling region, i.e. above the temperature T_x.

The theory was originally developed to describe the slow dynamics in simple liquids, i.e. liquids made by atoms or by molecules interacting through a spherically symmetric potential. Experimental [37,42–44,46,48] and numerical [14–17,24,49,50] results have shown that also molecular liquids behave, at least qualitatively, as predicted by the theory. An extension of the MCT equations to molecules of arbitrary shape has been recently developed [7,8] and predictions for the long time dynamics of the center of mass (COM) and angular correlators are now available for bulk samples [7–9,11] and for a single solute molecule in a simple solvent liquid [10]. The successful comparison between theoretical predictions and numerical data for a liquid of Lennard-Jones dumbbells and for the SPC/E case, we discuss here, strongly encourages further investigations in this direction.

One key element of MCT is that the static structure of the liquid (as revealed by the partial structure factors) in supercooled states controls the dynamic of the system. Dynamics is slaved to static. According to MCT, the slow dynamics of liquids with the same structure and the same number density is the same. Theories emphasizing the role of configurational entropy in controlling the dynamics in supercooled states [51,52] share such a prediction with MCT.

4. Supercooled SPC/E water – test of MCT

The data reviewed in this section refer to a series of 100 ns simulations, at several temperatures, down to $T = 207$ K. The SPC/E potential is characterized by a density maximum around $T = 250$ K at ambient pressure [53]. Thus, the lowest simulated temperature is about 40°C below the temperature of maximum density (TMD). In bulk water, experiments can be performed down to 35°C below the TMD.

Examples of (self) rotational and translational correlation functions for SPC/E water at different temperatures are shown in Fig. 1. In analogy with supercooled atomic liquids, all correlation functions show on cooling a two-step relaxation scenario. A well-defined plateau (whose value defines the so-called non-ergodicity parameter) follows a fast relaxation process. The nature of the first relaxation has been shown to be related, in the case of SPC/E, to harmonic motion within one single configuration-space basin [54,55]. In this respect, the first relaxation is not connected to dissipation processes but to the incoherent sum of harmonic oscillations distributed according to the system's density of states [54,55]. Instead, the long time relaxation (the so-called α-relaxation), is a truly dissipative process, related to the diffusion of the system in configuration space. As predicted by MCT, the early part of the α-relaxation (i.e. the departure from the plateau value f) can be well described by a power law $f + h_1 t^b + h_2 t^{2b}$, where the wavevector q (or the order of the Legendre polynomial l) dependence of f, h_1, h_2, shown in Figs. 2 and 3, has been successfully compared to theoretical predictions [25]. We note on passing, that the l dependence observed in Fig. 3 is consistent with recent MCT predictions for the

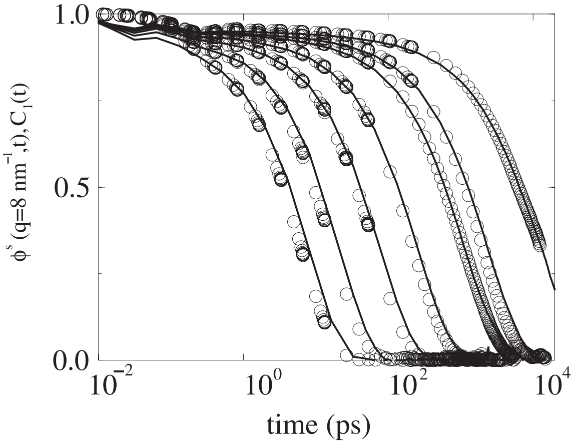

Fig. 1. Symbols: Time evolution of the angular correlators $C_1(t)$ (first Legendre polynomial) for the dipole moment as calculated from the MD data for seven different temperatures. From left to right: $T = 285$, 258, 238, 225, 213, 210 and 207 K. Lines: Time evolution of the incoherent density correlators for $q = 8\ \mathrm{nm}^{-1}$ at the same temperatures. No scaling has been applied to the data. The incoherent density correlation function is the autocorrelation function of $e^{i\mathbf{q}\cdot\mathbf{r}(t)}$, where $\mathbf{r}(t)$ is the position at time t of the tagged-molecule COM.

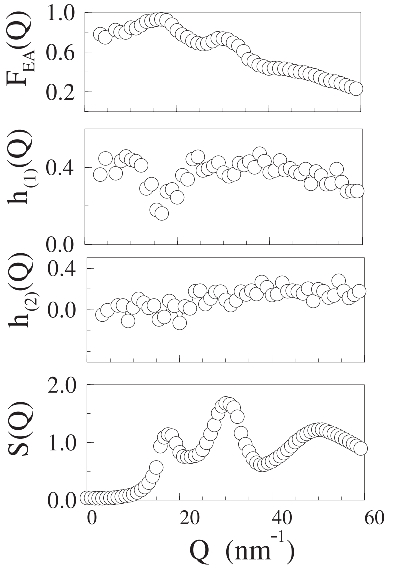

Fig. 2. q-Vector dependence of the non-ergodicity factor $f(q)$, of $h_1(q)$ and $h_2(q)$ for SPC/E water for the collective density–density correlation function. The bottom panel shows the corresponding structure factor. The collective density correlation function is the autocorrelation function of $\sum_j e^{i\mathbf{q}\cdot\mathbf{r}_j(t)}$, where $\mathbf{r}_j(t)$ is the position at time t of the j molecule COM.

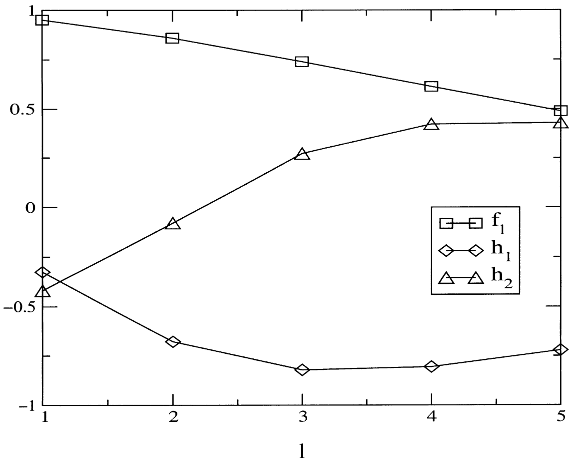

Fig. 3. l-Dependence of f, h_1 and h_2 for the SPC/E dipole $\vec{\mu}$ correlation function (Legendre polynomial of order l of $\vec{\mu}(t)\cdot\vec{\mu}$). h_1 and h_2 are in arbitrary units. Lines are guides to the eye.

self-motion of a dumbbell close to the mode coupling critical temperature [56], in the strong inderhance scenario.

Fig. 1 shows that a well-defined relation exists between angular and orientational displacements. Indeed, we observe that for all temperatures, decorrelation over distances $2\pi/q$ takes place on the same time scale as decorrelation over angles of π/l, suggesting a strong coupling between translation and rotations in the case of SPC/E water. Such a coupling has its origin in the strong directionality of the hydrogen bonding. In supercooled states, translational motions can be accomplished only when molecules rotate and hydrogen bonds are bend or broken.

Correlation functions at several temperatures can be scaled on a common master plot, as shown in Fig. 4 for the case of the collective density–density correlation function. The time dependence in the time region around the plateau is well described by the so-called β-correlator [38], whose analytic expression can be calculated within MCT. The inset shows the same correlation function as a function of t^b, with $b = 0.5$, to linearize the power-law region which follow the plateau.

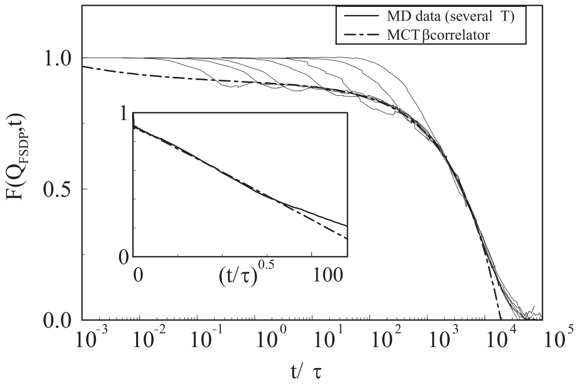

Fig. 4. Master curve for the collective density–density correlation function (intermediate scattering function) $F(Q_{\mathrm{FSDP}}, t)$. Q_{FSDP} is the $Q = 18$ nm^{-1} wave vector, corresponding to the position of the first pre-peak in the structure factor (the analogous of the so-called first sharp diffraction peak in silica). Full lines are the molecular dynamics data at $T = 207$, 210, 215, 225, 238, 258 and 285 K. Correlation functions have been shifted in time by τ. τ is defined as the time at which $F(Q_{\mathrm{FSDP}}, \tau) = 1/e$. Dashed line is the β-correlator predicted by MCT. The validity of the β-correlator is a priori limited to the region where $F(Q,t)$ is close to the plateau value. For clarity reason, we have plotted the β-correlator in a larger time range. The inset shows that the decay of the correlation functions calculated by the MD data after the plateau follows a power law with exponent 0.5.

MCT predicts also a relation between the exponent b introduced above and the exponent γ which controls the T-dependence of all characteristic times, as for example the inverse diffusivity. In the case of SPC/E, correlation times scale as $\tau \sim |T - T_x|^{-\gamma}$, where T_x is about 50 K below the temperature of maximum density at ambient pressure. By studying the slowing down of the dynamics along several different isochores, it is possible to calculate the ideal glass-transition line in the P–T plane, and compare the pressure dependence of γ and b with the MCT predictions. Such a calculation has been recently performed [56,57] and the results are shown in Fig. 5. The pressure dependence of γ in SPC/E is at odd with the pressure dependence of γ in water [59] but within the model the agreement with the MCT prediction is striking.

The agreement between the SPC/E data and MCT is very good both at qualitative and quantitative level and it has been discussed at length in Refs. [11,16,17,24,26,57,58]. In these references, it is shown in detail that, for both self and collective properties:

(1) In supercooled states, all correlators decay with a two-step process which spreads over several time decades. Correlation functions evaluated at different temperatures can be scaled on a common master curve (Fig. 4).

(2) The α-relaxation decay has an initial power-law behavior on leaving the plateau, whose range of validity is Q-dependent (see inset of Fig. 4). The exponent of the power law agrees with the predictions of MCT.

(3) The long time part of the decay can be well fitted by a stretched exponential function.

(4) The q-dependence of the parameters in the stretched exponential (i.e. amplitude, time and exponent) oscillates in phase with the static structure factor, in close analogy with the MCT predictions for simple liquids.

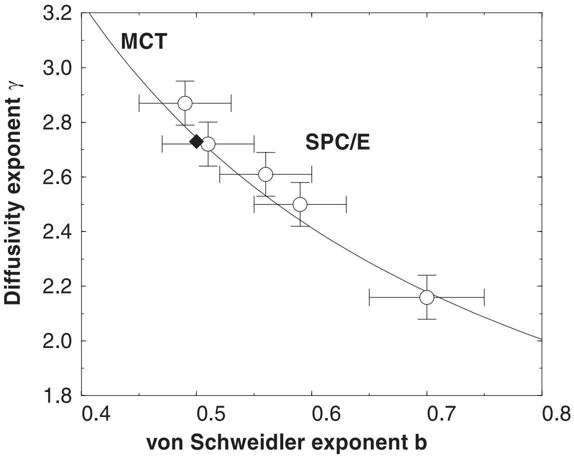

Fig. 5. The line shows the relationship between the exponents b and γ predicted by MCT. The symbols show the calculated values for the SPC/E model along different isochores. Reproduced from Refs. [57,58].

5. Test of molecular mode coupling theory

Very recently, MCT has been generalized to the case of molecular liquids. The generalization requires the introduction of angular degrees of freedom in the description of the dynamical processes. The dynamics of the liquid is now described by an infinite matrix of correlators:

$$S_{\kappa,\kappa'}(\vec{q},t) = \frac{1}{N}\langle \rho^*_\kappa(\vec{q},t)\rho_{\kappa'}(\vec{q})\rangle, \qquad (1)$$

where $\rho_\kappa(\vec{q},t)$ is the expansion of the microscopic density $\rho(\vec{r},\Omega,t) = \sum_j \delta(\vec{r} - \vec{r}_j(t))\delta(\Omega - \Omega_j(t))$ with respect to plane waves and to Wigner matrices $D^l_{mn}(\Omega)$. The index κ combines the angular indexes l, m and n while $\vec{r}_j$ and Ω_j are the COM position and the three Euler angles of molecule j.

The molecular mode-coupling theory (MMCT) provides equation of motion for the molecular correlators $S_{\kappa,\kappa'}(\vec{q},t)$, once the static angular correlators $S_{\kappa,\kappa'}(\vec{q},0)$ and the number density are provided. Of course, there are an infinite number of them and this forces a truncation of the MMCT equations to some ad hoc cut-off value in l. For the case of SPC/E, the static angular correlators have been evaluated and the MMCT equations have been recently solved, using $l = 2$ as a cut-off, both excluding [11] and including [60] the angular number n. The result of such calculations is the q-dependence of the non-ergodicity factor for all angular correlators with $l \leqslant 2$. Figs. 6 and 7 show a comparison of the non-ergodicity factor

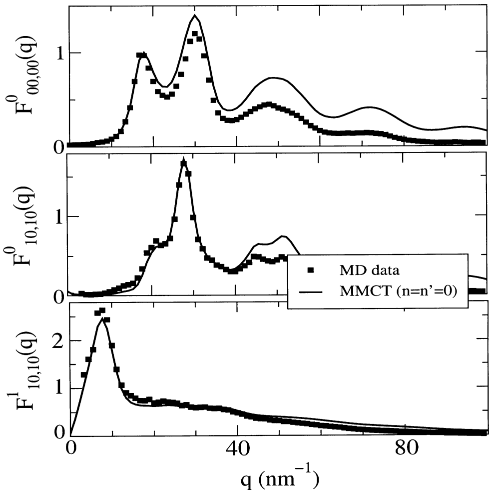

Fig. 6. Not normalized non-ergodicity parameter $F^m_{ln,l'n'}(q)$ for a few selected diagonal ($l = l'$, $m = m'$, $n = n'$) angular correlators. Symbols: MD simulation. Lines: theoretical MMCT predictions (redrawn from Ref. [11]).

evaluated from the molecular dynamics trajectories with the one calculated solving numerically the MMCT equations, in the approximation in which the angular number n can be neglected. The interested reader is referred to Ref. [11] for detailed information. Although the agreement is not of the same quality as for the simple liquid case [61,62], data in Fig. 6 support the view that MCT succeeds in describing in a quantitative way the dynamics of supercooled molecular liquids, even for network forming ones, in the early supercooled region.

6. Conclusions

Concluding this article, we like to stress that SPC/E is not, of course, a perfect modellization of water. Limitations in the ability of reproducing the behavior of water are intrinsic in the choice of a classical, non-polarizable and rigid potential. For example, it is known that this potential is not able to reproduce the liquid–ice I_h coexistence, simply because the SPC/E I_h free energy is greater than the liquid one. SPC/E crystallizes into a different structure [63]. Concerning dynamics, we call the reader attention on

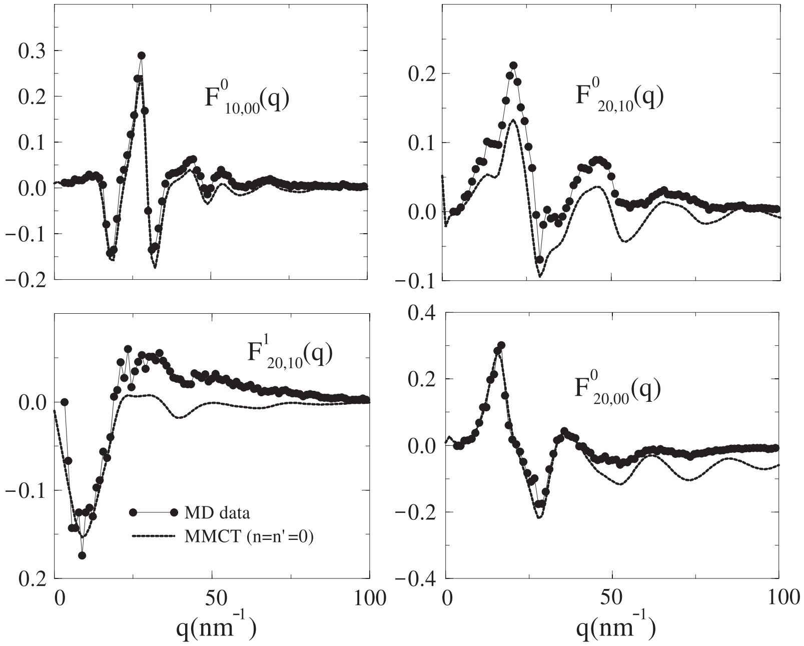

Fig. 7. Not normalized non-ergodicity parameter $F^m_{ln,l'n'}(q)$ for a few selected non-diagonal angular correlators. Symbols: MD simulation. Lines: theoretical MMCT predictions (redrawn from Ref. [11]).

the fact that the pressure dependence of $\gamma(P)$ is at odd with experiments. Unfortunately, a detailed study of the slow dynamics of water is not possible with the more accurate polarizable or quantum models.

This notwithstanding, we note that the analysis reviewed in this article [11,16,17,24,26,27] represent an important step towards the understanding of slow structural relaxation in complex glass forming liquids, independently from the ability of SPC/E of mimicking real water. From the theoretical point of view, SPC/E is a non-trivial molecular system, composed by molecules interacting via a strong anisotropic pair-wise additive interaction potential. Structural arrest in this system is not driven by packing constraints but by the formation of a strong network of tetrahedrally coordinated water molecules. The molecules are hindered in their translational and rotational motion by the presence of strong hydrogen bonds (energetic cages). The fact that MCT, which was originally developed for simple liquids, succeeds well in describing the dynamics in such a complicated molecular system, strongly support the existence of an universality in the self and collective behavior of liquids under supercooling.

The analysis of SPC/E water is also important with respect to the thermodynamic behavior of simulated water [31,32,64–68]. In this context, if SPC/E could be considered a sufficiently satisfactory modellization of real water, the data presented in this article would suggest that the so-called Angell temperature [30,69,70] is the critical temperature of MCT [16,17]. In this regard, the apparent power-law increase of transport coefficient in liquid water on supercooling is traced to the formation of cages and to the slow dynamics resulting from the presence of these long-living energetic cages. In other words, the divergence of transport coefficients does not need to rely on a thermodynamical instability, either connected to the re-entrance of the gas–liquid spinodal or to the presence of a critical point at high pressure and low temperature [66–70]. If SPC/E can represent the thermodynamic behavior of water sufficiently, we would conclude that at low pressure, there is a continuous path connecting the liquid state to the low density amorphous ice.

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