

Role of Pre-peaks in Glass-forming Liquids

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Abstract. Microstructural and dynamical properties resulting from the hydrogen bonding interactions between ibuprofen molecules in the liquid state have been investigated by means of molecular dynamics computer simulations. Individual and collective dipole autocorrelation functions were calculated. They reveal that the behavior of the long time collective dipole correlation is dominated by the individual function due to antiparallel dipoles correlations in agreement with a value of the Kirkwood correlation factor significantly smaller than unity. The exact numeration of hydrogen-bonding associating structures, their shapes cyclic or linear is a question that we have considered here. The existence of very stable small aggregates such as cyclic dimers and trimers is shown. The presence of these stable cyclic associating structures within homogeneous disordered phase are demonstrated to have a striking influence on the dynamical properties and might be at the origin of the unconventional Debye type process detected in this system. A comparison is made with the Debye-type relaxation found in microstructured monohydroxy alcohols.

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INTRODUCTION

In the framework of the glass transition phenomena, there has been recently revived interest for hydrogen-bonded (HB) liquids in order to characterize the complex mechanisms underlying the different relaxation dielectric processes and to precisely identify the dielectric contribution truly resulting from the structural relaxation^{1-4, 5, 6}.

HB liquids such as alcohols⁷ or substituted aromatics^{8, 9} to cite only a few belong to a special class of liquids: due to the strong directional hydrogen bonding, they tend to be locally more organized than ordinary van der Waals liquids. Indeed, it is well recognized from x-ray experiments that such liquids exhibit a small- Q peak of the structure factor $S(Q)$ below the first sharp diffraction peak in the domain where supra-molecular collective effects are expected¹⁰. The existence of this peak can thus be interpreted as the presence of some short range HB arrangements of nanometer scale⁷. However, it is not totally clear about which shapes these HB aggregates come in, as open chains, rings or self-micellization and in which proportions^{10, 11}. Multimers with parallel dipole orientations, competition between ring and open chains¹²⁻¹⁷ have been suggested from dielectric spectroscopy (DRS) investigations¹⁵ for a long time. Cyclic structures are also suggested from x-ray and neutron diffraction studies¹⁸ and heats of vaporization¹⁹ measurements of liquid alcohols. From Molecular dynamics (MD) simulation, a rich variety of HB

aggregates are usually seen such as open chains or rings¹⁰. However, linear HB winding chains associations seem privileged by this technique unlike to the existence of cyclic HB structures such as dimers and trimers which is clearly supported from *ab-initio* calculations^{20, 21}. The difference could be explained from the importance of the non-pairwise-additive cooperative interactions well considered in *ab-initio* calculation but not taken into account in the classical MD investigations in which the liquid interactions are approximated with empirical potential functions of pairwise-additive form.

A common feature known for decades from DRS experiments¹⁴ of some HB liquids mainly monohydroxy alcohols or amides in which the -OH or the -NH group is sterically accessible is the existence of an extremely large amplitude low frequency symmetrical peak corresponding to a simple exponential decay of the polarization according to the Debye-type relaxation. This peak (noted process I in the following) is always accompanied by a few decades smaller amplitude and a few decades higher frequency mainly non symmetrical relaxation (process II). A higher frequency relaxation is also frequently detected and often attributed to the so-called Johari-Goldstein process β_{J-G} ²² (process III). The problem of the origin of the Debye-type relaxation and the way it contributes to the liquid structural relaxation or its viscosity continues to be a matter of debate and has motivated many experiments and models but a complete understanding is still lacking. A few models