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The dynamical relaxation: a key to understand Water Anomalies. Results from bulk and confined water
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The anomalous behavior of thermodynamic response functions is an unsolved problem in the physics of water. The mechanism that causes the apparently indefinite increase in the heat capacity, the compressibility, and the coefficient of thermal expansion, inside the supercooled regime, is unknown. We explore this problem by analyzing both new and old experimental data coming out from the power spectrum $S(Q, \omega)$, on bulk and confined water at ambient pressure. On decreasing the temperature, we find that the liquid undergoes a structural transformation with the onset of an extended hydrogen bond network. Such a structure is at the basis of the marked viscoelastic behavior observed as a well defined frequency and wave vector dependence of the water sound velocity, and thus of the water response functions. All these observed properties appear consistent with the water polymorphism. We stress that, under these conditions, the thermal response functions and their corresponding fluctuations remain finite at ambient pressure. From the observation that the water density maximum dominating the system thermodynamics under ambient conditions is strongly P-dependent and disappears at a crossover pressure ($P_{cross} \approx 1.8 \text{ kbar}$) we have studied such a variable in a wide area of the T-P phase diagram. On these basis we have considered new and old data of both the isothermal compressibility $\kappa(T, P)$ and the coefficient of thermal expansion $\alpha(T, P)$. In the first case the main observation is that $\kappa(T)$ shows a minimum located at the same temperature ($T_{MC} \approx 315 \pm 5 \text{ K}$) for all the studied pressures. As in the $\kappa(T)$ case, also the behavior of α is surprising: all the $\alpha(T)$ curves measured at different P cross at T_{MC} ; specifically, the experimental data show a “singular and universal expansivity point” at $T_{MC} \approx 315 \text{ K}$ and $\alpha(T_{MC}) \approx 0.44 \cdot 10^{-3} \text{ K}^{-1}$. Moreover, on the contrary of other water singularities we stress that such temperature has a precise thermodynamical consistence lying in the relationship connecting the two studied response functions.