The 2PT approach for a molecular dipolar liquid

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Abstract

The two-phase thermodynamic model (2PT) has been developed to calculate absolute entropy, free energy and other thermodynamic magnitudes in fluids by using relatively short Molecular Dynamics simulations [1]. In the approach, velocity autocorrelation functions and vibrational densities of states are modeled as combinations of a solid-like component and a gas-like one. The solid-like part is intended to reproduce the harmonic behavior of the fluid. The gas-like component, which is responsible for diffusion, includes anharmonic dynamic processes. The method requires the fluidicity fraction that characterizes the gas-like proportion in the overall functions. A revisited 2PT version, including a redefinition of the fluidicity parameter, outperforms the classical approach when tested in Lennard-Jones systems and liquid metals [2]. We have extended this modified version of the original 2PT methodology in order to evaluate thermodynamic properties of molecular systems. The solid part has been approximated by that of a set of harmonic oscillators, whereas a subset composed of rough hard spheres [3,4] has been considered for the gas part. In this new approach, molecules are rotating hard spheres that experience elastic collisions. Different fluidicity factors for rotation and translation have been introduced in the model. The technique has been tested on a system made up of diatomic molecules with a dipole moment at a wide range of temperatures, from the liquid to the supercooled state. Additionally, instantaneous normal modes (INM) have been evaluated for the system. Translation and rotation 2PT solid components of the overall spectra have been compared to the stable wing of the corresponding INM vibrational densities of states, which are commonly associated with the purely harmonic dynamics of the system. It has been obtained that the 2PT approach reasonably reproduces INM spectra at short frequencies, overestimates the function at intermediate frequencies and slightly underestimates the high frequency part. The proposed methodology provides accurate results for total entropy, potential energy reference and heat capacity [5].

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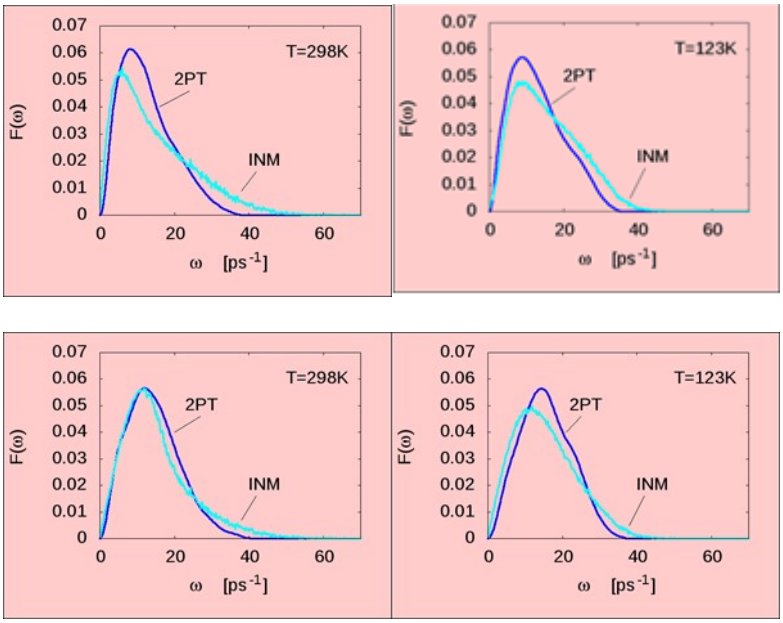

Figure 1: Solid components of vibrational densities of states evaluated within the 2PT approximation, compared with the harmonic instantaneous normal modes spectra (INM) associated with translation (up) and rotation (down) at liquid (298 K) and supercooled (123 K) states.

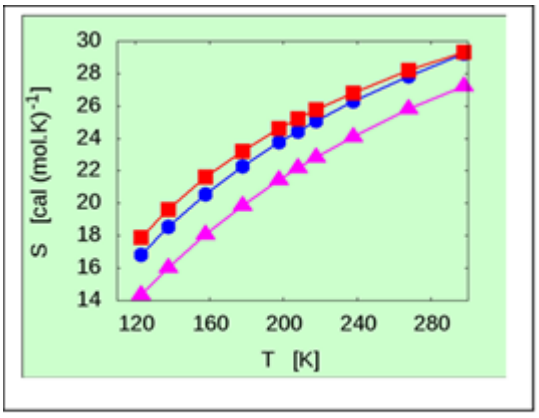

Figure 2: Entropy obtained by using the 2PT rough hard sphere approach (red squares) [5], and by considering the 2PT approach in [1] (pink triangles). Reference values are also shown (blue circles).