Inclusion of quantum nuclear effects in alkanes using PIMD techniques

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Diffusion is one of the key subjects of molecular modeling and simulation studies. However, there is an unresolved lack of consistency between Einstein-Smoluchowski (E-S) and Green-Kubo (G-K) methods for diffusion coefficient calculations in systems of complex molecules. We analyze this problem for the case of liquid n-triacontane. The non-conventional long-time tails of the velocity autocorrelation function (VACF) are found for this system. Temperature dependence of the VACF tail decay exponent is defined. The proper inclusion of the long-time tails contributions to the diffusion coefficient calculation results in the consistency between G-K and E-S methods [1, 2, 3].

Having considered the major factors influencing the precision of the diffusion rate calculations in comparison with experimental data (system size effects and force field parameters), we point to hydrogen nuclear quantum effects as, presumably, the last obstacle to fully consistent n-alkane description.

Path integral molecular dynamics methods are used to treat quantum nuclear effects in n-alkane liquid [4, 5, 6]. The comparison between classical and quantum simulation results is discussed.

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