Calculation of Thermodynamic Properties of Helium and Neon by Path Integral Monte Carlo Simulations using ab initio Potentials

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Based on Feynman's path integral formulation of quantum mechanics, nuclei can be treated quantum mechanically in a classical Monte Carlo simulation by representing particles as finite ring polymers within the classical isomorphism. We have applied the methodology of Lustig [1] to derive expressions, which enable the calculation of arbitrary thermodynamic properties of fluids using the path integral framework in the canonical and *NpT* ensembles. Path integral Monte Carlo simulations were performed for supercritical helium and neon applying highly accurate *ab initio* potentials to account for pairwise and non-additive three-body interactions for both helium [2,3] and neon [4,5]. The results for thermodynamic properties show excellent agreement with recent experimental speed-of-sound data [6] and reference equations of state, which confirms our approach. We investigate different simulation strategies including refined sampling techniques, such as the staging algorithm, and advanced methods to calculate thermodynamic properties based on virial estimators. We also performed semi-classical simulations applying the Feynman-Hibbs correction for quantum effects. These results allow us to assess the validity of this correction within the studied temperature and pressure ranges. Additional classical simulations enable the evaluation of the contribution of non-additive three-body interactions and quantum effects to different thermodynamic properties.

References

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