Thermodynamic Insights through the Prism of the Eight Statistical Ensembles

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In thermodynamics, there are eight boundary conditions that can be conceived in terms of three independent variables, and give rise to the eight natural “ensembles”. This line of thought was initiated by Josiah W. Gibbs in 1902, who outlined the isolated, closed and open material systems that correspond to the micro-canonical, canonical and grand-canonical ensembles. In general, the eight ensembles can be grouped according to the specified variables into: open vs. closed, adiabatic vs. isothermal and isobaric vs. isochoric.

With the advent of electronic computing around 1950, molecular simulation was prioritized to be one of the first application areas with the aim to evaluate the thermodynamic partition functions as introduced by Boltzmann. In the last seven decades, several of these ensembles have been identified to be beneficial for certain tasks, while others have hardly been applied at all.

The foundation for the availability of derivatives of the thermodynamic potential up to arbitrary order was laid in the seminal work of Lustig starting in 1994 for the micro-canonical ensemble. As a result, relevant thermodynamic properties for process engineering, like isochoric and isobaric heat capacity, speed of sound, isothermal compressibility or Joule-Thomson coefficient, can be determined in this ensemble. Subsequently, Lustig applied the same formalism to the canonical ensemble. It was not until recently that Ströker and Meier transferred the methodology to all remaining ensembles such that the above-mentioned properties can now be determined for any boundary condition.

On this account, a comparison of the eight statistical ensembles in the context of thermodynamic properties is made, offering a comprehensive analysis of these ensembles and shedding light on their applicability and performance for simulating thermodynamic systems. In this work, all eight ensembles, i.e. NVE, NVT, NpH, NpT, μVL, μVT, μpR and μpT, are assessed with respect to the entire set of respective thermodynamic potential function derivatives up to the second order. The according rigorous expressions arise as combinations of ensemble averages, which are evaluated on the fly during molecular simulation. Both the Monte Carlo and Molecular Dynamics simulation techniques are considered for this task. This study examines the size scaling behavior in terms of particle number, convergence and statistical quality, as well as stability of these ensembles across a wide range of homogeneous state points in the fluid region.

The results reveal that closed ensembles tend to yield higher-quality statistical data compared to open systems, since insertion and deletion inflict significant interferences. It is shown that the microcanonical ensemble consistently outperforms the other ensembles. Further, the long-standing prejudice that the generalized ensemble (μpT) is not useful for molecular simulation is eliminated and unveils that the resulting data are in fact statistically more accurate than in the other open ensembles.