Physical Validation of Properties of Small Grand Canonical Systems

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In thermodynamics, the main difference between small and large systems is the surface area to volume ratio. Since this ratio is much larger for small systems, the surface effects become much more significant, and the properties can no longer be directly compared to thermodynamic properties of macroscopic systems [1]. This difference becomes clear if we study the system's extensive properties. For small systems these properties are no longer proportional to volume, but higher order functions of size and shape. The Small System Method (SSM) [2], exploits the size dependency of these properties, and uses properties calculated for small systems to obtain the value of the same property for a macroscopic system. The small systems are created by placing small nonperiodic subsystems at random positions inside a larger periodic reservoir. SSM is therefore based on the assumption that these small systems are grand canonical. A method recently developed by Shirts [3] can be used to check whether this assumption is in fact valid. It uses paired simulations to investigate to what extent our measured probability distribution is satisfying the Boltzmann distribution of the grand canonical ensemble. Applying this test to the small systems generated by SSM will therefore give more insight to the method and the validity of its underlying assumptions.

[1] Hill TL. Thermodynamics of Small Systems. J Chem Phys. 1962;36(12):3182–3197.

[2] Schnell SK, Vlugt TJH, Simon JM, Bedeaux D, Kjelstrup S. Thermodynamics of a small system in a μT-reservoir. Chem Phys Lett. 2011;504(4):199 – 201.T-reservoir. Chem Phys Lett. 2011;504(4):199 – 201.

[3] Shirts MR. Simple quantitative tests to validate sampling from thermodynamic ensembles. J Chem. Theory Comput. 2013 feb;9(2):909–926