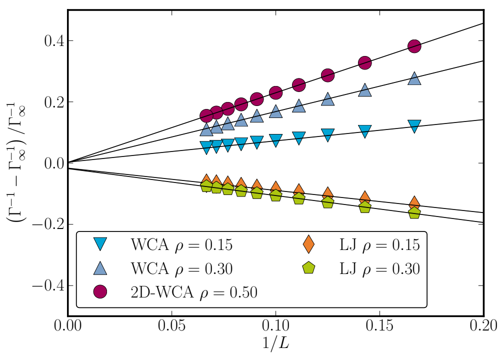
Thermodynamics of small systems in the μVT ensemble

S.K. Schnell[a)], T.J.H. Vlugt[a)], J.-M. Simon[b)], D. Bedeaux[c)] and S. Kjelstrup[a),c)]
$a)$ *Process and Energy Laboratory, Delft University of Technology, Leeghwaterstraat 44, 2628CA Delft, The Netherlands*
$b)$ *Institut Carnot de Bourgogne, UMR 5209 CNRS-Universite de Bourgogne, 21000 Dijon, France*
$c)$ *Department of Chemistry, Faculty of Natural Science and Technology, Norwegian University of Science and Technology, 7491 Trondheim, Norway*

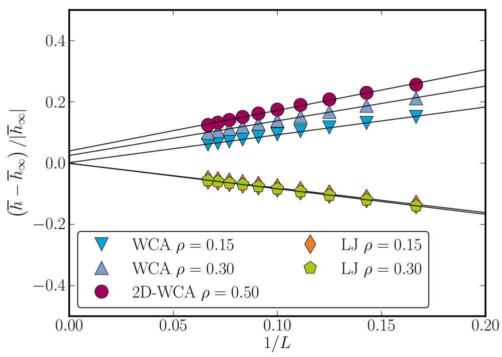
Due to advances in experimental techniques, processes and phenomena occurring at the nanoscale is now more available then ever. In fact, we can distinguish ensembles of particles on individual basis by taking images of them. Colloids, surfaces, and other systems on the nano-scale are getting more and more attention from the research community. However, thermodynamics on the small scale is different from thermodynamics in a macroscopic system, but the limit for when a system is small is often not well defined. Terrell L. Hill[1] proposed to use a correction for the size of the small system, thereby developing a tool that can make it possible to describe small systems using a correction to the more familiar thermodynamic equations.

Based on the guidelines proposed by Hill[1], we have developed a simple non-real model for a small system in the μVT ensemble, taking into account only the surface interaction of a small system. This model has been used to derive the finite size dependence of thermodynamic variables in μVT ensemble.

The size dependence of a system in the grand-canonical ensemble is found to be proportional to the inverse length of the system, $1/L$ for all thermodynamic properties. We use molecular simulations in the grand-canonical ensemble to calculate the thermodynamic correction factor, Γ, and the enthalpy, $\overline{h}$, for a range of small systems in the grand-canonical ensemble. Our numerical results unambiguously show that in order to obtain the correct macroscopic thermodynamics properties finite-size scaling should be used.



(a)



(b)

Figure 1: The relative difference between the macroscopic system and a range of small systems. (a) is the difference for the thermodynamic correction factor, while (b) is for the enthalpy.

[1] Terrell L. Hill, *Thermodynamics of Small Systems, Part 1.*, Benjamin, New York (1963)