

Thermodynamics for single - molecule stretching experiments: a molecular dynamics study

Eivind Bering

PoreLab, NTNU

Over 50 years after Hill's theory for small system thermodynamics was introduced it is still debated whether a non-equilibrium thermodynamic description applies for single molecular systems. According to Hill, the thermodynamic functions cease to be extensive at small length scales [1]. They obtain additional terms, from surface or line energy contributions. Strøm et al. have previously documented a scaling law between the thermodynamic and the molecular limit [2]. This indicates that the thermodynamic laws will indeed apply to the molecular level, provided that we use the additional terms arising from the system smallness. This is a direct contradiction of e.g. Keller, Swigon and Bustamante's claims from 2003 that there is no valid Gibbs-Duhem relationship applicable for single molecular systems [3]. It is well known and documented that the choice of ensemble will affect the thermodynamic potentials for small systems [4], however there appears to be a profound lack of literature investigating the scaling of the ensemble deviation with system size. By utilizing non-equilibrium molecular dynamics simulations to perform force controlled and length controlled virtual stretching experiments of chains of polyethylene oxide we aim to verify the rate laws presented by Rubi et al.

[1] T. L. Hill, *Thermodynamics of Small Systems*, W.A. Benjamin Inc, New York, 1963.

[2] B. A. Strøm, J.-M. Simon, S. K. Schnell, S. Kjelstrup, J. He & D. Bedeaux. *J. Phys. Chem.* 19 (2017).

[3] J. M. Rubi, D. Bedeaux & S. Kjelstrup, *J. Phys. Chem.* 110 (2006).

[4] C. Süzen, M. and Sega, M. and Holm. *Phys. Rev. E*, 79(5):051118, (2009).