Entropy Production Beyond the Thermodynamic Limit: Single-Molecule Stretching Simulations

Eivind Bering[S]
PoreLab, Department of Physics, Norwegian University of Science and Technology, Trondheim, Norway

Signe Kjelstrup [C] and Dick Bedeaux
PoreLab, Department of Chemistry, Norwegian University of Technology and Science, Trondheim, Norway
signe.kjelstrup@ntnu.no

J. Miguel Rubi
Department of Condensed Matter Physics, University of Barcelona, Barcelona, Spain

Astrid de Wijn
Department of Mechanical and Industrial Engineering, Norwegian University of Science and Technology, Trondheim, Norway

Single-molecular systems can serve as a test bed to answer questions on to what extent thermodynamics applies when the size of a system is drastically reduced. Isometric and isotensional single-molecule stretching experiments and their theoretical interpretations have shown a lack of a thermodynamic limit at those scales and nonequivalence between their corresponding statistical ensembles. This disparity between thermodynamic results obtained in both experimental protocols can also be observed in entropy production, as previous theoretical results have shown. In this work, we present results from molecular dynamics simulations from stretching of a typical polymer, polyethylene-oxide. We present a framework for analysis and obtain from molecular simulations the friction coefficients and entropy production that can be associated with stretching. In the smallest system with 12 monomers, the friction coefficients differ by factor of 2. For the bigger systems, the difference decreases with size predicted. In this way, we provide new numerical evidence that a thermodynamic description is meaningful for the case of single-molecule stretching.

References

[1] Bering et al. *J. Phys. Chem. B*, 2020, 124, 40, 8909–8917