

## MESOSCOPIC NON-EQUILIBRIUM THERMODYNAMICS

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### EXTENDED ABSTRACT

Classical thermodynamics is a theory for a collection of molecules in equilibrium. What happens if the number of molecules in the system becomes smaller and smaller, and the system boundaries reflect conditions further and further away from equilibrium? Can we still use thermodynamics? In our work we have found that the answer is yes. The field of non-equilibrium thermodynamics can be extended to mesoscopic systems and describe in a systematic manner even molecular behavior far from equilibrium conditions. Using the concept of internal variables along the reaction coordinate we derive the law of mass action. This shows that the mesoscopic analysis gives a natural explanation of the fact that the reaction rate is a nonlinear function of the Gibbs energy of the reaction. The theory can be applied to RNA stretching experiments. This application shows why stretching RNA leads to different results when one uses a constant force to stretch or when one stretches to a constant length. This relates to the fact that for small systems the results differ for different ensembles. Important work was done on this issue by Hill who wrote a book in the sixties of the last century on equilibrium thermodynamics of small systems. Furthermore the mesoscopic analysis can be applied to active transport by the Ca-ATPase. We were able to explain how temperature differences feature in this phenomenon. This understanding is relevant for instance to understand thermogenesis. In conclusion we find that mesoscopic non-equilibrium thermodynamic theory can be used, also on a molecular level.

### REFERENCES

- [1] S. Kjelstrup, D. Bedeaux, Isabella Inzoli, Jean-Marc Simon, Criteria for validity of thermodynamic equations from non-equilibrium molecular dynamics simulations, *Energy*, 33 (2008) 1185-1196
- [2] D. Bedeaux, J. Ortiz de Zárate, I. Pagonabarraga, J.V. Sengers and S. Kjelstrup, Concentration fluctuations in non-isothermal reaction-diffusion systems. II. The nonlinear case, *J. Chem. Phys.* 135 (2011) 124516
- [3] J.M. Rubi, D. Bedeaux and S. Kjelstrup, Thermodynamics for small molecule stretching experiments, *J. Phys. Chem. B*, 110 (2006) 12733-12737
- [4] T.L. Hill, *Thermodynamics of small systems*, Benjamin Inc. 1963; Dover, 1994
- [5] D. Bedeaux and S. Kjelstrup, The measurable heat flux that accompanies active transport by Ca-ATPase, *Phys. Chem. Chem. Phys.* 48 (2008) 7304-7317
- [6] A. Lervik, D. Bedeaux, and S. Kjelstrup, Kinetic and mesoscopic non-equilibrium description of the Ca<sup>2+</sup>-pump: a comparison, *Eur. Biophys. J.* 41 (2012) 437-448.