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Report on Doctoral Thesis

„Theoretical description of unequilibrium energy transformation processes on the level of molecular structures"

by Viktor Holubec

Various experimental techniques have advanced in recent years to measure energy transformation on microscopic scales down to the level of single molecules. This leads to unprecedented insight into the functioning of molecular motors and provides new options for the design of molecular machines in nanotechnology. In general, systems studied in respective experiments are driven far from thermodynamic equilibrium and are exposed to strong thermal fluctuations because of their small size. Both these aspects have to be taken into account in proper theoretical treatments. Work and heat quantities need to be considered as stochastic variables. Their mean values correspond to the ones of conventional thermodynamics. Problems of determining free energy differences between initial and target states in controlled processes, and of determining efficiency and optimizing of molecular machines need to be treated on the basis of stochastic thermodynamics. This theory has been strongly advanced over the past ten years, and it is further developed nowadays.

In his thesis, Viktor Holubec addresses challenging problems in this active field of current research: The question of obtaining exact analytical solutions of work and heat distributions for isothermal non-equilibrium processes in suitable models with discrete and continuous microscopic state variables, the question of obtaining corresponding exact analytical solutions for cyclic processes involving two different heat reservoirs, and the question of optimizing periodic driving protocols for such cyclic processes with respect to maximal output power, efficiency, and minimal power fluctuations. Exact analytical solutions for work and heat distributions are very important on different reasons. Firstly, they serve as reference for theoretical investigations of more complicated extended models, which may be tractable by similar techniques or which may be treated by some kind of perturbative treatment around the reference model. Secondly, they allow one to get insight into the structure of the tails of work distributions, in particular to the regime of work values much smaller than the mean work. Generic findings with respect to the tail structure in this regime are useful for developing improved estimators of free energy differences based on application of the Jarzynski equality. Thirdly, the exact solutions provide valuable test cases for simulation procedures of the underlying stochastic processes and they give information on the necessary number of stochastic trajectories that need to be generated in order to obtain faithful results for simulated work and heat distributions.

After a general introduction and a good overview of relevant achievements in the field of stochastic thermodynamics in chapter 1, Holubec first considers models with discrete state variables in chapter 2. For many independent two-level systems, he shows how the work distribution can be obtained by convolutions of the respective distribution for a single two-level system. For a specific type of driving protocol, a corresponding exact solution for such two-level system has been obtained by Subrt and Chvosta. With respect to many independent two-level systems, it would have been interesting also to investigate the heat distribution and to look at its singular component. In addition to singularities in form of Dirac-delta functions, which correspond to (commonly rare) realizations of the stochastic process without transitions during the driving period, I would expect jump discontinuities to appear in that distribution, which result from (also rare) trajectories with in total just one transition during the driving period. These jump singularities should occur only if there is more than a single two-level system present. For a homogeneous system of an infinite number of levels, where the backward and forward transitions between neighboring levels are the same functions of time, Holubec furthermore derives exact solutions for the Laplace-transformed work distribution.

As additional discrete model in chapter 2 he studies an extension of a zipper model that was suggested by Kittel to describe the "melting" (folded-unfolded state) transition of DNA molecules. In this extension, time-dependent Kramers-Bell type forward (folding) and backward (refolding) transition rates between molecular states with k and $(k+1)$ open base pairs are introduced. In case of neglect of refolding transitions, Holubec succeeds to derive exact results for the joint probability of state and work for an unzipping protocol, where the state free energies are linearly decreasing with time. He discusses in detail the energetics of this extended Kittel model and critically analyzes the meaning of his findings for single-molecule experiments, where DNA molecules can be unfolded and refolded with optical or magnetic tweezers. By performing additional kinetic Monte Carlo simulations of the model under inclusion of the backward transitions, he in particular discusses the limits of the assumption of zero backward transition rates in the analytical treatment. In addition he investigates the role of inhomogeneities in the free energy landscapes as a consequence of the different types of bases appearing in the sequence of DNA molecules.

In chapter 3, Holubec studies, as an example of a system with a continuous state variable, the Brownian motion of a particle in a harmonic oscillator potential. The particle is driven by an external time-dependent force, amounting to a corresponding time-dependent shift of the minimum of the oscillator potential. Applying either Gaussian functional or Lie operator techniques, he derives exact expression for the joint probability density of particle position and work.

In chapter 4, Holubec considers heat engines operating between two thermal reservoirs. He starts by analyzing a two-level system with piecewise periodic linear driving, for which he derives exact solutions for the time-dependent occupation probabilities from the master equation. By evaluating its stationary solution and, based on this, the mean values of work and heat quantities, he characterizes the engines' performance in the limit cycle. A thorough discussion is given of its dependence on the control parameters. Moreover, utilizing the previously derived exact result for the joint probability of state and work for the (non-cyclic) "ramp driven" system, he derives the distributions of work and heat for the limit cycle. Complete information thus is given for the energetic fluctuations of this microscopic heat engine. Among others, Holubec finds that an optimization of the control parameters with respect to maximum output power goes along with comparative large fluctuations of the output power. As a second type of heat engine, he studies a Brownian particle moving in a logarithmic-harmonic potential with reflecting boundary at the origin. Again two isothermal branches are considered, connected by ("instantaneous") adiabatic branches, where the particle position is kept fixed. During the isothermal branches the strength ("stiffness") of the harmonic potential is varied in time. His results obtained for this model may be directly compared to optical tweezer experiments with colloidal particles.

In summary, Holubec has impressively shown that he is capable to successfully work on challenging scientific problems at the forefront of current research. The topical background, the problems to be addressed, the methods and the results are clearly presented and thoroughly discussed in his thesis, and the figures nicely illustrate his findings. References to previous work in the literature are appropriate and up to date.

Holubec's studies on the energetics of driven small systems and the performance of microscopic heat engines have received much attention already on various international conferences, and they gave rise to in total 4 publications in international peer-reviewed journals and a further invited one in a peer-reviewed open access journal. Within the joint collaboration of our groups in Prague and Osnabrück, I had also the pleasure to work with Viktor Holubec and I can state that he is an original thinker and hard-working scientist.

In view of the very good work and results, I strongly recommend to accept his doctoral thesis.

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