Reviews of Nonlinear Dynamics and Complexity

Edited by
R. Klages, W. Just, and C. Jarzynski

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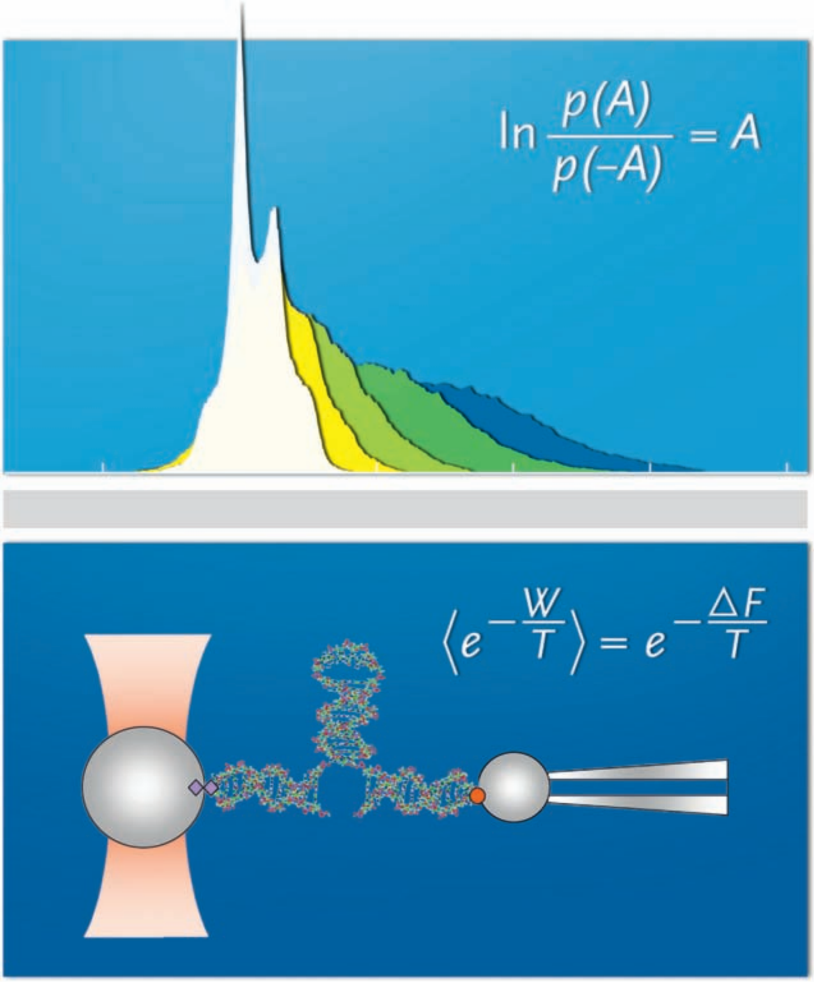
Nonequilibrium Statistical Physics of Small Systems

Fluctuation Relations and Beyond



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The Editors

Dr. Rainer Klages
Queen Mary University of London
School of Mathematical Sciences
London, UK
r.klages@qmul.ac.uk

Dr. Wolfram Just
Queen Mary University London
School of Mathematical Sciences
London, UK

Prof. Christopher Jarzynski
University of Maryland
Dept. of Chemistry & Biochemistry
Institute for Physical Science and Technology
College Park, USA

The Series Editor

Prof. Dr. Heinz Georg Schuster
Saarbrücken, Germany

Cover picture

Cover, upper picture by Prof. Dr. Sergio Ciliberto et al., Universite de Lyon, ENSL and CNRS
Distributions of the classical work of a Brownian particle trapped in a nonlinear double-well potential produced by two laser beams, and Fluctuation Theorem formula.
Cover, lower picture by Prof. Dr. Felix Ritort et al., Universitat de Barcelona
Experimental setup for the mechanical folding/unfolding of a DNA hairpin, and Jarzynski work relation.

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Contents

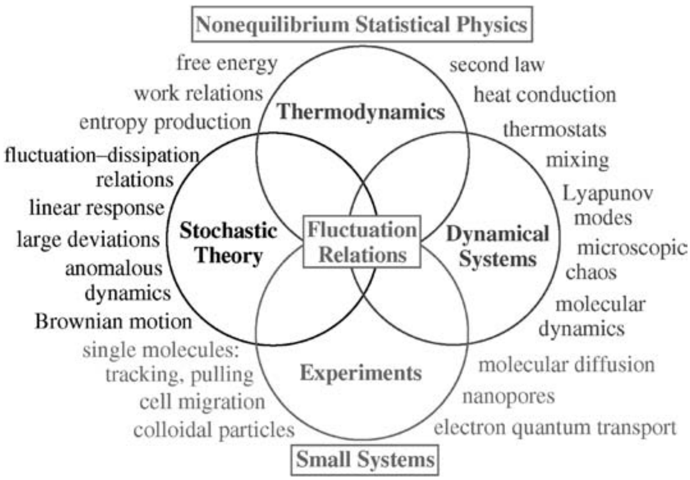
Preface

The term *small systems* denotes objects composed of a limited, small number of particles, as is typical for matter on meso- and nanoscales. The interest of the scientific community in small systems has been boosted by the recent advent of micromanipulation techniques and nanotechnologies. These provide scientific instruments capable of measuring tiny energies in physical systems under *non-equilibrium* conditions, that is, when these systems are exposed to external forces generated by gradients or fields. Prominent examples of small systems exhibiting nonequilibrium dynamics are biopolymers stretched by optical tweezers (as shown in the lower picture on the book cover), colloidal particles dragged through a fluid by optical traps, and single molecules diffusing through meso- and nanopores.

Understanding the *statistical physics* of such systems is particularly challenging, because their small size does not allow one to apply standard methods of statistical mechanics and thermodynamics, which presuppose large numbers of particles. Small systems often display an intricate interplay between microscopic nonlinear dynamical properties and macroscopic statistical behavior leading to highly non-trivial fluctuations of physical observables (cf. the upper picture on the book cover). They can thus serve as a laboratory for understanding the emergence of complexity and irreversibility, in the sense that for a system consisting of many entities the dynamics of the whole is more than the sum of its single parts.

Studying the behavior of small systems on different spatiotemporal scales becomes particularly interesting in view of nonequilibrium transport phenomena such as diffusion, heat conduction, and electronic transport. Understanding these phenomena in small systems requires novel theoretical concepts that blend ideas and techniques from nonequilibrium statistical physics, thermodynamics, stochastic theory, and dynamical systems theory. More recently, it has become clear that a central role in this field is played by *fluctuation relations*, which generalize fundamental thermodynamic relations to small systems in nonequilibrium situations.

The aim of this book is to provide an introduction for both theorists and experimentalists to small systems physics, fluctuation relations, and the associated research topics listed in the word cloud diagram shown below. The book should also be useful for graduate-level students who want to explore this new field of research. The single chapters have been written by internationally recognized experts in small systems physics and provide in-depth introductions to the directions of their research. This approach of a multi-author reference book appeared to be particularly useful in view of the vast amount of literature available on different forms of fluctuation relations. While there exist excellent reviews highlighting single facets of fluctuation relations, we feel that the field lacks a reference that brings together the most important contributions to this topic in a comprehensive manner. This book is an attempt to fill the gap. In a way, it may act itself as a complex system, in the sense that the book as a whole ideally yields a new picture on small systems physics and fluctuation relations emerging from a synergy of the individual chapters. Along these lines, our intention was to embed research on fluctuation relations into a wider context of small systems research by pointing out cross-links to other theories and experiments. We thus hope that this book may serve as a catalyst both to fuse existing theories on fluctuation relations and to open up new directions of inquiry in the rapidly growing area of small systems research.



Accordingly, the book is organized into two parts. Part I introduces both the theoretical and experimental foundations of *fluctuation relations*. It starts with a threefold opening on basic theoretical ideas. The first chapter features a pedagogical introduction to fluctuation relations based on an approach that was coined "stochastic thermodynamics." The second chapter outlines a fully deterministic theory of fluctuation relations by working it out both analytically and numerically for a particle in an optical trap. The third chapter generalizes these deterministic ideas by also establishing cross-links to the Gallavotti–Cohen fluctuation theorem, which historically was the first to be established, with mathematical rigor, for nonequilibrium steady states. After this theoretical opening, the following two chapters summarize groundbreaking experimental work on two fundamental types of fluctuation relations. Along the lines of Gallavotti and Cohen, the first subset of them is often referred to as "fluctuation theorems" generalizing the second law of thermodynamics to small systems (see the first formula on the book cover). This type of fluctuation formulas is tested experimentally in systems where particles are confined by optical traps under nonequilibrium conditions. "Work relations," on the other hand, generalize an equilibrium relation between work and free energy to nonequilibrium (see the second formula on the book cover). The result is tested in experiments where single DNA and RNA chains are unzipped by optical tweezers. The remaining three chapters of Part I elaborate on aspects of fluctuation relations that moved into the focus of small systems research more recently. The first one introduces the nonequilibrium thermodynamics of information processing by using feedback control. The second one reviews quantum mechanical generalizations of fluctuation relations applied to electron transport in mesoscopic circuits. The third one discusses generalizations of fluctuation relations for stochastic anomalous dynamics with cross-links to experiments on biological cell migration.

Part II goes *beyond fluctuation relations* by reviewing topics that, while centered around nonequilibrium fluctuations in small systems, do not elaborate in particular on fluctuation relations. It starts with a discussion of fluctuation–dissipation relations, which are intimately related to, but may not be confused with, fluctuation relations. A cross-link to the foregoing chapter is provided in terms of partially studying anomalous dynamics, a topic that becomes particularly important for heat conduction in nanostructures, as is demonstrated from both an experimental and a theoretical point of view in the subsequent chapter. Fluctuation relations bear an important relation to large deviation theory, as is outlined in the next chapter, with applications to interacting particle systems. The book concludes with a summary about Lyapunov modes, which provide important information about the phase space dynamics in deterministically chaotic interacting many-particle systems, and experiments about diffusion in meso- and nanopores by performing single-molecule spectroscopy.

We finally remark that the various points of view expressed in the single chapters may not always be in full agreement with each other. This became clear in lively discussions between different groups of authors when the book was in preparation. As editors, we do not necessarily aim to achieve a complete consensus among all authors, as differences in opinions are typical for a very active field of research such as the one presented in this book.

We are most grateful to Heinz-Georg Schuster, the editor of the series *Reviews of Nonlinear Dynamics and Complexity*, in which this book is published as a Special Issue, for his invitation to edit this book, and for his help in getting the project started. We also thank Vera Palmer and Ulrike Werner from Wiley-VCH Publishers for their kind and efficient assistance in editing this book. C.J. gratefully acknowledges financial support from the National Science Foundation (USA) under grant DMR-0906601. W.J. is grateful for support from the British EPSRC by grant EP/H04812X/1. We finally thank all book chapter authors for sharing their expertise in this multi-author monograph. Their strong efforts and enthusiasm for this project were indispensable for bringing it to success.

Summer 2012

London *Rainer Klages*
London *Wolfram Just*
College Park, MD *Christopher Jarzynski*

List of Contributors

Anna Alemany
Universitat de Barcelona
Departament de Física Fonamental
Small Biosystems Lab
Avda. Diagonal 647
08028 Barcelona
Spain

and

Instituto de Salud Carlos III
CIBER-BBN de Bioingeniería
Biomateriales y Nanomedicina
C/ Sinesio Delgado 4
28029 Madrid
Spain

L. Bellon
Université de Lyon
Ecole Normale Supérieure de Lyon
Laboratoire de Physique (CNRS
UMR 5672)
46 Allée d'Italie
69364 Lyon Cedex 07
France

Christoph Bräuchle
Ludwig-Maximilians-Universität
München
Department Chemie
Lehrstuhl für Physikalische
Chemie I
Butenandtstr. 11
81377 Munich
Germany

Aleksei V. Chechkin
National Science Center "Kharkov
Institute of Physics and Technology"
(NSC KIPT)
Institute for Theoretical Physics
Akademicheskaya Street 1
Kharkov 61108
Ukraine

Sergio Ciliberto
Université de Lyon
Ecole Normale Supérieure de Lyon
Laboratoire de Physique (CNRS
UMR 5672)
46 Allée d'Italie
69364 Lyon Cedex 07
France

Peter Dieterich
Technische Universität Dresden
Medizinische Fakultaet "Carl Gustav Carus"
Institut für Physiologie
Fetscherstrasse 74
01307 Dresden
Germany

Denis J. Evans
Australian National University
Research School of Chemistry
Building 35 Science Rd
Canberra, ACT 0200
Australia

Ian Ford
University College London
Department of Physics and Astronomy and London Centre for Nanotechnology
Gower Street
London WC1E 6BT
UK

Pierre Gaspard
Université Libre de Bruxelles
Center for Nonlinear Phenomena and Complex Systems and Department of Physics
Campus Plaine
Code Postal 231
Boulevard du Triomphe
1050 Brussels
Belgium

J.R. Gomez-Solano
Université de Lyon
Ecole Normale Supérieure de Lyon
Laboratoire de Physique (CNRS UMR 5672)
46 Allée d'Italie
69364 Lyon Cedex 07
France

G. Gradenigo
Universita degli Studi di Roma "La Sapienza"
Dipartimento di Fisica
Piazzale A. Moro 2
00185 Rome
Italy

Rosemary J. Harris
Queen Mary University of London
School of Mathematical Sciences
Mile End Road
London E1 4NS
UK

O.G. Jepps
Griffith University
School of Biomolecular and Physical Sciences
Queensland Micro- and Nanotechnology Centre
170 Kessels Road
Brisbane, Qld 4111
Australia

Rainer Klages
Queen Mary University of London
School of Mathematical Sciences
Mile End Road
London E1 4NS
UK

Baowen Li
National University of Singapore
Department of Physics and Centre for Computational Science and Engineering
Science Drive 2
Singapore 117542
Singapore

and

NUS Graduate School for Integrative Sciences and Engineering
28 Medical Drive
Singapore 117456
Singapore

Sha Liu
National University of Singapore
Department of Physics and Centre for Computational Science and Engineering
Science Drive 2
Singapore 117542
Singapore

and

NUS Graduate School for Integrative Sciences and Engineering
28 Medical Drive
Singapore 117456
Singapore

Stephan Mackowiak
Ludwig-Maximilians-Universität München
Department Chemie
Lehrstuhl für Physikalische Chemie I
Butenandtstr. 11
81377 Munich
Germany

A. Petrosyan
Université de Lyon
Ecole Normale Supérieure de Lyon
Laboratoire de Physique (CNRS UMR 5672)
46 Allée d'Italie
69364 Lyon Cedex 07
France

A. Puglisi
Universita degli Studi di Roma "La Sapienza"
Dipartimento di Fisica
Piazzale A. Moro 2
00185 Rome
Italy

Günter Radons
Chemnitz University of Technology
Institute of Mechatronics and Institute of Physics
09107 Chemnitz
Germany

James C. Reid
The University of Queensland
Australian Institute for Bioengineering and Nanotechnology
AIBN Building (75)
Corner Cooper & College Roads
Brisbane, Qld 4072
Australia

Marco Ribezzi-Crivellari
Universitat de Barcelona
Departament de Fisica Fonamental
Small Biosystems Lab
Barcelona
Spain

and

Instituto de Salud Carlos III
CIBER-BBN de Bioingenieria Biomateriales y Nanomedicina
Madrid
Spain

Felix Ritort
Universitat de Barcelona
Departament de Fisica Fonamental
Small Biosystems Lab
Barcelona
Spain

and

Instituto de Salud Carlos III
CIBER-BBN de Bioingenieria Biomateriales y Nanomedicina
Madrid
Spain

Lamberto Rondoni
Dipartimento di Scienze
Matematiche
Politecnico di Torino
Corso Duca degli Abruzzi 24
10129 Torino
INFN, Sezione di Torino
Via P. Giuria 1
10125 Torino, Italy

Takahiro Sagawa
Kyoto University
The Hakubi Center for Advanced
Research
iCeMS Complex 1 West Wing
Yoshida-Ushinomiya-cho, Sakyo-ku
Kyoto 606-8302
Japan

and

Kyoto University
Yukawa Institute of Theoretical
Physics
Kitashirakawa Oiwake-Cho, Sakyo-ku
Kyoto 606-8502
Japan

A. Sarracino
Universita degli Studi di Roma
"La Sapienza"
Dipartimento di Fisica
Piazzale A. Moro 2
00185 Rome
Italy

Debra J. Searles
The University of Queensland
Australian Institute for
Bioengineering and Nanotechnology
and School of Chemistry and
Molecular Biosciences
AIBN Building (75)
Corner Cooper & College Roads
Brisbane, Qld 4072
Australia

Richard Spinney
University College London
Department of Physics and
Astronomy and London Centre
for Nanotechnology
Gower Street
London WC1E 6BT
UK

Hugo Touchette
Queen Mary University of London
School of Mathematical Sciences
Mile End Road
London E1 4NS
UK

Masahito Ueda
The University of Tokyo
Department of Physics
7-3-1 Hongo, Bunkyo-ku
Tokyo 113-0033
Japan

D. Villamaina
Universita degli Studi di Roma
"La Sapienza"
Dipartimento di Fisica
Piazzale A. Moro 2
00185 Rome
Italy

A. Vulpiani
Universita degli Studi di Roma
"La Sapienza"
Dipartimento di Fisica
Piazzale A. Moro 2
00185 Rome
Italy

Stephen R. Williams
Australian National University
Research School of Chemistry
Building 35 Science Rd
Canberra, ACT 0200
Australia

Hong-Liu Yang
Chemnitz University of Technology
Institute of Mechatronics and
Institute of Physics
09107 Chemnitz
Germany

Gang Zhang
Peking University
Key Laboratory for the Physics and
Chemistry of Nanodevices and
Department of Electronics
Yiheyuan Road 5
Beijing 100871
China

and

National University of Singapore
Department of Physics and Centre
for Computational Science and
Engineering
Science Drive 2
Singapore 117542
Singapore

Color Plates

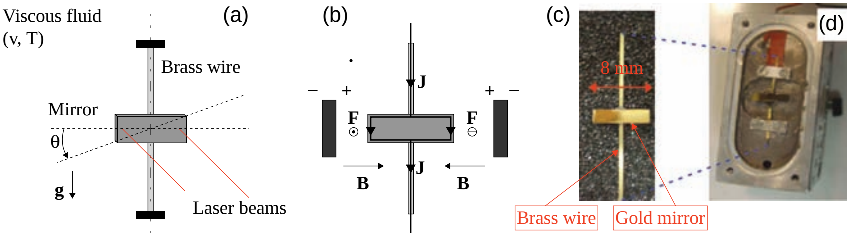


Figure 4.1 (a) The torsion pendulum. (b) The magnetostatic forcing. (c) Picture of the pendulum. (d) Cell where the pendulum is installed.

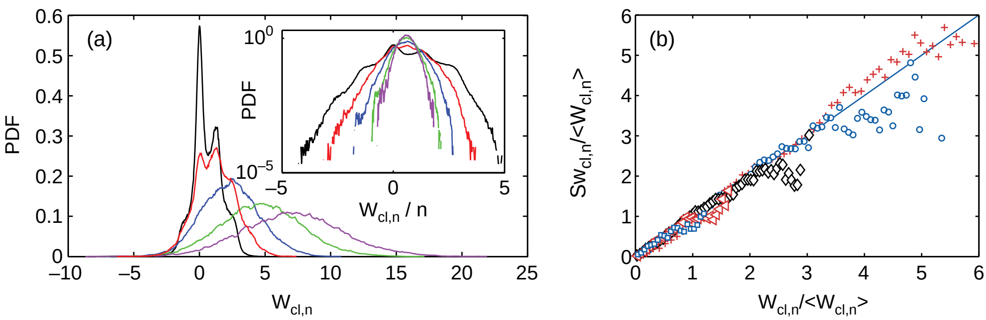


Figure 4.12 (a) Distribution of classical work W_{cl} for different numbers of period $n = 1, 2, 4, 8$, and 12 ($f = 0.25$ Hz). *Inset*: Same data in lin-log. (b) Normalized symmetry function as a function of the normalized work for $n = 1$ (+), 2 (○), 4 (◇), 8 (Δ), and 12 (□).

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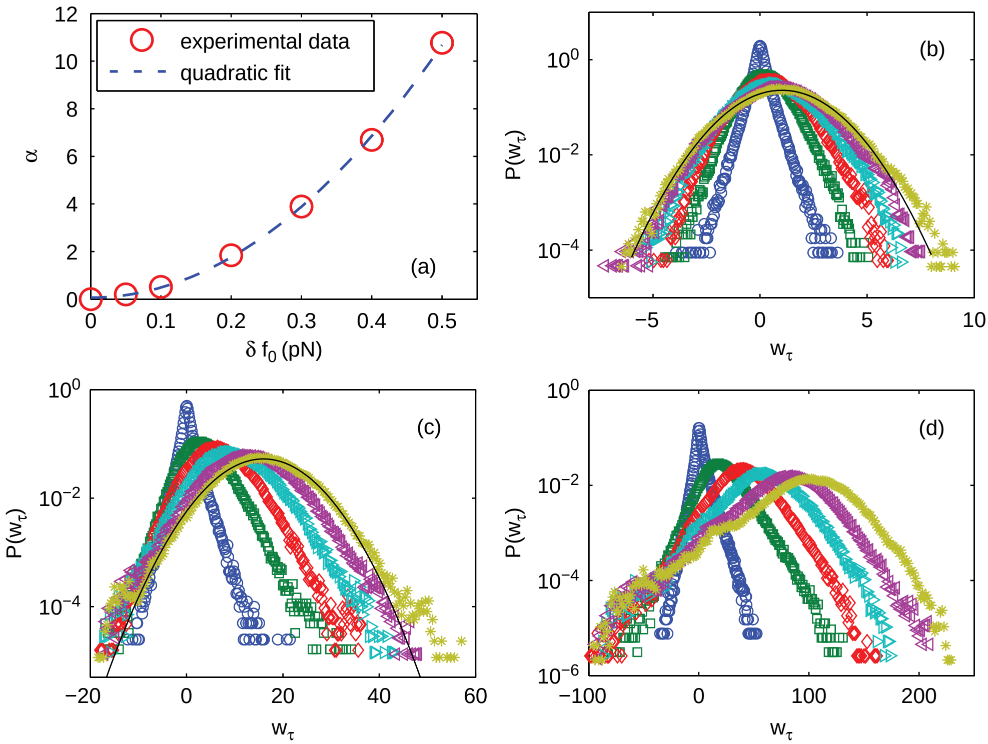

Figure 4.14 (a) Dependence of the parameter α on the standard deviation of the Gaussian exponentially correlated external force f_0 acting on the colloidal particle. Probability density functions of the work w_τ for (b) $\alpha = 0.20$, (c) $\alpha = 3.89$, and (d) $\alpha = 10.77$. The symbols correspond to integration times $\tau = 5$ ms (○), 55 ms (□), 105 ms (◇), 155 ms (◁), 205 ms (▷), and 255 ms (∗). The solid black lines in (b) and (c) are Gaussian fits.

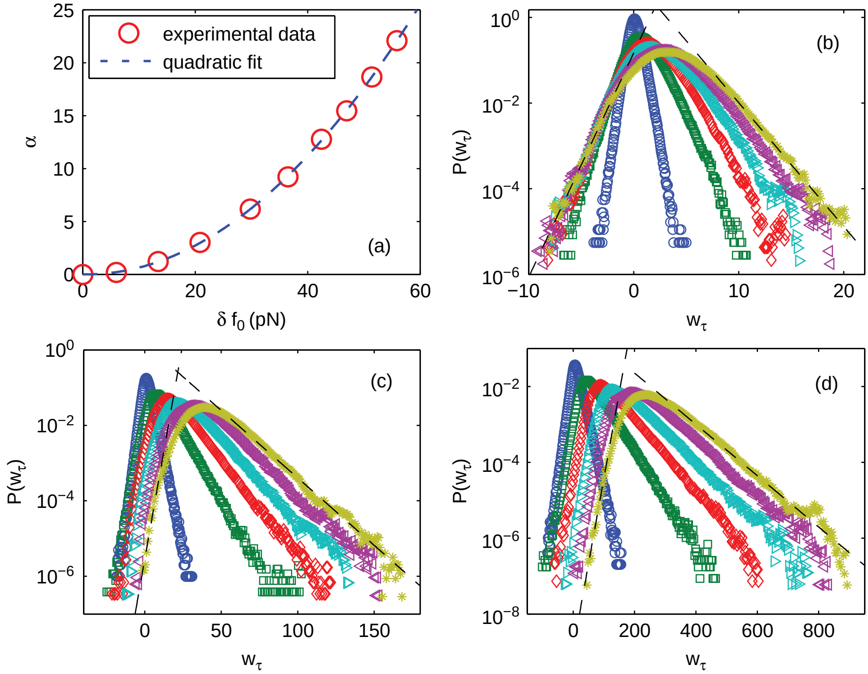

Figure 4.16 (a) Dependence of the parameter α on the standard deviation of the Gaussian white external force f_0 acting on the cantilever. Probability density functions of the work w_τ for (b) $\alpha = 0.19$, (c) $\alpha = 3.03$, and (d) $\alpha = 18.66$. The symbols correspond to integration times $\tau = 97\ \mu s$ (○), 1.074 μs (□), 2.051 ms (◇), 3.027 ms (◁), 4.004 ms (▷), and 4.981 ms (∗). The black dashed lines in (b)–(d) represent the exponential fits of the corresponding tails.

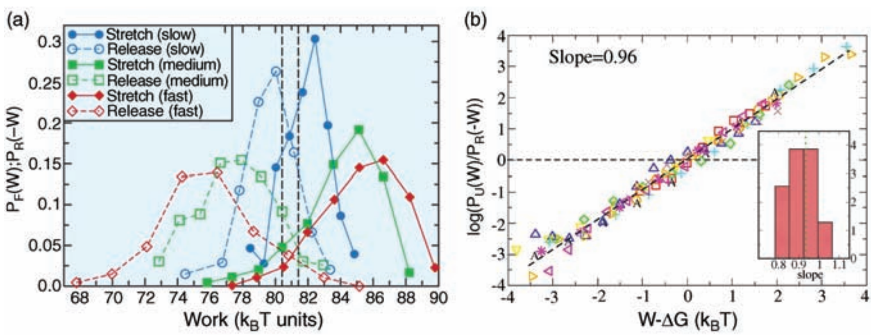

Figure 5.3 The Crooks fluctuation relation. (a) Work distributions for the hairpin shown in Figure 5.1 measured at three different pulling speeds: 50 nm s^{-1} (blue), 100 nm s^{-1} (green), and 300 nm s^{-1} (red). Unfolding or forward (continuous lines) and refolding or reverse work distributions (dashed lines) cross each other at a value of $81.0 \pm 0.2\ k_B T$ independent of the pulling speed. (b) Experimental test of the CFR for 10 different molecules pulled at different speeds. The log of the ratio between the unfolding and refolding work distributions is equal to $(W - \Delta G)$ in $k_B T$ units. The inset shows the distribution of slopes for the different molecules that are clustered around an average value of 0.96. (Figure taken from Ref. [19].)

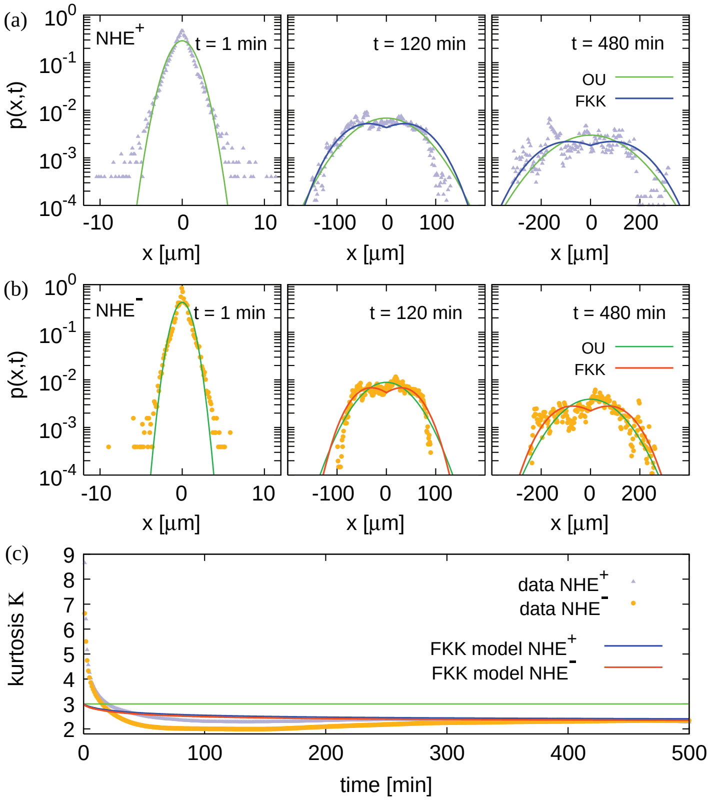

Figure 8.8 Spatiotemporal probability distributions $P(x, t)$. (a and b) Experimental data for both cell types at different times in semilogarithmic representation. The dark lines, labeled FKK, show the long-time asymptotic solutions of our model (Eq. (8.31)) with the same parameter set used for the MSD fit. The light lines, labeled OU, depict fits by the Gaussian distributions (Eq. (8.11)) representing Brownian motion. For $t = 1$ min, both $P(x, t)$ show a peaked structure clearly deviating from a Gaussian form. (c) The kurtosis $\kappa(t)$ of $P(x, t)$ (cf. Eq. (8.30)) plotted as a function of time saturates at a value different from that of Brownian motion (line at $\kappa = 3$). The other two lines represent $\kappa(t)$ obtained from the model (Eq. (8.31)) [43].

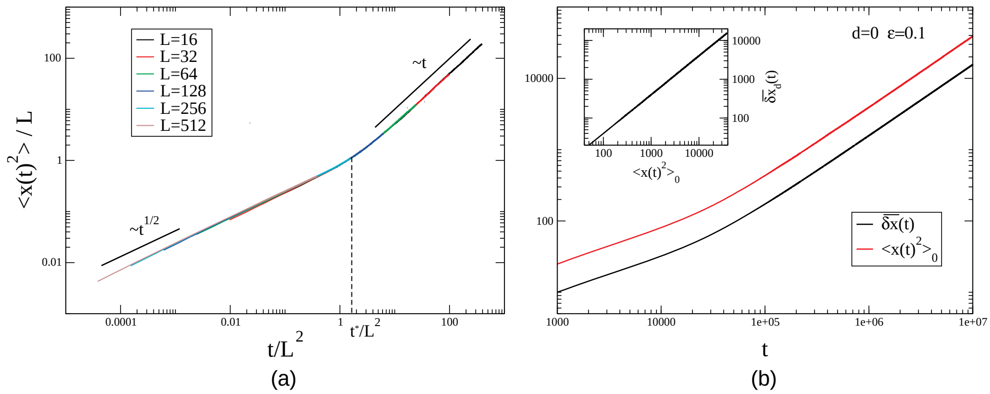

Figure 9.1 (a) $\langle x^2(t)\rangle_0/L$ versus t/L^2 plotted for several values of L in the comb model. (b) $\langle x^2(t)\rangle_0$ and the response function $\overline{\delta x}(t)$ for $L = 512$. *Inset*: The parametric plot of $\overline{\delta x}(t)$ versus $\langle x^2(t)\rangle_0$.

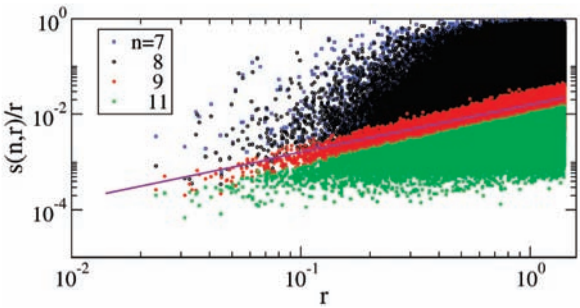

Figure 12.18 Variation of the normalized projection error $s(n, r)/r$ with the distance to the reference state r with $n = 7$, 8, 9, and 11, respectively. To improve the statistics, data from 200 reference states are presented together. A line with slope 1 is shown to guide the eyes.

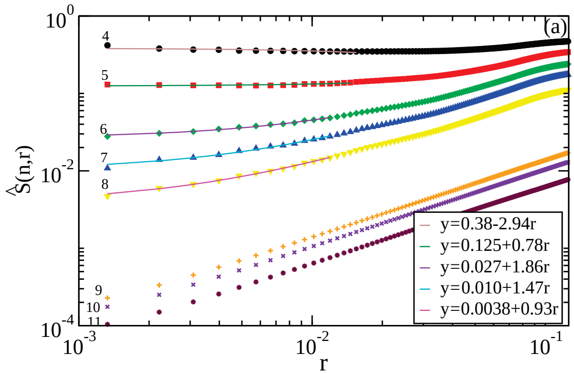

Figure 12.19 The normalized average projection error $S(n, r)/r$ versus the distance to the reference state r with n from 4 to 11. Linear fittings of data for $n < M$ confirms the saturation of $S(n, r)/r$ to a nonzero constant value.

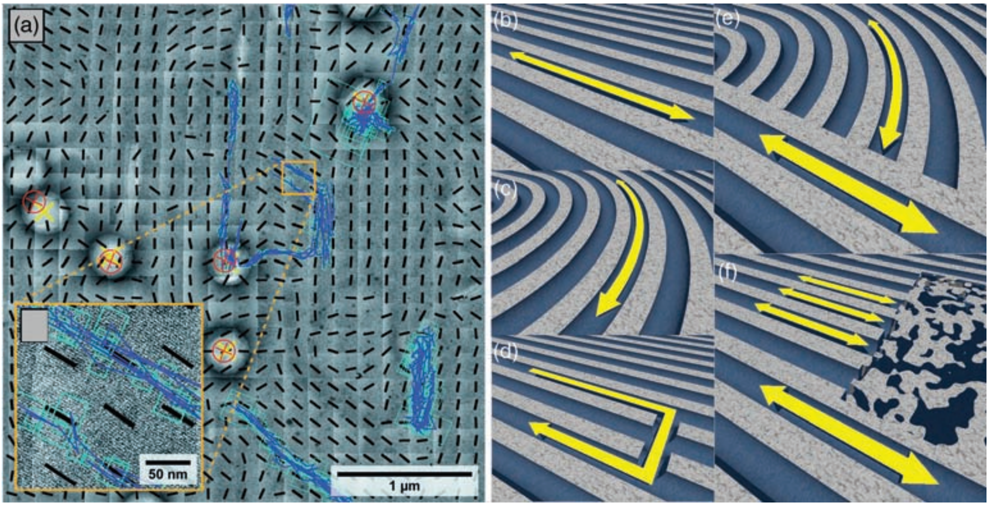

Figure 13.3 (a) Overlay of TEM image (gray) and FFT directors (black bars) with single-molecule trajectories (dark blue). The polystyrene beads, used for the overlay, are indicated by the yellow (TEM) and red (SMM) crosses. The light blue boxes show the positioning error of the SM trajectories. (b–f) Possible movement patterns of a single molecule in various structural features found in the hexagonal mesoporous films.