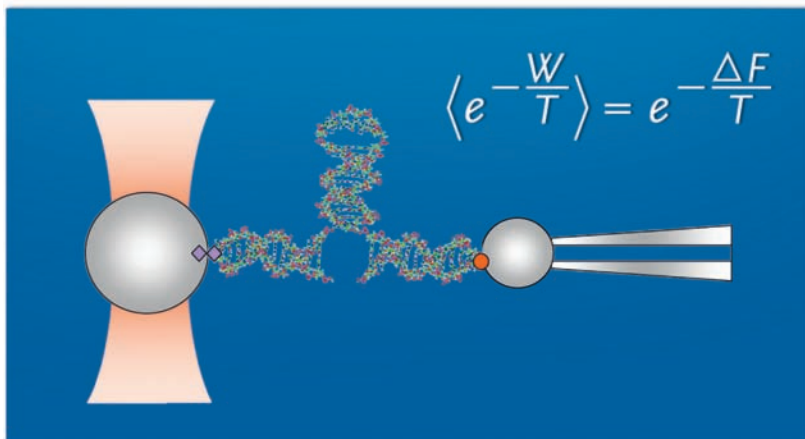
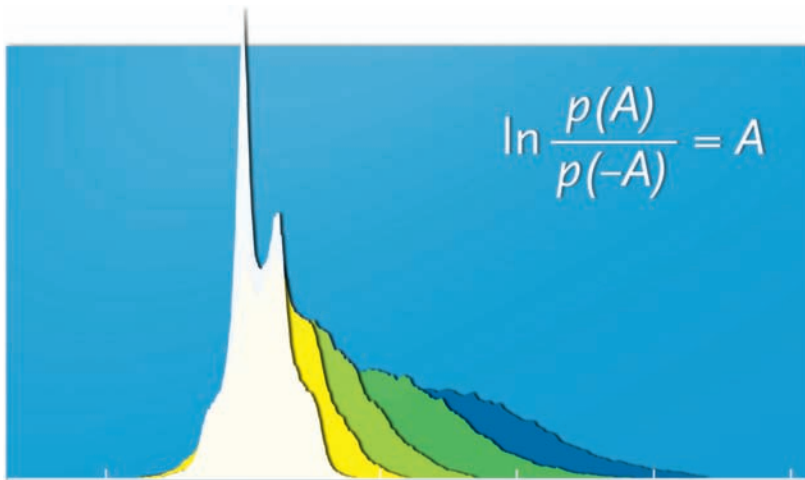


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R. Klages, W. Just, and C. Jarzynski

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Fluctuation Relations and Beyond



Edited by
Rainer Klages, Wolfram Just,
and Christopher Jarzynski

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Cover picture

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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.

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Preface

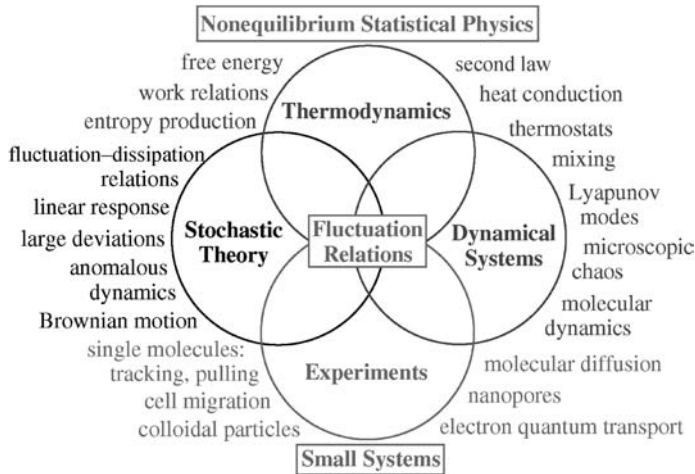
The term *small systems* denotes objects composed of a limited, small number of particles, as is typical for matter on meso- and nanoscales. The interest of the scientific community in small systems has been boosted by the recent advent of micromanipulation techniques and nanotechnologies. These provide 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.

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Summer 2012

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Color Plates

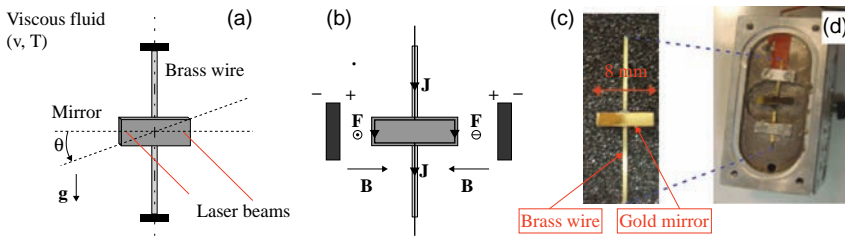


Figure 4.1 (a) The torsion pendulum. (b) The magnetostatic forcing. (c) Picture of the pendulum. (d) Cell where the pendulum is installed.

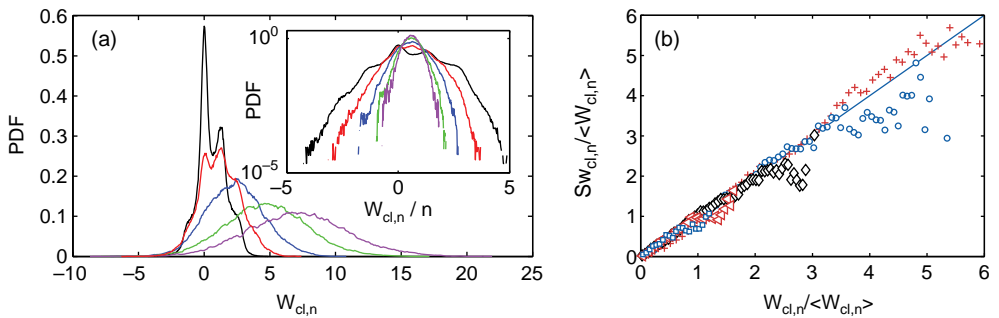


Figure 4.12 (a) Distribution of classical work W_{cl} for different numbers of period $n = 1, 2, 4, 8,$ and 12 ($f = 0.25$ Hz). *Inset:* Same data in lin-log. (b) Normalized symmetry function as a function of the normalized work for $n = 1$ (+), 2 (o), 4 (◇), 8 (Δ), and 12 (□).

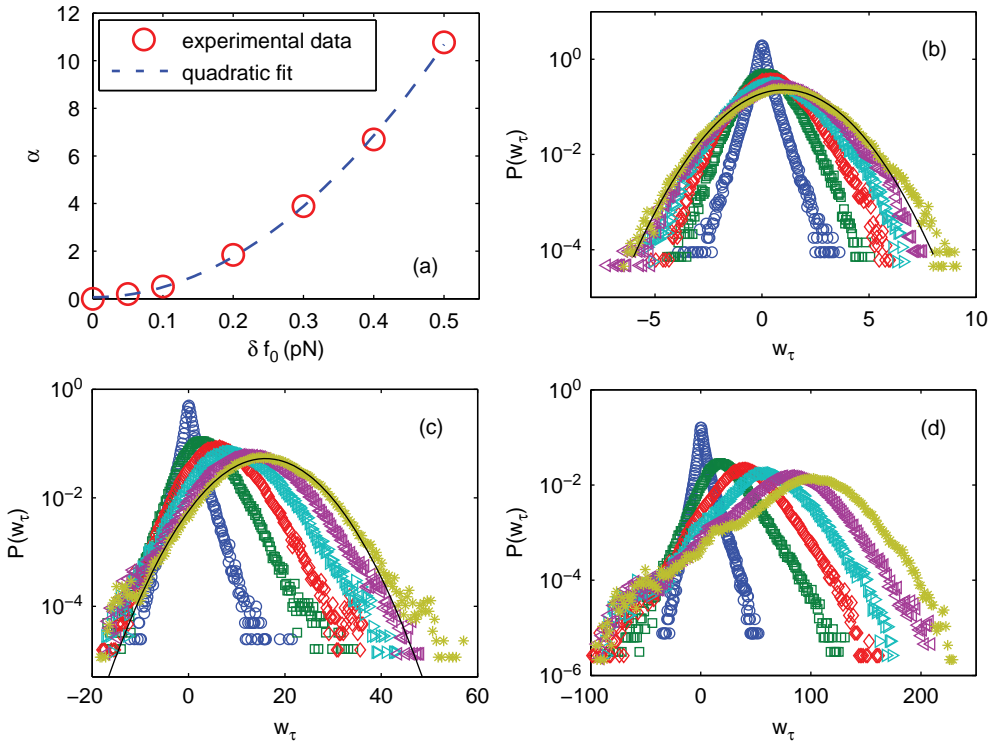


Figure 4.14 (a) Dependence of the parameter α on the standard deviation of the Gaussian exponentially correlated external force f_0 acting on the colloidal particle. Probability density functions of the work w_τ for (b) $\alpha = 0.20$, (c) $\alpha = 3.89$, and (d) $\alpha = 10.77$. The symbols correspond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

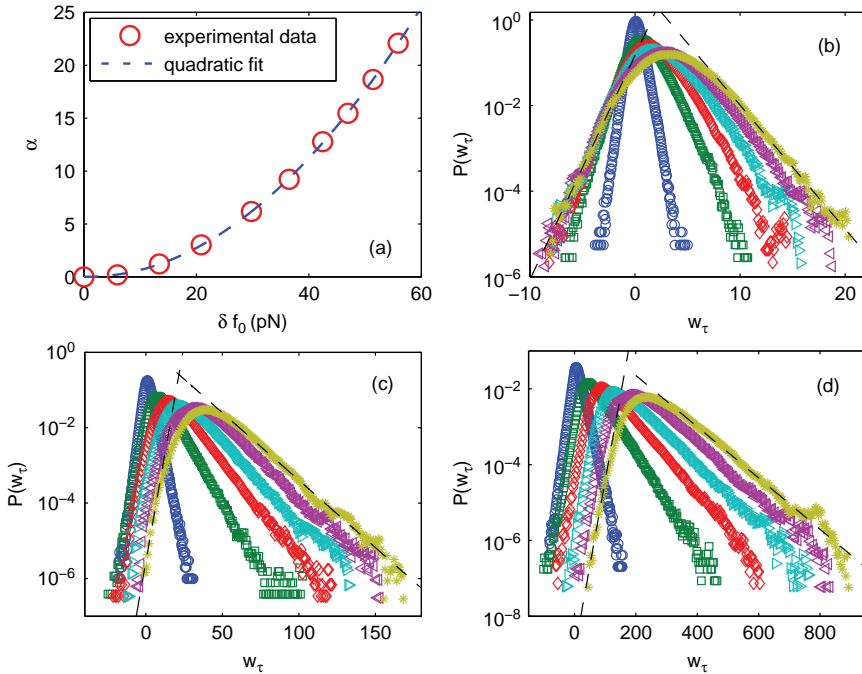


Figure 4.16 (a) Dependence of the parameter α on the standard deviation of the Gaussian white external force f_0 acting on the cantilever. Probability density functions of the work w_τ for (b) $\alpha = 0.19$, (c) $\alpha = 3.03$, and (d) $\alpha = 18.66$.

The symbols correspond to integration times $\tau = 97 \mu\text{s}$ (\circ), $1.074 \mu\text{s}$ (\square), 2.051ms (\diamond), 3.027ms (\triangleleft), 4.004ms (\triangleright), and 4.981ms ($*$). The black dashed lines in (b)–(d) represent the exponential fits of the corresponding tails.

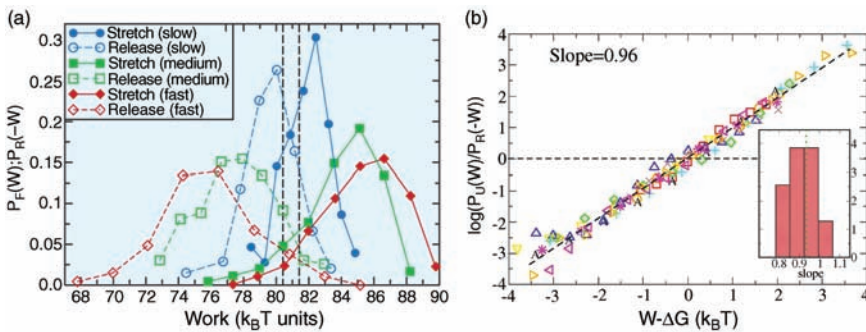


Figure 5.3 The Crooks fluctuation relation. (a) Work distributions for the hairpin shown in Figure 5.1 measured at three different pulling speeds: 50nm s^{-1} (blue), 100nm s^{-1} (green), and 300nm s^{-1} (red). Unfolding or forward (continuous lines) and refolding or reverse work distributions (dashed 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].)

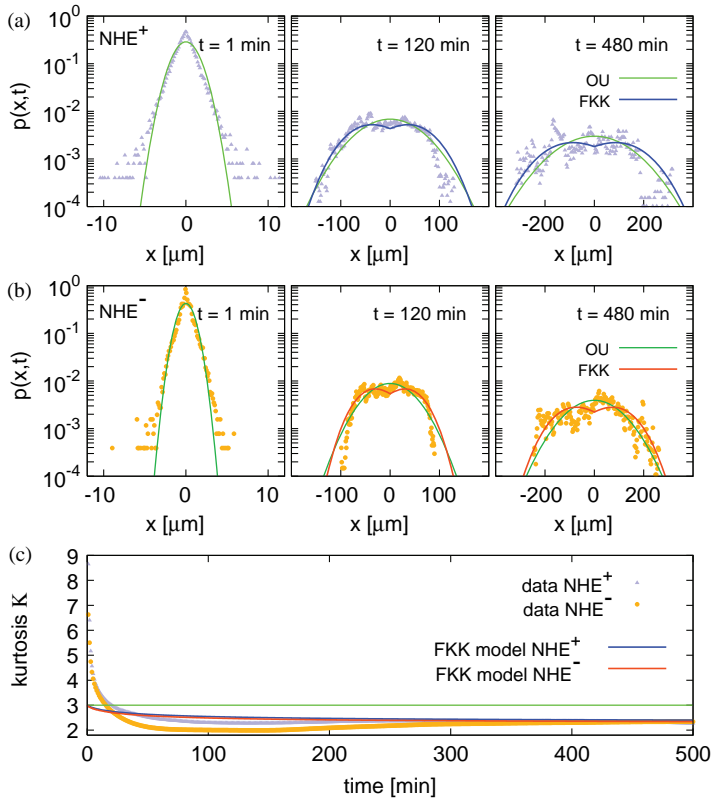


Figure 8.8 Spatiotemporal probability distributions $P(x, t)$. (a and b) Experimental data for both cell types at different times in semilogarithmic representation. The dark lines, labeled FKK, show the long-time asymptotic solutions of our model (Eq. (8.31)) with the same parameter set used for the 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].

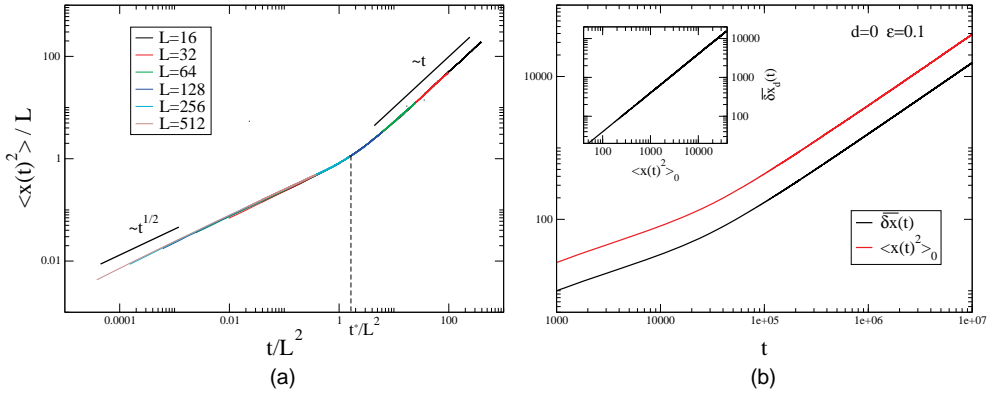


Figure 9.1 (a) $\langle x^2(t) \rangle_0 / L$ versus t/L^2 plotted for several values of L in the comb model. (b) $\langle x^2(t) \rangle_0$ and the response function $\delta x(t)$ for $L = 512$. *Inset:* The parametric plot of $\delta x(t)$ versus $\langle x^2(t) \rangle_0$.

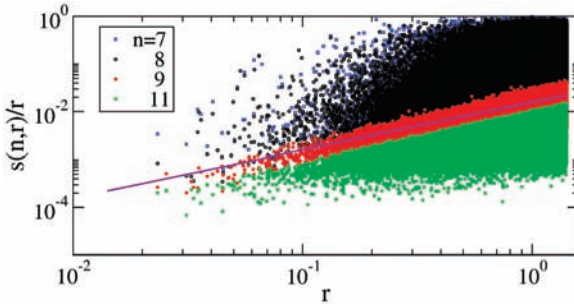


Figure 12.18 Variation of the normalized projection error $s(n,r)/r$ with the distance to the reference state r with $n = 7, 8, 9$, and 11 , respectively. To improve the statistics, data from 200 reference states are presented together. A line with slope 1 is shown to guide the eyes.

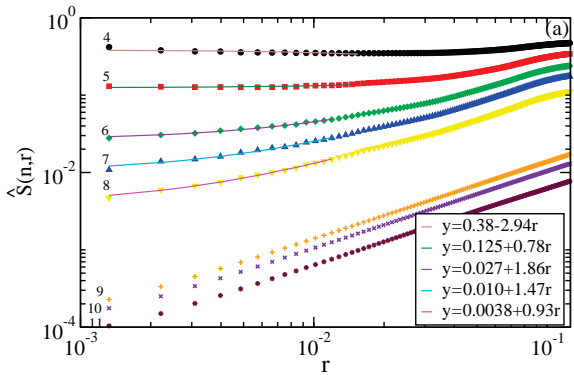


Figure 12.19 The normalized average projection error $\hat{S}(n,r)/r$ versus the distance to the reference state r with n from 4 to 11. Linear fittings of data for $n < M$ confirms the saturation of $\hat{S}(n,r)/r$ to a nonzero constant value.

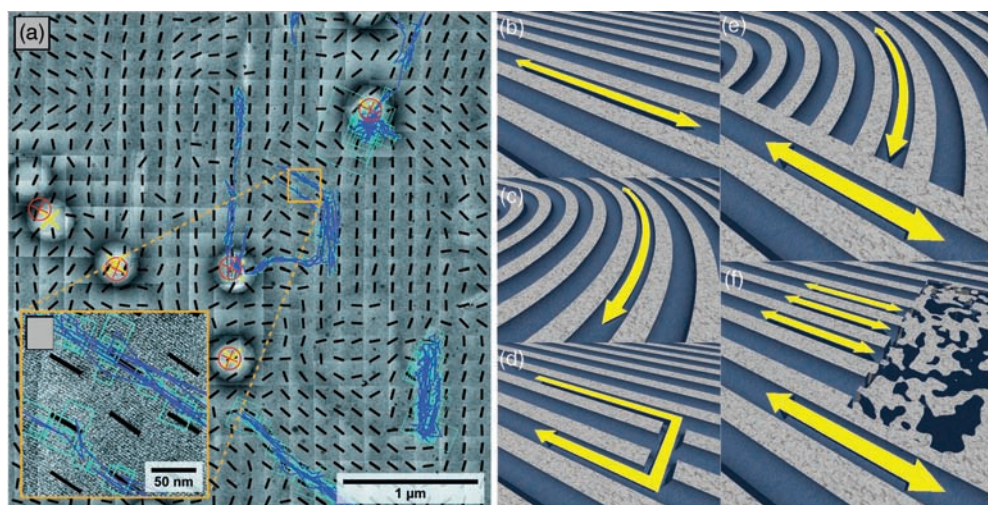


Figure 13.3 (a) Overlay of TEM image (gray) and FFT directors (black bars) with single-molecule trajectories (dark blue). The polystyrene beads, used for the overlay, are indicated by the yellow (TEM) and red (SMM)

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.