

The Thermodynamics of Small Driven Systems

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Abstract

In the present thesis, a thermodynamic theory is developed for driven soft matter systems like polymer solutions and colloidal suspensions. Within this theory, notions like the work applied to the system externally and the heat dissipated into a heat reservoir will be defined consistently. Going beyond mean values, all quantities are defined along a single trajectory. This thermodynamic approach is completed through a nonequilibrium generalized entropy.

Recent theoretical progress has led to the formulation of a class of nonequilibrium fluctuation relations holding in great generality beyond the well-understood linear response regime. We derive these relations and show how they are connected to the thermodynamic quantities introduced before. Since these quantities are defined on the level of single trajectories, stochasticity of the system implies probability distributions for them. The nonequilibrium fluctuation relations like the Jarzynski relation for the work then basically restrict these probability distributions. In order to obtain the still nonuniversal distribution functions, we show how these functions can be obtained through deriving equations of motion for the joint probability including the stochastic state of the system.

As a third issue, we show how Onsager's principle leading to the fluctuation-dissipation theorem may be generalized in nonequilibrium steady states. Explicitly, we derive the nonequilibrium fluctuation-dissipation theorem for the stochastic velocity and show how the equilibrium form of the fluctuation-dissipation theorem may be restored.

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Kurzfassung

In den letzten Jahren hat die Erforschung von Nichtgleichgewichtsphänomenen große Fortschritte mit der Formulierung so genannter Fluktuationstheoreme oder auch Nichtgleichgewichts-Fluktuations-Relationen gemacht. Zum ersten Mal wurde ein Fluktuationstheorem für die Entropieproduktion in einer simulierten gescherten Flüssigkeit, also einem Nichtgleichgewichtssystem, gefunden. Zwei Besonderheiten traten bei diesem Computerexperiment hervor. Zum einen gab es Simulationsläufe, bei denen sich die Teilchen der Flüssigkeit kurzzeitig spontan ordneten, die Entropie also verringert wurde. Zum anderen wurde gezeigt, dass eine negative Entropieproduktion nicht willkürlich auftritt, sondern dass vielmehr die Wahrscheinlichkeitsverteilung $p(\sigma)$ der Entropieproduktionsrate σ die Beziehung $p(-\sigma)/p(\sigma) \sim e^{-\sigma t}$ im Limes langer Zeiten t erfüllt. Diese Relation fand viel Beachtung, da sie eine der wenigen, allgemein gültigen Aussagen über das Nichtgleichgewicht jenseits des Linearen Response darstellt. Eine unmittelbare Folge der Beziehung ist, dass der Mittelwert der Entropieproduktionsrate in Übereinstimmung mit dem zweiten Hauptsatz der Thermodynamik immer nichtnegativ ist. Zentrales Thema dieser Dissertation ist eine Reihe ähnlicher Relationen, welche aus einem allgemeinen Zugang abgeleitet werden.

Während diese neuen Nichtgleichgewichtsrelationen generell gelten, so haben sie doch vor allem Bedeutung für Systeme, in denen Fluktuationen eine essentielle Rolle spielen. Dies sind vor allem *kleine Systeme*, wobei *klein* nicht notwendigerweise bedeutet, dass das System nur aus wenigen Teilchen besteht oder von molekularer Größe ist. Vielmehr ist entscheidend, dass die Energie, die mit der Umgebung als Arbeit oder Wärme ausgetauscht wird, so klein ist, dass ihre Fluktuationen beobachtbar sind. So kann durchaus ein makroskopisches Objekt wie ein Torsionspendel als experimentelle Realisierung eines kleinen Systems verstanden werden. In erster Linie zielt die zu entwickelnde Theorie jedoch auf Systeme, die der weichen Materie zugeordnet werden können. Das sind zum einen Moleküle mit biologischen Funktionen wie z.B. DNA- und RNA-Moleküle, Proteine wie das Muskelprotein Titin oder auch Motorproteine, die für aktive Zellprozesse zuständig sind wie Kinesin und Myosin; zum anderen sind das Polymere und Kolloide. Besonders kolloidale Systeme nehmen einen wichtigen Platz in der experimentellen Überprüfung der neuen Nichtgleichgewichtsrelationen ein und ein Großteil der existierenden Experimente arbeitet mit kolloidalen Partikeln. Systeme der weichen Materie, wie die eben genannten, sind in der Regel in eine viskose, inkompressible Flüssigkeit suspendiert. Diese Flüssigkeit hat eine wohldefinierte, konstante Temperatur und agiert in unserem Zugang als das Wärmebad, deren Freiheitsgrade wir weder kontrollieren noch deren Dynamik explizit beschreiben können. Die Flüssigkeit muss nicht notwendigerweise ruhen,

sondern kann durch äußere Einwirkungen stationär oder auch zeitabhängig fließen. Von einem hydrodynamischen Standpunkt aus zeichnen sich Systeme der weichen Materie durch eine niedrige Reynolds-Zahl aus, d.h. Trägheitseffekte sind vernachlässigbar und die Dynamik ist überdämpft, es gibt also keine Bewegung ohne Kraft. Die Gesamtheit aller Partikelpositionen oder allgemein der Freiheitsgrade wird als *Konfiguration* bezeichnet.

In der vorliegenden Arbeit wird die überdämpfte Dynamik von Systemen der weichen Materie als stochastisch angenommen und auf zwei Ebenen modelliert. Die zeitliche Entwicklung der Wahrscheinlichkeitsverteilung wird durch die Smoluchowski-Gleichung beschrieben. Als entscheidende Größe tritt in dieser die lokale mittlere Geschwindigkeit der Teilchen auf, welche auf zwei Weisen physikalisch interpretiert werden kann. Auf der einen Seite ist sie der Mittelwert der stochastischen tatsächlichen Geschwindigkeit, wobei aber nur über die Untermenge an Trajektorien gemittelt wird, die durch eine gegebene Konfiguration verlaufen. Andererseits muss ein Unterschied zwischen lokaler mittlerer Geschwindigkeit und der Geschwindigkeit des äußeren Flusses durch eine Kraft bedingt sein, welche sich aus drei Teilen zusammensetzt: einer konservativen Kraft aufgrund eines Potentials, möglichen nichtkonservativen Kräften und der thermodynamischen Kraft, welche das Erreichen der Gibbs-Boltzmann-Verteilung als Gleichgewichtsverteilung sicherstellt. Eine alternative Beschreibung der Dynamik auf der Ebene einzelner Trajektorien ist die Langevin-Gleichung. Hierbei wird die Interaktion mit dem Wärmebad durch einen stochastischen Kraftterm direkt modelliert. Für eine korrekte Beschreibung der Dynamik in Gegenwart hydrodynamischer Wechselwirkungen muss diese stochastische Kraft jedoch durch eine zusätzliche Drift vervollständigt werden.

Ausgehend von zwei Axiomen stellen wir in Kapitel 3 eine Thermodynamik kleiner Systeme auf. Das erste Axiom definiert Arbeit als kontrollierbare Energieänderung des Systems, welche von außen verursacht wird. Das zweite Axiom besagt, dass entlang jedweder Trajektorie Energieerhaltung und damit der erste Hauptsatz der Thermodynamik gilt. Die (negative) Differenz zwischen Änderung der potentiellen Energie und der Arbeit wird dann als dissipierte Wärme, also nicht kontrollierte Energieänderung, interpretiert. Im Gegensatz zur klassischen Thermodynamik ist das System nicht durch einige wenige Zustandsvariablen charakterisiert, sondern durch seine Konfiguration. Eine vollständige Beschreibung makroskopischer Systeme ist damit weder möglich noch sinnvoll. Die Prozessgrößen Wärme und Arbeit werden für stochastische Systeme, wie wir sie im Blick haben, zu Zufallsgrößen mit einer Verteilung. Für ein System, das aus dem Gleichgewicht durch zeitabhängige Änderung eines Kontrollparameters getrieben wird, demonstrieren wir dieses Konzept experimentell. Dafür messen wir die Trajektorie eines einzelnen kolloidalen Teilchens, welches sich vor einer Glasplatte bewegt. Das Teilchen wird von einer stark fokussierten Laserfalle auf eine eindimensionale Bewegung senkrecht zur Glasplatte unter Einwirkung der Gravitation eingeschränkt. Eine zweite, defokussierte optische Falle drückt dann das Teilchen zeitabhängig gegen die gleich geladene Glasplatte.

Im nächsten Schritt erweitern wir die Theorie auf nichtkonservative Kräfte sowie äußere Flüsse. Während die Arbeit, die von den nichtkonservativen Kräften verrichtet wird, ein-

fach Kraft mal Weg ist, ist die Arbeit des äußeren Flusses schwieriger zu bestimmen. Ausgehend von dem Grundsatz, dass die Arbeit invariant unter einem zeitabhängigen Wechsel des Bezugssystems sein muss, finden wir als Generalisierung, dass nun die konvektive Ableitung an die Stelle der partiellen Zeitableitung tritt. Vervollständigt wird unsere thermodynamische Beschreibung durch die Einführung einer generalisierten Systementropie definiert auf der Ebene der Einzeltrajektorien. Somit ist auch die Entropie eine Zufallsgröße mit einer Verteilung. Die totale Entropieproduktion spaltet sich auf in einen Term, der die Änderung der Systementropie beschreibt und einen Anteil, der in das umgebene Medium, also die Flüssigkeit, dissipiert wird. Da das Medium eine wohldefinierte Temperatur aufweist, kann der Zusammenhang zwischen dissipierter Wärme und Entropieänderung über die Clausius Formel hergestellt werden.

Als drittes Element diskutieren wir unseren Formalismus für stationäre Nichtgleichgewichtszustände. Einer phänomenologischen Theorie folgend wird in einem stationären Nichtgleichgewichtszustand die Wärme dissipiert als Reaktion auf die Arbeit, die aufgewendet werden muss, um diesen Zustand aufrecht zu erhalten. Dieser Anteil der Wärme, die *Housekeeping*-Wärme, muss dann in Übergängen zwischen stationären Zuständen unterschieden werden von der Überschusswärme. Auch für diese Größen leiten wir explizite, trajektorienabhängige Ausdrücke her.

Das Kapitel 4 ist zweigeteilt. Im ersten Teil werden die bekannten, historisch bedingt verschieden hergeleiteten Nichtgleichgewichtsrelationen aus einem vereinigenden Zugang abgeleitet. Grob zerfallen diese für eine Prozessgröße R (z.B. Arbeit oder Wärme) in zwei Klassen, die integralen Relationen in der Form $\langle e^{-R} \rangle = 1$, welche die möglichen Verteilungen beschränken ähnlich der Normierungsbedingung, sowie ferner die detaillierten Relationen, $p(-R)/p(R) = e^{-R}$, welche die Wahrscheinlichkeitsverteilung von Ereignissen mit negativem R aus der von Ereignissen mit positivem R bestimmen. Es wird gezeigt, dass die bekannten Relationen (und im Prinzip unendlich viele weitere) alle aus dem Verhalten des antisymmetrischen Anteiles der Pfadwahrscheinlichkeit einer Trajektorie unter Zeitumkehr folgen. Die Vielfalt der Relationen hat zwei Gründe: zum einen haben wir die Freiheit, die Wahrscheinlichkeitsdichte des finalen Zustandes frei zu wählen und zum anderen kann die Operation der Zeitumkehr auf den Prozess, die Dynamik des Systems, oder auf beide angewendet werden. Explizit gezeigt und diskutiert werden allerdings nur die Relationen, die Aussagen über eine der im vorhergehenden Kapitel eingeführten thermodynamischen Größen machen.

Die detaillierten Fluktuationsrelationen bestimmen zwar die Verteilung von Ereignissen mit negativem R , allerdings ist die Verteilungsfunktion $p(R \geq 0)$ immer noch eine nicht-universelle Funktion, über die wir mit den bisherigen Mitteln keine Aussagen treffen können. Im zweiten Teil des Kapitels 4 wenden wir uns daher Bewegungsgleichungen für die Verteilungsfunktion zu. Der gewählte Zugang kann wie folgt motiviert werden: Die Dynamik des Systems wird beschrieben durch die Smoluchowski-Gleichung. Die zeitliche Änderung einer Prozessgröße hängt nur ab von der momentanen Konfiguration des Systems. Wir betrachten daher die Verbundwahrscheinlichkeit, dass ein Wert von R in der Zeit t akkumuliert wurde und sich das System zum Zeitpunkt t in einem bestimmten

Zustand befindet. In anderen Worten ist die Verbundwahrscheinlichkeit die Wahrscheinlichkeit eines Wertes R für die Menge aller Trajektorien, die in einem bestimmten Zustand enden. Für diese Verbundwahrscheinlichkeit lässt sich eine Bewegungsgleichung ableiten und die Verteilung für R folgt dann durch Integration über alle möglichen Endzustände. Die Bewegungsgleichung für die Verteilung erlaubt darüber hinaus, die verschiedenen Fluktuationsrelationen zu beweisen. Explizit geben wir die Bewegungsgleichungen für Arbeit und *Housekeeping*-Wärme an.

Als System, das von unserer Agenda abweicht aber trotzdem sehr interessante Eigenschaften aufweist, diskutieren in Kapitel 5 eine Fehlstelle in einem Diamant. Die Fehlstelle kann für unsere Zwecke als ein diskretes Zwei-Niveau-System dargestellt werden. Das Besondere an diesem System ist, dass die Entropieproduktion im Medium abstrakt definiert ist, da ein Wärmebad mit einer definierten Temperatur fehlt. Trotzdem können die Konzepte, die wir bislang für Systeme in Kontakt mit einem Wärmebad entwickelt haben, auch auf diskrete Systeme angewendet werden.

Die Lineare Response-Theorie ist ein zentraler Bestandteil der statistischen Mechanik und wird im letzten Kapitel für Systeme der weichen Materie untersucht. Im Gleichgewicht verknüpft das Fluktuations-Dissipations-Theorem die Antwortfunktion einer Observablen auf eine kleine Störung mit der Ableitung der Korrelationsfunktion dieser Observablen mit ihrer durch die innere Energie konjugierten Größe. Das wohl bekannteste Beispiel für ein Fluktuations-Dissipations-Theorem erhält man für die Geschwindigkeit eines freien Teilchens, dessen integrierte Version zur Einstein-Relation führt. Diese verknüpft die Mobilität des freien Teilchens mit der Diffusionskonstanten durch die Temperatur der Flüssigkeit.

Während sich die Antwortfunktion auch auf das Nichtgleichgewicht ausdehnen lässt, so ist hingegen die physikalische Interpretation eines generalisierten Fluktuations-Dissipations-Theorems weitaus schwieriger. Der Grund dafür ist, dass nun die Korrelationsfunktion nicht mehr mit der gleichgewichts-konjugierten Observablen, sondern mit dem abstrakten, generalisierten Potential gebildet wird. Wir zeigen, dass es dennoch möglich ist, das generalisierte Fluktuations-Dissipations-Theorem für die Geschwindigkeit durch physikalisch messbare Größen auszudrücken, und finden als neue konjugierte Größe die relative Geschwindigkeit, also die Differenz zwischen aktueller stochastischer und lokaler mittlerer Geschwindigkeit. Als Anwendung diskutieren wir die Verallgemeinerung der Einstein-Relation auf einen stationären Nichtgleichgewichtszustand numerisch und experimentell.

Zusammenfassend haben wir in dieser Arbeit eine Theorie entwickelt, die als zentralen Punkt Aussagen über die Wahrscheinlichkeitsverteilungen thermodynamischer Größen wie Arbeit und Wärme in kleinen, getriebenen Systemen macht. Als essentielle Bausteine dieser Theorie haben wir konsistente Definitionen von Prozessgrößen wie Arbeit und Wärme sowie Entropie gegeben und ihre Wahrscheinlichkeitsverteilungen durch die Angabe von Bewegungsgleichungen bestimmt.

Notations and Symbols

α	discretization parameter
β	any scalar function; friction kernel
γ	control parameter
Γ	protocol
ε	small parameter (small time step, etc.)
$\dot{\varepsilon}$	strain rate
μ, μ_0	mobility tensor, bare mobility
$\psi, \psi_s, \psi_{\text{eq}}, \psi_\varepsilon$	state (probability distribution), steady state, equilibrium state, perturbed state
Φ	nonequilibrium generalized potential
\mathcal{A}	dynamical free energy
A, B, \mathcal{B}	general observable; conjugate observable, in nonequilibrium
D, D_0	diffusion tensor, bare diffusion coefficient
$\mathbf{d}, \mathbf{d}^\alpha$	drift vector, spurious drift
\mathbf{f}, \mathbf{F}	nonconservative, total force
\mathcal{F}	equilibrium free energy
g	generating function
I	violation function
k_B	Boltzmann's constant
$\hat{L}, \hat{L}_s, \hat{L}_{\text{eq}}, \lambda$	time evolution operator, in a steady state, in equilibrium; their eigenvalues
m	conditional moment; mass
\mathbf{m}	mean displacement
N	number of particles
\mathbf{p}	momentum
p, ρ	probability, joint probability distribution
P	transition probability
\mathcal{P}	path probability
\hat{P}	projecting operator
$Q, Q_{\text{hk}}, Q_{\text{ex}}$	total, housekeeping, excess heat
\mathbf{r}	position
R, r	skew-symmetric part of the action, its explicit value
$\mathcal{R}, \mathcal{R}^{\text{eq}}$	response function, in equilibrium
$\Delta s, \Delta s_m, \Delta s_{\text{tot}}$	change of system, medium, total entropy
t	time

Notations and Symbols

τ	time scale (e.g., relaxation time)
$T, k_B T$	temperature, thermal energy
U	inner energy
\hat{U}	propagator
$\mathbf{v}, \mathbf{v}^s, \delta\mathbf{v}$	local mean velocity, in a steady state; relative velocity
W	work
$\mathcal{W}, \mathcal{W}_s$	dissipation function, in a steady state
x	microstate (collection of particle positions)
X	trajectory
Y	transition functional
\mathcal{Z}	partition function

1 Introduction

Thermodynamics is a branch of physics which emerged in the early 19th century in conjunction with the development of steam engines [1]. Classical thermodynamics is a phenomenological theory describing processes in macroscopic systems composed of many particles on the order of the Avogadro constant 10^{23} . Somewhat counter-intuitively, this large number allows to describe macroscopic systems at equilibrium by a set of relatively few state variables like pressure, energy, temperature, etc. Later, the microscopic foundations of thermodynamics have been laid by the work of Boltzmann, giving thermodynamics a probabilistic interpretation based on the motion of molecules and atoms and leading eventually to the formulation of equilibrium statistical mechanics [2].

In contrast to equilibrium, our understanding of nonequilibrium is still far from complete despite constant theoretical progress. Of course, in equilibrium there are still open questions left to be answered, but from a fundamental point of view the Boltzmann-Gibbs distribution gives a complete description of any system in equilibrium with a large heat reservoir. In the sense of this universality, a comparable theory for nonequilibrium systems is lacking and may even, in full generality, never arise.

For a certain class of small driven systems as reviewed in [3, 4, 5, 6], however, unexpected and significant progress occurred during the last decade with the formulation of exact relations like the fluctuation theorem [7, 8, 9, 10], the Jarzynski relation [11], and various extensions [12, 13, 14, 15, 16], all holding beyond the well understood linear response regime. Characteristically, these systems consist of a few degrees of freedom embedded in a heat bath of well-defined temperature. External mechanical forces or flows drive these few degrees of freedom out of their equilibrium while still in contact with an equilibrium bath of well-defined temperature. The common theme of all these nonequilibrium relations is that they apply to whole probability distribution instead of just to mean values. This shows that fluctuations play a prominent role and we only have the chance to verify and use these relations in what we will call *small systems*.

1.1 The theoretical perspective: A short history

The study of thermal fluctuations dates back to the work of Einstein on Brownian motion [17] in 1905, where the first fluctuation-dissipation relation for a sedimenting suspension under the influence of gravitation was given. Einstein's work revealed that (Gaussian) fluctuations determine essential properties of equilibrium systems like transport coefficients, e.g., the mobility of a Brownian particle. Transport coefficients have been

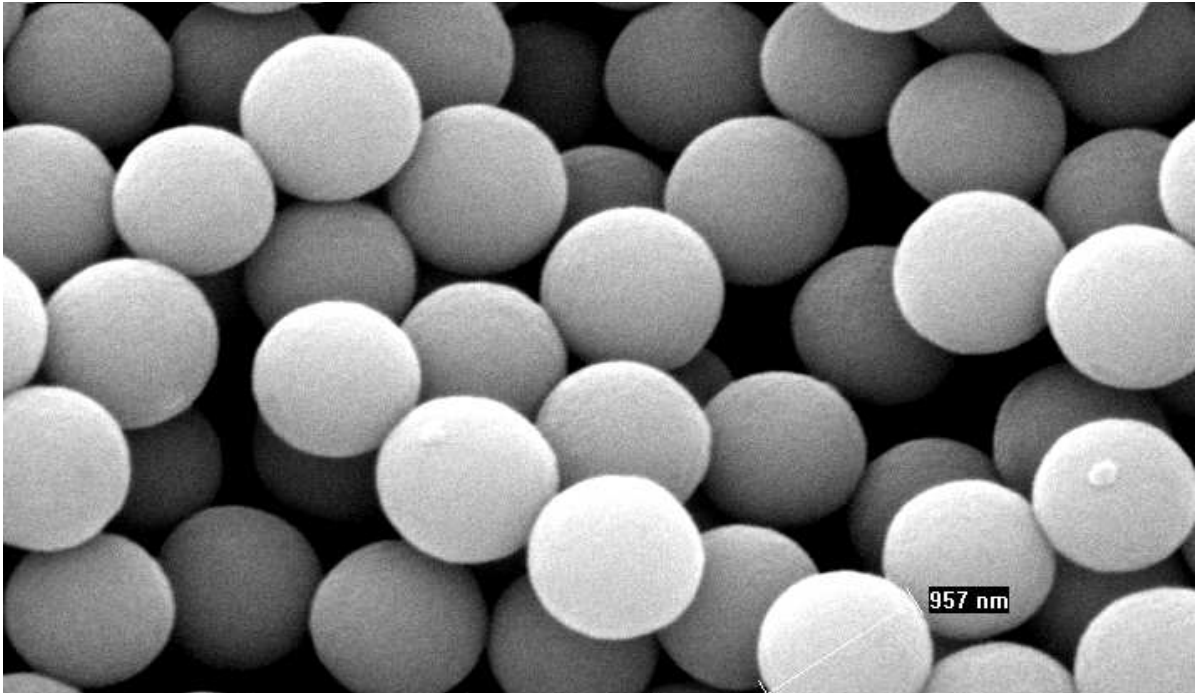


Figure 1.1: Scanning electron micrograph image of titania colloidal beads. Colloids are mesoscopic particles which are suspended in a liquid with typical particle sizes between 10 and 1000 nm. They have developed into an ideal system to experimentally test new nonequilibrium relations. (Picture from <http://hera.physik.uni-konstanz.de>)

calculated first by Nyquist for linear electrical circuits [18] and then extended by Onsager [19, 20] to thermal systems through the formulation of the fluctuation-dissipation theorem. Since then, the focus has gradually shifted towards nonequilibrium systems. However, nonequilibrium concerns a much wider range of phenomena compared to equilibrium and its state is far from complete lacking a universal description comparable to the Boltzmann-Gibbs distribution.

In 1993, Evans, Cohen, and Morriss gave the study of nonequilibrium systems a new turn [7]. They investigated a simple two-dimensional sheared fluid numerically [21]. In these simulations, the Newtonian equations of motion for all particles of the fluid are integrated. Driving the fluid would lead to an increasing kinetic energy and additional constructs, called thermostats, have to be used. These thermostats constrain, e.g., the kinetic energy of all particles and keep the so defined temperature fixed through introducing additional degrees of freedom. The phase space volume then is not conserved anymore and its contraction rate can be related to the entropy produced in one or more thermostats mimicking thermal baths. Two things were observed. First, sometimes a negative entropy production was found, i.e., entropy in the bath was annihilated. Second, these negative

events do not occur randomly but they obey the symmetry

$$\frac{p(-\sigma)}{p(+\sigma)} \sim e^{-\sigma t}, \quad (1.1)$$

where σ is the phase space contraction rate and $p(\sigma)$ its probability distribution. The symbol \sim indicates that the ratio approaches the right hand side in the long time limit.

Two years later, Gallavotti and Cohen placed the fluctuation theorem on solid mathematical ground [8]. They proved it under certain conditions, particularly the chaotic hypothesis. Loosely speaking, the chaotic hypothesis assumes that a nonequilibrium steady state is a hyperbolic attractor having both positive and negative Lyapunov exponents. Regarding this hypothesis as a technical ingredient, it was conjectured [22] that the fluctuation theorem holds more generally. Kurchan gave the first hints how the fluctuation theorem arises for stochastic dynamics [9] and how it is connected to the entropy production in these systems. In a seminal paper, Lebowitz and Spohn gave the proof for general Markov processes and discussed several systems governed by stochastic dynamics [10]. Stochastic systems are easier to handle in the sense that technical difficulties arising in deterministic dynamics like ergodic issues and the nonexistence of a stationary measure on strange attractors are bypassed.

Another branch of development started with the formulation of the Jarzynski relation [11] showing that fluctuation relations can be found also for other quantities than the entropy production. The Jarzynski relation

$$\langle e^{-W/T} \rangle = e^{-\Delta\mathcal{F}/T} \quad (1.2)$$

turns the second law

$$\langle W \rangle \geq \Delta\mathcal{F} \quad (1.3)$$

for a process connecting two equilibrium states with a free energy difference $\Delta\mathcal{F}$ into an equality. Whereas the equality in (1.3) only holds for quasistatical processes, the equation (1.2) is valid for any process and implies (1.3) through the Jensen inequality $\langle \exp(x) \rangle \geq \exp(\langle x \rangle)$. The brackets $\langle \dots \rangle$ denote the average over the corresponding probability distribution. A relation similar to (1.2) has been found already in the 70s [23, 24], albeit invoking a different definition of the work [25]. Crooks has then derived a symmetry related to the fluctuation theorem (1.1) based on microscopic reversibility [12, 13]. The Jarzynski and Crooks relations have received the largest attention among the nonequilibrium fluctuation relation due to their practical importance. In particular, they can be used to recover the free energy profile of some reaction coordinate [26, 27, 28, 29, 30, 31, 32]. To assess their practical applicability in experiments and numerical studies, convergence and statistical properties have been studied [33, 34].

The Hatano-Sasa relation [35] has conceptually advanced the study of nonequilibrium steady states as it provides a bridge to steady state thermodynamics. Steady state ther-

modynamics [36] is a phenomenological theory which promotes the splitting of the dissipated heat $Q = Q_{\text{hk}} + Q_{\text{ex}}$ into the housekeeping heat Q_{hk} needed to maintain a nonequilibrium steady state and the excess heat Q_{ex} . From the Hatano-Sasa relation

$$\langle e^{-Q_{\text{ex}}/T - \Delta\Phi} \rangle = 1, \quad (1.4)$$

a generalized second law

$$T \Delta S \geq -\langle Q_{\text{ex}} \rangle$$

can be derived through the Jensen inequality. Here, $\Delta S = \langle \Delta\Phi \rangle$ is the change of (Shannon) entropy due to a transition between nonequilibrium steady states.

The short survey given above is far from complete and represents a highly personal point of view as to which theoretical papers have contributed most to this exciting field. The list of literature by now is large and continuously growing. Unfortunately, an all-encompassing review has not yet been written and so for further information and references, the interested reader is referred to the reviews [3, 5, 6, 37].

1.2 The experimental perspective: What are small systems?

Up to now we said that we aim to study small systems. This is not a very precise term and the need arises for a more accurate definition. F. Ritort answers this question in [38] with the definition:

Small systems are those in which the energy exchanged with the environment is a few times $k_B T$ and energy fluctuations are observable. A few can be 10 or 1000 depending on the system. A small system must not necessarily be of molecular size or contain a few number of molecules.

Examples of small systems in this sense include single colloidal particles but also colloidal suspensions (figure 1.1), motor proteins (figure 1.2), and large molecules like DNA, Titin, or proteins (figure 1.3) to name just the most important ones. However, also apparently

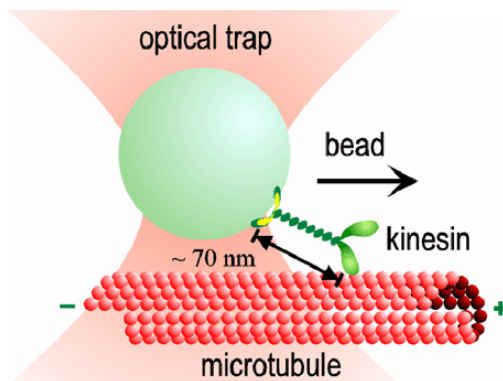


Figure 1.2: A paradigm for small driven systems are biological systems like motor proteins. The intracellular aqueous solution provides an environment with constant, well-defined temperature. Sketched is a possible experiment exerting a force on a kinesin molecule which walks along a microtubule. (Picture from <http://www.imprs-mcbb.de>)

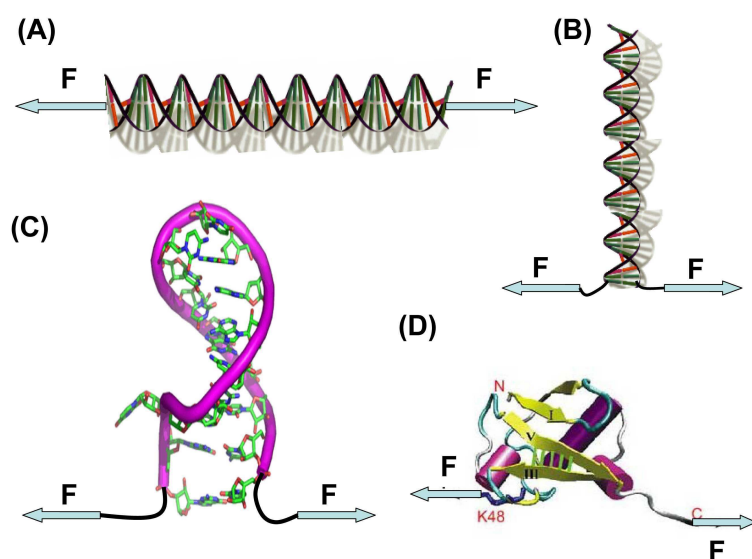


Figure 1.3: Mechanical manipulation of small systems has become feasible through the development of optical traps and the atomic force microscope. An example are single molecule pulling experiments: (A) stretching DNA, (B) unzipping DNA, (C) mechanical unfolding of RNA, and (D) mechanical unfolding of proteins. (Figure taken from [38].)

macroscopic systems like a torsion pendulum may be regarded as small system and can be used to verify the fluctuation theorem [39].

Direct manipulation of single molecules and colloids in experiments became feasible with the advent of two devices, the atomic force microscope [40] and the optical tweezers [41, 42]. Especially colloidal particles driven by time-dependent laser traps [43, 44, 45, 46] have become the ideal systems for quantitatively studying nonequilibrium fluctuation relations experimentally for essentially two reasons. First, individual trajectories can be recorded allowing thus to compute the probability distribution of observables in contrast to ensemble quantities typically obtained in scattering experiments. Second, even though the particles are driven into a genuine nonequilibrium state, the surrounding fluid still faithfully behaves like an equilibrium bath. Consequently, a large number of experimental tests have used single colloidal particles. The first test was reported by Wang *et al* [43]. It claimed to demonstrate the fluctuation theorem for the entropy production but closer inspection shows that it really demonstrated the Jarzynski relation and the Crooks symmetry for the work. Later tests include [44, 46]. The Hatano-Sasa relation was demonstrated successfully also using a colloidal particle [45].

The probably most exciting perspective is offered through the understanding and modeling of biological systems. These systems are generically out of equilibrium. Still, for most processes in cell biology taking place on the level of a single (or few) molecules, the intracellular aqueous solution provides an environment with constant temperature. The genuine source of nonequilibrium are not temperature gradients but rather mechanical or chemical stimuli provided by external forces or imbalanced chemical reactions. Hence, single molecule experiments and experimental studies of biomolecules like proteins or DNA can be regarded as a paradigm for small systems. Indeed, the first real world test of

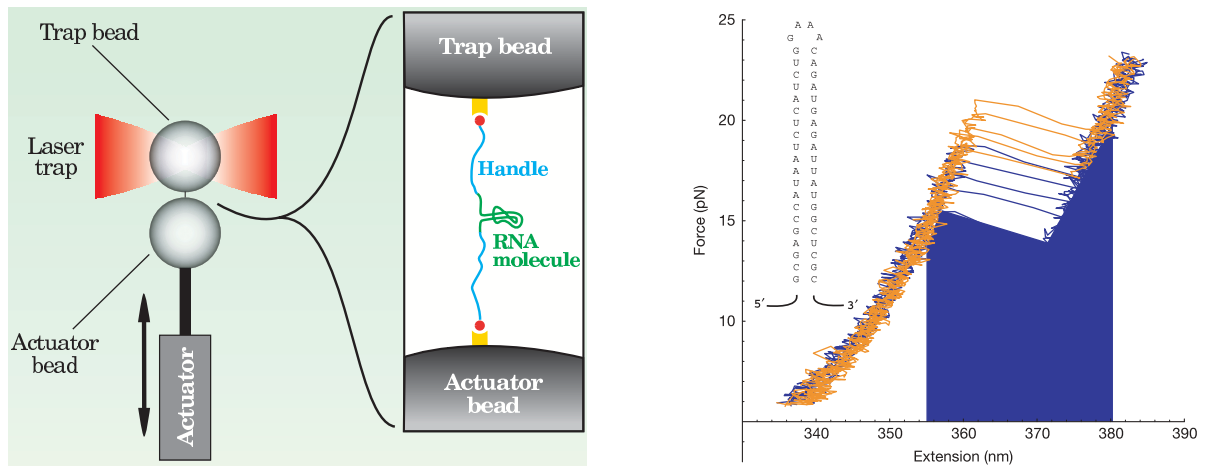


Figure 1.4: Experimental test of the Jarzynski relation (1.2). Left: A molecule of RNA is attached to two beads and subjected to reversible and irreversible cycles of folding and unfolding. A piezoelectric actuator controls the position of the bottom bead, which, when moved, stretches the RNA. An optical trap formed by two opposing lasers captures the top bead. The difference in positions of the bottom and top beads gives the end-to-end length of the molecule. The blowup shows how the RNA molecule (green) is coupled with the two beads via molecular handles (blue). The handles end in chemical groups (red) that can be stuck to complementary groups (yellow) on the bead. (Figure and caption taken from [4], the described experiment is [47].) Right: Typical unfolding (orange) and refolding (blue) force extension curves for the RNA hairpin from a similar experiment [30]. The blue area under the curve represents the work returned as the molecule switches from the unfolded to the folded state.

the Jarzynski relation has been the recovering of the free energy profile of RNA molecules through recording the work in stretching experiments [47], see also figure 1.4. Other experimental and numerical studies on specific systems have followed. The Crooks relation has been tested as well [30]. Directed transport in noisy environments such as cells is also studied in the context of ratchets [48, 49, 50, 51] and Brownian motors [52, 53].

Since their first formulation, nonequilibrium fluctuation relations have been anticipated to play an important role in our understanding of biological processes, in the design of devices on the nanoscale, and in the development of a thermodynamical theory for finite, small systems. The motivation of this thesis is to sketch such a theory for systems governed by stochastic dynamics and embedded into an environment of constant temperature.

1.3 Organization of the thesis

The thesis is organized as follows. The three building blocks of the thermodynamics of small driven systems are: a consistent formulation of work, heat, and entropy introduced

in chapter 3, the discussion of the nonequilibrium relations in chapter 4 and the linear response theory of chapter 6. But first, in order to lay the foundations, we define the stochastic dynamics in chapter 2 of the systems we aim to study. We introduce the time evolution operator in a very general way and then specialize to overdamped Markovian dynamics. Our basic model throughout the thesis will be the Smoluchowski equation. Only in chapter 5 we will turn off the main road and study the discrete dynamics of a two-level system whose dynamics is governed by the master equation.

The appendix is organized separately. It contains the more complex calculations and is ordered such that single calculations build upon former results derived in the course of the appendix. The appendix does not depend on definitions nor results derived in the main text. The main text uses and references equations and relations obtained in the appendix, however, these references do not occur in the same order as in the appendix.

Throughout most parts of the thesis, we will work with dimensionless quantities. For example, we assume that all lengths have been made dimensionless through choosing an appropriate length scale. In particular, probability distributions are real numbers. The Boltzmann constant k_B is set to unity, making the entropy dimensionless. The temperature T is measured in units of the thermal energy $k_B T$. The only exception are values for experimental parameters and measured quantities, which we give with the proper units.

1.4 Publications

Part of the work used to compile this thesis has been published previously:

- “The Jarzynski relation, fluctuation theorems, and stochastic thermodynamics for non-Markovian processes”
T. Speck and U. Seifert, *J. Stat. Mech.* L09002 (2007)
- “Einstein relation generalized to nonequilibrium”
V. Blickle, T. Speck, C. Lutz, U. Seifert, and C. Bechinger, *Phys. Rev. Lett.* **98**, 210601 (2007)
- “Measurement of Stochastic Entropy Production”
C. Tietz, S. Schuler, T. Speck, U. Seifert, and J. Wrachtrup, *Phys. Rev. Lett.* **97**, 050602 (2006)
- “Restoring a fluctuation-dissipation theorem in a nonequilibrium steady state”
T. Speck and U. Seifert, *Europhys. Lett.* **74**, 391 (2006)
- “Thermodynamics of a Colloidal Particle in a Time-Dependent Nonharmonic Potential”
V. Blickle, T. Speck, L. Helden, U. Seifert, and C. Bechinger, *Phys. Rev. Lett.* **96**, 070603 (2006)

- “Integral fluctuation theorem for the housekeeping heat”
T. Speck and U. Seifert, *J. Phys. A: Math. Gen.* **38**, L581 (2005)
- “Experimental Test of the Fluctuation Theorem for a Driven Two-Level System with Time-Dependent Rates”
S. Schuler, T. Speck, C. Tietz, J. Wrachtrup, and U. Seifert, *Phys. Rev. Lett.* **94**, 180602 (2005)

2 Dynamics

2.1 Introduction

The principal difference between a system in equilibrium with a large heat reservoir and a system driven into nonequilibrium is dynamics. In equilibrium, the probability to find the system in a specific configuration, called the *microstate*, is solely determined by the energy associated with this microstate. This is achieved through the Gibbs-Boltzmann distribution, the basic relation of equilibrium statistical mechanics. Quite in contrast, nonequilibrium systems must be characterized through their dynamics. Consequentially, in our approach the basic equation

$$\partial_t \psi(t) = \hat{L}(t) \psi(t) \quad (2.1)$$

describes the time evolution of a, by now abstract, *state* $\psi(t)$ which is governed by the operator \hat{L} . Throughout the thesis, we differentiate between the state of the system containing global information and the microstate the system actually occupies. The evolution operator may depend on time but it is independent of ψ itself and hence (2.1) is a linear equation. The status of this equation can be compared to the Schrödinger equation in quantum mechanics.

2.2 State space

2.2.1 Continuous state space

For continuous systems, we aim to describe the dynamics of d degrees of freedom which we collect in the microstate $x \equiv \{x^1, \dots, x^d\}$. The set of all microstates forms the state space. The state function $\psi(x, t)$ is nonnegative everywhere and normalized,

$$\psi(x, t) \geq 0, \quad \int dx \psi(x, t) = 1. \quad (2.2)$$

We distinguish between:

Deterministic dynamics

In the case of deterministic dynamics of an isolated system, the time evolution operator becomes the Liouville operator which can be stated as $\hat{L} \cdot = \{H, \cdot\}$, where H is the system's

Hamiltonian and $\{\cdot, \cdot\}$ denote the Poisson brackets [54]. Hence, \hat{L} is a differential operator. The state space is the phase space of the system and the state function $\psi(x, t)$ corresponds to the phase space density.

For driven systems some constraints, e.g., in order to keep the kinetic energy fixed, have to be imposed. This is achieved through so called thermostats [21]. Although these systems could be included in proofs of nonequilibrium relations based on (2.1), we will not investigate thermostated systems in detail.

Stochastic dynamics

If a small system is coupled to a heat bath then one possibility to tackle the evolution of the small system is to regard its dynamics as stochastic. The state $\psi(x, t)$ then emerges as the probability density of a certain microstate and we simply call $\psi(x, t)$ the distribution function. This kind of dynamics is often called Brownian dynamics or motion. The picture behind this name is that of particles immersed in a fluid undergoing a “zig-zag” motion. However, and although we will use single colloidal particles both as motivation and to demonstrate our theory, the methods we will develop are much more powerful and not restricted to particles. The operator \hat{L} is again a differential operator but takes into account the interactions with the heat bath explicitly. For general stochastic processes, the evolution operator is called the Fokker-Planck operator [55]. However, for the overdamped dynamics of colloidal particles and polymers it is more common to call it the Smoluchowski operator [56, 57]. The set of all microstates in this case forms the *configuration space* and a single microstate is also called a configuration.

2.2.2 Discrete state space

Stochastic dynamics can also be formulated on discrete state spaces where the system changes its microstate with a rate $w(x \rightarrow x')$. This is in a way more abstract since no heat bath is required as the source of randomness. The state $\psi(x, t)$ is now the probability of the microstate labeled x and it is subject to the constraints

$$\psi(x, t) \geq 0, \quad \sum_x \psi(x, t) = 1.$$

The dynamics are governed by the *master equation*

$$\partial_t \psi(x, t) = \sum_{x'} L_{xx'} \psi(x', t), \quad L_{xx'} = w(x' \rightarrow x) - \delta_{xx'} \sum_{x''} w(x \rightarrow x''), \quad (2.3)$$

where the entries $L_{xx'}$ of the stochastic matrix are determined by the hopping rates with $w(x \rightarrow x) = 0$. The first term quantifies the “gain” and the second term the “loss”.

2.3 Stochastic processes

When the system evolves in time, the microstate changes randomly. The chronological sequence of microstates

$$X \equiv \{x(t) : t_0 \leq t \leq t_1\} \quad (2.4)$$

is then called a *trajectory*. On the level of the evolution of the state ψ , stochastic processes can be classified as either Markovian or non-Markovian.

2.3.1 Markov processes

For any stochastic process there exists a *propagator* $\hat{U}(t, t')$ which propagates an initial state $\psi(t')$

$$\psi(t) = \hat{U}(t|t')\psi(t') \quad (2.5)$$

towards a later time $t \geq t'$ with $\hat{U}(t|t) = \mathbf{1}$. The propagator determines the transition probability through

$$P(x, t|x', t') = \hat{U}(t|t')\delta(x - x').$$

The stochastic process is called a *Markov process* if its propagators form a semi-group with property

$$\hat{U}(t|t') = \hat{U}(t|t'')\hat{U}(t''|t'). \quad (t \geq t'' \geq t') \quad (2.6)$$

In the present context, this equation is known as the Chapman-Kolmogorov equation. The time evolution operator is then the infinitesimal generator of the semi-group,

$$\hat{L}(t) = \left. \frac{\partial}{\partial t'} \hat{U}(t'|t) \right|_{t'=t}. \quad (2.7)$$

The most important property of Markov processes is that they have no memory. Using the semi-group property (2.6), we find as equation of motion for the propagators

$$\partial_t \hat{U}(t|t') = \partial_t \hat{U}(t|t'')\hat{U}(t''|t') \Big|_{t''=t} = \hat{L}(t)\hat{U}(t|t'),$$

which does not depend on times before t' . Hence, all informations about the process is already contained in the generator \hat{L} . In particular, we can construct the joint two-point distribution

$$\psi^{(2)}(x, t; x', t') = P(x, t|x', t')\psi(x', t')$$

and following the same route, higher n -point distributions can be constructed from the transition probability alone.

The basic properties of the operator \hat{L} can already be discussed in a general way even though we do not know it explicitly. To this end we realize that the states $\{\psi\}$ form a real vector space with 1-norm.¹ Its dual space is the vector space of linear functionals

$$\bar{\psi}[\psi] \equiv \langle \bar{\psi}, \psi \rangle \mapsto \mathbb{R}$$

mapping the state ψ to a real number. We introduce the adjoint operator through

$$\langle \bar{\psi}, \hat{L}\psi \rangle = \langle \hat{L}^\dagger \bar{\psi}, \psi \rangle.$$

A bi-orthonormal set $\{\bar{\varphi}_k, \varphi_k\}$ must fulfill both the orthonormal and the completeness condition,

$$\langle \bar{\varphi}_k, \varphi_l \rangle = \delta_{kl}, \quad \sum_{k=0}^{\infty} \bar{\varphi}_k(x) \varphi_k(x') = \delta(x - x'),$$

respectively. For discrete systems, the δ -function in the last equation should be replaced by the Kronecker symbol $\delta_{xx'}$.

We can map a system with continuous configuration space onto a discrete state space through expanding a state into the series

$$\psi(t) = \sum_{k=0}^n c_k(t) \varphi_k$$

with n coefficients $c_k(t) = \langle \bar{\varphi}_k, \psi(t) \rangle$. An operator is then represented by a $n \times n$ matrix,

$$L_{kl}(t) = \langle \bar{\varphi}_k, \hat{L}(t) \varphi_l \rangle.$$

Although the continuous system corresponds in principle to an infinite-dimensional state space, we assume that it is well approximated by a large but finite number n . This allows us to make the following statements. For a constant operator \hat{L} , we define its eigenstates through

$$\hat{L}\varphi_k = -\lambda_k \varphi_k$$

with sorted eigenvalues $\lambda_0 < |\lambda_1| \leq |\lambda_2| \leq \dots$. The lowest eigenvalue $\lambda_0 = 0$ is unique and corresponds to the stationary state. This property is a consequence of the Perron-Frobenius theorem [58]. Higher eigenvalues can be complex numbers but with positive real part such that the corresponding eigenstates relax on time scales $(\Re \lambda_k)^{-1}$ and therefore $\psi(t)$ approaches the stationary state φ_0 in the long-time limit. The smallest nonzero eigenvalue λ_1 defines the *relaxation time* $\tau \equiv 1/|\lambda_1|$. If we exclude the stationary state

¹We choose the 1-norm because it is compatible with the normalization condition (2.2).

then we can assume that the inverse operator \hat{L}^{-1} exists. Further, the inverse is bounded with operator norm

$$\|\hat{L}^{-1}\| \equiv \sup_{\|\psi\|=1} \|\hat{L}^{-1}\psi\|.$$

Since we have chosen the 1-norm, we can calculate the norm easily in the diagonal matrix representation $L_{kl}^{-1} = -(1/\lambda_k)\delta_{kl}$, leading to

$$\|\hat{L}^{-1}\| = \max_l \sum_{k=1} |L_{kl}^{-1}| = \tau.$$

In appendix A.3, the eigenvalue spectrum of a simple operator \hat{L} is calculated explicitly. In section A.1, the existence and boundness of \hat{L}^{-1} are the crucial ingredients for a time scale separation.

2.3.2 Non-Markovian processes

Markov processes constitute a special, albeit the most studied, class of stochastic processes. In general processes, the transition probability depends on the history before t' and the propagators do not form a semi-group. There is no general theory for these non-Markovian processes. However, in section 4.4 we will show that in some cases the evolution equation (2.1) can be generalized even to non-Markovian processes.

2.4 Overdamped continuous dynamics

The main focus in this thesis lies on soft matter systems composed of N particles at positions \mathbf{r}_k . We will neglect inertial effects which are only important at short time scales, typically less than 10^{-7} s in soft matter systems. The microstate $x = (\mathbf{r}_1, \dots, \mathbf{r}_N)$ therefore is the collection of all particle positions. Soft matter systems like colloidal particles and polymers are usually immersed in an incompressible fluid acting as a heat reservoir with well-defined temperature T . In addition, the fluid may flow according to an imposed velocity profile $\mathbf{u}(\mathbf{r})$ caused by external stirring.

2.4.1 Notation

We first fix the notation used throughout the thesis and, in particular, in the appendix. To ease the notational overhead, we will use the following operations on vectors $\mathbf{a} = (a_k)$ and matrices $A = (A_{kl})$: The dot product contracts vectors

$$\mathbf{a} \cdot \mathbf{b} \equiv \sum_k a_k b_k, \quad \mathbf{a} \cdot A \equiv \sum_k a_k A_{kl} = A^T \mathbf{a},$$

and the double-dot product contracts matrices

$$\mathbf{A} : \mathbf{B} \equiv \sum_{kl} A_{kl} B_{lk} = \text{Tr}(\mathbf{A}\mathbf{B}).$$

For two matrices, the double-dot product is a shortcut for the trace of the matrix product. The superscript T denotes the transposed matrix. Indices as in \mathbf{r}_k indicate the particle number. We follow the convention to sum over same indices.

2.4.2 Smoluchowski equation

The time evolution of the probability density $\psi(x, t)$ is governed by the Smoluchowski equation [56, 57]

$$\partial_t \psi + \nabla_k \cdot (\mathbf{v}_k \psi) = 0. \quad (2.8)$$

Equation (2.8) is written in the form of a continuity equation in order to preserve probability which is demanded by the normalization constraint (2.2). The Smoluchowski equation balances the local change of the probability with the divergence of the current $\mathbf{v}_k \psi$. Any deviation of the velocity

$$\mathbf{v}_k = \mathbf{u}(\mathbf{r}_k) + \mu_{kl} \mathbf{F}_l = \mathbf{u}(\mathbf{r}_k) + \mu_{kl} (-\nabla_l U + \mathbf{f}_l - T \nabla_l \ln \psi) \quad (2.9)$$

from the imposed flow profile $\mathbf{u}(\mathbf{r})$ has to be caused by a force \mathbf{F}_l exerted on the l^{th} particle. This force may lead to a distortion of the flow which couples back to the other particles. These hydrodynamic interactions are taken into account through the symmetric mobility tensors $\mu_{kl}(x)$. The mobility tensors are positive semidefinite,

$$\mathbf{r}_k \cdot \mu_{kl} \mathbf{r}_l \geq 0, \quad (2.10)$$

for any vectors \mathbf{r}_k . Moreover, we assume that the inverse tensors μ_{km}^{-1} defined through

$$\mu_{km}^{-1} \mu_{ml} = \mathbf{1} \delta_{kl}$$

exist.

The force \mathbf{F}_k stems from three sources. First, the gradient of the potential energy $U(x)$. This potential energy can be split into an inner energy due to interactions and the contribution of external potentials. Second, the system can be driven through nonconservative forces \mathbf{f}_k which cannot be written as gradient of a potential. And third, we have to take into account a ‘‘thermodynamic’’ force arising from the stochastic interactions between system and the surrounding fluid. In equilibrium, i.e., in the absence of external flows and nonconservative forces, detailed balance must hold which amounts to $\mathbf{v}_k = 0$. The thermodynamic force then ensures that

$$\nabla_k (U + T \ln \psi) = 0$$

leads to the correct equilibrium distribution $\psi_{\text{eq}} \sim e^{-U/T}$, which is of course the Gibbs-Boltzmann distribution.

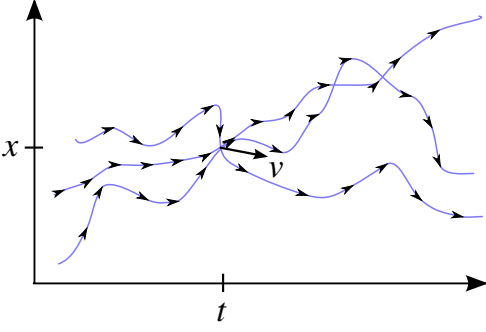


Figure 2.1: The local mean velocity v as determined in (2.12). It is the stochastic particle velocity \dot{x} averaged over the subset of trajectories passing through a certain microstate, here x in one dimension.

2.4.3 Local mean velocity

The velocity \mathbf{v}_k defined in (2.9) has an immediate physical meaning as a local average. In equilibrium, the joint probability $\Psi_0(x, x_p) = \varphi_{\text{MB}}(x_p)\psi_{\text{eq}}(x)$ of particle positions and momenta $x_p \equiv (\mathbf{p}_1, \dots, \mathbf{p}_N)$ is the product of the Maxwell-Boltzmann distribution (A.19) and the equilibrium distribution ψ_{eq} . If we drive the systems, position and momentum become correlated. In appendix A.5, we calculate the deviation Ψ_1 from the equilibrium case in the overdamped limit. With the operator expression (A.24), it can be written as

$$\Psi_1 \simeq -\hat{L}_0^{-1}\hat{L}_1\Psi_0 = T^{-1}\mathbf{p}_k \cdot \mathbf{v}_k\Psi_0.$$

The joint probability therefore is

$$\Psi(x, x_p, t) = [1 + T^{-1}\mathbf{p}_k \cdot \mathbf{v}_k]\Psi_0(x, x_p, t). \quad (2.11)$$

We define the mean local velocity as the conditional mean

$$\langle \dot{\mathbf{r}}_k(t)|x \rangle = \frac{\int dx_p (\mathbf{p}_k/m)\Psi(x, x_p, t)}{\psi(x, t)} = \mathbf{v}_k(x, t), \quad (2.12)$$

which reduces to \mathbf{v}_k after inserting (2.11) and carrying out the Gaussian integration over the momenta. In words, the local mean velocity is the average of the stochastic velocity $\dot{\mathbf{r}}_k$ over the subset of trajectories passing through a given microstate x at time t .

2.4.4 Langevin equation

A description complementary to the Smoluchowski equation on the level of a single trajectory is the Langevin equation [59]

$$\dot{\mathbf{r}}_k = \mathbf{u}(\mathbf{r}_k) + \mu_{kl}(-\nabla_l U + \mathbf{f}_l) + \mathbf{d}_k^\alpha + \zeta_k. \quad (2.13)$$

The first two terms are the external flow and the direct forces exerted on the k^{th} particle, respectively. The noise term ζ_k models the thermal environment with short-ranged correlations

$$\langle \zeta_k(t)\zeta_l^T(t') \rangle = 2D_{kl}\delta(t - t') \quad (2.14)$$

and zero mean.

The term \mathbf{d}_k^α takes into account an additional drift caused by the hydrodynamic interactions. We have to include it in order for the system to reach the correct equilibrium state in the absence of driving forces and flows [60]. In appendix A.2, the Fokker-Planck equation is derived. Together with the moments from A.4, we can rewrite the Fokker-Planck equation in form of the continuity equation

$$\partial_t \psi + \nabla_k \cdot [(\mathbf{d}_k + \alpha \mathbf{G}_{lm} : \nabla_m \mathbf{G}_{kl} - \nabla_l \cdot \mathbf{D}_{kl} - \mathbf{D}_{kl} \nabla_l \ln \psi) \psi] = 0.$$

Hence, for the parenthesis to coincide with the velocity (2.9), we make the two identifications

$$\mathbf{D}_{kl} = T \mu_{kl}, \quad (2.15)$$

$$\mathbf{d}_k^\alpha = \nabla_l \cdot \mathbf{D}_{kl} - \alpha \mathbf{G}_{lm} : \nabla_m \mathbf{G}_{kl}. \quad (\mathbf{D}_{kl} = \mathbf{G}_{km} \mathbf{G}_{ml}) \quad (2.16)$$

The last equation quantifies the additional drift. It vanishes for spatially uniform mobility tensors. As detailed in A.4, it depends on our interpretation of multiplicative noise through the parameter α . Equation (2.15) is the famous Einstein relation. It relates the short-time diffusion tensors

$$\mathbf{D}_{kl}(\mathbf{r}) \equiv \lim_{\varepsilon \rightarrow 0} \frac{1}{2\varepsilon} \langle [\mathbf{r}_k(t + \varepsilon) - \mathbf{r}_k][\mathbf{r}_l(t + \varepsilon) - \mathbf{r}_l]^T \rangle$$

with the mobility tensors through the temperature T of the heat bath.

The thus introduced Smoluchowski and Langevin equations define the dynamics of the systems we aim to study. Other evolution equations are thinkable for interacting many-body systems, e.g., on the level of the density [61, 62]. However, the investigation of these equations is beyond the scope of this thesis and remains for future study. In the next chapter, we will introduce a thermodynamical description independent of the underlying dynamics leading to expressions for work and heat. In chapter 4, the Smoluchowski equation will appear in evolution equations for the probability distribution of work and heat. The Langevin equation will become crucial in the linear response theory developed in chapter 6.

3 Thermodynamics of Small Systems

3.1 Introduction

The idea that even stochastic dynamics like the Brownian motion of a particle must conserve energy when coupled to a heat bath could have been formulated back in the days of Einstein. Somewhat surprisingly, as late as in 1997 Sekimoto was the first to realize this fact and to formulate the first law of thermodynamics along a single stochastic trajectory [63, 64] using a one-dimensional Langevin equation. In this chapter, we will give a coherent reformulation of thermodynamic notions like work and heat along a single trajectory for general driven systems. We will then discuss the concept of a trajectory-dependent entropy arising in this context. Furthermore, the role of nonequilibrium steady states is elucidated and we attempt the construction of a steady state thermodynamics.

3.2 Work and heat

Every good theory starts with just a few axioms from which anything else can be deduced. In our case, we will require the following:

- (A1) *Work* is the *energy* change of the *system* caused *externally*.
- (A2) The first law of thermodynamics holds, i.e., *energy* is conserved along single trajectories as well as mean values.

These axioms regard the energetics of the system and should hold universally independent of the underlying dynamics. They contain notions which we have to explain in more detail. We consider a small *system* governed by overdamped motion. Suppose the potential *energy* of the system $U(x; \gamma)$ depends on a parameter γ which can be controlled with high precision. The system is manipulated *externally* through varying γ according to some prescribed protocol $\Gamma \equiv \{\gamma(t) : t_0 \leq t \leq t_1\}$. The infinitesimal change of the energy is

$$dU = \frac{\partial U}{\partial \gamma} d\gamma + (\nabla_k U) \cdot d\mathbf{r}_k$$

employing the chain rule. We identify as work the energy change

$$dW \equiv \frac{\partial U}{\partial \gamma} d\gamma \tag{3.1}$$

caused by some outer agent. In particular, it is not the mechanical work spent by the conservative force $-\nabla U$ arising from the potential.

Following the first law of thermodynamics, the heat dissipated is then

$$\bar{d}Q \equiv -(dU - \bar{d}W) = -(\nabla_k U) \cdot d\mathbf{r}_k. \quad (3.2)$$

The sign of heat and work is convention and it is reversed if we compare it to classical thermodynamics. The heat is positive for energy dissipated into the reservoir and negative for energy which is extracted from the system's surroundings whereas the work is positive if put into the system. Both heat and work are process quantities, i.e., they are not exact differentials and depend on the whole path Γ in parameter space and the trajectory $x(t)$ through configuration space. Small changes are therefore represented by \bar{d} instead of d which is reserved for total differentials.

In classical thermodynamics, the internal energy is a function of a few extensive quantities like volume and the particle number. In the case of small systems, these few observables are replaced by the relevant degrees of freedom x . To see this connection, we identify the parameter $\gamma = V$ with the confining volume of a gas which we control, e.g., through moving a piston. With the pressure $p = -\partial U / \partial V$, equation (3.1) then yields the well-known expression $\bar{d}W = -pdV$ for the work. In contrast to macroscopic systems, the dependence on the relevant degrees of freedom means that if the dynamics of the system is stochastic then work and heat also will acquire a stochastic nature. It is then clear that their actual values will depend on the temporal coarse-graining of the trajectory, i.e., our capability to observe it experimentally.

From the definitions (3.1) and (3.2) we can deduce the following cases immediately. If the parameter γ is constant then no work is performed. If the system is isolated then the accessible microstates in configuration space $U(x; \gamma) = E(\gamma)$ have the same energy and hence no heat is dissipated. If γ is constant but the system is coupled to a heat reservoir then heat exchange takes place. It is zero on average if the system is in equilibrium with the bath.

3.2.1 Quasi-static processes

We drive the system from an initial state A to a final state B . We change the parameter $\Gamma : \gamma_A \mapsto \gamma_B$ quasi-statically, i.e., so slowly that the system passes through a sequence of consecutive equilibrium states with Gibbs-Boltzmann distribution

$$\psi_{\text{eq}}(x; \gamma) = \frac{1}{\mathcal{Z}(\gamma)} e^{-U(x; \gamma)/T}, \quad (3.3)$$

where the partition function $\mathcal{Z}(\gamma)$ depends on the actual value of the control parameter. Following (3.1), the mean work spent in such a transition

$$\langle W \rangle = \int_{\gamma_A}^{\gamma_B} d\gamma \langle \partial_\gamma U \rangle = \int_{\gamma_A}^{\gamma_B} d\gamma \partial_\gamma [-T \ln \mathcal{Z}(\gamma)] = \mathcal{F}(\gamma_B) - \mathcal{F}(\gamma_A) \equiv \Delta \mathcal{F}$$

equals the change of free energy $\Delta\mathcal{F}$ independent of the path through parameter space, where the equilibrium free energy is defined as $\mathcal{F}(\gamma) \equiv -T \ln \mathcal{Z}(\gamma)$. This shows that the definition of the work (3.1) is compatible with the statements obtained from equilibrium statistical mechanics [2].

3.2.2 An experimental study: The case of a single colloidal particle

Let us look at a specific system which we studied experimentally. In this experiment, particle trajectories were determined using total internal reflection microscopy (TIRM), where a single colloidal particle is illuminated under evanescent field conditions. This field is created by total internal reflection of a laser beam at a glass–water interface. The scattered intensity of a bead near the interface is proportional to $\exp(-\zeta x)$, with $\zeta^{-1} \simeq 200$ nm the decay length of the evanescent field and x the particle–wall distance [65]. Measuring the scattered intensity of a fluctuating Brownian particle as a function of time thus yields its vertical position with a spatial resolution of about 5 nm.

To drive the colloidal particle between two equilibrium states, it was subjected to the light pressure of an optical tweezers incident from below while a tightly focused second laser beam was directed vertically from the top, confining the particle motion to an one-dimensional trajectory in x -direction (cf. figure 3.1). The control parameter in this experiment is the intensity of the first laser. It was modulated according to a time-dependent symmetric protocol $\gamma(t) = \gamma(t_s - t)$ in the interval $0 \leq t \leq t_s$, where t_s is the pulse duration. To ensure that the system is out of equilibrium, t_s must be smaller than the particle relaxation time.

The total potential in which the particle is moving is given by [65]

$$U(x; \gamma) = A_0 \exp(-\kappa x) + B_0 x + C_0 \gamma x \quad (3.4)$$

with four parameters A_0 , κ , B_0 , and C_0 . The first term describes the double-layer interaction between the negatively charged colloidal particle and the likely charged wall with A_0 depending on the corresponding surface charges and κ^{-1} the Debye screening length, which depends on the salt concentration in the fluid. The second term accounts for the

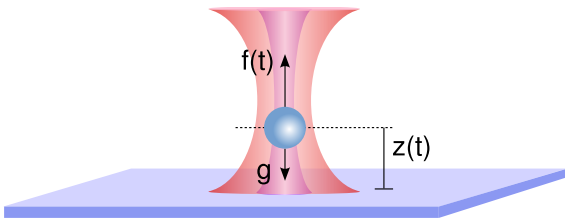


Figure 3.1: Experimental setup. A polystyrene bead in aqueous solution is moving above a glass surface. A tightly focused laser beam confines the motion of the bead to one dimension perpendicular to the surface. A second, defocused optical tweezers drives the particle by exerting a force $f(t)$ counterbalancing the gravitational force g .

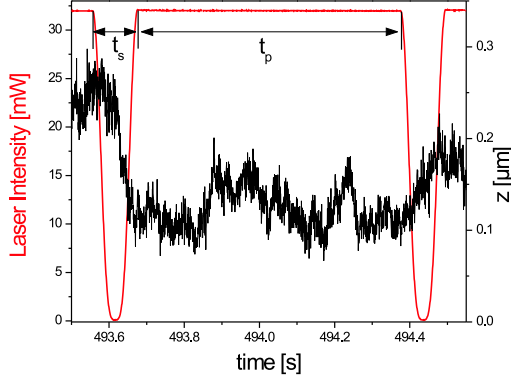


Figure 3.2: Measured tweezers intensity $\gamma(t)$ and particle trajectory $x(t)$. During the first pulse the particle is pressed towards the surface. During the second pulse thermal fluctuations support the particle and it is able to move away from the wall. Hence the applied work is positive for the first pulse and negative for the second. The pause t_p between two consecutive pulses of duration t_s must be longer than the particle relaxation time to guarantee equilibration of the system.

weight of the particle and the additionally exerted light pressure from the upper tweezers, which both depend linearly on the particle distance x [66]. The last term considers the time-dependent optical forces induced by the lower tweezers. Through measuring the equilibrium distribution $\psi_{\text{eq}}(x)$ of the particle position, the potential up to an irrelevant constant is determined as

$$U(x) = -T \ln \psi_{\text{eq}}(x),$$

from which the parameters in (3.4) are obtained.

Integration of (3.1) along a single trajectory $x(t)$ leads to the work functional

$$W = \int_0^{t_s} dt \frac{\partial U(x(t); \gamma(t))}{\partial \gamma} \dot{\gamma}(t) = C_0 \Delta t \sum_n \dot{\gamma}(t_n) x(t_n), \quad (3.5)$$

where we have inserted the potential (3.4). The right hand side of equation (3.5) accounts for the discrete sampling of the particle trajectory during our experiments with rate $(\Delta t)^{-1}$ at times $t_n = n\Delta t$. In figure 3.2, the sampled trajectory is shown with two pulses, one pulse with a positive work and the other leading to negative work supported by thermal fluctuations.

We want to test experimentally to which precision energy conservation of the particle on its trajectory is maintained, thus demonstrating the interplay of applied work and

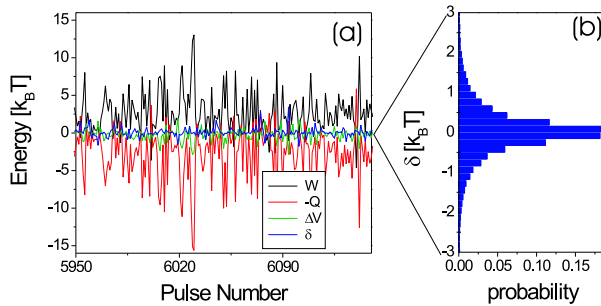


Figure 3.3: Experimental demonstration of the first law of thermodynamics along a single trajectory. The stochastic quantities W , $-Q$, and ΔU for about 100 periods of the protocol $\gamma(t)$ are shown. (b) Distribution histogram of $\delta = W - Q - \Delta U$, the experimentally observed “deviation” from the first law.

exchanged heat when the system is non-adiabatically driven. Therefore, in addition to the work W exerted on the particle we need to determine its heat exchange Q with the environment. Because the velocity autocorrelation of a Brownian particle decays on a timescale of some 10 ns, the velocity

$$\bar{\dot{x}}(t_n) = \frac{1}{\Delta t} \int_{t_n}^{t_{n+1}} dt \dot{x}(t)$$

determined from a trajectory measured with sample frequency 2 kHz is not identical to the instant particle velocity \dot{x} . However, since $\partial U/\partial x$ varies on a timescale much larger than Δt , the heat along a single trajectory $x(t)$ can be written as

$$\begin{aligned} Q &= - \int_0^{t_s} dt \frac{\partial U(x(t); \gamma(t))}{\partial x} \dot{x}(t) = - \sum_n \frac{\partial U(x(t_n); \gamma(t_n))}{\partial x} \int_{t_n}^{t_{n+1}} dt \dot{x}(t) \\ &= -\Delta t \sum_n \frac{\partial U(x(t_n); \gamma(t_n))}{\partial x} \bar{\dot{x}}(t_n). \end{aligned} \quad (3.6)$$

Introducing $\Delta U \equiv U(x(t_s); \gamma(t_s)) - U(x(0); \gamma(0))$, we finally obtain a stochastic version

$$W - Q - \Delta U = 0$$

of the first law of thermodynamics. Figure 3.3(a) shows work W , heat Q , and change of inner energy ΔU for the trajectory of a single particle where the protocol $\gamma(t)$ was repeated about 100 times. For W and Q maximal energies of about $15 k_B T$ are observed, whereas ΔU is on the order of a few $k_B T$. Obviously, Q and W are not independent quantities. Usually trajectories resulting in a large work W are also accompanied by a large value of Q . But only when taking all three energies into consideration, the distribution of the deviation shown in figure 3.3(b) is centered around zero, having a half-width of about $0.7 k_B T$. Assuming that the three terms have the same contribution to the total error, the error of these energies is about one quarter of $k_B T$.

3.3 Work and heat in the presence of nonconservative forces and external flows

The approach to a coherent definition of work and heat for a driven transition between equilibrium states given at the start of the previous section only depends on the internal energy $U(x; \gamma)$ of the system. In order to drive the system into a nonequilibrium steady state, we must consider additional forces. These may arise from two sources: nonconservative forces $\mathbf{f}_k(x; \gamma)$ applied directly to the k^{th} particle or an external flow $\mathbf{u}(\mathbf{r}; \gamma)$. While for the nonconservative forces the applied work increment is simply $\mathbf{f}_k \cdot d\mathbf{r}_k$, the work spent by flows requires a more careful analysis.

3.3.1 An introductory example

To get an idea of how the work spent by flows should look like, we consider a very simple example. A colloidal particle at position x is trapped by optical tweezers which are moving with a constant velocity $\dot{\gamma} = u_0$. The trap strength is k and hence the potential energy is $U(x; \gamma) = (k/2)(x - \gamma)^2$. The motion of the particle neglecting hydrodynamic interactions, e.g., with a wall, is governed by the Langevin equation

$$\dot{x}(t) = -\tau^{-1}[x(t) - u_0 t] + \zeta(t), \quad (3.7)$$

where the noise $\zeta(t)$ has correlations (2.14), μ_0 is the bare mobility, and $\tau \equiv (\mu_0 k)^{-1}$ is the relaxation time. The work rate reads

$$\dot{W} = \frac{\partial U}{\partial \gamma} \dot{\gamma} = k(x - u_0 t)(-u_0).$$

Now suppose that we change to the comoving frame through $y(t) = x(t) - u_0 t$. The potential energy $U(y) = (k/2)y^2$ then becomes explicitly time-independent and following the definition (3.1), the work rate vanishes, $\dot{W} = 0$. However, physical intuition tells us that the work should really be the same in both frames. The solution to this apparent contradiction is that in the comoving frame the fluid is not resting but moving with uniform velocity $u = -u_0$. Demanding that the work is the same in any frame, we find

$$\dot{W} = k(x - u_0 t)(-u_0) = ky(-u_0) = \frac{\partial U}{\partial y} u.$$

Hence, the work rate can be expressed as force times the flow's velocity. The same can be done for the heat,

$$\dot{Q} = -\frac{\partial U}{\partial x} \dot{x} = -k(x - \gamma)\dot{x} = -ky(\dot{y} + u_0) = -\frac{\partial U}{\partial y}(\dot{y} - u),$$

which vanishes if the particle moves along with the velocity of the flow as then no heat due to friction is dissipated.

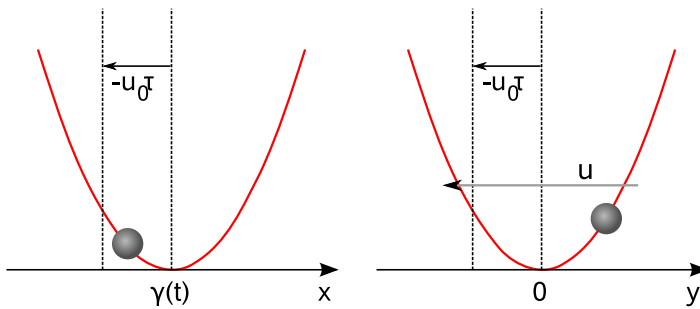


Figure 3.4: A colloidal particle is trapped by optical tweezers. In the left panel, the trap is moving with velocity $\dot{\gamma} = u_0$. In the right panel, the trap is stationary but the fluid is moving with velocity $u = -u_0$. The mean trails behind a distance $u_0 \tau$, where τ is the relaxation time.

3.3.2 General expressions for work and heat

The previous example shows that by choosing a coordinate system moving with the external flow, we can eliminate this flow in tradeoff for a time-dependent inner energy and vice versa. The work, however, must be invariant under such a change of frame. For a refinement of the expressions for work (3.1) and heat (3.2) taking into account both external flows and frame invariance, consider the convective derivative

$$\frac{DU}{Dt} \equiv \dot{\gamma} \frac{\partial U}{\partial \gamma} + \mathbf{u}(\mathbf{r}_k) \cdot \nabla_k U.$$

Suppose the particles are noninteracting and moving deterministically according to $\dot{\mathbf{r}}_k = \mathbf{u}(\mathbf{r}_k)$, i.e., in figure 3.5 they are moving along a fluid trajectory. Then the total change of energy along these trajectories becomes the work increment, $dU = dW = (DU/Dt)dt$, as no heat is dissipated. Particle–particle and particle–fluid interactions lead to dissipation through leaving the trajectory prescribed through the fluid. Adding the contribution of the nonconservative forces, the work therefore is found to be

$$dW \equiv \frac{DU}{Dt} dt + \mathbf{f}_k \cdot [d\mathbf{r}_k - \mathbf{u}(\mathbf{r}_k)dt]. \quad (3.8)$$

The new expression for the heat then follows from the first law as

$$dQ \equiv -(dU - dW) = [-\nabla_k U + \mathbf{f}_k] \cdot [d\mathbf{r}_k - \mathbf{u}(\mathbf{r}_k)dt]. \quad (3.9)$$

It is straightforward to check both that these expressions reduce to either (3.1) or (3.9) in the absence of external flow and nonconservative forces and that the work is invariant with respect to a change of frame. The deeper physical reason is that we can distinguish a resting fluid from a moving fluid through dissipation. The fluid velocity therefore appears explicitly in the expressions for work (3.8) and heat (3.9).

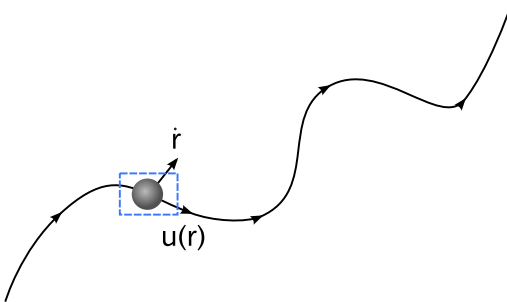


Figure 3.5: A particle at \mathbf{r} in a fluid element. The fluid element moves along the sketched trajectory. If the particle stays within the fluid element and moves with velocity $\mathbf{u}(\mathbf{r})$, no heat is dissipated and the work is the change of inner energy. However, due to interactions, the particle moves with $\dot{\mathbf{r}}$ leaving the fluid element thus leading to the dissipation of heat.

3.4 Entropy production

One cornerstone of equilibrium statistical mechanics is entropy [2]. For a system at equilibrium with a large heat reservoir, it can be written as

$$S_{\text{eq}} \equiv - \int dx \psi_{\text{eq}}(x) \ln \psi_{\text{eq}}(x)$$

based on the equilibrium probability distribution $\psi_{\text{eq}}(x)$. Seeking a generalization of the concept of entropy to driven systems on the level of a single trajectory, it has been proposed [16] to define

$$s(t) \equiv - \ln \psi(x(t), t). \quad (3.10)$$

The quantity s is, like our definitions of work and heat, a trajectory based quantity. A single stochastic trajectory $x(t)$ is parameterized by the time t . The definition (3.10) then assign a scalar value s at any time t to the trajectory $x(t)$. Given two times t_0 and t_1 , we can ask for the change of system entropy along this trajectory,

$$\Delta s \equiv s(t_1) - s(t_0) = \int_{t_0}^{t_1} dt \dot{s}(t),$$

where $\dot{s} \equiv ds/dt$. Suppose we start at t_0 in equilibrium and drive the system into another equilibrium state. If we choose t_1 large enough such that the system has been equilibrated again, we clearly have $\Delta S_{\text{eq}} = \langle \Delta s \rangle$. We therefore have a trajectory dependent expression the mean of which agrees with what we know from equilibrium statistical mechanics.

Driving the system causes energy to be dissipated in form of heat into the surroundings. This is in our case the fluid but more formally, one calls it the medium. Dissipation takes place while the system is driven but continues even after the driving has stopped as the system relaxes towards equilibrium, where the dissipated heat Q leads to an increase of medium entropy Δs_{m} . Both can be related by Clausius' famous formula

$$\Delta s_{\text{m}} = \int \frac{dQ}{T} \quad (3.11)$$

if we assume that the surrounding fluid itself is and remains in equilibrium with temperature T . At the first glance, this seems like a severe restriction of the applicability of our formalism. However, any physical realization of fluid plus system is itself embedded into an environment acting as an equilibrium super reservoir. The dissipated heat then eventually leads to a change of entropy in the super reservoir, where equation (3.11) holds. The sum

$$\Delta s_{\text{tot}} = \Delta s + \Delta s_{\text{m}}$$

thus is the total entropy change of the universe.

3.4.1 Equation of motion

The rate of change of the system entropy (3.10) is

$$\begin{aligned}\dot{s}(t) &= -\partial_t \ln \psi - [\dot{\mathbf{r}}_k - \mathbf{u}(\mathbf{r}_k)] \cdot \nabla_k \ln \psi - \mathbf{u}(\mathbf{r}_k) \cdot \nabla_k \ln \psi \\ &= \frac{Ds}{Dt} + \frac{1}{T} \mathbf{F}_k \cdot [\dot{\mathbf{r}}_k - \mathbf{u}(\mathbf{r}_k)] - \frac{1}{T} \underbrace{[-\nabla_k U + \mathbf{f}_k] \cdot [\dot{\mathbf{r}}_k - \mathbf{u}(\mathbf{r}_k)]}_{\dot{Q}=T\dot{s}_m}.\end{aligned}$$

Going from the first to the second line, we have inserted the force following from (2.9). The first term is the convective derivative of the entropy (3.10). The last term is the dissipated heat rate, see (3.9). The total entropy production rate $\dot{s}_{\text{tot}} = \dot{s} + \dot{s}_m$ therefore becomes

$$\dot{s}_{\text{tot}}(t) = [\partial_t + \mathbf{u}(\mathbf{r}_k) \cdot \nabla_k][-\ln \psi] + \frac{1}{T} [\dot{\mathbf{r}}_k - \mathbf{u}(\mathbf{r}_k)] \cdot \mathbf{F}_k. \quad (3.12)$$

This rate can be positive corresponding to a production of entropy but it can also be negative corresponding to the annihilation of entropy. In equilibrium, the rate (3.12) vanishes.

Calculating the mean total entropy production rate, we first look at the mean of the convective derivative,

$$\int dx [\partial_t \psi + \mathbf{u}(\mathbf{r}_k) \cdot \nabla_k \psi] = \partial_t \int dx \psi + \int dx \nabla_k \cdot [\mathbf{u}(\mathbf{r}_k) \psi] = 0.$$

The first term vanishes due to the conservation of probability. The second term vanishes because we look at (i) incompressible fluids with $\nabla \cdot \mathbf{u} = 0$ and (ii) neglect boundary terms. The mean total entropy production rate then becomes

$$T \langle \dot{s}_{\text{tot}} \rangle = \langle [\dot{\mathbf{r}}_k - \mathbf{u}(\mathbf{r}_k)] \cdot \mathbf{F}_k \rangle = \langle [\mathbf{v}_k - \mathbf{u}(\mathbf{r}_k)] \cdot \mathbf{F}_k \rangle = \langle \mathbf{F}_k \cdot \mu_{kl} \mathbf{F}_l \rangle \geq 0 \quad (3.13)$$

following equation (2.9). It is always nonnegative because the mobility tensors are positive semidefinite (2.10). The calculation of the mean is done in two steps: first we average over all trajectories passing through a given microstate x which results in replacing the actual velocity by the local mean velocity. We then average with the probability distribution $\psi(x, t)$ leading to (3.13). The fact that $\langle \dot{s}_{\text{tot}} \rangle$ is nonnegative can be regarded as a manifestation of the second law of thermodynamics. The equal sign holds in equilibrium only.

3.4.2 Dissipation function

In a phenomenological approach to the dynamics of polymers and colloidal suspensions, one starts from the total dissipation rate functional [57]

$$K[\psi, \{\mathbf{v}_k\}] \equiv \langle \mathcal{W} \rangle + \dot{\mathcal{A}} - \dot{\mathcal{W}}_f, \quad (3.14)$$

where we regard the distribution function and the local mean velocities as independent variables. This functional captures the three sources of dissipation. First, the nonnegative *dissipation function*

$$\mathcal{W}(x, t) \equiv \frac{1}{2} [\mathbf{v}_k - \mathbf{u}(\mathbf{r}_k)] \cdot \mu_{kl}^{-1} [\mathbf{v}_l - \mathbf{u}(\mathbf{r}_l)] \geq 0 \quad (3.15)$$

takes into account dissipation due to friction. Second, relaxation of the system is related to a dynamical “free energy”

$$\mathcal{A}(t) \equiv \int dx \psi [U + T \ln \psi] = \langle U \rangle - TS.$$

And third, the mean work rate done by the nonconservative forces is

$$\dot{\mathcal{W}}_f(t) \equiv \langle \dot{\mathbf{r}}_k \cdot \mathbf{f}_k \rangle = \langle \mathbf{v}_k \cdot \mathbf{f}_k \rangle = \int dx \psi \mathbf{v}_k \cdot \mathbf{f}_k.$$

The mean is again evaluated in two steps, first over trajectories passing a certain microstate and then over all microstates.

The time derivative of the dynamical free energy becomes

$$\begin{aligned} \dot{\mathcal{A}} &= \int dx (\partial_t \psi) [U + T \ln \psi] = - \int dx [U + T \ln \psi] \nabla_k \cdot (\mathbf{v}_k \psi) \\ &= \int dx \psi \mathbf{v}_k \cdot \nabla_k [U + T \ln \psi] \end{aligned}$$

after inserting the continuity equation (2.8) and one integration by parts where we neglect the boundary terms. Putting everything together, we obtain

$$K = \int dx \psi \left\{ \frac{1}{2} [\mathbf{v}_k - \mathbf{u}(\mathbf{r}_k)] \cdot \mu_{kl}^{-1} [\mathbf{v}_l - \mathbf{u}(\mathbf{r}_l)] - \mathbf{v}_k \cdot [-\nabla_k U + \mathbf{f}_k - T \nabla_k \ln \psi] \right\}.$$

Remembering that we regard the velocities as independent, minimization of the functional (3.14) amounts to

$$\frac{\partial K}{\partial \mathbf{v}_k} = \int dx \psi \left\{ \mu_{kl}^{-1} [\mathbf{v}_l - \mathbf{u}(\mathbf{r}_l)] - \mathbf{F}_k \right\} \stackrel{!}{=} 0,$$

leading for distributions $\psi(x, t) > 0$ to the dynamics (2.9). Hence, the dynamics which minimizes (3.14) implies that the total entropy production rate (3.13) equals two times the dissipation function, $T \langle \dot{s}_{\text{tot}} \rangle = 2 \langle \mathcal{W} \rangle$.

3.5 Steady state thermodynamics

In the definition of the entropy (3.10), the actual probability distribution $\psi(x, t)$ enters. In contrast, work (3.8) and heat (3.9) are defined on the basis of energy, nonconservative force, and external flow only. Among the accessible states, the steady states play a prominent role. We thus attempt a description in terms of transitions between nonequilibrium steady states characterized by the external control parameter γ in analogy to transitions between equilibrium states. The term *steady state thermodynamics* has been coined for a phenomenological theory [36, 67] promoting the splitting of the heat into the housekeeping and the excess heat, a concept which we will also use.

In contrast to equilibrium which is determined by the energy alone, a nonequilibrium steady state is described by two quantities. First, the stationary distribution which we write as

$$\psi_s(x; \gamma) = e^{-\Phi(x; \gamma)} \quad (3.16)$$

introducing the pseudo-“potential” $\Phi(x; \gamma)$ in analogy to the Gibbs-Boltzmann distribution (3.3). Second, the stationary probability distribution $\psi_s(x; \gamma)$ leads to a local mean velocity (2.9) reading

$$\mathbf{v}_k^s(x; \gamma) = \mathbf{u}(\mathbf{r}_k; \gamma) + \mu_{kl}[-\nabla_l U(x; \gamma) + \mathbf{f}_l(x; \gamma) + T \nabla_l \Phi(x; \gamma)].$$

With these two quantities, we split the total heat rate (3.9)

$$\dot{Q} = [\mathbf{v}_k^s - \mathbf{u}(\mathbf{r}_k)] \cdot \mu_{kl}^{-1}[\dot{\mathbf{r}}_l - \mathbf{u}(\mathbf{r}_l)] + T[\dot{\gamma} \partial_\gamma + \mathbf{u}(\mathbf{r}_k) \cdot \nabla_k] \Phi - T \frac{d\Phi}{dt} \quad (3.17)$$

into three terms. The structure we thus obtain is similar to the splitting of the entropy (3.12). It involves, however, the stationary distribution $\psi_s(x; \gamma)$ belonging to the current value γ of the control parameter instead of the actual distribution $\psi(x, t)$.

From (3.17) we define, first, the *housekeeping heat* with rate

$$\dot{Q}_{\text{hk}} \equiv [\mathbf{v}_k^s - \mathbf{u}(\mathbf{r}_k)] \cdot \mu_{kl}^{-1}[\dot{\mathbf{r}}_l - \mathbf{u}(\mathbf{r}_l)] + T \mathbf{u}(\mathbf{r}_k) \cdot \nabla_k \Phi. \quad (3.18)$$

It quantifies the heat which is dissipated in response to the work put into the system just to keep it in a nonequilibrium steady state, hence the name “housekeeping”. Further, we define the *transition functional*

$$Y[x(t); \gamma(t)] \equiv \int_{t_0}^{t_1} dt \dot{\gamma}(t) \frac{\partial \Phi}{\partial \gamma}(x(t); \gamma(t)) \quad (3.19)$$

along a specific stochastic trajectory $x(t)$. The transition functional vanishes for $\dot{\gamma} = 0$, i.e., if there is no transition. Finally, the last term in (3.17) gives rise to a pure boundary term

$\Delta\Phi \equiv \Phi(x(t_1)) - \Phi(x(t_0))$ rooted in the different stochastic initial and final microstates of the trajectory. The excess heat finally is defined as

$$Q_{\text{ex}} \equiv Q - Q_{\text{hk}} = TY - T\Delta\Phi. \quad (3.20)$$

It is the heat dissipated in a transition minus the boundary term which is always present.

If the stationary state corresponding to all values γ of the control parameter reached during a transition is equilibrium, we have $\mathbf{v}_k^s = 0$. The housekeeping heat vanishes and (3.20) becomes the first law of thermodynamics with

$$TY = W - \Delta\mathcal{F}, \quad T\Delta\Phi = \Delta U - \Delta\mathcal{F}$$

after inserting $\Phi(x; \gamma) = U(x; \gamma) - \mathcal{F}(\gamma)$.

3.6 An illustration: a dumbbell in simple shear flow

Let us finally illustrate the concepts and notions we have introduced in this chapter in the case of a simple solvable model: two particles connected by a linear spring and driven by simple shear flow in two dimensions.

The two particles are at positions $x = (\mathbf{r}_1, \mathbf{r}_2)$. The external flow is

$$\mathbf{u}(\mathbf{r}) = \dot{\epsilon} \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \mathbf{r}$$

with strain rate $\dot{\epsilon}$. The inner energy $U(\mathbf{r}) = (k/2)\mathbf{r}^2$ is a quadratic function of the particle displacement $\mathbf{r} \equiv \mathbf{r}_1 - \mathbf{r}_2 = (x, y)^T$. We neglect hydrodynamic interactions and obtain as local mean velocities

$$\mathbf{v}_{1,2} = \mathbf{u}(\mathbf{r}_{1,2}) - \mu_0 \nabla_{1,2}[U + T \ln \psi]$$

with bare mobility μ_0 . We assume an infinite system and concentrate on the relative coordinate \mathbf{r} . The relative local mean velocity thus is

$$\mathbf{v}(\mathbf{r}) \equiv \mathbf{v}_1 - \mathbf{v}_2 = \mathbf{u}(\mathbf{r}) - 2\mu_0 \nabla[U + T \ln \psi] \quad (3.21)$$

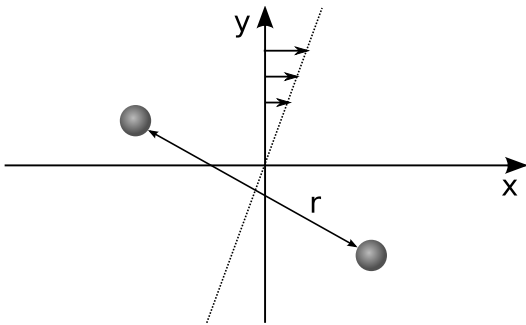


Figure 3.6: Two particles with displacement \mathbf{r} coupled by a linear force $-k\mathbf{r}$ in shear flow. The velocity profile of the simple shear flow is linear in y -direction with strain rate $\dot{\epsilon}$.

with $\nabla_1 U = \nabla U$ and $\nabla_2 U = -\nabla U$. The stationary distribution is obtained from the differential equation

$$0 = \nabla \cdot (\mathbf{v}^s \psi_s) = \nabla \cdot [\mathbf{u}(\mathbf{r}) - 2\mu_0 k \mathbf{r} - 2\mu_0 T \nabla] \psi_s.$$

The equations of motion are linear and hence the solution is a Gaussian

$$\psi_s(\mathbf{r}) = \frac{\exp[-\frac{1}{2} \mathbf{r} \cdot \mathbf{S}^{-1} \mathbf{r}]}{\sqrt{(2\pi)^2 \det \mathbf{S}}} \quad (3.22)$$

with covariance matrix [68]

$$\mathbf{S}(\gamma) = \frac{T}{k} \begin{pmatrix} 1 + 2\gamma^2 & \gamma \\ \gamma & 1 \end{pmatrix}. \quad (3.23)$$

We have defined $\gamma \equiv \dot{\epsilon} \tau / 2$, where the relaxation time is $\tau \equiv (2\mu_0 k)^{-1}$. The system is controlled by two parameters: the strength of the potential k and the strain rate $\dot{\epsilon}$. We use as the external control parameter the reduced strain rate γ . Equilibrium corresponds to $\gamma = 0$ and we can force the system into different nonequilibrium steady states by varying the strain rate $\dot{\epsilon}$.

For the work rate, we find from (3.8)

$$\dot{W} = \sum_{k=1}^2 \mathbf{u}(\mathbf{r}_k) \cdot \nabla_k U = \mathbf{u}(\mathbf{r}) \cdot \nabla U = k \dot{\epsilon} x y$$

with mean rate

$$\langle \dot{W} \rangle = k \dot{\epsilon} \langle x y \rangle = 2(T/\tau) \gamma^2,$$

where the moment $\langle x y \rangle$ can be read off the off-diagonal of the covariance matrix (3.23) directly. The local mean velocity in a steady state with respect to the flow becomes after inserting (3.22) into (3.21)

$$\mathbf{v}^s(\mathbf{r}; \gamma) - \mathbf{u}(\mathbf{r}; \gamma) = \tau^{-1} \mathbf{V}(\gamma) \mathbf{r}, \quad \mathbf{V}(\gamma) \equiv \frac{\gamma}{1 + \gamma^2} \begin{pmatrix} -\gamma & -1 \\ -1 & \gamma \end{pmatrix}.$$

With

$$\mathbf{v}_1^s - \mathbf{u}(\mathbf{r}_1) = +\frac{1}{2} [\mathbf{v}^s - \mathbf{u}(\mathbf{r})], \quad \mathbf{v}_2^s - \mathbf{u}(\mathbf{r}_2) = -\frac{1}{2} [\mathbf{v}^s - \mathbf{u}(\mathbf{r})],$$

the housekeeping heat rate (3.18) can be rewritten

$$\begin{aligned} \dot{Q}_{\text{hk}} &= \frac{1}{2\mu_0} [\mathbf{v}^s - \mathbf{u}(\mathbf{r})] \cdot [\dot{\mathbf{r}} - \mathbf{u}(\mathbf{r})] + T \mathbf{u}(\mathbf{r}) \cdot \nabla \Phi \\ &= k \mathbf{V} \mathbf{r} \cdot [\dot{\mathbf{r}} - \mathbf{u}(\mathbf{r})] + T \mathbf{u}(\mathbf{r}) \cdot \mathbf{S}^{-1} \mathbf{r} = \frac{k}{2} \frac{d}{dt} [\mathbf{V} \mathbf{r}]^2 - k \mathbf{u}(\mathbf{r}) \cdot \mathbf{V} \mathbf{r} + T \mathbf{u}(\mathbf{r}) \cdot \mathbf{S}^{-1} \mathbf{r}. \end{aligned}$$

as a function of the displacement \mathbf{r} only. The center of mass undergoes free diffusion and hence does not contribute to the housekeeping heat. When averaging with the corresponding stationary probability distribution, the first and the last term become zero. Only the second term is extensive in time and leads to the mean rate

$$\langle \dot{Q}_{\text{hk}} \rangle = k\dot{\varepsilon} \left[\gamma \langle xy \rangle + \langle y^2 \rangle \right] \frac{\gamma}{1 + \gamma^2} = \frac{2T}{\tau} \gamma^2 = \langle \dot{W} \rangle.$$

Hence, the work put into the system to maintain the nonequilibrium steady state is dissipated as the housekeeping heat as expected.

3.7 Outlook

The equations of motion for work and heat in driven systems in the theory we have developed are determined through two quantities, the stationary probability and the stationary local mean velocity. Up to now, experimental tests have been mostly restricted to a single degree of freedom. However, their natural extension to many-body systems is confronted with the problem that the stationary probability beyond linear systems as in the previous section is not known analytically. Moreover, this probability distribution is accessible neither experimentally nor through numerical simulations. Instead, one has to settle with reduced information as is contained, e.g., in the pair correlations distribution. A major challenge for the future development therefore is to find expressions and to develop approximations for work and heat incorporating these reduced quantities for complex systems.

4 Probability Distributions of Work, Heat, and Entropy

4.1 Introduction

In this chapter, we first introduce a family of exact nonequilibrium relations all holding far from equilibrium. All these relations restrict the probability distribution $p(R)$ of a stochastic trajectory functional R defined as the asymmetric part of the path action under a given map. In the second part of this chapter, we then derive various equations governing the evolution of the probability distribution $p(R)$.

4.2 Nonequilibrium fluctuation relations: Path integral formalism

In the first part of this chapter, we exploit another approach to nonequilibrium systems complementary to the dynamics defined in section 2.4. The path integral formalism [69, 70] offers another perspective which is especially appropriate for the trajectory based quantities like work and heat we have in mind. To this end, we assign a probability density $\mathcal{P}(X) > 0$ to every trajectory X . The path-independent functional measure $\mathcal{D}X$ is determined through the normalization condition

$$\int \mathcal{D}X \mathcal{P}(X) = 1 \tag{4.1}$$

when summing over all possible trajectories. It will be convenient to introduce a path action functional $\mathcal{S}(X)$ through

$$\mathcal{P}(X) \equiv \exp[-\mathcal{S}(X)].$$

The path integral introduced in (4.1) indicates continuous dynamics. The developed formalism, however, will also hold for discrete dynamics where the path integral sums over all trajectories of discrete jumps. The presentation in this section is particularly inspired by the work of Chernyak *et al* [71] and Maes [72, 73].

4.2.1 Trajectory involutions

The various nonequilibrium fluctuation relations we are going to discuss can all be derived from a general “master approach”. The only ingredient is an involution $I(X)$ acting on trajectories X with $I^2 = 1$. This means that mapping a trajectory twice will restore its original form. An involution necessarily has unity Jacobian and therefore preserves the functional measure of trajectories. The most obvious involution is the identity $I(X) = X$. Other possibilities include any permutation involutions of the microstates. More generally, for a discretized trajectory, I can be represented by a matrix. This matrix can be diagonalized with entries ± 1 on the diagonal while the determinant is equal to one.

The most studied involution is time reversal since it leads to expressions which allow for a direct physical interpretation and in the following, we will restrict our discussion to time reversal. A time reversed trajectory is defined as

$$X^* \equiv \{x(t_1 + t_0 - t) : t_0 \leq t \leq t_1\}.$$

In equilibrium, the detailed balance condition

$$P(x', t' | x, t; \gamma) \psi_{\text{eq}}(x; \gamma) = P(x, t | x', t'; \gamma) \psi_{\text{eq}}(x'; \gamma) \quad (4.2)$$

holds for all values γ of the control parameter. It is then easy to show that the probability of both original and mirrored trajectory are the same, $\mathcal{P}(X) = \mathcal{P}(X^*)$. One can therefore expect that the skew-symmetric part of the action is connected with, in general, dissipation, and particularly with the entropy production.

Stationary processes

We will first turn to stationary processes, i.e., constant γ . The crucial ingredient is (two times) the skew-symmetric part of the action under time reversal,

$$R(X) \equiv \mathcal{S}(X^*) - \mathcal{S}(X) = -R(X^*). \quad (4.3)$$

The fluctuation relations essentially exploit this skew-symmetry in the calculation of the mean of an arbitrary function $G(R)$,

$$\begin{aligned} \langle G(R) \rangle &= \int \mathcal{D}X G(R(X)) \mathcal{P}(X) \\ &= \int \mathcal{D}X G(R(X)) e^{R(X)} \mathcal{P}(X^*). \end{aligned}$$

In the second line, we replace the original trajectory X by X^* and use that the functional measure is preserved, leading to

$$\langle G(R) \rangle = \langle G(-R) e^{-R} \rangle. \quad (4.4)$$

This is our first master formula from which nonequilibrium relations can be derived by specifying $I(X)$ and the function $G(R)$. The two most important classes of nonequilibrium relations are: the integral fluctuation relations

$$\langle e^{-R} \rangle = 1 \quad (4.5)$$

for $G(R) = 1$ and the detailed fluctuation relations

$$\frac{p(-r)}{p(+r)} = e^{-r} \quad (4.6)$$

for $G(R) = \delta(r - R)$ because of $p(r = R) = \langle \delta(r - R) \rangle$. The latter relation determines universally the probability of events leading to a negative R through the probability for positive R . The function $p(r \geq 0)$, however, is a nonuniversal distribution depending on the details of the system and the process. Further relations can be generated easily, e.g., for the moments $G(R) = R^n$ we obtain

$$\langle R^n \rangle = (-1)^n \langle R^n e^{-R} \rangle.$$

Nonstationary processes

If we change the control parameter during the process then the path action $S(X; \Gamma)$ depends on both the trajectory X and the protocol Γ . We combine both paths into the vector $\mathbf{X} \equiv (X, \Gamma)$ with time reversal $\mathbf{X}^* = (X^*, \Gamma^*)$. The original protocol is called the forward processes and its time-reversal is called the backward processes. We then repeat the steps leading to equation (4.4) replacing X by \mathbf{X} . However, the average on the left hand side is now carried out for the reverse process. We make this clear by modifying the master formula (4.4) to

$$\langle G(R) \rangle = \langle G(-R) e^{-R} \rangle^*. \quad (4.7)$$

With $G(R) = e^{-R}$, the integral fluctuation relation remains (4.5) whereas the detailed fluctuation relation (4.6) becomes

$$\frac{p^*(-r)}{p(+r)} = e^{-r} \quad (4.8)$$

because we have to measure the probability distribution of R with respect to either the forward or the reverse process. A special case constitute symmetric protocols $\Gamma^* = \Gamma$ for which a distinction between forward and reverse process is not necessary anymore and therefore (4.7) reduces to (4.4).

End-point distribution

Beside choosing an involution, we have an additional freedom which can be used to tailor the functional R . To this end, we split the trajectory probability

$$\mathcal{P}(\mathbf{X}) = \mathcal{P}(\mathbf{X}|x_0)\psi_0(x_0)$$

into a conditional probability for trajectories starting in microstate x_0 and the initial probability distribution $\psi_0(x)$. We do the same for the transformed trajectory, leading to

$$\mathcal{P}(\mathbf{X}^*) = \mathcal{P}(\mathbf{X}^*|x_f)\psi_1(x_f)$$

with another function $\psi_1(x)$ specifying the probability of the final microstate x_f , which is the initial microstate of the reversed process. The skew-symmetric functional R becomes the sum

$$R = \bar{R} + \ln \frac{\psi_0(x_0)}{\psi_1(x_f)} \quad \text{with} \quad \bar{R} \equiv \mathcal{S}(\mathbf{X}^*|x_f) - \mathcal{S}(\mathbf{X}|x_0). \quad (4.9)$$

This apparently leaves us with two functions ψ_0 and ψ_1 which can be chosen freely. However, in order to give the left hand side of the master formula (4.7) the meaning of an average over an existing process, the function ψ_0 is fixed as the initial state. A normalized function ψ_1 together with $G(R) = e^{-R}$ therefore leads to the integral fluctuation relation (4.5) but with the freedom to choose a normalized else arbitrary function as the distribution of final states.

4.2.2 Connection to heat dissipation

In the previous section, we have introduced a scheme exploiting a functional R from which various exact relations follow. To complete this scheme, we have to establish a link to observable physical quantities, and this link is provided by the dissipated heat. For an explicit calculation, we assume the noise to be Gaussian with action functional

$$\mathcal{S}(\zeta) = \frac{1}{4} \int_{t_0}^{t_1} dt \zeta_k(t) \cdot D_{kl}^{-1} \zeta_l(t).$$

For simplicity, we only regard constant diffusion tensors D_{kl} . We replace the noise through the Langevin equation (2.13) with

$$\zeta_k = [\dot{\mathbf{r}}_k - \mathbf{u}(\mathbf{r}_k)] - \mu_{kl}[-\nabla_l U + \mathbf{f}_l], \quad (4.10)$$

leading to the conditional action $\mathcal{S}(\mathbf{X}|x_0)$ which has to be augmented by the initial state x_0 . In addition, a change of variables gives rise to a Jacobian.

We have already split the noise (4.10) into an asymmetric and a symmetric part under time reversal. The velocities in the first square brackets change their sign for the reversed process whereas¹ the second term remains invariant as does the Jacobian. The skew-symmetric functional (4.9) therefore reads

$$\bar{R} = \mathcal{S}(\mathbf{X}^*|x_f) - \mathcal{S}(\mathbf{X}|x_0) = \frac{1}{T} \int_{t_0}^{t_1} dt [\dot{\mathbf{r}}_k - \mathbf{u}(\mathbf{r}_k)] \cdot [-\nabla_k U + \mathbf{f}_k] = \frac{Q}{T} \quad (4.11)$$

¹This convention corresponds to the time-reversal of the external flow, i.e., we invert the velocities of all fluid particles. Yet another form of the fluctuation relations would arise for invariant velocities $\mathbf{u}(\mathbf{r})$.

with the heat (3.9). This is the sought link, which will turn in the discussion below the yet abstract relations into nonequilibrium fluctuation relations for measurable quantities.

4.2.3 Reversed dynamics

Up to now we have considered the behavior of the system under the time reversal of trajectory and protocol but obeying the same dynamics like the original process. We go now one step further and also reverse the dynamics of the process which leads to a modified path probability

$$\mathcal{P}^*(\mathbf{X}) = \exp[-\mathcal{S}^*(\mathbf{X})].$$

To this end, we introduce the adjoint transition probability P^* for a backward transition through a generalization of the detailed balance condition (4.2),

$$P^*(x', t' | x, t; \gamma) \psi_s(x; \gamma) = P(x, t | x', t'; \gamma) \psi_s(x'; \gamma). \quad (4.12)$$

We discretize a trajectory X into $n + 1$ microstates $x_k \equiv x(t_k)$ at times $t_0 < t_1 < \dots < t_n$ with final microstate $x_n = x_f$. The same is done for the protocol. For a Markovian process starting in a stationary state corresponding to γ_0 , the conditional trajectory probability can be expressed as the joint probability

$$\mathcal{P}(\mathbf{X} | x_0) = P(x_n | x_{n-1}; \gamma_{n-1}) \cdots P(x_1 | x_0; \gamma_0)$$

of all these microstates $\{x_k\}$. We now explore two obvious choices for the skew-symmetric functional R :

Reversed dynamics

The first possibility is to only reverse the dynamics through considering

$$R(\mathbf{X}) = \mathcal{S}^*(\mathbf{X}) - \mathcal{S}(\mathbf{X}).$$

This amounts to

$$\begin{aligned} \mathcal{P}^*(\mathbf{X} | x_0) &= P^*(x_n | x_{n-1}; \gamma_{n-1}) \cdots P^*(x_1 | x_0; \gamma_0) \\ &= \mathcal{P}(\mathbf{X}^* | x_f) \left[\prod_{k=0}^{n-1} \frac{\psi_s(x_{k+1}; \gamma_k)}{\psi_s(x_k; \gamma_k)} \right]. \end{aligned} \quad (4.13)$$

Reversed dynamics and process

Another possibility is setting

$$R(\mathbf{X}) = \mathcal{S}^*(\mathbf{X}^*) - \mathcal{S}(\mathbf{X}),$$

amounting to the time reversal of both the dynamics and the process. The corresponding trajectory probability then reads

$$\mathcal{P}^*(\mathbf{X}^*|x_f) = P^*(x_0|x_f; \gamma_0) \cdots P^*(x_{n-1}|x_n; \gamma_{n-1}).$$

Using (4.12) to replace the backward transition probabilities, we get

$$\mathcal{P}^*(\mathbf{X}^*|x_f) = \mathcal{P}(\mathbf{X}|x_0) \left[\prod_{k=0}^{n-1} \frac{\psi_s(x_k; \gamma_k)}{\psi_s(x_{k+1}; \gamma_k)} \right]. \quad (4.14)$$

4.2.4 The relations

We will now present and discuss the various existing fluctuation relations and show how they arise from the general scheme we just developed.

Fluctuation theorem

Through Clausius' formula (3.11), we have $\bar{R} = \Delta s_m$. Historically, the term *fluctuation theorem* is connected to systems driven into a nonequilibrium steady state. We then define the entropy production rate $\sigma \equiv \Delta s_m/t$ along a trajectory of length t . If the temporal boundary term in (4.9) is bounded or grows sublinear, then

$$\lim_{t \rightarrow \infty} \frac{1}{t} R = \sigma$$

and the fluctuation theorem (1.1)

$$\frac{p(-\sigma)}{p(+\sigma)} \sim e^{-\sigma t}$$

follows from (4.6). The fluctuation theorem is also discussed in deterministic systems [8, 3], where, however, certain notions like isoenergetic and isokinetic ensembles as well as technical issues like the chaotic hypothesis have to be distinguished carefully. For stochastic systems, the fluctuation theorem can be regarded as a special case of the following relation.

Total entropy production

The definition of the entropy (3.10) turns the fluctuation theorem into a relation for the total entropy production holding for any trajectory length t . Using the freedom to specify any distribution for the final microstates, we choose the actual distribution, $\psi_1(x) = \psi(x, t)$. We then find

$$R = \Delta s_m + \Delta s = \Delta s_{\text{tot}}$$

and consequently

$$\frac{p^*(-\Delta s_{\text{tot}})}{p(+\Delta s_{\text{tot}})} = e^{-\Delta s_{\text{tot}}}, \quad \langle e^{-\Delta s_{\text{tot}}} \rangle = 1$$

first derived in [16].

Jarzynski relation

The most prominent nonequilibrium fluctuation relation is arguably the Jarzynski relation derived in 1997 [11, 74]. Suppose we drive the system from equilibrium state A to equilibrium state B . Furthermore, the stationary states belonging to the values of the control parameter γ reached during the transition $\gamma_A \rightarrow \gamma_B$ are equilibrium states, $\psi_s(x; \gamma) = \psi_{\text{eq}}(x; \gamma)$. This has to be distinguished from the actual distribution $\psi(x, t)$ which is the solution of the Smoluchowski equation (2.8). We choose $\psi_1(x) = \psi_{\text{eq}}(x; \gamma_B)$, the equilibrium state belonging to the final value of the control parameter. Then

$$R = \bar{R} + \ln \frac{\psi_{\text{eq}}(x_0; \gamma_A)}{\psi_{\text{eq}}(x_f; \gamma_B)} = [Q + \Delta U - \Delta \mathcal{F}] / T$$

together with the first law of thermodynamics $W = Q + \Delta U$ leads from (4.5) to

$$\langle e^{-W/T} \rangle = e^{-\Delta \mathcal{F}/T},$$

the famous Jarzynski relation.

Crooks relation

The Crooks relation [12, 13] is the detailed version of the Jarzynski relation,

$$\frac{p^*(-W)}{p(+W)} = e^{-(W - \Delta \mathcal{F})/T}.$$

Here, the distinction between forward and reversed process is crucial.

Hatano-Sasa relation

The first relation involving reversed dynamics is the Hatano-Sasa relation [35]. It can be derived from (4.14) including the boundary term for a transition starting in a steady state and with $\psi_1(x) = \psi_s(x; \gamma_n)$,

$$R = -\ln \left[\frac{1}{\psi_s(x_0; \gamma_0)} \frac{\psi_s(x_0; \gamma_0) \psi_s(x_1; \gamma_1)}{\psi_s(x_1; \gamma_0) \psi_s(x_2; \gamma_1)} \dots \frac{\psi_s(x_{n-1}; \gamma_{n-1})}{\psi_s(x_n; \gamma_{n-1})} \psi_s(x_n; \gamma_n) \right].$$

If we use further the expression (3.16) for the stationary probability, we can rewrite the square brackets as

$$\exp \left\{ - \sum_{k=1}^n [\Phi(x_k; \gamma_k) - \Phi(x_k; \gamma_{k-1})] \right\} \rightarrow \exp \left\{ - \int_{t_0}^{t_1} dt \dot{\gamma} \frac{\partial \Phi}{\partial \gamma} \right\},$$

where the last expression follows in the limit $n \rightarrow \infty$ for fixed trajectory length. Hence, $R = Y$ and the integral relation $\langle \exp[-Y] \rangle = 1$ is known as the Hatano-Sasa relation. Of

course, any other relation stemming from a function $G(R)$ like the detailed relation (4.6) for $R = Y$ is possible, too.

Housekeeping heat

For the housekeeping heat, we start with (4.13) but set $\psi_1 = \psi_0$, i.e., we discard the boundary term. This leads to

$$R = \bar{R} = \ln \frac{\mathcal{P}(\mathbf{X}|x_0)}{\mathcal{P}(\mathbf{X}^*|x_f)} + \ln \left[\frac{\psi_s(x_0; \gamma_0) \psi_s(x_1; \gamma_1)}{\psi_s(x_1; \gamma_0) \psi_s(x_2; \gamma_1)} \dots \frac{\psi_s(x_{n-1}; \gamma_{n-1})}{\psi_s(x_n; \gamma_{n-1})} \right],$$

where the first term is the heat, see (4.11). Evaluating the square brackets the same way we did for the Hatano-Sasa relation, we obtain the result

$$R = \frac{Q}{T} - Y + \Delta\Phi = \frac{Q_{\text{hk}}}{T}.$$

Hence, also the housekeeping heat fulfills a fluctuation relation.

Steady state thermodynamics

As the final result, we repeat the approach to the Jarzynski relation but generalized to transitions between nonequilibrium steady states. We set $\psi_1(x) = \psi_s(x; \gamma_B)$ and obtain from (4.9)

$$R = \bar{R} + \ln \frac{\psi_{\text{eq}}(x_0; \gamma_A)}{\psi_{\text{eq}}(x_f; \gamma_B)} = Q/T + \Delta\Phi$$

for the original dynamics. Hence, both the housekeeping and the excess heat (modulo the boundary term) as well as their sum

$$Q_{\text{hk}}/T, \quad Q_{\text{ex}}/T + \Delta\Phi, \quad Q/T + \Delta\Phi$$

independently fulfill a nonequilibrium fluctuation relation.

This list can be further extended due to the arbitrariness of the end-point distribution, e.g., the relation of Bochkov and Kuzovlev [23, 24] can be recovered by setting ψ_1 to the initial distribution [25, 37]. Nevertheless, we will stop here and turn to the second part of this chapter.

4.3 Evolution of path functionals

The path functionals R for heat and work discussed so far have a common property, they can be written as integral

$$R(X; \Gamma) = \int_{t_0}^{t_1} dt \dot{r}(x(t), \dot{x}(t); \gamma(t)) \quad (4.15)$$

with a *rate function* $\dot{r}(x, \dot{x}; \gamma)$ depending on the positions, possibly the velocities, and on time through the control parameter γ . Integration is carried out along a single trajectory X in the time interval $t_0 \leq t \leq t_1$. We call this property *time-local*. It allows us to find an also time-local evolution equation for the joint probability distribution $\rho(x, r, t)$ of the system to be in microstate x at time $t \leq t_1$ and to have accumulated an amount $r = R$ since t_0 . This evolution equation is found by treating r as another degree of freedom. The explicit calculation is presented in the appendix A.6. For the general *ansatz*

$$\dot{r} \equiv [\dot{\mathbf{r}}_k - \mathbf{u}(\mathbf{r}_k)] \cdot \mathbf{a}_k + \beta$$

with yet arbitrary vectors $\mathbf{a}_k(x; \gamma)$ and scalar function $\beta(x; \gamma)$, we obtain as equation of motion $\partial_t \rho = \hat{L} \rho$ with operator (A.28)

$$\hat{L} = \hat{L}_{\text{SM}} - \{\mathbf{a}_k \cdot [\hat{\mathbf{v}}_k - \mathbf{u}(\mathbf{r}_k)] - \nabla_k \cdot \mathbf{D}_{kl} \mathbf{a}_l + \beta\} \partial_r + \mathbf{a}_k \cdot \mathbf{D}_{kl} \mathbf{a}_l \partial_r^2, \quad (4.16)$$

where \hat{L}_{SM} is the Smoluchowski operator (A.26) and $\hat{\mathbf{v}}_k$ is the velocity operator (A.21). Evolution operators similar to, or special cases of, the operator (4.16) have been derived previously [75, 76, 77, 78].

4.3.1 Generating function and fluctuation relations

Our main tool for proving fluctuation relations based on the joint probability $\rho(x, r, t)$ will be the generating functions. First, we note that the probability distribution of R is obtained through integration over all final microstates,

$$p(r, t) = \int dx \rho(x, r, t).$$

The generating functions are defined as

$$g_z(x, t) \equiv \int_{-\infty}^{+\infty} dr e^{-zr} \rho(x, r, t), \quad \bar{g}_z(t) \equiv \int dx g_z(x, t) \quad (4.17)$$

with $g_0(x, t) = \psi(x, t)$. We distinguish between the generating function $g_z(x, t)$ still depending on the microstate and its integral $\bar{g}_z(t)$. The nonequilibrium fluctuation relations will be expressed as conditions on \bar{g}_z but only for g_z we find the explicit equation of motion

$$\partial_t g_z = \hat{L}_z g_z \quad (4.18)$$

with operator

$$\hat{L}_z = \hat{L}_{\text{SM}} - \{\mathbf{a}_k \cdot [\hat{\mathbf{v}}_k - \mathbf{u}(\mathbf{r}_k)] - \nabla_k \cdot \mathbf{D}_{kl} \mathbf{a}_l + \beta\} z + \mathbf{a}_k \cdot \mathbf{D}_{kl} \mathbf{a}_l z^2, \quad (4.19)$$

which is obtained through inserting (4.16) into (4.17) and integration by parts with respect to r . The boundary terms vanish since the probability distribution $p(r)$ has natural boundary conditions, i.e., $p(r \rightarrow \pm\infty) \rightarrow 0$.

The Taylor expansion of the generating function g_z around $z = 0$ yields for the conditional moments

$$m_n(x, t) \equiv \int dr r^n \rho(x, r, t)$$

the relation

$$\left. \frac{\partial^n}{\partial z^n} g_z(x, t) \right|_{z=0} = (-1)^n m_n(x, t). \quad (4.20)$$

An equation of motion for the conditional moments is then obtained through differentiating (4.18) with respect to z .

The nonequilibrium fluctuation relations can now be traced back to certain conditions on the generating function. For any integral relation, we have

$$\langle e^{-R} \rangle = \int dr e^{-r} p(r, t) = \int dx g_1(x, t) = \bar{g}_1(t) = 1,$$

i.e., any at $z = 1$ normalized generating function fulfills an integral fluctuation relation. Note that in contrast to the derivation based on the path integral, here we need no statement about the time reversal of process or dynamics. Rather, the existence of integral fluctuation relations restricts the set of possible operators (4.19) and therefore the set of path functionals R . For the sake of brevity, we will restrict the discussion of detailed fluctuation relations to steady states. Inserting (4.6) into the definition (4.17), we find the symmetry

$$\bar{g}_z(t) = \int dr e^{-zr+r} p(-r, t) = \bar{g}_{1-z}(t) \quad (4.21)$$

after a change of variables $r \mapsto -r$, leading to the detailed fluctuation relation. Due to normalization, $\bar{g}_0(t) = \bar{g}_1(t) = 1$ for all times t .

4.3.2 Transition functional and work distribution

For the evolution equation of the transition functional Y , we set $\beta = \dot{\gamma} \partial_\gamma \Phi$ and $\mathbf{a}_k = 0$, leading to

$$\hat{L}_z = \hat{L}_{\text{SM}} - \dot{\gamma} \frac{\partial \Phi}{\partial \gamma} z.$$

The normalized solution of the evolution equation at $z = 1$ involving this operator is $g_1(x, t) = \psi_s(x; \gamma(t))$.

The transition functional reduces to the dissipated work $W - \Delta\mathcal{F}$ if the stationary state at any γ reached during the transition is equilibrium. Setting $\beta = \dot{\gamma} \partial_\gamma U$, the condition on the generating function in order to yield the Jarzynski relation becomes slightly different,

$$\bar{g}_1(t) = \int dx g_1(x, t) = \mathcal{Z}_B / \mathcal{Z}_A,$$

where $\mathcal{Z}_{A,B}$ is the partition function of the initial and final state, respectively. The solution of (4.18) fulfilling this condition and also the initial equilibrium condition is

$$g_1(x, t) = (\mathcal{Z}_A)^{-1} \exp[-U(x; \gamma(t))/T]$$

with $g_1(x, t_0) = \psi_{\text{eq}}(x; \gamma_A)$.

4.3.3 Experimental work distribution

In section 3.2.2, we introduced an experiment demonstrating the conservation of energy along a single trajectory. In particular, we determined the work from experimentally measured trajectories. We now want to compare the distribution obtained from this measured trajectories with the theoretical prediction obtained from the evolution equation for the work distribution. To this end, it is advantageous to consider the equation of motion for the conditional moments m_n obtained through (4.20) from the evolution equation for the generating function (4.18), reading

$$\partial_t m_n = \hat{L}_{\text{SM}} m_n + n \dot{\gamma} \frac{\partial U}{\partial \gamma} m_{n-1}. \quad (4.22)$$

These equations form a hierarchy of inhomogeneous differential equations which couple the evolution of the n^{th} conditional moment to that of the $(n - 1)^{\text{th}}$ moment. The lowest moment $m_0(x, t) = \psi(x, t)$ is the solution of the Smoluchowski equation with initial condition $m_0(x, t_0) = \psi_{\text{eq}}(x; \gamma_A)$. All higher moments have initial condition $m_n(x, t_0) = 0$ for $n \geq 1$. The formal solution of (4.22) can be written as a Dyson series.

The equations (4.22) are to be solved numerically for the first three conditional moments. The Smoluchowski operator reads

$$\hat{L}_{\text{SM}} = \partial_x D_\perp(x) \{ [\partial_x U(x; \gamma)] + \partial_x \}$$

for the distance x between particle and glass surface with potential energy (3.4). The fact that the particle is moving perpendicular but close to a surface drastically influences the diffusion coefficient due to hydrodynamic interactions of the colloidal bead with the surface. We take this into account through the distance-dependent diffusion coefficient

$$D_\perp(x) \approx D_0 [1 + a_0/(x - a_0)]^{-1},$$

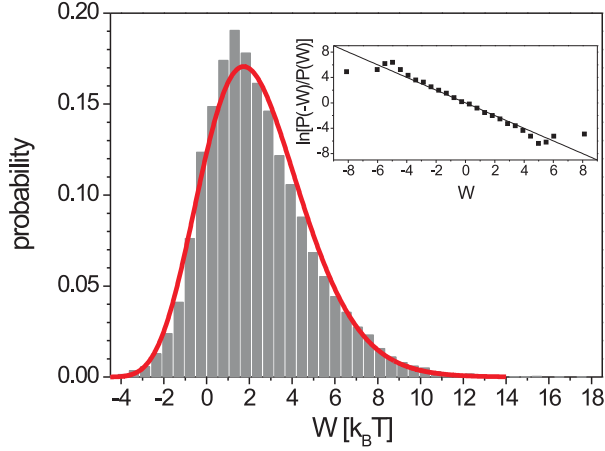


Figure 4.1: Experimental non-Gaussian work distribution. The data was taken from about 16000 trajectories, where the average work done on the particle was about $2.4 k_B T$. The solid line shows the Pearson type III distribution (4.23) corresponding to the theoretically obtained moments, see main text. Inset: Logarithm of the ratio of the probability to find trajectories with work $-W$ to those with work $+W$. The solid line shows the expected slope of -1 .

where a_0 is the radius of the particle [79].

For a comparison with the experimental histogram, we seek a probability distribution function which roughly resembles the histogram, i.e., it is non-Gaussian with a skew-symmetry towards larger work values. The most simple normalized non-Gaussian is the Pearson type III distribution [80]

$$p(r) = \frac{1}{\beta \Gamma(p)} \left(\frac{r - \alpha}{\beta} \right)^{p-1} \exp \left[-\frac{r - \alpha}{\beta} \right] \quad (4.23)$$

with three parameters $\alpha, \beta > 0, p > 0$ determining its form. In this expression, $\Gamma(p)$ is the gamma function. This function cannot be the exact distribution since it has a sharp lower bound and negative events are cut off for $r < \alpha$. However, it is a good approximation to the measured histogram, see figure 4.1. The three parameters are easily obtained from the three numerically determined moments through the relations

$$\kappa_1 = \alpha + \beta p, \quad \kappa_n = p \beta^n \Gamma(n),$$

for $n > 1$ where κ_n is the n^{th} cumulant. In particular, with

$$\begin{aligned} \kappa_1(t) &= \int dx m_1(x, t), & \kappa_2(t) &= \int dx m_2(x, t) - \kappa_1^2(t), \\ \kappa_3(t) &= \int dx m_3(x, t) - 3\kappa_1(t)\kappa_2(t) - \kappa_1^3(t) \end{aligned}$$

the parameters become

$$\alpha = \kappa_1 - \frac{2\kappa_2^2}{\kappa_3}, \quad \beta = \frac{\kappa_3}{2\kappa_2}, \quad p = \frac{4\kappa_2^3}{\kappa_3^2}.$$

For the comparison, we take a full cycle of the symmetric protocol with $t = t_s$. In figure 4.1, also the Crooks relation is tested experimentally as shown in the inset. The deviation is due to the poor statistics of large negative work values $W \lesssim -4 k_B T$.

4.3.4 Housekeeping heat

The derivation of the evolution equation for the housekeeping heat is straightforward. From the expression (3.18), we identify $\mathbf{a}_k = D_{kl}^{-1}[\mathbf{v}_l^s - \mathbf{u}(\mathbf{r}_l)]$ and $\beta = \mathbf{u}(\mathbf{r}_k) \cdot \nabla_k \Phi$. We can relate

$$T \mathbf{a}_k \cdot D_{kl} \mathbf{a}_l = [\mathbf{v}_k^s - \mathbf{u}(\mathbf{r}_k)] \mu_{kl}^{-1} [\mathbf{v}_l^s - \mathbf{u}(\mathbf{r}_l)] \equiv 2\mathcal{W}_s$$

to the dissipation function $\mathcal{W}_s(x; \gamma)$ in the steady state corresponding to γ . In the next step, we expand the velocity operator (A.21) as follows,

$$\hat{\mathbf{v}}_k = \mathbf{v}_k^s - D_{kl} [(\nabla_l \Phi) + \nabla_l].$$

The term proportional to z in (4.19) then reads

$$2\mathcal{W}_s/T - [\mathbf{v}_k^s - \mathbf{u}(\mathbf{r}_k)] \cdot [(\nabla_k \Phi) + \nabla_k] - \nabla_k \cdot [\mathbf{v}_k^s - \mathbf{u}(\mathbf{r}_k)] + \mathbf{u}(\mathbf{r}_k) \cdot (\nabla_k \Phi).$$

Pulling the derivative in the second term in front and using $\nabla \cdot \mathbf{u} = 0$, we can simplify this expression to

$$2\mathcal{W}_s/T - 2\nabla_k \cdot [\mathbf{v}_k^s - \mathbf{u}(\mathbf{r}_k)] + [(\nabla_k \cdot \mathbf{v}_k^s) - \mathbf{v}_k^s \cdot (\nabla_k \Phi)] + 2\mathbf{u}(\mathbf{r}_k) \cdot (\nabla_k \Phi).$$

The sum in the third term cancels, leading us to the evolution operator

$$\hat{L}_z = \hat{L}_{SM} + 2 \{ \nabla_k \cdot [\mathbf{v}_k^s - \mathbf{u}(\mathbf{r}_k)] - \mathbf{u}(\mathbf{r}_k) \cdot (\nabla_k \Phi) - (\mathcal{W}_s/T) \} z + 2(\mathcal{W}_s/T) z^2 \quad (4.24)$$

for the housekeeping heat $R = Q_{hk}/T$.

For the integral fluctuation relation at $z = 1$, we find

$$\partial_t \bar{g}_1(t) = \int dx \hat{L}_1 g_1 = -2 \int dx \mathbf{u}(\mathbf{r}_k) \cdot (\nabla_k \Phi) g_1 = 0. \quad (4.25)$$

For $z = 1$, the last two terms in (4.24) involving \mathcal{W}_s cancel. The integration over the Smoluchowski operator vanishes due to the conservation of probability. The second term leads to a boundary term which also vanishes. Finally, the remaining term becomes a boundary term for $g_1(x, t) = \psi_s(x; \gamma(t))$, the same choice as for the transition functional. Moreover, for this choice the stricter result $\hat{L}_1 g_1 = 0$ also holds. Hence, for the initial condition $\bar{g}_1(0) = 1$ it follows $\bar{g}_1(t) = 1$ for all times t and the integral relation for the housekeeping heat holds as expected. Note that without external flow, relation (4.25) is valid for any choice of $g_1(x, t)$.

In a nonequilibrium steady state, there are two limits where the generating function can be approximated by the product form $g_z(x, t) \approx \bar{g}_z(t) \psi_s(x)$. First, this *ansatz* becomes exact for vanishing potential energy and an approximation if the nonconservative forces or the flow forces are much larger than the conservative forces arising from the potential.

Second, this form also holds near equilibrium for small nonconservative forces or flows. The equation of motion reads

$$\partial_t \bar{g}_z(t) = \left[\int dx \hat{L}_z \psi_s(x) \right] \bar{g}_z(t) = -\langle \dot{s}_{\text{tot}} \rangle z(1-z) \bar{g}_z(t)$$

with mean entropy production rate $\langle \dot{s}_{\text{tot}} \rangle = \langle \dot{s}_{\text{m}} \rangle = 2\langle \mathcal{W}_s \rangle / T$ in a nonequilibrium steady state. The solution for the generating function

$$\bar{g}_z(t) = \exp [-\langle \dot{s}_{\text{tot}} \rangle z(1-z)t]$$

is a Gaussian and therefore the probability distribution for both the housekeeping heat and the total entropy production in these limits are Gaussians, too. Obviously, this solution obeys the symmetry (4.21) and therefore the fluctuation theorem (4.6).

4.4 Extension to non-Markovian processes

The time-local property of the functional (4.15) can be used to extend the proofs in section 4.3.1 of the nonequilibrium fluctuation relations through the generating function to non-Markovian dynamics. The only condition on the non-Markovian process is that it still has a unique stationary state.²

The crucial ingredient for an extension of the proofs is that the time evolution equation (2.1)

$$\partial_t \psi(x, t) = \hat{L}(t; t_0) \psi(x, t) \tag{4.26}$$

for the distribution $\psi(x, t)$ still holds as in the case of a Markov process. It is somewhat surprising that the same, apparently time-local, equation (4.26) holds also for non-Markovian processes [82, 83]. This can be understood by realizing that the complete information about processes with memory is contained in the transition probability rather than in the single-point distribution $\psi(x, t)$. We denote with $\hat{U}(t|t'; t_0)$ the operator that propagates the non-Markovian system from time $t' < t$ to the later time t . These propagators do not form a semi-group (2.6) and the fact that the propagator depends on the whole history in principle back to the time of preparation is made explicit through the dependence on t_0 . The propagator actually depends on the protocol Γ up to t since any change of the protocol will have consequences for the following evolution.

Using the propagator as the starting point, we define an evolution operator

$$\hat{L}_{\text{NM}}(t; t_0) \equiv \partial_t \hat{U}(t|t'; t_0) \Big|_{t'=t} \tag{4.27}$$

²Non-ergodic systems result in non-Markovian processes which then do not relax towards a stationary state, for a discussion of such processes see, e.g., [81].

describing a “substitute”, non-stationary Markov process leading to the same single-point distribution $\psi(x, t)$ but to a different transition probability than the non-Markovian process [82]. In particular, knowledge of the operator (4.27) is not sufficient to calculate correlation functions. In contrast to the Markov case, the dependence on the control parameter γ of the operator (4.27) is implicit.

We restrict our proof to dynamics with a unique steady state, i.e., for fixed γ the system will relax towards a unique probability distribution $\psi_s(x; \gamma)$ depending on the control parameter,

$$\lim_{t \rightarrow \infty} \psi(x, t) \rightarrow \psi_s(x; \gamma). \quad (4.28)$$

This statement is equivalent to assuming an ergodic process with or without memory. The second ingredient to the proof is the existence of a stationary solution

$$\hat{L}(t; t_0)\psi_s(x; \gamma(t)) = 0 \quad (4.29)$$

for the corresponding value $\gamma = \gamma(t)$ of the control parameter. Whereas this is evident in the case of a Markovian operator, due to the implicit dependence on γ it is not so obvious in the non-Markovian case and we give a proof by contradiction. First, we note that for a proper Markovian substitute process, the operator (4.27) must have a stationary solution. Now suppose that at time t' we stop the process and hold the parameter fixed with value $\gamma = \gamma(t')$. Under very general conditions, which are fulfilled by any transition probability, the Perron-Frobenius theorem ensures that the propagator $\hat{U}(t|t'; t_0)$ has an eigenstate $\psi_1(x; t, t')$ corresponding to the eigenvalue 1 depending on t' and in principle also depending on t , i.e.,

$$\hat{U}(t|t'; t_0)\psi_1(t, t') = \psi_1(t, t'). \quad (4.30)$$

Furthermore, this eigenstate $\psi_1(x; t, t')$ is ensured to be a normalized, nonnegative probability distribution. From the definition (4.27), we calculate

$$\hat{L}_{\text{NM}}(t'; t_0)\psi_1(t, t') = \lim_{\varepsilon \rightarrow 0} \frac{1}{\varepsilon} [\hat{U}(t' + \varepsilon|t'; t_0)\psi_1(t, t') - \psi_1(t, t')] \neq 0 \quad (4.31)$$

which is nonzero for both arbitrary functions ψ_1 and for the eigenfunction $\psi_1(t, t')$ of the propagator if the latter would depend on t since t then does not match the leading time argument of the propagator. This would mean that the substitute operator (4.27) has no stationary solution. This contradiction is resolved only if the eigenfunction $\psi_1(t')$ is independent of t . Moreover, taking then the limit $t \rightarrow \infty$ in (4.30), we find from the ergodicity condition (4.28) that $\psi_1(x, t') = \psi_s(x; \gamma)$. Finally, we note that due to causality, we do not have to actually stop the process at a t' since the system cannot depend on the future protocol and (4.29) must hold for all times t .

With these ingredients, the generalized proof of nonequilibrium fluctuation relations becomes easy. Inspecting the expression for the function (4.15), we see that its instantaneous change $\dot{r}(x, \dot{x}; \gamma)$ only depends on the actual state x the system is in. Hence,

the time-local operator $\hat{L}(t; t_0)$ is all we need and the generalized proof goes along the same line as in section 4.3.1, but with the Smoluchowski operator \hat{L}_{SM} replaced by the substitute operator \hat{L}_{NM} .

4.4.1 Substitute operator for a moving trap

The Markovian substitute process is defined through the operator (4.27). Unlike the Markov case, explicit expressions for this operator are hard to come by. One exception are Gaussian processes for which these substitute operators can be calculated since we know the explicit transition probability. As an illustration, we calculate the substitute operator in case of a particle moving in one dimension with position x which is trapped in a harmonic potential $U(x; \gamma) = (k/2)(x - \gamma)^2$. The generalized Langevin equation

$$\int_0^t dt' \beta(t - t') \dot{x}(t') = -\partial_x U(x(t); \gamma(t)) + \zeta(t)$$

with friction kernel $\beta(t)$ then becomes linear and can be solved by Laplace transformation as

$$x(t) = G_1(t)x_0 + \int_0^t dt' G_2(t - t')[k\gamma(t') + \zeta(t')],$$

where the two kernels are given as the inverse Laplace transform of $\hat{G}_1(s) = \hat{\beta}(s)\hat{G}_2(s)$ and $\hat{G}_2(s) = [s\hat{\beta}(s) + k]^{-1}$, respectively. The system is prepared at time t_0 in equilibrium with initial position x_0 drawn from $\psi_{eq}(x; \gamma(t_0))$. Due to the change of the external parameter γ , the mean

$$m(t; \Gamma) \equiv \langle x(t) \rangle = \int_0^t dt kG_2(t - t')\gamma(t')$$

is a functional of the protocol Γ . Without loss of generality, we have set $\gamma(0) = 0$ and hence $\langle x_0 \rangle = 0$.

The substitute operator for one-dimensional Gaussian processes has been worked out explicitly in [82] reading in general

$$\hat{L}_{NM}(t) = -\partial_x \left[\dot{\chi}(t)x + \dot{\mu}(t) - \frac{1}{2}\dot{\sigma}(t)\partial_x \right].$$

The functions $\dot{\mu}(t)$ and $\dot{\sigma}(t)$ are determined through the differential equations

$$\dot{m}(t) = \dot{\mu}(t) + \dot{\chi}(t)m(t), \quad \dot{v}(t) = \dot{\sigma}(t) + 2\dot{\chi}(t)v(t)$$

with time-dependent mean $m(t)$ and variance $v(t)$. The correlation function

$$\chi(t, t') \equiv \frac{\langle [x(t) - m(t)][x(t') - m(t')] \rangle}{v(t')} \quad (4.32)$$

with $\chi(t, t) = 1$ determines $\dot{\chi}(t) \equiv \partial_t \chi(t, t')|_{t'=t}$.

To be more specific, we choose an exponential friction kernel

$$\beta(t) = \kappa e^{-\kappa t} \Rightarrow \hat{\beta}(s) = \frac{\kappa}{s + \kappa} \Rightarrow G_2(t) = (\bar{\kappa}/k)^2 e^{-\bar{\kappa} t} + \frac{\delta(t)}{\kappa + k}$$

with inverse time scale $\bar{\kappa} \equiv \kappa k / (\kappa + k)$. In the Markov limit, $\kappa \rightarrow \infty$ yields $\bar{\kappa} \rightarrow k$ as expected. Using the explicit expression for the kernel $G_2(t)$, we calculate the mean

$$m(t) = e^{-\bar{\kappa}(t-t')} m(t') + \gamma [1 - e^{-\bar{\kappa}(t-t')}]$$

where we have stopped the process at t' with parameter $\gamma = \gamma(t')$. This equation shows the basic features of ergodic non-Markovian processes. For fixed γ , the mean $m(t \rightarrow \infty) \rightarrow \gamma$ relaxes towards the value of the control parameter. It is a functional of the protocol Γ up to t' and afterwards depends on the time difference $t - t'$ only. The time derivative yields $\dot{m}(t) = -\bar{\kappa} m(t) + \bar{\kappa} \gamma$ and indeed a straightforward calculation of (4.32) confirms $\dot{\chi} = -\bar{\kappa}$. Therefore, we have $\dot{\mu} = \bar{\kappa} \gamma$ and since we do not change the strength of the trap, the variance is $\nu = T/k$ leading to $\dot{\sigma} = 2\bar{\kappa} T/k$. Hence, the substitute operator for fixed γ becomes

$$\hat{L}_{\text{NM}}(\gamma) = \bar{\kappa} \partial_x [(x - \gamma) + (T/k) \partial_x]$$

with stationary solution $\psi_{\text{eq}}(x; \gamma) \propto \exp[-k/(2T)(x - \gamma)^2]$ for all times $t \geq t'$.

4.5 Conclusions

The nonequilibrium fluctuation relations compromise a class of exact results holding arbitrarily far from equilibrium. They arise from the behavior of the path action for a time reversed process and/or reversed dynamics of the system. Mathematically, any skew-symmetric form on the space of trajectories will generate a similar structure. However, without an explicit link to physical quantities, the value of the resulting relations is doubtful. It therefore seems that time reversal is exceptional since it is connected to the entropy production. Then a wealth of relations involving real physical quantities like the transition functional and the housekeeping heat can be derived. Nevertheless, future studies of other trajectory transformations might yield surprising results.

5 Discrete Systems

5.1 Introduction

The concepts introduced and discussed in the previous chapters for mechanically driven systems can be extended to systems with a discrete configuration space in a very straightforward manner. This has been pioneered in [84] for death–birth processes. In this chapter, we will study the extension of the Jarzynski relation and the entropy production along a single stochastic trajectory for the specific system of a single defect center in diamond. Moreover, the defect center is an athermal system, i.e., it is not coupled to a heat bath with a well-defined temperature providing thermal noise. However, since the relations we will study essentially derive from the behavior of the system under time-reversal, they can be defined for other dynamics as well. We will restrict our discussion to the transition functional Y and the concept of a nonequilibrium entropy. A more thorough extension to discrete systems driven by chemical gradients has been given in [85].

5.2 The system: A single defect center in diamond

The simple energy level scheme 5.1 describes the observed optical properties of the defect center in diamond as two coupled two-level systems (TLS). In the first TLS, the center can be excited with red light of wavelength 680 nm, responding with a Stokes shifted fluorescence of rate $k_b^{-1} = 5.5$ ns. The second TLS is excited with green light of wavelength 514 nm and decays non-radiatively with rate k_d . Since these nano-second transitions are not resolved, the first TLS appears as bright whereas the second TLS is dark. Depending on the intensity of the red excitation light, the bright TLS decays with another rate b into

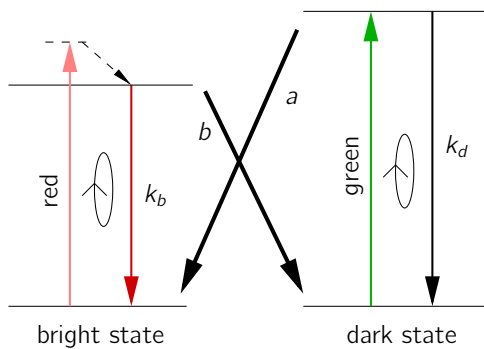


Figure 5.1: A single defect center in diamond described as an effective two-level system with a dark and a detectable, fluorescent bright state. It consists of two coupled two-level systems, where the fluorescent state is driven by a red laser and the dark state is driven by a tuneable green laser. The system switches between these two states with rates a and b .

the dark TLS, from which it can be pumped back with rate a using the green laser. The transition rates a and b between the two TLSs are several orders of magnitude smaller than k_b and k_d and depend linearly on the intensities of the green (rate a) and red (rate b) laser, respectively. Hence, it is sufficient to consider the whole system as one effective two-level system with a dark and a bright state,



with transition rates a and b . The stochastic trajectory $X \equiv \{n(t) : 0 \leq t \leq t_1\}$ of the state occupied by the system at time t consists of N consecutive jumps at times t_i between state $n = 0$ and state $n = 1$, where $t_0 = 0$ and $t_{N+1} = t$. In the i^{th} interval $t_i \leq t \leq t_{i+1}$, the state is denoted by n_i .

The system is driven out of the initial equilibrium by modulating the intensity of the green laser with a sinusoidal protocol $\gamma(t)$ with modulation period t_m . This leads to the time-dependent rate

$$a(t) = a_0[1 + \delta\gamma(t)] \quad (5.2)$$

with protocol

$$\gamma(t) \equiv \sin(2\pi t/t_m), \quad (5.3)$$

where $0 < \delta < 1$ is the strength of the modulation. The intensity of the red laser is constant and therefore $b = b_0$. The state of the system is the vector $\psi = (\psi_0, \psi_1)$. For fixed γ , the system relaxes towards the steady state

$$\psi_0(\gamma) = \frac{b_0}{a(\gamma) + b_0} = 1 - \psi_1(\gamma), \quad (5.4)$$

which, for a two-level system, is necessarily an equilibrium state.

5.3 The transition functional

In an athermal system, due to the lack of a bath, the notions heat and work lose their immediate physical meaning. We therefore elude to more abstract concepts like the transition functional and the entropy production. The transition functional (3.19) reads

$$Y(X; \Gamma) = \int_0^{t_1} dt \dot{\gamma}(t) \frac{\partial \Phi_{n(t)}(\gamma(t))}{\partial \gamma}, \quad (5.5)$$

where $\Phi_n(\gamma) \equiv -\ln \psi_n(\gamma)$ defined from (5.4) corresponds to a ‘‘pseudo’’ energy. Along the trajectory X , the transition functional can be rewritten as

$$Y(X; \Gamma) = - \sum_{i=0}^N n_i \ln \frac{a(t_{i+1})}{a(t_i)} + \ln \frac{a(t) + b_0}{a_0 + b_0} \quad (5.6)$$

exploiting the discrete nature of the system. The second term vanishes if we start and end the driving at the same laser intensity.

We distinguish moderate driving from strong driving by comparing the intrinsic relaxation time of the unmodulated system

$$\tau = (a_0 + b_0)^{-1} \quad (5.7)$$

with the modulation period t_m . For the first two experiments, $\tau = 14$ ms compared to $t_m = 50$ ms means that the system is only moderately driven into non-equilibrium. For the third run, the modulation period is reduced to $t_m = 20$ ms compared to a relaxation time $\tau = 20$ ms. In this case modulation period and intrinsic relaxation time are approximately equal, which corresponds to a strongly driven system.

5.3.1 Probability distribution

Insight into the statistical properties is gained by looking directly at the probability distribution $p(Y)$. For the calculation of this distribution, it is convenient to introduce the joint probability $\rho_n \equiv \rho_n(Y, t)$, which is the probability of the system to be in state n at time t and to have accumulated an amount Y up to this time. Starting from the master equation (2.3), the time evolution of ρ_n is then governed by the differential Chapman-Kolmogorov equation [75, 76]

$$\partial_t \rho_n = \sum_{m=0}^1 L_{nm}(t) \rho_m - \dot{\gamma} \frac{\partial \Phi_n}{\partial \gamma} \frac{\partial \rho_n}{\partial Y}, \quad (5.8)$$

where $L_{10} = -L_{00} = a(t)$ and $L_{01} = -L_{11} = b_0$. Since we start out of equilibrium, the initial condition is $\rho_n(Y, 0) = \psi_n(0) \delta(Y)$. In general, equation (5.8) must be solved numerically. The distribution

$$p(Y, t) = \rho_0(Y, t) + \rho_1(Y, t)$$

can then be obtained by adding the contributions of the two possible final states.

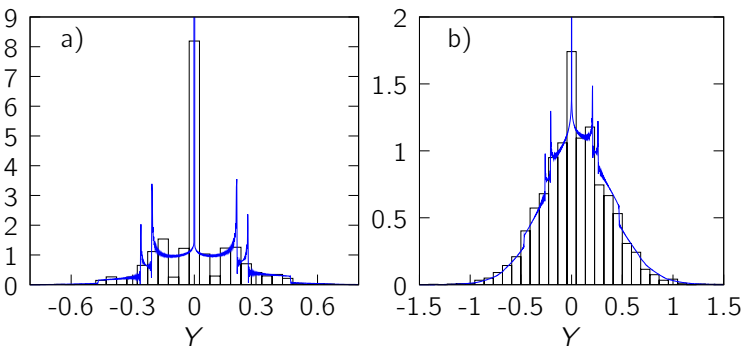


Figure 5.2: Comparison of the numerically calculated probability distribution $P(Y)$ with the experimentally obtained normalized histogram at times a) $t = 60$ ms and b) $t = 200$ ms. (In both cases: $a_0^{-1} = 64$ ms, $b_0^{-1} = 30$ ms, $t_m = 20$ ms, and $\delta = 0.23$.)

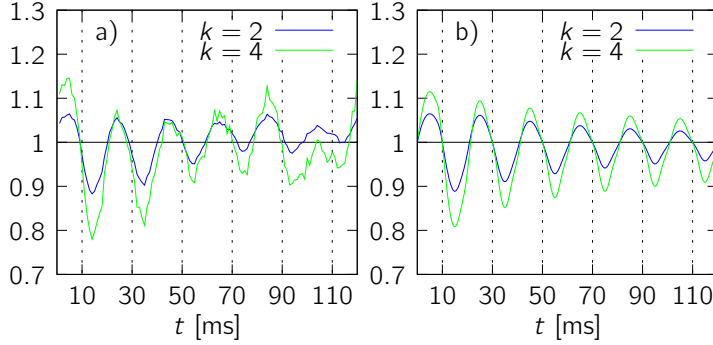


Figure 5.3: Test of the moment relation (5.10) for the second ($k = 2$) and fourth ($k = 4$) moment. The plots show the ratio $\langle Y^k e^{-Y} \rangle / \langle Y^k \rangle$ over trajectory length t for $t_m = 20$ ms. At the vertical dashed lines the protocol becomes symmetric, see Eq. (5.9). a) Experimental data; b) Numerical data. (Parameters are as in Fig. 5.2.)

For sufficiently slow driving, i.e., if the relaxation time of the system is much smaller than the modulation period t_m , the distribution $p(Y)$ is expected to be a Gaussian. For large t , our experimental results and numerical calculations indicate that $p(Y)$ again is a Gaussian. In the intermediate regime of short trajectories and fast driving, the distribution $p(R)$ shows distinctly non-Gaussian behavior with a pronounced peak structure, as shown in Fig. 5.2. Here, we compare experimentally obtained histograms for two different trajectory lengths to the basically exact numerical solution.

The numerically obtained center peak and the four narrow side peaks can be resolved partially by the experimental histograms. These peaks can only be observed for short trajectories, where there are at most a few jumps. The center peak derives from trajectories which do not jump within t . The positions of the other four peaks are at $Y = \pm \ln(1 \pm \delta)$, independent of the driving frequency, which demonstrates that this is not a resonance phenomena. Rather the explanation is as follows. Independent of the probability density $p(t_i)$ to jump at t_i , the most probable value of a is either near the maximum $a = a_0(1 + \delta)$ or the minimum $a = a_0(1 - \delta)$, as can be seen by inverting $p(a)da = p(a(t_i))dt_i$. For a jump at those values of a , Y in (5.6) picks up a contribution $\pm \ln(1 \pm \delta)$ corresponding to the location of the peaks. Therefore, these peaks are a consequence of the discrete nature of the system and the shape of the protocol $\gamma(t)$.

For particular protocols obeying the symmetry relation

$$\gamma(t_1 - t) = \gamma(t), \quad (5.9)$$

adaption of the arguments developed by Crooks [13] show that then the distribution $P(Y)$ obeys even the stronger fluctuation theorem (4.6). This relation implies in particular an intriguing condition on the k -th moment

$$\langle Y^k e^{-Y} \rangle = (-1)^k \langle Y^k \rangle. \quad (5.10)$$

In Fig. 5.3, we show the ratio between the two sides of this relation as a function of the length t of the trajectory. The theoretically calculated curves show clearly that the moment relation is valid for symmetric protocols, i.e., for $t = lt_m$ where $l = 1/2, 3/2, 5/2, \dots$. For

other values of t the relations (4.6) and (5.10) do not hold. The oscillations of the ratio are damped and hence the moment relation will become valid for all t in the limit $t \rightarrow \infty$. Even though the experimental data are somewhat noisy, they also illustrate this particular feature of a symmetric protocol which is a consequence of the fluctuation theorem.

5.4 Entropy production

For an extension of the concept of a nonequilibrium entropy to discrete systems, we define

$$s(t) \equiv -\ln p_{n(t)}(t)$$

analog to (3.10), where now $p_n(t)$ is the time-dependent solution of the master equation (2.3) to be distinguished from the equilibrium solution $\psi(\gamma)$. The measured probability p_n is evaluated at the actual state $n(t)$ at time t . Fig. 5.4a shows the protocol $a(t)$ together with the probability $p_1(t)$ to dwell in the bright state. Fig. 5.4b displays a sample binary trajectory $n(t)$ jumping between the two states. In Fig. 5.4c we see that the evolution of $s(t)$ is governed by two effects. First, the time-dependent driving of the rates leads to an evolving probability resulting in a continuous contribution. Second, a jump between the two states gives rise to a contribution $-\ln[p_+/p_-]$, where p_- and p_+ are the probabilities of the states immediately before and after the jump, respectively.

Beside the entropy of the system itself, energy exchange and dissipation lead, in general, to a change in medium entropy. For an athermal system, this change in medium entropy Δs_m can not be inferred from the exchanged heat. Rather it has to be defined. In Ref. [16], the choice

$$\Delta s_m = \ln \frac{w(i \rightarrow j)}{w(j \rightarrow i)} \tag{5.11}$$

for a jump from state i to state j with instantaneous rate $w(i \rightarrow j)$ [$w(j \rightarrow i)$ being the backward rate] has been motivated in analogy to the thermal case. In our case it becomes $\Delta s_m = -\ln[a(t)/b]$ for a jump $1 \rightarrow 0$ and $\Delta s_m = -\ln[b/a(t)]$ for a jump $0 \rightarrow 1$. As demonstrated in Fig. 5.4d, the medium entropy changes only when the system jumps, thereby balancing to some degree the change of $s(t)$.

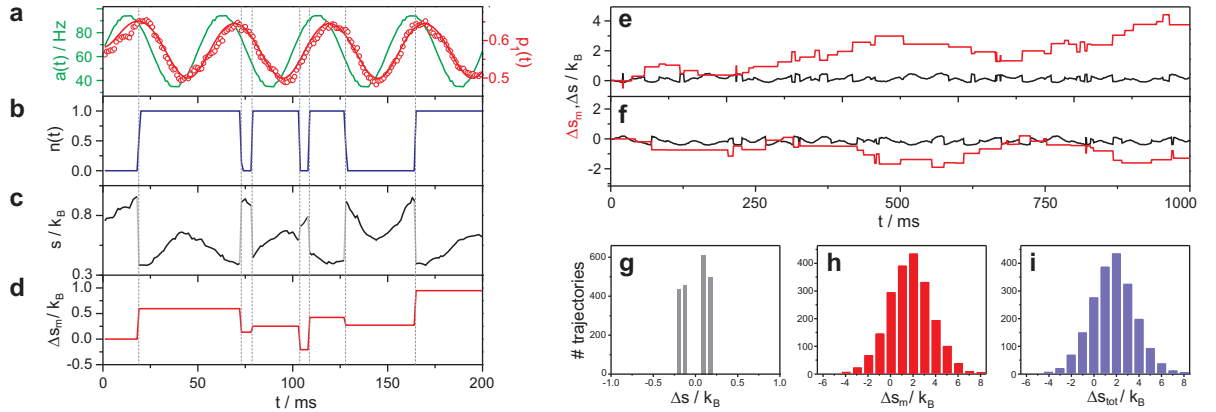


Figure 5.4: Entropy production in a single two-level system with parameters $a_0 = (15.6 \text{ ms})^{-1}$, $b = (21.8 \text{ ms})^{-1}$, $t_m = 50 \text{ ms}$, and $\delta = 0.46$. (a) Transition rate $a(t)$ (green line) and probability of the bright state $p_1(t)$ (red circles – measured, red line – theoretical prediction) over 4 periods. (b) Single trajectory $n(t)$. (c) Evolution of the system entropy. The gray lines correspond to jumps (vertical dotted lines) of the system whereas the dark lines show the continuous evolution due to the driving. (d) Entropy change of the medium, where only jumps contribute. (e,f) Examples of (e) entropy producing and (f) entropy annihilating trajectories. The change of system entropy $\Delta s = s(t) - s(0)$ (black) fluctuates around zero without effective entropy production, whereas in (e) Δs_m (red) produces a net entropy over time. In (f), Δs_m consumes an entropy of about 1 after 20 periods. (g-i) Histograms taken from 2,000 trajectories of the system (g), medium (h), and total entropy change (i). The system entropy shows four peaks corresponding to four possibilities for the trajectory to start and end ($0 \rightarrow 1$, $1 \rightarrow 0$, $0 \rightarrow 0$, and $1 \rightarrow 1$). The distribution (h) of the medium entropy change has mean $\langle \Delta s_m \rangle = 1.7$ and width $\sigma = 3.7$, on this scale it differs only slightly from the distribution of the total entropy change (i).

6 Linear Response Theory

6.1 Introduction

The behavior of systems in response to small perturbations lies at the heart of many disciplines in physics, e.g., the electrodynamics of macroscopic media, and in particular at the heart of statistical mechanics. The linear response of equilibrium systems defines the linear response regime. In this regime, loosely speaking following Onsager, the decay of a fluctuation is independent of whether it has been created spontaneously due to thermal noise or whether it has been induced by a small applied force. The physical picture behind this regression principle is manifested in the fluctuation-dissipation theorem relating a response function with the equilibrium correlations of the thermodynamically conjugated observable [86, 87]. Beyond the linear response regime, a generalized fluctuation-dissipation theorem has been found, which, however, does not allow for an interpretation in terms of thermodynamic observables anymore [88, 83]. The question we attempt to answer in this final chapter is whether the thermodynamics for small driven systems we have constructed so far may point to a generalization of Onsager's regression principle for nonequilibrium steady states.

6.2 Fluctuation-dissipation theorem

6.2.1 Equilibrium

In its most general form for thermal systems, the equilibrium fluctuation-dissipation theorem

$$T\mathcal{R}_{A,h}^{\text{eq}}(t-t') = -\partial_t \langle A(t)B(t') \rangle_0 \quad (6.1)$$

relates the response function $\mathcal{R}_{A,h}^{\text{eq}}$ with an equilibrium correlation function through the temperature T . The observable $B(x)$ appearing in (6.1) is not arbitrary but fixed through the external perturbation h . In equilibrium, a perturbation causes a shift in energy of the type

$$U \mapsto U - Bh, \quad (6.2)$$

where B is the observable conjugated to h in the energy.

The response function is defined as

$$\mathcal{R}_{A,h}(t-t') \equiv \left. \frac{\delta \langle A(t) \rangle_\varepsilon}{\delta [\varepsilon h(t')]} \right|_{\varepsilon=0}. \quad (t \geq t') \quad (6.3)$$

It quantifies the change of the average of an arbitrary observable $A(x)$ at time t in response to a small perturbation $h(t')$ of order ε applied to the system at an earlier time t' , where the average is measured in the perturbed system. The response function follows from Taylor expanding the perturbed mean,

$$\langle A(t) \rangle_\varepsilon = \langle A \rangle_0 + \varepsilon \int_{-\infty}^t dt' \mathcal{R}_{A,h}(t-t') h(t') + \mathcal{O}(\varepsilon^2).$$

Such a response function can be defined not only for a perturbation out of equilibrium but also for a perturbation out of a nonequilibrium steady state. In both cases, due to stationarity, the response function depends only on the time difference. Causality requires $\mathcal{R}_{A,h}(t) = 0$ for times $t < 0$. In the following, we always assume nonnegative times for response functions.

6.2.2 General Markov processes

We will now summarize two long-known relations for the linear response of Markovian stochastic processes. The first relation is based on an operator approach [83], whereas the second relation quantifies the response of the noise [89, 90].

Smoluchowski equation

In appendix A.5, we have derived the Smoluchowski operator (A.26) as

$$\hat{L}_{SM}(t) = -\nabla_k \cdot \hat{\mathbf{v}}_k(t).$$

Let us assume that the system is in a nonequilibrium steady state and that it is then responding to a small external perturbation. We make this explicit by splitting the operator

$$\hat{L}_{SM}(t) = \hat{L}_s + \varepsilon \hat{L}_p(h(t))$$

into a constant part corresponding to the steady state $\hat{L}_s \psi_s = 0$ and a part of order ε which is time dependent through its dependence on the external field $h(t)$. We further assume that the distribution function can be expanded in powers of ε ,

$$\psi_\varepsilon(t) = \psi_s + \varepsilon \psi_p(t) + \mathcal{O}(\varepsilon^2). \quad (6.4)$$

The equation of motion for the deviation from the steady state up to first order then becomes

$$\partial_t \psi_p(t) = \hat{L}_s \psi_p(t) + \hat{L}_p(h(t)) \psi_s$$

with formal solution

$$\psi_p(t) = \int_{-\infty}^t dt' e^{\hat{L}_s(t-t')} \hat{L}_p(h(t')) \psi_s.$$

The initial condition is $\psi_p(t \rightarrow -\infty) = 0$.

To obtain the response function (6.3), we write out the average of an observable $A(x)$

$$\langle A(t) \rangle_\varepsilon = \int dx A(x) \psi_\varepsilon(x, t).$$

The time dependence is completely contained in the perturbed distribution function $\psi_\varepsilon(t)$. Inserting the expansion (6.4), we obtain

$$\frac{\delta \langle A(t) \rangle_\varepsilon}{\delta [\varepsilon h(t')]} = \int dx A(x) \frac{\delta \psi_p(x, t)}{\delta h(t')} = \int dx A(x) e^{\hat{L}_s(t-t')} \frac{\partial \hat{L}_p}{\partial h} \psi_s(x).$$

We can write the last expression in the form of a fluctuation-dissipation theorem

$$T \mathcal{R}_{A,h}(t-t') = \langle A(t) \mathcal{B}(t') \rangle_0 \quad (6.5)$$

similar to (6.1) but with the “conjugate observable” $\mathcal{B}(x)$ now given as

$$\mathcal{B} \equiv T \psi_s^{-1} \frac{\partial \hat{L}_p}{\partial h} \psi_s. \quad (6.6)$$

Moreover, correlations $\langle \cdot \rangle_0$ are now measured in a nonequilibrium steady state.

In the linear response regime near equilibrium, both expressions (6.1) and (6.5) should of course become equal. To this end, we calculate the time derivative in (6.1) and obtain

$$-\frac{\partial}{\partial t} \int dx A(x) e^{\hat{L}_{\text{eq}}(t-t')} \mathcal{B}(x) \psi_{\text{eq}}(x) = \int dx A(x) e^{\hat{L}_{\text{eq}}(t-t')} [-\psi_{\text{eq}}^{-1} \hat{L}_{\text{eq}} \mathcal{B} \psi_{\text{eq}}] \psi_{\text{eq}}(x).$$

The Smoluchowski operator in equilibrium reads

$$\hat{L}_{\text{eq}} = -\nabla_k \cdot \mu_{kl} [-(\nabla_l U) - T \nabla_l] \quad (6.7)$$

and the term in square brackets can be worked out to give

$$\begin{aligned} -\psi_{\text{eq}}^{-1} \hat{L}_{\text{eq}} \mathcal{B} \psi_{\text{eq}} &= -T \psi_{\text{eq}}^{-1} \nabla_k \cdot \mu_{kl} (\nabla_l \mathcal{B}) \psi_{\text{eq}} + \psi_{\text{eq}}^{-1} \nabla_k \cdot \mu_{kl} \mathcal{B} [-(\nabla_l U) - T \nabla_l] \psi_{\text{eq}} \\ &= -T \psi_{\text{eq}}^{-1} \nabla_k \cdot \mu_{kl} (\nabla_l \mathcal{B}) \psi_{\text{eq}}. \end{aligned}$$

On the other hand, with (6.2) we obtain from (6.7) the perturbation operator

$$\hat{L}_p = -\nabla_k \cdot \mu_{kl} [\nabla_l (Bh)]$$

with

$$\mathcal{B} = -T\psi_{\text{eq}}^{-1}\nabla_k \cdot \mu_{kl}(\nabla_l B)\psi_{\text{eq}},$$

which shows the equivalence of both fluctuation-dissipation theorems in the linear response regime.

Noise response

For a second relation involving explicitly the noise, we realize that the current microstate $x(t)$ is a functional $x(\zeta; t)$ of the noise trajectory ζ up to time t . The probability of a given noise history in the case of Gaussian noise is

$$\mathcal{P}(\zeta) = \exp \left\{ -\frac{1}{4T} \int dt \zeta_k(t) \cdot \mu_{kl}^{-1} \zeta_l(t) \right\}.$$

This probability is normalized according to the path integral over all noise histories

$$\int \mathcal{D}\zeta \mathcal{P}(\zeta) = 1,$$

which determines the functional measure $\mathcal{D}\zeta$.

An external perturbation now leads to different trajectories and we calculate the response with respect to a change of the noise trajectory as

$$\begin{aligned} \left\langle \frac{\delta A(t)}{\delta \zeta_k(t')} \right\rangle &= \int \mathcal{D}\zeta \frac{\delta A(x(\zeta; t))}{\delta \zeta_k(t')} \mathcal{P}(\zeta) = - \int \mathcal{D}\zeta A(x(\zeta; t)) \frac{\delta \mathcal{P}(\zeta)}{\delta \zeta_k(t')} \\ &= \frac{1}{2T} \int \mathcal{D}\zeta \left[A(x(\zeta; t)) \mu_{kl}^{-1}(x(\zeta; t')) \zeta_l(t') \right] \mathcal{P}(\zeta) \\ &= \frac{1}{2T} \langle A(t) \mu_{kl}^{-1}(t') \zeta_l(t') \rangle. \end{aligned} \quad (6.8)$$

To arrive at the second line, we perform a functional integration by parts.

6.3 The nonequilibrium velocity fluctuation-dissipation theorem

6.3.1 Derivation

We consider a system in a nonequilibrium steady state which is perturbed through a small, spatially homogeneous change of the nonconservative force

$$h \mapsto \delta \mathbf{f}_m$$

exerted on the m^{th} particle. The response function can be rewritten as

$$\begin{aligned} T\mathcal{R}_{A,\delta\mathbf{f}_m}(t-t') &= T \left\langle \frac{\delta A(t)}{\delta \mathbf{f}_m(t')} \right\rangle = T \left\langle \frac{\delta A(t)}{\delta \zeta_k(t')} \cdot \frac{\partial \zeta_k}{\partial \mathbf{f}_m} \right\rangle \\ &= T \left\langle \frac{\delta A(t)}{\delta \zeta_k(t')} \cdot \mu_{km}(t') \right\rangle \end{aligned} \quad (6.9)$$

employing the chain rule. To obtain the last expression, we use that within the brackets, the trajectory is fixed. The Langevin equation (2.13) solved for the noise is then a function of the velocities and, in particular, of the nonconservative forces. Partial differentiation with respect to \mathbf{f}_m then leads to the mobility matrices μ_{km} . The response function is now a vectorial quantity where the components are given by the functional derivative with respect to the components of \mathbf{f}_m . We follow the steps outlined in the end of the previous section and perform a functional integration by parts of (6.9), leading to

$$T\mathcal{R}_{A,\delta\mathbf{f}_m}(t-t') = -T \int \mathcal{D}\zeta A(x(\zeta; t)) \frac{\delta \mu_{km}(x(\zeta; t')) \mathcal{P}(\zeta)}{\delta \zeta_k(t')}.$$

However, here we are confronted with the treatment of multiplicative noise due to the spatial dependence of the mobility tensors.¹ For the sake of simplicity, we set $\alpha = 0$ corresponding to the Itô calculus. Then $\langle \mathbf{r}_k(t) \zeta_l^T(t) \rangle = 0$ holds at same times which implies that microstate and noise are independent variables leading to the response function

$$T\mathcal{R}_{A,\delta\mathbf{f}_m}(t-t') = \frac{1}{2} \langle A(t) \zeta_m(t') \rangle. \quad (6.10)$$

With this intermediate result, we can now calculate the observable conjugate to the non-conservative force in a nonequilibrium steady state.

The conjugate observable in general is given by (6.6). The perturbation operator is found to be

$$\hat{L}_p(\delta\mathbf{f}_m) = -\nabla_k \cdot \mu_{km} \delta\mathbf{f}_m$$

and we obtain the vector

$$\mathcal{B} = -\nabla_k \cdot D_{mk} - D_{mk}(\nabla_k \ln \psi_s)$$

employing the Einstein relation (2.15). This is certainly correct but seems not very useful. However, combining the Langevin equation (2.13) with the local mean velocity (2.9), we find the Langevin equation (remember $\alpha = 0$)

$$\dot{\mathbf{r}}_m = \mathbf{v}_m^s + D_{mk}(\nabla_k \ln \psi_s) + \nabla_k \cdot D_{mk} + \zeta_m$$

¹See appendix A.4.

and hence

$$\mathcal{B} = \zeta_m - (\dot{\mathbf{r}}_m - \mathbf{v}_m^s).$$

The fluctuation-dissipation theorem (6.5) amounts to

$$T\mathcal{R}_{A,\delta\mathbf{f}_m}(t-t') = \langle A(t)\mathcal{B}(t') \rangle_0 = -\langle A(t)[\dot{\mathbf{r}}_m(t') - \mathbf{v}_m^s(t')] \rangle_0 + \langle A(t)\zeta_m(t') \rangle$$

and finally, using (6.10), we arrive at the velocity fluctuation-dissipation theorem

$$T\mathcal{R}_{A,\delta\mathbf{f}_m}(t-t') = \langle A(t)\delta\mathbf{v}_m(t') \rangle_0 \quad (6.11)$$

involving the *relative velocity*

$$\delta\mathbf{v}_m(t) \equiv \dot{\mathbf{r}}_m(t) - \mathbf{v}_m^s(x(t)). \quad (6.12)$$

Hence, through combining the two known relations introduced in the previous section, we could show that the abstract expression (6.6) equals the relative velocity (6.12).

6.3.2 Restoring the equilibrium form and a violation function

In equilibrium, the velocity fluctuation-dissipation theorem (6.1) reads

$$T\mathcal{R}_{\dot{\mathbf{r}}_n,\delta\mathbf{f}_m}^{\text{eq}}(t-t') = \frac{\partial}{\partial t'} \langle \dot{\mathbf{r}}_n(t)\mathbf{r}_m^T(t') \rangle_0 = \langle \dot{\mathbf{r}}_n(t)\dot{\mathbf{r}}_m^T(t') \rangle_0,$$

where the response function now is a response matrix. The conjugate variable of the force is the position \mathbf{r}_m . We have shifted the derivative to the earlier time t' and due to linearity, we can pull the time derivative within the brackets. From (6.11), the same form holds in nonequilibrium steady states but for the relative velocity,

$$T\mathcal{R}_{\delta\mathbf{v}_n,\delta\mathbf{f}_m}(t-t') = \langle \delta\mathbf{v}_n(t)\delta\mathbf{v}_m^T(t') \rangle_0. \quad (6.13)$$

This is not the equilibrium fluctuation-dissipation theorem since the response is defined with respect to a perturbation out of a nonequilibrium steady state but it strongly resembles the form of the fluctuation-dissipation theorem in equilibrium.

Equation (6.13) demonstrates the role of the three velocities involved: the actual velocity $\dot{\mathbf{r}}_k$, the local mean velocity \mathbf{v}_k^s , and the global mean velocity $\langle \dot{\mathbf{r}}_k \rangle$. Surprisingly, in order to recover the equilibrium form of the fluctuation-dissipation theorem, the actual velocity has to be measured with respect to the local mean velocity which depends on the microstate of the system in contrast to the global mean velocity. At least for the velocity, this implies a modification of Onsager's principle: forced fluctuations out of a nonequilibrium steady state cannot be distinguished from spontaneous fluctuations *with respect to the local mean*.

The fact that the equilibrium form is contained in (6.11) also for a general observable A suggests that we introduce a “violation function”

$$I_{A,\delta f_m}(t-t') \equiv \langle [A(t) - \langle A \rangle][\mathbf{v}_m^s(t') - \langle \dot{\mathbf{r}}_m \rangle] \rangle_0 \quad (6.14)$$

measuring the excess. The so defined violation function vanishes in equilibrium. In principle, the fluctuation-dissipation theorem is not “violated” in the sense that a prerequisite, namely detailed balance, is no longer met. It is, however, a convenient and commonly used term. Violations of the fluctuation-dissipation theorem have been studied mostly in the context of glassy systems [91, 92, 93, 90, 94], where time-translational invariance is broken but the entropy production rate is small. In contrast to our result leading to an additive violation (6.14), the concept of an effective temperature [95, 93, 90] aims to keep the simple form (6.1) at the expense of a temperature different from that of the fluid. The concept of an effective temperature has been applied also to driven systems [96, 97].

6.3.3 Generalized Einstein relation

In chapter 2 we already met the Einstein relation (2.15) connecting the short-time diffusion tensors to the mobility tensors through the temperature T . This relation holds strictly only in equilibrium but we have required it to be valid even when we drive the system. In principle it corresponds to the assumption that driving the small system of interest does not affect the strength of fluctuations determined by the larger heat bath, i.e., the fluid.

In the following discussion of a generalized Einstein relation, we consider the one-dimensional case with particle position x . The particle is moving in a periodic potential $U(x+L) = U(x)$ with periodicity L . We introduce a second definition for the diffusion coefficient as

$$D \equiv \lim_{t \rightarrow \infty} \frac{1}{2t} \left[\langle x^2(t) \rangle - \langle x(t) \rangle^2 \right] \quad (6.15)$$

with particle position x . Whereas (A.9) defines the short-time diffusion coefficient D_0 determining also the noise strength, D from (6.15) defines the effective long-time diffusion coefficient. The free diffusion coefficient D_0 is a property of the bath alone and does not depend on external potentials nor particle–particle interactions. For a better understanding, consider a deep potential where the particle is trapped. Then clearly $D = 0$ but $D_0 \neq 0$ as the particle still diffuses within the potential minimum. In equilibrium, $D \leq D_0$ since interactions hinder the diffusion of the particle, where the equal sign holds for a free particle only. It has been shown that in a periodic potential under nonequilibrium conditions, i.e., a nonconservative force f is driving the particle, the effective diffusion is enhanced [98, 99] with $D \gg D_0$ under certain conditions. We will now show that the excess of the diffusion coefficient is quantitatively given by the violation function.

In one dimension, the violation function (6.14) becomes

$$I(t) = \langle [\dot{x}(t'+t) - \langle \dot{x} \rangle][v^s(x(t')) - \langle \dot{x} \rangle] \rangle, \quad (6.16)$$

which is a function of the time difference t . The offset t' is arbitrary because of time-translational invariance in a steady state, and in the following we set $t' = 0$. The diffusion coefficient (6.15) can be rewritten through the Green-Kubo formula

$$D = \int_0^{\infty} dt \langle [\dot{x}(t) - \langle \dot{x} \rangle][\dot{x}(0) - \langle \dot{x} \rangle] \rangle. \quad (6.17)$$

This suggests to integrate the fluctuation-dissipation theorem over time, leading to

$$T \int_0^{\infty} dt \mathcal{R}_{\dot{x},f}(t) = D - \int_0^{\infty} dt I(t).$$

However, the left hand side is the effective mobility of the particle defined as the response with respect to a small variation of the driving force,

$$\mu \equiv \frac{\partial \langle \dot{x} \rangle}{\partial f} = \int_0^{\infty} dt \mathcal{R}_{\dot{x},f}(t). \quad (6.18)$$

Therefore, the integrated version of the fluctuation-dissipation theorem (6.13) holding in nonequilibrium implies a generalized Einstein relation

$$D = T\mu + \int_0^{\infty} dt I(t), \quad (6.19)$$

which reduces to $D = T\mu$ in equilibrium. Hence, in equilibrium the Einstein relations for bare and effective diffusion coincide. Driving the system into a nonequilibrium steady state, the ‘‘bath’’ Einstein relation for the bare diffusion coefficient still holds but the effective diffusion attains an additional contribution given by the integrated violation function.

For the one-dimensional case, explicit formulas for both the global mean velocity

$$\langle \dot{x} \rangle = \frac{1 - \exp(-Lf/T)}{\int_0^L dx I_+(x)/L}, \quad I_{\pm}(x) \equiv \frac{1}{D_0} \int_0^L dz \exp\{\pm[V(x) - V(x \mp z)]/T\}$$

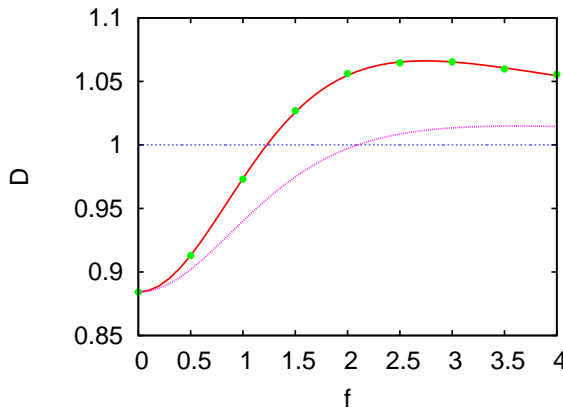


Figure 6.1: The effective diffusion constant D over the force f for the periodic model potential $V(x) = V_0 \cos 2x$ (with $V_0 = \frac{1}{2}$, $D = T = 1$). The solid line shows the analytical solution (6.20) whereas the closed circles are obtained numerically. The dotted line shows the effective mobility (6.18).

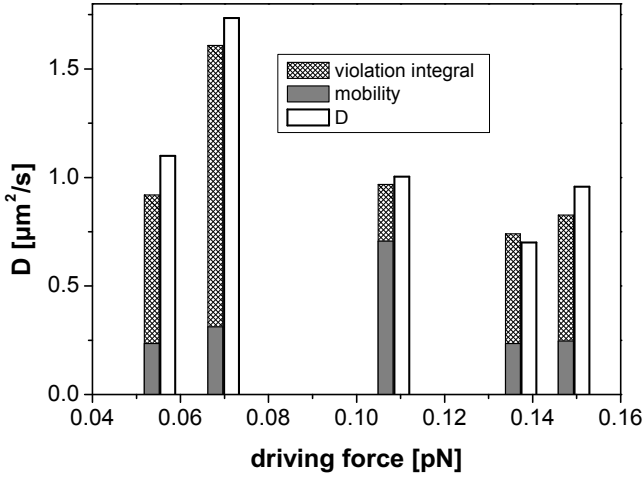


Figure 6.2: Experimental test of Eq. (6.19) for different driving forces f . The open bars show the measured diffusion coefficients D . The stacked bars are mobility (gray bar) and integrated violation (hatched bar), respectively.

and the diffusion coefficient

$$D = D_0 L^2 \left[\int_0^L dx I_+(x) \right]^{-3} \int_0^L dx I_+^2(x) I_-(x) \quad (6.20)$$

with $V(x) \equiv U(x) - fx$ exist [98]. With these exact results, we compare the generalized Einstein relation versus numerical data in figure 6.1.

We have also tested the Einstein relation experimentally, see figures 6.2 and 6.3. To this end, a single colloidal particle is moving in a toroidal optical trap which restricts the motion of the particle effectively to one dimension. The diffusion coefficient and the violation function can be calculated from a single trajectory. First, global mean velocity and the stationary probability distribution $\psi_s(x)$ are determined. From these quantities, the local mean velocity follows as $v^s(x) = \langle \dot{x} \rangle / [L\psi_s(x)]$. The correlation function (6.16) is then calculated along the trajectory, resulting in the violation function which is finally integrated. The diffusion coefficient is obtained from (6.15). For the effective mobility, the force is varied experimentally by a small amount and a short trajectory is recorded. The difference of the global mean velocity finally leads to the mobility (6.18).

6.4 Outlook

These final remarks concerning the extension of the fluctuation-dissipation theorem to nonequilibrium steady states conclude our efforts to build a thermodynamics of small systems. The method described in this chapter yields a promising approach, which hopefully can be extended to other quantities than the velocity. Especially the extension of the Onsager principle seems to be of greater generality than just concerning velocities. The remaining task of finding the correct local mean for other observables, however, will certainly be challenging.

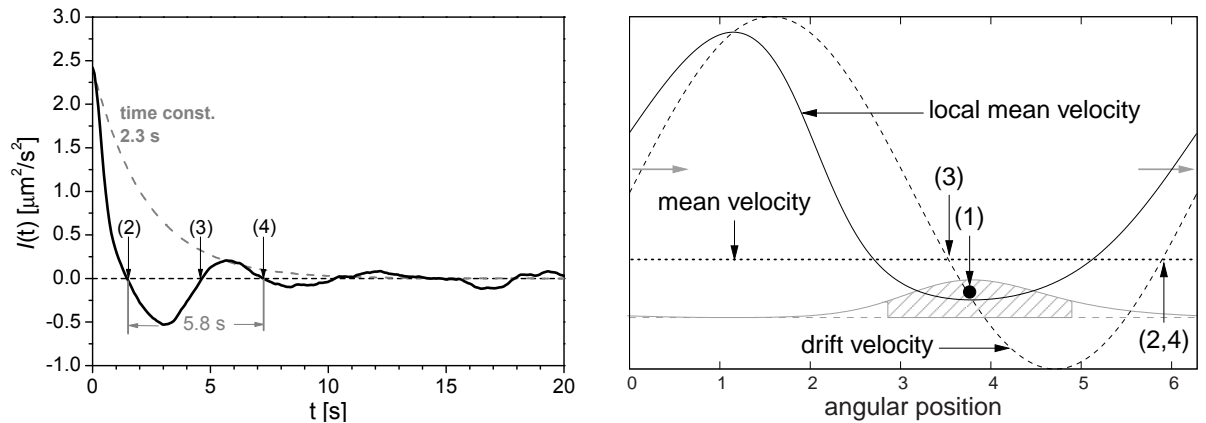


Figure 6.3: Left: Experimentally measured violation function $I(t)$ (solid line). Right: Comparison of the velocities involved in the violation function $I(t)$. For an ideal cosine potential, we sketch the probability distribution $\psi_s(x)$ (solid gray line), the local mean velocity $v^s(x)$ together with the drift velocity and their mean $\langle \dot{x} \rangle$ versus the angular particle position. The drift velocity is the deterministic part of the actual velocity \dot{x} . The sign change in $I(t)$ at (2), (3), and (4) can be understood as follows. In a steady state, a single particle trajectory will start with highest probability in the shaded region and, for an illustration, we choose its maximum as starting point (1) determining the value $v^s(x(t))$ in Eq. (6.16). Neglecting thermal fluctuations, the particle would follow the dashed line and during a small time step τ the product of drift velocity time $v^s(x(t'))$ is positive. If the particle passes (2), the product will become negative. The sign changes again if the particle passes (3) and then (4) and so on due to the periodic nature of the potential. Thermal noise and averaging over all trajectories does not change this behavior responsible for the oscillations of $I(t)$.

A Appendix

A.1 Projected processes

There are in general two kinds of projected processes. The *Zwanzig-Mori formalism* allows to derive exact equations of motion for configuration space functions including the mean of an observable, correlation functions, etc [91]. This has found applications in the mode-coupling theory of glasses [100] but also driven colloidal suspensions [101]. The second technique, also called *adiabatic elimination* [55, 102], reduces the configuration space by means of a time scale separation which allows to project out unwanted degrees of freedom. We will use the latter method to get rid of the particle momenta in the overdamped regime.

We assume that the time evolution

$$\partial_t \Psi(t) = \hat{L} \Psi(t) \quad (\text{A.1})$$

of a state $\Psi(x, x', t)$ is governed by the linear, constant operator \hat{L} . Let us denote $\langle \cdot, \cdot \rangle$ the linear functionals with respect to the space $\{x'\}$. We aim to describe the evolution of the process depending on x alone, i.e., we look for the function $\psi(x, t)$ given by the projection

$$\hat{P} \Psi(t) = \psi(x, t) \varphi_0(x'). \quad (\text{A.2})$$

The projector is defined as

$$\hat{P} \cdot \equiv \langle \bar{\varphi}_0, \cdot \rangle \varphi_0,$$

where $\varphi_0(x')$ and $\bar{\varphi}_0(x')$ are two yet arbitrary functions which must fulfill $\langle \bar{\varphi}_0, \varphi_0 \rangle = 1$ to ensure idempotency $\hat{P}^2 = \hat{P}$.

The specific application we have in mind is that of a process $\partial_t \varphi(x', t) = \hat{L}_0 \varphi(x', t)$ to which the evolution of another process is coupled. We model this through $\hat{L} = \hat{L}_0 + \hat{L}_1$ and choose to project onto the null space of \hat{L}_0 . Hence, $\hat{L}_0 \varphi_0 = 0$ and $\hat{L}_0^\dagger \bar{\varphi}_0 = 0$ lead to

$$\hat{L}_0 \hat{P} = \hat{P} \hat{L}_0 = 0. \quad (\text{A.3})$$

Applying the projector to (A.1) and using (A.3), we can rewrite the evolution equation as the two coupled equations

$$\partial_t \Psi_0(t) = \hat{P} \hat{L}_1 \Psi_0(t) + \hat{P} \hat{L}_1 \Psi_1(t), \quad (\text{A.4})$$

$$\partial_t \Psi_1(t) = (\hat{L}_0 + \hat{P}' \hat{L}_1) \Psi_1(t) + \hat{P}' \hat{L}_1 \Psi_0(t), \quad (\text{A.5})$$

where $\Psi_0 \equiv \hat{P}\Psi = \psi\varphi_0$ is the projected state and $\Psi_1 \equiv \hat{P}'\Psi \equiv (1 - \hat{P})\Psi$ is the deviation from the projected state. The formal solution of (A.5) for time independent operators \hat{L}_0 and \hat{L}_1 is

$$\Psi_1(t) = \exp[(\hat{L}_0 + \hat{P}'\hat{L}_1)t]\Psi_1(0) + \int_0^t dt' \exp[(\hat{L}_0 + \hat{P}'\hat{L}_1)(t - t')]\hat{P}'\hat{L}_1\Psi_0(t').$$

The generalization to time-dependent operators is straightforward through a time-ordered exponential. Putting this solution back into (A.4) would lead to an integro-differential equation for $\psi(x, t)$ but to little avail since the memory kernel can only be expressed formally.

We can proceed further assuming that the time scales on which the two processes evolve are very different. The first time scale is set by the relaxation time $\tau_0 = \|\hat{L}_0^{-1}\|$. We define

$$\varepsilon = \|\hat{L}_0^{-1}(\partial_t - \hat{P}'\hat{L}_1)\| \leq \|\hat{L}_0^{-1}\| \cdot \|\partial_t - \hat{P}'\hat{L}_1\| = \tau_0 \|\partial_t - \hat{P}'\hat{L}_1\| \ll 1$$

as the ratio of the relaxation time and the typical rate of change of the coupled process. Equation (A.5) is solved as

$$\Psi_1(t) = [\partial_t - (\hat{L}_0 + \hat{P}'\hat{L}_1)]^{-1}\hat{P}'\hat{L}_1\Psi_0(t).$$

Assuming ε to be small, we can expand

$$[(\partial_t - \hat{P}'\hat{L}_1) - \hat{L}_0]^{-1} = -[1 - \hat{L}_0^{-1}(\partial_t - \hat{P}'\hat{L}_1)]^{-1}\hat{L}_0^{-1} \simeq -\hat{L}_0^{-1} + \mathcal{O}(\varepsilon),$$

leading to a deviation

$$\Psi_1(t) \simeq -\hat{L}_0^{-1}\hat{P}'\hat{L}_1\Psi_0(t).$$

The equation of motion for the reduced process thus reads

$$\partial_t \psi(t) = \hat{L}_{\text{red}}\psi(t), \quad \hat{L}_{\text{red}} \equiv \langle \bar{\varphi}_0, \hat{L}_1\varphi_0 \rangle - \langle \bar{\varphi}_0, \hat{L}_1\hat{L}_0^{-1}\hat{P}'\hat{L}_1\varphi_0 \rangle.$$

Through discarding the component of the coupled process in the nullspace of \hat{L}_0 , the projector \hat{P}' makes sure that we can always apply the inverse \hat{L}_0^{-1} . If $\hat{P}'\hat{L}_1\varphi_0 = 0$ then the reduced evolution operator simplifies to

$$\hat{L}_{\text{red}} = -\langle \bar{\varphi}_0, \hat{L}_1\hat{L}_0^{-1}\hat{L}_1\varphi_0 \rangle. \tag{A.6}$$

A.2 Derivation of the Fokker-Planck equation

The Fokker-Planck equation is the equation of motion for the probability distribution of a general Markov process [55]. In this section, we basically apply the methods of stochastic processes as introduced in textbooks [55, 103] to many-particle systems while keeping

in mind Lau and Lubensky's more recent discussion of the correct interpretation of multiplicative noise [60] following in the next section.

Derivations usually start from the propagation of the probability distribution (2.5)

$$\psi(x, t + \varepsilon) = \int dx' P(x, t + \varepsilon | x', t) \psi(x', t) \quad (\text{A.7})$$

using the transition probability. The transition probability is normalized according to

$$\int dx P(x, t + \varepsilon | x', t) = 1.$$

The probability for the transition $x' \rightarrow x$ during the small time step ε is defined as

$$P(x, t + \varepsilon | x', t) = \langle \delta(x - x(t + \varepsilon)) \rangle_{|x(t)=x'},$$

where the mean is over the noise for trajectories starting in x' . Taylor expanding the δ -function around x' yields

$$\begin{aligned} \delta(x - x(t + \varepsilon)) &= \delta(x - x') - [\mathbf{r}_k(t + \varepsilon) - \mathbf{r}'_k] \cdot \nabla_k \delta(x - x') \\ &\quad + \frac{1}{2} [\mathbf{r}_k(t + \varepsilon) - \mathbf{r}'_k] [\mathbf{r}_l(t + \varepsilon) - \mathbf{r}'_l]^T : \Delta_{kl} \delta(x - x') + \dots \end{aligned}$$

where $\Delta_{kl} \equiv \nabla_k \nabla_l^T$ is the symmetric matrix of second-order derivatives. The minus sign in the second term arises because we shift the derivative to the first argument. We expand the Taylor series up to second order since for normal diffusion the first two moments,

$$\langle [\mathbf{r}_k(t + \varepsilon) - \mathbf{r}'_k] \rangle \equiv \mathbf{m}_k(x') \varepsilon, \quad (\text{A.8})$$

$$\langle [\mathbf{r}_k(t + \varepsilon) - \mathbf{r}'_k] [\mathbf{r}_l(t + \varepsilon) - \mathbf{r}'_l]^T \rangle \equiv 2D_{kl}(x') \varepsilon, \quad (\text{A.9})$$

are of order ε and higher moments are at least of order ε^2 [55]. These moments are the mean displacements \mathbf{m}_k and the short-time diffusion matrices D_{kl} , respectively.

We put the resulting transition probability

$$P(x, t + \varepsilon | x', t) = \delta(x - x') - \varepsilon [\mathbf{m}_k(x') \cdot \nabla_k \delta(x - x') - D_{kl}(x') : \Delta_{kl} \delta(x - x')]$$

back into (A.7) and pull the derivatives in front of the integral. With the time derivative

$$\frac{\partial \psi}{\partial t} = \lim_{\varepsilon \rightarrow 0} \frac{\psi(x, t + \varepsilon) - \psi(x, t)}{\varepsilon}$$

and using the properties of the δ -function, we arrive at the Fokker-Planck equation

$$\partial_t \psi + [\nabla_k \cdot (\mathbf{m}_k \psi) - \Delta_{kl} : (D_{kl} \psi)] = 0. \quad (\text{A.10})$$

The Fokker-Planck equation is a partial differential equation of second order. The explicit expressions of the mean displacements \mathbf{m}_k and short-time diffusion matrices D_{kl} depend on our interpretation of the actual stochastic processes as defined by the Langevin equation.

A.3 Time evolution operator: The harmonic oscillator

The simplest Fokker-Planck operator is

$$\hat{L} = \tau^{-1} \partial_x [x + \partial_x] \quad (\text{A.11})$$

which describes motion in one dimension with a linear restoring force. The eigenvalue equation becomes

$$-\lambda_k \psi_k(x) = \hat{L} \psi_k(x) = \tau^{-1} [\psi_k(x) + x \psi_k'(x) + \psi_k''(x)],$$

where the prime denotes derivation with respect to x . With the *ansatz* $\psi_k(x) = e^{-x^2/2} \varphi_k(x)$ we obtain

$$\varphi_k''(x) - x \varphi_k'(x) + \lambda_k \tau \varphi_k(x) = 0,$$

the generating differential equation – replace x by $2x$ – for the Hermite polynomials $H_k(x)$. The normalized eigenfunctions of the operator (A.11) are therefore

$$\psi_k(x) = \frac{e^{-x^2/2}}{\sqrt{2\pi}} H_k(x/\sqrt{2})$$

with nonnegative eigenvalues $\lambda_k = k/\tau$. For the definition of the inverse operator we exclude the null space ($k = 0$) and since there is a gap between zero and the smallest nonzero eigenvalue $1/\tau$ the inverse is a bounded operator with norm

$$\|\hat{L}^{-1}\| = \tau,$$

i.e., all its eigenvalues are positive and smaller than τ .

A.4 Multiplicative noise

In this section, we write the Langevin equation as

$$\dot{\mathbf{r}}_k = \mathbf{d}_k + G_{kl} \xi_l \quad (\text{A.12})$$

with arbitrary drift vectors \mathbf{d}_k . The noise has zero mean and correlations

$$\langle \xi_k(t) \xi_l^T(t') \rangle = \mathbf{21} \delta_{kl} \delta(t - t'). \quad (\text{A.13})$$

If the strength of the noise $G_{kl}(x)$ depends on the microstate itself, we are confronted with the problem of multiplicative noise

$$G(x[\xi(t)]) \xi(t), \quad (\text{A.14})$$

which carries an ambiguity due to the δ -correlated nature of the noise. To understand the problem, consider the integral

$$\int_t^{t+\varepsilon} dt' G(x(t'))\xi(t') \rightarrow G(x(\bar{t})) \int_t^{t+\varepsilon} dt' \xi(t')$$

over a short time interval with the uniquely determined time $t < \bar{t} < t + \varepsilon$. The right hand side conclusion follows from the first integral mean-value theorem which only holds for continuous functions. However, the noise $\xi(t)$ is a discontinuous function. Stochastic products of the kind (A.14) have therefore to be augmented by the answer to the question of how the function $G(x)$ is to be evaluated. In [60], the following rule

$$x(\bar{t}) \mapsto \bar{x} \equiv (1 - \alpha)x(t) + \alpha x(t + \varepsilon) \quad (\text{A.15})$$

involving a parameter $0 \leq \alpha \leq 1$ has been proposed. In particular, it reduces to the Itô convention for $\alpha = 0$ and to the Stratonovich convention for $\alpha = 1/2$ [55].

In the previous section, we have derived the Fokker-Planck equation (A.10). Using the rule (A.15), we can calculate the involved moments from the particle's displacement

$$\mathbf{r}_k(t + \varepsilon) - \mathbf{r}_k(t) = \int_t^{t+\varepsilon} dt' \dot{\mathbf{r}}_k(t') = \mathbf{d}_k(\bar{x})\varepsilon + \mathbf{G}_{kl}(\bar{x}) \int_t^{t+\varepsilon} dt' \xi_l(t') \quad (\text{A.16})$$

using the Langevin equation (A.12). Taylor expanding a function depending on \bar{x} around $x = x(t)$ up to first order in ε yields

$$G(\bar{x}) \simeq G(x) + \left. \frac{dG}{d\varepsilon} \right|_{\varepsilon=0} \varepsilon = G(x) + \alpha [\dot{\mathbf{r}}_k \cdot \nabla_k G(x)] \varepsilon.$$

Putting this expression back into (A.16) and taking the mean over the noise leads to an additional contribution

$$\langle \dot{\mathbf{r}}_k(t) \xi_l^T(t') \rangle = \mathbf{d}_k(x) \langle \xi_l^T \rangle + \mathbf{G}_{km}(x) \langle \xi_m(t) \xi_l^T(t') \rangle = 2\mathbf{G}_{kl}(x) \delta(t - t')$$

to the mean displacement \mathbf{m}_k besides the drift \mathbf{d}_k . Integrals over the δ -function are evaluated according to

$$\int_t^{t+\varepsilon} dt' \delta(t - t') = \frac{1}{2}, \quad \int_t^{t+\varepsilon} dt' \int_t^{t+\varepsilon} dt'' \delta(t' - t'') = \varepsilon.$$

The moments as defined in (A.8) and (A.9) then become

$$\begin{aligned} \mathbf{m}_k &= \mathbf{d}_k + \alpha \mathbf{G}_{lm} : \nabla_m \mathbf{G}_{kl}, \\ D_{kl} &= \mathbf{G}_{km} \mathbf{G}_{ml}. \end{aligned}$$

Here, we have assumed that the \mathbf{G}_{kl} are symmetric matrices. We can assume this because the D_{kl} must be symmetric matrices (and also symmetric with respect to $k \leftrightarrow l$), which does not determine the \mathbf{G}_{kl} uniquely.

A.5 Derivation of the Smoluchowski equation

In section 2.4.2, the Smoluchowski equation has been introduced phenomenologically. However, it can also be derived from the Fokker-Planck equation (A.10) if we consider inertial particles and then project out their momenta $\{\mathbf{p}_k\}$.

For the derivation of the Fokker-Planck equation, we start with the coupled equations of motion

$$\dot{\mathbf{r}}_k = \mathbf{p}_k/m, \quad \dot{\mathbf{p}}_k = -\nabla_k U + \mathbf{f}_k - \mu_{kl}^{-1} [\mathbf{p}_l/m - \mathbf{u}(\mathbf{r}_l)] + \xi_k,$$

where m is the mass of the particles. The noise has correlations

$$\langle \xi_k(t) \xi_l^T(t') \rangle = 2T \mu_{kl}^{-1} \delta(t - t').$$

The equations of motion for the momenta are linear with additive noise since the mobility tensors $\mu_{kl}(x)$ do not depend on the momenta. It therefore does not suffer from the ambiguities we discussed in section A.4.

Besides the positions x we gather the momenta $x_p \equiv (\mathbf{p}_1, \dots, \mathbf{p}_N)$ such that the configuration space turns into phase space with microstate (x, x_p) . The state $\Psi(x, x_p, t)$ is then the joint probability distribution of both particle positions and momenta. The Fokker-Planck equation is obtained from (A.10) and we write it in the form

$$\partial_t \Psi(t) = [\hat{L}_0 + \hat{L}_1] \Psi(t)$$

with operators

$$\hat{L}_0 \equiv \frac{\mu_{kl}^{-1}}{m} \frac{\partial}{\partial \mathbf{p}_k} \cdot \left[\mathbf{p}_l + mT \frac{\partial}{\partial \mathbf{p}_l} \right], \quad (\text{A.17})$$

$$\hat{L}_1 \equiv -\frac{\mathbf{p}_k}{m} \cdot \nabla_k - [-\nabla_k U + \mathbf{f}_k] \cdot \frac{\partial}{\partial \mathbf{p}_k} - \mu_{kl}^{-1} \mathbf{u}(\mathbf{r}_l) \cdot \frac{\partial}{\partial \mathbf{p}_k}. \quad (\text{A.18})$$

The benefit of splitting the operator in this way is that \hat{L}_0 acts and depends on the momenta only, which are the variables we want to get rid of. The splitting therefore is amenable to the projecting scheme we developed in section A.1. The relaxation time τ_0 is the maximal eigenvalue of $m\mu_{kl}$. For the projecting scheme to hold, τ_0 must be larger than the typical time scale on which we observe the positions of the particles.

A.5.1 Reduced time evolution operator

For the explicit calculation of the reduced time evolution operator, we need the stationary solution of $\hat{L}_0 \varphi_0 = 0$ which is of course the Maxwell-Boltzmann distribution (in three dimensions)

$$\varphi_0(x_p) = \varphi_{\text{MB}}(x_p) \equiv \left(\frac{1}{2\pi mT} \right)^{\frac{3N}{2}} \exp \left\{ -\sum_{k=1}^N \frac{\mathbf{p}_k^2}{2mT} \right\}. \quad (\text{A.19})$$

Its gradient becomes

$$\frac{\partial \varphi_{\text{MB}}}{\partial \mathbf{p}_k} = -\frac{\mathbf{p}_k}{mT} \varphi_{\text{MB}}. \quad (\text{A.20})$$

We define the brackets as the integral

$$\langle \cdot, \cdot \rangle \equiv \int dx_p \cdot (x_p) \cdot (x_p)$$

and accordingly, $\bar{\varphi}_0 = 1$.

The first step is to calculate

$$\hat{L}_1 \varphi_0 = \varphi_0 \frac{\mathbf{p}_k}{mT} \cdot \left[-T \nabla_k + (-\nabla_k U + \mathbf{f}_k) + \mu_{kl}^{-1} \mathbf{u}(\mathbf{r}_l) \right] \equiv \varphi_0 \frac{\mathbf{p}_k}{mT} \cdot \mu_{kl}^{-1} \hat{\mathbf{v}}_l,$$

where we have introduced the velocity operator

$$\hat{\mathbf{v}}_k \equiv \mathbf{u}(\mathbf{r}_k) + \mu_{kl} \left[-\nabla_l U + \mathbf{f}_l - T \nabla_l \right]. \quad (\text{A.21})$$

Applying this operator to the probability distribution $\psi(x, t)$ leads to the local mean velocity (2.9),

$$\hat{\mathbf{v}}_k \psi = \mathbf{v}_k \psi.$$

Applying the projector (A.2) shows that

$$\hat{P} \hat{L}_1 \varphi_0 = \langle \bar{\varphi}_0, \hat{L}_1 \varphi_0 \rangle \varphi_0 = \varphi_0 \langle \mathbf{1}, \mathbf{p}_k / (mT) \varphi_{\text{MB}} \rangle \cdot \mu_{kl}^{-1} \hat{\mathbf{v}}_l = 0$$

vanishes because of the Gaussian integral $\int dx_p \mathbf{p}_k \varphi_{\text{MB}} = 0$. Therefore, the Smoluchowski operator is given by the expression (A.6),

$$\hat{L}_{\text{SM}} = -\langle \bar{\varphi}_0, \hat{L}_1 \hat{L}_0^{-1} \hat{L}_1 \varphi_0 \rangle. \quad (\text{A.22})$$

In the next step, we have to calculate $\hat{L}_0^{-1} \hat{L}_1 \varphi_0$ involving

$$\hat{L}_0^{-1} \mathbf{p}_k \varphi_0 = -m \mu_{kl} \mathbf{p}_l \varphi_0. \quad (\text{A.23})$$

Hence,

$$\hat{L}_0^{-1} \hat{L}_1 \varphi_0 = \frac{1}{mT} (\hat{L}_0^{-1} \mathbf{p}_k \varphi_0) \cdot \mu_{kl}^{-1} \hat{\mathbf{v}}_l = -\varphi_0 \frac{\mathbf{p}_k}{T} \cdot \hat{\mathbf{v}}_k. \quad (\text{A.24})$$

The last step is to apply the operator \hat{L}_1 again. It involves the derivative

$$\frac{\partial}{\partial \mathbf{p}_k} (\mathbf{p}_l \varphi_0) = \mathbf{1} \delta_{kl} \varphi_0 - \frac{\mathbf{p}_k \mathbf{p}_l^T}{mT} \varphi_0$$

which is, however, zero if we integrate over the momenta. As the result, most terms cancel in the integral

$$\int dx_p \hat{L}_1 \mathbf{p}_k \varphi_0 = -T \nabla_k. \quad (\text{A.25})$$

Finally, putting everything together, we obtain the Smoluchowski operator

$$\hat{L}_{SM} = \langle \bar{\varphi}_0, \hat{L}_1(\mathbf{p}_k \varphi_0) / T \rangle \cdot \hat{\mathbf{v}}_k = -\nabla_k \cdot \hat{\mathbf{v}}_k \quad (\text{A.26})$$

as the reduced time evolution operator in the overdamped limit.

A.6 Evolution of time-local functionals

The derivation of the evolution equation for time-local functionals goes along the same lines as in the derivation of the Smoluchowski equation in the previous section. We start from the equations

$$\begin{aligned} \dot{\mathbf{r}}_k &= \mathbf{p}_k / m, \\ \dot{\mathbf{p}}_k &= -\nabla_k U + \mathbf{f}_k - \mu_{kl}^{-1} [\mathbf{p}_l / m - \mathbf{u}(\mathbf{r}_l)] + \xi_k, \\ \dot{r} &= [\mathbf{p}_k / m - \mathbf{u}(\mathbf{r}_k)] \cdot \mathbf{a}_k + \beta, \end{aligned}$$

where the first two are the same as in the previous section and the last equation is an *ansatz* with arbitrary vectors $\mathbf{a}_k(x; \gamma)$ and a scalar function $\beta(x; \gamma)$ justified in section 4.3 in the main text.

The state is $\Psi(x, x_p, r, t)$ obeying

$$\partial \Psi(t) = [\hat{L}_0 + \hat{L}_1 + \hat{L}_r] \Psi(t).$$

The operators \hat{L}_0 and \hat{L}_1 are given in (A.17) and (A.18), respectively. In addition, there is an operator

$$\hat{L}_r \equiv -\{[\mathbf{p}_k / m - \mathbf{u}(\mathbf{r}_k)] \cdot \mathbf{a}_k + \beta\} \partial_r \quad (\text{A.27})$$

acting on r . First, we note that due to the additional operator now there is a component in the null space of \hat{L}_0^{-1} ,

$$\hat{P}(\hat{L}_1 + \hat{L}_r) \varphi_0 = \hat{P} \hat{L}_r \varphi_0 = \varphi_0 [\mathbf{u}(\mathbf{r}_k) \cdot \mathbf{a}_k - \beta] \partial_r,$$

and hence

$$\hat{P}'(\hat{L}_1 + \hat{L}_r) \varphi_0 = [\hat{L}_1 - (\mathbf{p}_k / m) \cdot \mathbf{a}_k \partial_r] \varphi_0.$$

The time evolution operator for the reduced joint probability $\rho(x, r, t)$ without the momenta then becomes

$$\hat{L} = [\mathbf{u}(\mathbf{r}_k) \cdot \mathbf{a}_k - \beta] \partial_r - \langle \bar{\varphi}_0, (\hat{L}_1 + \hat{L}_r) \hat{L}_0^{-1} [\hat{L}_1 - (\mathbf{p}_k/m) \cdot \mathbf{a}_k \partial_r] \varphi_0 \rangle.$$

This expression contains the Smoluchowski operator (A.26). The first part of the remaining operator reads

$$\int dx_p \hat{L}_1 \hat{L}_0^{-1} (\mathbf{p}_k/m) \cdot \mathbf{a}_k \partial_r \varphi_0 = - \int dx_p \hat{L}_1 \mathbf{p}_k \cdot \mu_{kl} \mathbf{a}_l \partial_r \varphi_0 = T \nabla_k \cdot \mu_{kl} \mathbf{a}_l \partial_r$$

using (A.23) and (A.25). The second part is slightly more complicated and we proceed in two steps. First,

$$\hat{L}_0^{-1} [\hat{L}_1 - (\mathbf{p}_k/m) \cdot \mathbf{a}_k \partial_r] \varphi_0 = - \left[\frac{\mathbf{p}_k}{T} \cdot \hat{\mathbf{v}}_k - \mathbf{p}_k \cdot \mu_{kl} \mathbf{a}_l \partial_r \right] \varphi_0$$

employing (A.24) and again (A.23). This operator is proportional to \mathbf{p}_k . Now we apply the operator (A.27) but only the first term containing the momentum will survive the following integration, leading to the result

$$\mathbf{a}_k \cdot \hat{\mathbf{v}}_k \partial_r - T \mathbf{a}_k \cdot \mu_{kl} \mathbf{a}_l \partial_r^2.$$

Collecting everything together, we obtain the evolution operator

$$\hat{L} = \hat{L}_{SM} - \{ \mathbf{a}_k \cdot [\hat{\mathbf{v}}_k - \mathbf{u}(\mathbf{r}_k)] - \nabla_k \cdot \mathbf{D}_{kl} \mathbf{a}_l + \beta \} \partial_r + \mathbf{a}_k \cdot \mathbf{D}_{kl} \mathbf{a}_l \partial_r^2. \quad (\text{A.28})$$

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