ADVANCES IN CHEMICAL PHYSICS VOL. [illegible]

Editor
STUART A. RICE

ADVANCES IN CHEMICAL PHYSICS

064
P945
V.140

ADVANCES IN CHEMICAL PHYSICS

VOLUME 140

Series Editor

STUART A. RICE

Department of Chemistry
and
The James Franck Institute
The University of Chicago
Chicago, Illinois

WILEY

A JOHN WILEY & SONS, INC. PUBLICATION

ADVANCES IN CHEMICAL PHYSICS

VOLUME 140

EDITORIAL BOARD

BRUCE J. BERNE, Department of Chemistry, Columbia University, New York, New York, U.S.A.

KURT BINDER, Institut für Physik, Johannes Gutenberg-Universität Mainz, Mainz, Germany

A. WELFORD CASTLEMAN, JR., Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania, U.S.A.

DAVID CHANDLER, Department of Chemistry, University of California, Berkeley, California, U.S.A.

M. S. CHILD, Department of Theoretical Chemistry, University of Oxford, Oxford, U.K.

WILLIAM T. COFFEY, Department of Microelectronics and Electrical Engineering, Trinity College, University of Dublin, Dublin, Ireland

F. FLEMING CRIM, Department of Chemistry, University of Wisconsin, Madison, Wisconsin, U.S.A.

ERNEST R. DAVIDSON, Department of Chemistry, Indiana Univeristy, Bloomington, Indiana, U.S.A.

GRAHAM R. FLEMING, Department of Chemistry, The University of California, Berkeley, California, U.S.A.

KARL F. FREED, The James Franck Institute, The University of Chicago, Chicago, Illinois, U.S.A.

PIERRE GASPARD, Center for Nonlinear Phenomena and Complex Systems, Université Libre de Bruxelles, Brussels, Belgium

ERIC J. HELLER, Department of Chemistry, Harvard-Smithsonian Center for Astrophysics, Cambridge, Massachusetts, U.S.A.

ROBIN M. HOCHSTRASSER, Department of Chemistry, The University of Pennsylvania, Philadelphia, Pennsylvania, U.S.A.

R. KOSLOFF, The Fritz Haber Research Center for Molecular Dynamics and Department of Physical Chemistry, The Hebrew University of Jerusalem, Jerusalem, Israel

RUDOLPH A. MARCUS, Department of Chemistry, California Institute of Technology, Pasadena, California, U.S.A.

G. NICOLIS, Center for Nonlinear Phenomena and Complex Systems, Université Libre de Bruxelles, Brussels, Belgium

THOMAS P. RUSSELL, Department of Polymer Science, University of Massachusetts, Amherst, Massachusetts, U.S.A.

DONALD G. TRUHLAR, Department of Chemistry, University of Minnesota, Minneapolis, Minnesota, U.S.A.

JOHN D. WEEKS, Institute for Physical Science and Technology and Department of Chemistry, University of Maryland, College Park, Maryland, U.S.A.

PETER G. WOLYNES, Department of Chemistry, University of California, San Diego, California, U.S.A.

CONTRIBUTORS TO VOLUME 140

PHIL ATTARD, School of Chemistry F11, University of Sydney, NSW 2006 Australia

THOMAS BARTSCH, Department of Mathematical Sciences, Loughborough University, Loughborough LE11 3TU, United Kingdom

RAJAT K. CHAUDHURI, Indian Institute of Astrophysics, Bangalore 560034, India

ROBERT J. GORDON, Department of Chemistry, University of Illinois at Chicago, Chicago, Illinois 60607 USA

RIGOBERTO HERNANDEZ, Center for Computational Molecular Science and Technology, Georgia Institute of Technology, Atlanta, Georgia 30332 USA

RAYMOND KAPRAL, University of Toronto, Toronto, Canada

SHINNOSUKE KAWAI, Molecule and Life Nonlinear Sciences Laboratory, Research Institute for Electronic Science (RIES), Hokkaido University, Sapporo 060-0812 Japan

JEREMY M. MOIX, Center for Computational Molecular Science and Technology, Georgia Institute of Technology, Atlanta, Georgia 30332 USA

MALAYA K. NAYAK, Indian Institute of Astrophysics, Bangalore 560034, India

TAMAR SEIDEMAN, Department of Chemistry, Northwestern University, Evanston, Illinois 60208 USA

T. UZER, Center for Nonlinear Science, Georgia Institute of Technology, Atlanta, Georgia 30332 USA

此为试读,需要完整PDF请访问: www.ertongbook.com

INTRODUCTION

Few of us can any longer keep up with the flood of scientific literature, even in specialized subfields. Any attempt to do more and be broadly educated with respect to a large domain of science has the appearance of tilting at windmills. Yet the synthesis of ideas drawn from different subjects into new, powerful, general concepts is as valuable as ever, and the desire to remain educated persists in all scientists. This series, *Advances in Chemical Physics*, is devoted to helping the reader obtain general information about a wide variety of topics in chemical physics, a field that we interpret very broadly. Our intent is to have experts present comprehensive analyses of subjects of interest and to encourage the expression of individual points of view. We hope that this approach to the presentation of an overview of a subject will both stimulate new research and serve as a personalized learning text for beginners in a field.

STUART A. RICE

CONTENTS

THE SECOND LAW OF NONEQUILIBRIUM THERMODYNAMICS: HOW FAST TIME FLIES 1
By Phil Attard

MULTIPARTICLE COLLISION DYNAMICS: SIMULATION OF COMPLEX SYSTEMS ON MESOSCALES 89
By Raymond Kapral

TWO-PATHWAY EXCITATION AS A COHERENCE SPECTROSCOPY 147
By Tamar Seideman and Robert J. Gordon

TIME-DEPENDENT TRANSITION STATE THEORY 191
By Thomas Bartsch, Jeremy M. Moix, Rigoberto Hernandez, Shinnosuke Kawai, and T. Uzer

ELECTRONIC STRUCTURE REFERENCE CALCULATIONS FOR DESIGNING AND INTERPRETING P AND T VIOLATION EXPERIMENTS 239
By Malaya K. Nayak and Rajat K. Chaudhuri

AUTHOR INDEX 267

SUBJECT INDEX 277

THE SECOND LAW OF NONEQUILIBRIUM THERMODYNAMICS: HOW FAST TIME FLIES

PHIL ATTARD

School of Chemistry F11, University of Sydney, NSW 2006 Australia

CONTENTS

I. Introduction
  A. Review and Preview
II. Linear Thermodynamics
  A. Formalities
  B. Quadratic Expansion
  C. Time Scaling
    1. Optimum Point
  D. Regression Theorem
    1. Asymmetry of the Transport Matrix
  E. Entropy Production
  F. Reservoir
  G. Intermediate Regime and Maximum Flux
III. Nonlinear Thermodynamics
  A. Quadratic Expansion
  B. Parity
  C. Time Scaling
    1. Optimum Intermediate Point
  D. Linear Limit of Nonlinear Coefficients
  E. Exchange with a Reservoir
  F. Rate of Entropy Production
IV. Nonequilibrium Statistical Mechanics
  A. Steady-State Probability Distribution
  B. Relationship with Green–Kubo Theory
  C. Microstate Transitions
    1. Adiabatic Evolution
    2. Stochastic Transition
    3. Stationary Steady-State Probability
    4. Forward and Reverse Transitions

Advances in Chemical Physics, Volume 140, edited by Stuart A. Rice
Copyright © 2008 John Wiley & Sons, Inc.

V. Time-Dependent Mechanical Work
A. Phase Space Probability
B. Transition Probability
VI. Nonequilibrium Quantum Statistical Mechanics
VII. Heat Flow
A. Thermodynamic Variables
B. Gaussian Approximation
C. Second Entropy
1. Isolated System
2. Reservoirs
3. Rate of Entropy Production
D. Phase Space Probability Distribution
VIII. Monte Carlo Simulations of Heat Flow
A. System Details
B. Metropolis Algorithm
C. Nonequilibrium Molecular Dynamics
D. Monte Carlo Results
1. Structure
2. Dynamics
IX. Conclusion
Acknowledgments
References

I. INTRODUCTION

The Second Law of Equilibrium Thermodynamics may be stated:

> The entropy increases during spontaneous changes in the structure of the total system (1)

This is a law about the equilibrium state, when macroscopic change has ceased; it is the state, according to the law, of maximum entropy. It is not really a law about nonequilibrium *per se*, not in any quantitative sense, although the law does introduce the notion of a nonequilibrium state constrained with respect to structure. By implication, entropy is perfectly well defined in such a nonequilibrium macrostate (otherwise, how could it increase?), and this constrained entropy is less than the equilibrium entropy. Entropy itself is left undefined by the Second Law, and it was only later that Boltzmann provided the physical interpretation of entropy as the number of molecular configurations in a macrostate. This gave birth to his probability distribution and hence to equilibrium statistical mechanics.

The reason that the Second Law has no quantitative relevance to nonequilibrium states is that it gives the direction of change, not the rate of change. So although it allows the calculation of the thermodynamic force that drives the system toward equilibrium, it does not provide a basis for calculating the all

important rate at which the system evolves. A full theory for the nonequilibrium state cannot be based solely on the Second Law or the entropy it invokes.

This begs the question of whether a comparable law exists for nonequilibrium systems. This chapter presents a theory for nonequilibrium thermodynamics and statistical mechanics based on such a law written in a form analogous to the equilibrium version:

> The second entropy increases during spontaneous changes in the dynamic structure of the total system (2)

Here dynamic structure gives a macroscopic flux or rate; it is a transition between macrostates in a specified time. The law invokes the notion of constrained fluxes and the notion that fluxes cease to change in the optimum state, which, in common parlance, is the steady state. In other words, the principle governing nonequilibrium systems is that in the transient regime fluxes develop and evolve to increase the second entropy, and that in the steady state the macroscopic fluxes no longer change and the second entropy is maximal. The second entropy could also be called the transition entropy, and as the reader has probably already guessed, it is the number of molecular configurations associated with a transition between macrostates in a specified time.

This nonequilibrium Second Law provides a basis for a theory for nonequilibrium thermodynamics. The physical identification of the second entropy in terms of molecular configurations allows the development of the nonequilibrium probability distribution, which in turn is the centerpiece for nonequilibrium statistical mechanics. The two theories span the very large and the very small. The aim of this chapter is to present a coherent and self-contained account of these theories, which have been developed by the author and presented in a series of papers [1–7]. The theory up to the fifth paper has been reviewed previously [8], and the present chapter consolidates some of this material and adds the more recent developments.

Because the focus is on a single, albeit rather general, theory, only a limited historical review of the nonequilibrium field is given (see Section IA). That is not to say that other work is not mentioned in context in other parts of this chapter. An effort has been made to identify where results of the present theory have been obtained by others, and in these cases some discussion of the similarities and differences is made, using the nomenclature and perspective of the present author. In particular, the notion and notation of constraints and exchange with a reservoir that form the basis of the author's approach to equilibrium thermodynamics and statistical mechanics [9] are used as well for the present nonequilibrium theory.

A. Review and Preview

The present theory can be placed in some sort of perspective by dividing the nonequilibrium field into thermodynamics and statistical mechanics. As will become clearer later, the division between the two is fuzzy, but for the present purposes nonequilibrium thermodynamics will be considered that phenomenological theory that takes the existence of the transport coefficients and laws as axiomatic. Nonequilibrium statistical mechanics will be taken to be that field that deals with molecular-level (i.e., phase space) quantities such as probabilities and time correlation functions. The probability, fluctuations, and evolution of macrostates belong to the overlap of the two fields.

Perhaps the best starting point in a review of the nonequilibrium field, and certainly the work that most directly influenced the present theory, is Onsager's celebrated 1931 paper on the reciprocal relations [10]. This showed that the symmetry of the linear hydrodynamic transport matrix was a consequence of the time reversibility of Hamilton's equations of motion. This is an early example of the overlap between macroscopic thermodynamics and microscopic statistical mechanics. The consequences of time reversibility play an essential role in the present nonequilibrium theory, and in various fluctuation and work theorems to be discussed shortly.

Moving upward to the macroscopic level, the most elementary phenomenological theories for nonequilibrium thermodynamics are basically hydrodynamics plus localized equilibrium thermodynamics [11, 12]. In the so-called soft sciences, including, as examples, biological, environmental, geological, planetary, atmospheric, climatological, and paleontological sciences, the study of evolution and rates of change is all important. This has necessarily stimulated much discussion of nonequilibrium principles and approaches, which are generally related to the phenomenological theories just described [13–18]. More advanced phenomenological theories for nonequilibrium thermodynamics in its own right have been pursued [19–23]. The phenomenological theories generally assert the existence of a nonequilibrium potential that is a function of the fluxes, and whose derivatives are consistent with the transport laws and other symmetry requirements.

In view of the opening discussion of the two second laws of thermodynamics, in analyzing all theories, phenomenological and otherwise, it is important to ask two questions:

$$\text{Does the theory invoke the second entropy, or only the first entropy and its rate of change?} \tag{3}$$

and

$$\text{Is the relationship being invoked true in general, or is it only true in the optimum or steady state?} \tag{4}$$

此为试读,需要完整PDF请访问: www.ertongbook.com

If the approach does not go beyond the ordinary entropy, or if it applies an optimized result to a constrained state, then one can immediately conclude that a quantitative theory for the nonequilibrium state is unlikely to emerge. Regrettably, for phenomenological theories of the type just discussed, the answer to both questions is usually negative. The contribution of Prigogine, in particular, will be critically assessed from these twin perspectives (see Section IIE).

Moving downward to the molecular level, a number of lines of research flowed from Onsager's seminal work on the reciprocal relations. The symmetry rule was extended to cases of mixed parity by Casimir [24], and to nonlinear transport by Grabert et al. [25] Onsager, in his second paper [10], expressed the linear transport coefficient as an equilibrium average of the product of the present and future macrostates. Nowadays, this is called a time correlation function, and the expression is called Green–Kubo theory [26–30].

The transport coefficient gives the ratio of the flux (or future macrostate velocity) to the conjugate driving force (mechanical or thermodynamic). It governs the dissipative force during the stochastic and driven motion of a macrostate, and it is related to the strength of the fluctuations by the fluctuation-dissipation theorem [31]. Onsager and Machlup [32] recognized that the transport theory gave rise to a related stochastic differential equation for the evolution of a macrostate that is called the Langevin equation (or the Smoluchowski equation in the overdamped case). Applied to the evolution of a probability distribution it is the Fokker–Planck equation [33]. In the opinion of the present author, stochastic differential equations such as these result from a fundamental, molecular-level nonequilibrium theory, but in themselves are not fundamental and they do not provide a basis for constructing a full nonequilibrium theory.

Onsager and Machlup [32] gave expressions for the probability of a path of macrostates and, in particular, for the probability of a transition between two macrostates. The former may be regarded as the solution of a stochastic differential equation. It is technically a Gaussian Markov process, also known as an Ornstein–Uhlenbeck process. More general stochastic processes include, for example, the effects of spatial curvature and nonlinear transport [33–35]. These have been accounted for by generalizing the Onsager–Machlup functional to give the so-called thermodynamic Lagrangian [35–42]. Other thermodynamic Lagrangians have been given [43–46]. The minimization of this functional gives the most probable evolution in time of the macrostate, and hence one might expect the thermodynamic Lagrangian to be related (by a minus sign) to the second entropy that is the basis of the present theory. However, the Onsager–Machlup functional [32] (and those generalizations of it) [35–42] fails both questions posed above: **(1)** it invokes solely the rate of production of first entropy, and **(2)** both expressions that it invokes for this are only valid in the steady state, not in the constrained states that are the subject of the optimization procedure (see Section IIE). The Onsager–Machlup functional (in two-state

transition form) is tested against computer simulation data for the thermal conductivity time correlation function in Fig. 8.

On a related point, there have been other variational principles enunciated as a basis for nonequilibrium thermodynamics. Hashitsume [47], Gyarmati [48, 49], and Bochkov and Kuzovlev [50] all assert that in the steady state the rate of first entropy production is an extremum, and all invoke a function identical to that underlying the Onsager–Machlup functional [32]. As mentioned earlier, Prigogine [11] (and workers in the broader sciences) [13–18] variously asserts that the rate of first entropy production is a maximum or a minimum and invokes the same two functions for the optimum rate of first entropy production that were used by Onsager and Machlup [32] (see Section IIE).

Evans and Baranyai [51, 52] have explored what they describe as a nonlinear generalization of Prigogine's principle of minimum entropy production. In their theory the rate of (first) entropy production is equated to the rate of phase space compression. Since phase space is incompressible under Hamilton's equations of motion, which all real systems obey, the compression of phase space that occurs in nonequilibrium molecular dynamics (NEMD) simulations is purely an artifact of the non-Hamiltonian equations of motion that arise in implementing the Evans–Hoover thermostat [53, 54]. (See Section VIIIC for a critical discussion of the NEMD method.) While the NEMD method is a valid simulation approach in the linear regime, the phase space compression induced by the thermostat awaits physical interpretation; even if it does turn out to be related to the rate of first entropy production, then the hurdle posed by Question (3) remains to be surmounted.

In recent years there has been an awakening of interest in fundamental molecular-level theorems in nonequilibrium statistical mechanics. This spurt of theoretical and experimental activity was kindled by the work theorem published by Jarzynski in 1997 [55]. The work theorem is in fact a trivial consequence of the fluctuation theorem published by Evans, Cohen, and Morriss in 1993, [56, 57] and both theorems were explicitly given earlier by Bochkov and Kuzovlev in 1977 [58–60]. As mentioned earlier, since Onsager's work in 1931 [10], time reversibility has played an essential role in nonequilibrium theory. Bochkov and Kuzovlev [60], and subsequent authors including the present one [4], have found it exceedingly fruitful to consider the ratio of the probability of a forward trajectory to that of the reversed trajectory. Using time reversibility, this ratio can be related to the first entropy produced on the forward trajectory, and it has come to be called the fluctuation theorem [56, 57]. An alternative derivation assuming Markovian behavior of the macrostate path probability has been given [61, 62], and it has been demonstrated experimentally [63]. From this ratio one can show that the average of the exponential of the negative of the entropy produced (minus work divided by temperature) equals the exponential of the difference in initial and final

Helmholtz free energies divided by temperature, which is the work theorem [55]. For a cyclic process, the latter difference is zero, and hence the average is unity, as shown by Bochkov and Kuzovlev [58–60]. The work theorem has been rederived in different fashions [57, 64, 65] and verified experimentally [66]. What is remarkable about the work theorem is that it holds for arbitrary rates of nonequilibrium work, and there is little restriction beyond the assumption of equilibration at the beginning and end of the work and sufficiently long time interval to neglect end effects. (See Sections IVC4 and VB for details and generalizations.)

With the exception of the present theory, derivations of the fluctuation and work theorems are generally for a system that is isolated during the performance of the work (adiabatic trajectories), and the effects of a thermal or other reservoir on the true nonequilibrium probability distribution or transition probability are neglected. The existence and form for the nonequilibrium probability distribution, both in the steady state and more generally, may be said to be the holy grail of nonequilibrium statistical mechanics. The Boltzmann distribution is the summit of the equilibrium field [67], and so there have been many attempts to formulate its analogue in a nonequilibrium context. The most well known is the Yamada–Kawasaki distribution [68, 69]. It must be stressed that this distribution is an adiabatic distribution, which is to say that it assumes that the system was in thermal equilibrium in the past, and that it was subsequently isolated from the thermal reservoirs while the work was being performed so that no heat was exchanged during the time-dependent process. This is obviously a very restrictive assumption. Attempts have been made to formulate a thermostatted form of the Yamada–Kawasaki distribution, but this has been found to be computationally intractable [53, 70, 71]. As pointed out earlier, most derivations of the fluctuation and work theorems are predicated on the adiabatic assumption, and a number of authors invoke or derive the Yamada–Kawasaki distribution, apparently unaware of its prior publication and of its restricted applicability.

An alternative approximation to the adiabatic probability is to invoke an instantaneous equilibrium-like probability. In the context of the work theorem, Hatano and Sasa [72] analyzed a nonequilibrium probability distribution that had no memory, and others have also invoked a nonequilibrium probability distribution that is essentially a Boltzmann factor of the instantaneous value of the time-dependent potential [73, 74].

In Sections IVA, VA, and VI the nonequilibrium probability distribution is given in phase space for steady-state thermodynamic flows, mechanical work, and quantum systems, respectively. (The second entropy derived in Section II gives the probability of fluctuations in macrostates, and as such it represents the nonequilibrium analogue of thermodynamic fluctuation theory.) The present phase space distribution differs from the Yamada–Kawasaki distribution in that

it correctly takes into account heat exchange with a reservoir during the mechanical work or thermodynamic flux. The probability distribution is the product of a Boltzmann-like term, which is reversible in time, and a new term, which is odd in time, and which once more emphasizes Onsager's [10] foresight in identifying time reversibility as the key to nonequilibrium behavior. In Section IVB this phase space probability is used to derive the Green–Kubo relations, in Section VIIIB it is used to develop a nonequilibrium Monte Carlo algorithm, and in Fig. 7 it is shown that the algorithm is computationally feasible and that it gives a thermal conductivity in full agreement with conventional NEMD results.

In addition to these nonequilibrium probability densities, the present theory also gives expressions for the transition probability and for the probability of a phase space trajectory, in both equilibrium and nonequilibrium contexts, (Sections IVC and VB). These sections contain the derivations and generalizations of the fluctuation and work theorems alluded to earlier. As for the probability density, one has to be aware that some work in the literature is based on adiabatic transitions, whereas the present approach includes the effect of heat flow on the transition. One also has to distinguish works that deal with macrostate transitions, from the present approach based in phase space, which of course includes macrostate transition by integration over the microstates. The second entropy, which is the basis for the nonequilibrium second law advocated earlier, determines such transitions pairwise, and for an interval divided into segments of intermediate length, it determines a macrostate path by a Markov procedure (Sections IIC and IIIC). The phase space trajectory probability contains an adiabatic term and a stochastic term. The latter contains in essence half the difference between the target and initial reservoir entropies. This term may be seen to be essentially the one that is invoked in Glauber or Kawasaki dynamics [75–78]. This form for the conditional stochastic transition probability satisfies detailed balance for an equilibrium Boltzmann distribution, and it has been used successfully in hybrid equilibrium molecular dynamics algorithms [79–81]. Using the term on its own without the adiabatic development, as in Glauber or Kawasaki dynamics, corresponds to neglecting the coupling inherent in the second entropy, and to losing the speed of time.

II. LINEAR THERMODYNAMICS

A. Formalities

Consider an isolated system containing N molecules, and let $\mathbf{\Gamma} \equiv \{\mathbf{q}^N, \mathbf{p}^N\}$ be a point in phase space, where the ith molecule has position $\mathbf{q}_i$ and momentum $\mathbf{p}_i$. In developing the nonequilibrium theory, it will be important to discuss the behavior of the system under time reversal. Accordingly, define the conjugate

point in phase space as that point with all the velocities reversed, $\mathbf{\Gamma}^\dagger \equiv \{\mathbf{q}^N, (-\mathbf{p})^N\}$. If $\mathbf{\Gamma}_2 = \mathbf{\Gamma}_0(t|\mathbf{\Gamma}_1)$ is the position of the isolated system at time t given that it was at $\mathbf{\Gamma}_1$ at time $t = 0$, then $\mathbf{\Gamma}_1^\dagger = \mathbf{\Gamma}_0(t|\mathbf{\Gamma}_2^\dagger)$, as follows from the reversibility of Hamilton's equations of motion. One also has, by definition of the trajectory, that $\mathbf{\Gamma}_1 = \mathbf{\Gamma}_0(-t|\mathbf{\Gamma}_2)$.

Macrostates are collections of microstates [9], which is to say that they are volumes of phase space on which certain phase functions have specified values. The current macrostate of the system gives its structure. Examples are the position or velocity of a Brownian particle, the moments of energy or density, their rates of change, the progress of a chemical reaction, a reaction rate, and so on. Let $\mathbf{x}$ label the macrostates of interest, and let $\hat{\mathbf{x}}(\mathbf{\Gamma})$ be the associated phase function. The first entropy of the macrostate is

$$S^{(1)}(\mathbf{x}|\mathbf{E}) = k_B \ln \int d\mathbf{\Gamma}\, \delta(\mathcal{H}(\mathbf{\Gamma}) - E)\, \delta(\hat{\mathbf{x}}(\mathbf{\Gamma}) - \mathbf{x}) \tag{5}$$

neglecting an arbitrary constant. This is the ordinary entropy; here it is called the first entropy, to distinguish it from the second or transition entropy that is introduced later. Here the Hamiltonian appears, and all microstates of the isolated system with energy E are taken to be equally likely [9]. This is the constrained entropy, since the system is constrained to be in a particular macrostate. By definition, the probability of the macrostate is proportional to the exponential of the entropy,

$$\wp(\mathbf{x}|E) = \frac{1}{W(E)} \exp S^{(1)}(\mathbf{x}|E)/k_B \tag{6}$$

The normalizing factor is related to the unconstrained entropy by

$$\begin{aligned} S^{(1)}(E) \equiv k_B \ln W(E) &= k_B \ln \int d\mathbf{x}\, \exp S(\mathbf{x}|E)/k_B \\ &= k_B \ln \int d\mathbf{\Gamma}\, \delta(\mathcal{H}(\mathbf{\Gamma}) - E) \end{aligned} \tag{7}$$

The equilibrium state, which is denoted $\bar{\mathbf{x}}$, is by definition both the most likely state, $\wp(\bar{\mathbf{x}}|E) \geq \wp(\mathbf{x}|E)$, and the state of maximum constrained entropy, $S^{(1)}(\bar{\mathbf{x}}|E) \geq S^{(1)}(\mathbf{x}|E)$. This is the statistical mechanical justification for much of the import of the Second Law of Equilibrium Thermodynamics. The unconstrained entropy, as a sum of positive terms, is strictly greater than the maximal constrained entropy, which is the largest term, $S^{(1)}(E) > S^{(1)}(\bar{\mathbf{x}}|E)$. However, in the thermodynamic limit when fluctuations are relatively negligible, these may be equated with relatively little error, $S^{(1)}(E) \approx S^{(1)}(\bar{\mathbf{x}}|E)$.

The macrostates can have either even or odd parity, which refers to their behavior under time reversal or conjugation. Let $\epsilon_i = \pm 1$ denote the parity of the ith microstate, so that $\hat{x}_i(\mathbf{\Gamma}^\dagger) = \epsilon_i \hat{x}_i(\mathbf{\Gamma})$. (It is assumed that each state is purely even or odd; any state of mixed parity can be written as the sum of two states of pure parity.) Loosely speaking, variables with even parity may be called position variables, and variables with odd parity may be called velocity variables. One can form the diagonal matrix $\underline{\underline{\epsilon}}$, with elements $\epsilon_i \delta_{ij}$, so that $\hat{\mathbf{x}}(\mathbf{\Gamma}^\dagger) = \underline{\underline{\epsilon}}\hat{\mathbf{x}}(\mathbf{\Gamma})$. The parity matrix is its own inverse, $\underline{\underline{\epsilon}}\,\underline{\underline{\epsilon}} = \underline{\underline{I}}$.

The Hamiltonian is insensitive to the direction of time, $\mathcal{H}(\mathbf{\Gamma}) = \mathcal{H}(\mathbf{\Gamma}^\dagger)$, since it is a quadratic function of the molecular velocities. (Since external Lorentz or Coriolis forces arise from currents or velocities, they automatically reverse direction under time reversal.) Hence both $\mathbf{\Gamma}$ and $\mathbf{\Gamma}^\dagger$ have equal weight. From this it is easily shown that $S^{(1)}(\mathbf{x}|E) = S^{(1)}(\underline{\underline{\epsilon}}\mathbf{x}|E)$.

The unconditional transition probability between macrostates in time τ for the isolated system satisfies

$$\begin{aligned}
\wp(\mathbf{x}' \leftarrow \mathbf{x}|\tau, E) &= \Lambda(\mathbf{x}'|\mathbf{x}, \tau, E)\wp(\mathbf{x}|E) \\
&= W_E^{-1} \int \mathrm{d}\mathbf{\Gamma}_1\, \mathrm{d}\mathbf{\Gamma}_2\, \delta(\mathbf{x}' - \hat{\mathbf{x}}(\mathbf{\Gamma}_2))\delta(\mathbf{x} - \hat{\mathbf{x}}(\mathbf{\Gamma}_1))\, \delta(\mathbf{\Gamma}_2 - \mathbf{\Gamma}_0(\tau|\mathbf{\Gamma}_1))\, \delta(\mathcal{H}(\mathbf{\Gamma}_1) - E) \\
&= W_E^{-1} \int \mathrm{d}\mathbf{\Gamma}_1^\dagger\, \mathrm{d}\mathbf{\Gamma}_2^\dagger\, \delta(\mathbf{x}' - \underline{\underline{\epsilon}}\hat{\mathbf{x}}(\mathbf{\Gamma}_2^\dagger))\delta(\mathbf{x} - \underline{\underline{\epsilon}}\hat{\mathbf{x}}(\mathbf{\Gamma}_1^\dagger))\, \delta(\mathbf{\Gamma}_1^\dagger - \mathbf{\Gamma}_0(\tau|\mathbf{\Gamma}_2^\dagger))\delta(\mathcal{H}(\mathbf{\Gamma}_1^\dagger) - E) \\
&= \wp(\underline{\underline{\epsilon}}\mathbf{x} \leftarrow \underline{\underline{\epsilon}}\mathbf{x}'|\tau, E)
\end{aligned} \tag{8}$$

This uses the fact that $\mathrm{d}\mathbf{\Gamma} = \mathrm{d}\mathbf{\Gamma}^\dagger$. For macrostates all of even parity, this says that for an isolated system the forward transition $\mathbf{x} \to \mathbf{x}'$ will be observed as frequently as the reverse $\mathbf{x}' \to \mathbf{x}$. This is what Onsager meant by the principle of dynamical reversibility, which he stated as "in the end every type of motion is just as likely to occur as its reverse" [10, p. 412]. Note that for velocity-type variables, the sign is reversed for the reverse transition.

The second or transition entropy is the weight of molecular configurations associated with a transition occurring in time τ,

$$S^{(2)}(\mathbf{x}', \mathbf{x}|\tau, E) = k_\mathrm{B} \ln \int \mathrm{d}\mathbf{\Gamma}_1\, \delta(\hat{\mathbf{x}}(\mathbf{\Gamma}_0(\tau|\mathbf{\Gamma}_1)) - \mathbf{x}')\, \delta(\hat{\mathbf{x}}(\mathbf{\Gamma}_1) - \mathbf{x})\, \delta(\mathcal{H}(\mathbf{\Gamma}_1) - E) \tag{9}$$

up to an arbitrary constant. The unconditional transition probability for $\mathbf{x} \to \mathbf{x}'$ in time τ is related to the second entropy by [2, 8]

$$\wp(\mathbf{x}', \mathbf{x}|\tau, E) = \frac{1}{W(E)} \exp S^{(2)}(\mathbf{x}', \mathbf{x}|\tau, E)/k_\mathrm{B} \tag{10}$$

此为试读,需要完整PDF请访问: www.ertongbook.com