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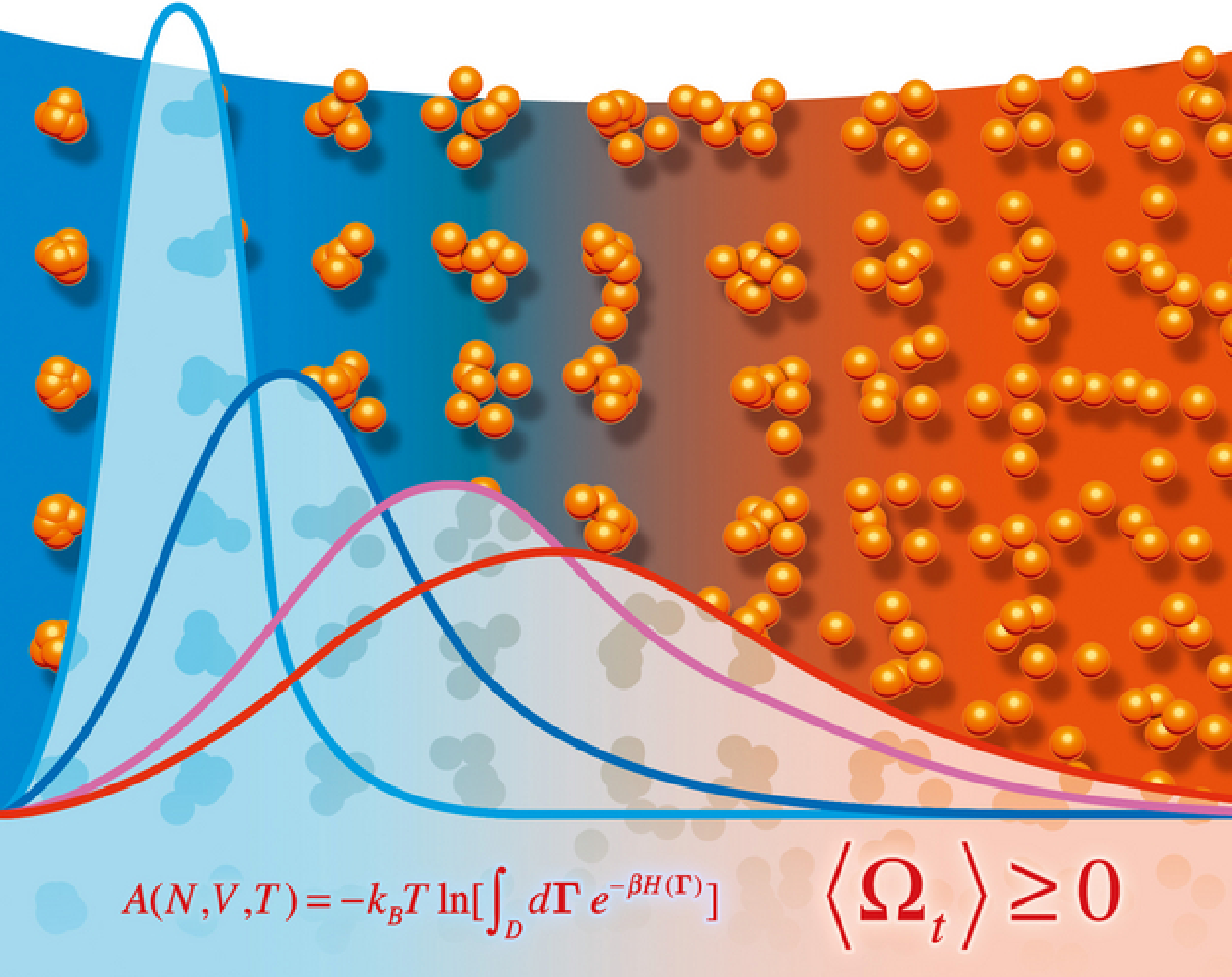
and Stephen R. Williams

Fundamentals of Classical Statistical Thermodynamics

Dissipation, Relaxation, and Fluctuation Theorems



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Contents

List of Symbols

Microscopic Dynamics

N	Number of particles in the system.
D_C	Cartesian dimensions of the system – usually three.
D	Accessible phase space domain
$\mathbf{q}$	ND_C-dimensional vector, representing the particle positions.
$\mathbf{p}$	ND_C-dimensional vector, representing the particle momenta.
$\mathbf{\Gamma}$	$2ND_C$-dimensional phase space vector, representing all $\mathbf{q}$'s and $\mathbf{p}$'s.
$\delta V_{\mathbf{\Gamma}}(S^t\mathbf{\Gamma})$	Very small volume element of phase space centered on $S^t\mathbf{\Gamma} \equiv \exp[iL(\mathbf{\Gamma})t]\mathbf{\Gamma}_{.}$
$p(\delta V_{\mathbf{\Gamma}}(\mathbf{\Gamma}); t)$	Probability of observing sets of trajectories inside $\delta V_{\mathbf{\Gamma}}(\mathbf{\Gamma})$ at time t.
$d(S^t\mathbf{\Gamma})$	Infinitesimal phase space volume centered on $S^t\mathbf{\Gamma}_{.}$
$p_{+/-}(t)$	Probability that the time-integrated dissipation function is plus/minus over the time interval $(0,t)$.
M^T	Time reversal map $M^T(\mathbf{q}, \mathbf{p}) \equiv (\mathbf{q}, -\mathbf{p})M^T_{.}$
M^K	Kawasaki or K-map of phase space vector for planar Couette flow, $M^K(x, y, z, p_x, p_y, p_z, \dot{\gamma}) \equiv (x, -y, z, -p_x, p_y, -p_z, \dot{\gamma})M^K_{,}$ where $\dot{\gamma} \equiv \partial u_x/\partial y$ is the xy component of the strain rate tensor.
L	f-Liouvillean.
$\exp[-i\mathrm{L}(\mathbf{\Gamma})t] \ldots$	f-propagator.
L	p-Liouvillean.
$\exp[iL(\mathbf{\Gamma})t]$	p-propagator.
S^t	p-propagator.
$K(\mathbf{p})$	Peculiar kinetic energy.
$\Phi(\mathbf{q})$	Interparticle potential energy.
$\phi_{i,j}(r_{ij})$	Pair potential of particle i with particle j.
$\mathbf{r}_{ij} \equiv \mathbf{r}_j - \mathbf{r}_i$	Position vector from particle i to particle j.
$r_{ij} \equiv \lvert\mathbf{r}_j - \mathbf{r}_i\rvert$	Distance between particles i and j.
$\mathbf{F}_{ij}$	Force on particle i due to particle j

$\nabla_{\mathbf{q}}$	$\equiv (\partial/\partial\mathbf{q}_1, \ldots, \partial/\partial\mathbf{q}_N$.
$H_0(\mathbf{\Gamma})$	Internal energy, $H_0 = K + \Phi$.
$H(\mathbf{\Gamma})$	Hamiltonian at phase vector $\mathbf{\Gamma}$.
$g(\mathbf{\Gamma})$	Deviation function – even in the momenta.
H_E	Extended Hamiltonian for Nosé–Hoover dynamics.
K_{th}	Peculiar kinetic energy of thermostatted particles $= D_C N_{\text{th}} k_{\text{B}} T_{\text{th}}/2 + O(1)$, where T_{th} is the kinetic temperate of the thermostat. If the system is isokinetic, $T_{\text{th}} = T$ – see thermodynamic variables below.
N_{th}	Number of thermostatted particles.
α	Gaussian or Nosé–Hoover thermostat or ergostat multiplier.
τ	Time constant.
$\dot{Q}_{\text{th/soi}}$	Rate of transfer of heat to the thermostat/system of interest.
Λ	Phase space expansion factor.
S_i	Switch function.
$\mathbf{J}(\mathbf{\Gamma})$	Dissipative flux.
$\mathbf{F}_e$	Dissipative external field.
m	Particle mass.
$\mathsf{T} \equiv \partial\dot{\mathbf{\Gamma}}(\mathbf{\Gamma})/\partial\mathbf{\Gamma}$	Stability matrix.
$\exp_L$	Time-ordered exponential operator, latest times to left.
$\mathbf{\Xi}(\mathbf{\Gamma}; t)$	Tangent vector propagator $\equiv \exp_L\left(\int_0^t ds\ \mathsf{T}(S^s\mathbf{\Gamma})\right)$.
λ_i	ith Lyapunov exponent.
$\lambda_{\text{max/min}}$	Largest/smallest Lyapunov exponent for steady or equilibrium state.

Statistical Mechanics

$\overline{A}_t$	Time average of some phase variable, $A(\mathbf{\Gamma})$.
$\langle A(t)\rangle$	Ensemble average of A at time t, on a time-evolved path.
$f(\mathbf{\Gamma}; t)$	Time-dependent phase space distribution function.
$\langle\cdots\rangle_{\mu c}$	Equilibrium microcanonical ensemble average.
$\langle\cdots\rangle_c$	Equilibrium canonical ensemble average,
$f_c(\mathbf{\Gamma})$	Equilibrium canonical distribution.
$f_{\mu c}(\mathbf{\Gamma})$	Equilibrium microcanonical distribution.
Λ	Phase space expansion factor.
$\Omega(S^{t_1}\mathbf{\Gamma}; t_2)$	The instantaneous dissipation function, at time t_1 on a phase space trajectory that started at phase $\mathbf{\Gamma}$ and defined with respect to the distribution function at time t_2. $\Omega(S^{t_1}\mathbf{\Gamma}; 0) \equiv \Omega(S^{t_1}\mathbf{\Gamma})$,
$\Omega(S^{t_1}\mathbf{\Gamma})$	$\Omega(S^{t_1}\mathbf{\Gamma}) \equiv \Omega(S^{t_1}\mathbf{\Gamma}; 0)$.
$\mathbf{r}$	Three-dimensional position vector.

$\mathbf{u}(\mathbf{r}, t)$	Three-dimensional local fluid streaming velocity, at Cartesian position $\mathbf{r}$ and time t.
$S_G(t)$	Fine-grained Gibbs entropy, $\equiv -k_{\mathrm{B}} \int_D d\mathbf{\Gamma} f(\mathbf{\Gamma}; t) \ln(f(\mathbf{\Gamma}; t)) \overset{\text{equilibrium}}{\Rightarrow} k_{\mathrm{B}} \ln(Z_{\mu c})$.
Z	Partition function – normalization for the equilibrium phase space distribution.
Z_c	Canonical partition function.
$Z_{\mu c}$	Microcanonical partition function.

Mechanical Variables

Q	Heat of thermostat.
V	Volume of system of interest.
U	Internal energy, $U = \langle H_0 \rangle$ of the system of interest.
W	Work performed on system of interest.
Y	Purely dissipative generalized dimensionless work.
X	Generalized dimensionless work.

Thermodynamic Variables

T	Equilibrium temperature the system will relax to if it is so allowed.
β	Boltzmann factor (reciprocal temperature) $\equiv 1/k_{\mathrm{B}}T$.
S_{ir}	Irreversible calorimetric entropy, defined by $\Delta S_{\mathrm{ir}} \equiv \int dt\, \dot{Q}(t)/T(t)$, where $T(t)$ is the instantaneous equilibrium temperature the system would relax to if it was so allowed. In Section 5.7, we show that the Gibbs entropy and the irreversible calorimetric entropy are equal, up to an additive constant.
$S_{\mathrm{eq}} \equiv S$	The calorimetric entropy defined in classical thermodynamics as $\Delta S_{\mathrm{eq}} \equiv \Delta S \equiv_{\mathrm{qs}} \int_1^2 dt\ \dot{Q}(t)/T(t)$, where T is equilibrium temperature of the system. This entropy is a state function.
A	Helmholtz free energy; $= -k_{\mathrm{B}}T \ln(Z_c) = U - TS_{\mathrm{eq}}$.
A_{ne}	Nonequilibrium Helmholtz free energy; $= U - TS_{\mathrm{ir}}$. This is not a state function.
$\langle \Sigma(t) \rangle$	Total entropy production – only defined in the weak field limit close to equilibrium.
G_0	Zero-frequency elastic shear modulus.
G_∞	Infinite-frequency shear modulus.

Transport

γ	Strain (note: γ is sometimes used to fix the system's total momentum).
$\delta\gamma$	Small strain.
$\dot{\gamma}$	Strain rate.
P_{xy}	xy element of the pressure tensor.
$-\langle P_{xy} \rangle$	xy element of the ensemble averaged stress tensor.
$\widetilde{\eta}_{0^+}$	Limiting zero-frequency shear viscosity of a solid.
η	Zero-frequency shear viscosity of a fluid.
τ_M	Maxwell relaxation time.
$\mathbf{J}(\boldsymbol{\Gamma})$	Dissipative flux.
$J_\perp(k_y, t)$	Wavector dependent transverse momentum density.
$\eta_M(t)$	Maxwell model memory function for shear viscosity.
η_M	Zero-frequency shear viscosity of a Maxwell fluid.

Mathematics

$\Theta(t)$	Heaviside step function at $t = 0$.
$\forall$	For all.
$\forall!$	For almost all. The exceptions have zero measure.
λ	Arbitrary scaling parameter.
$\widetilde{F}(s)$	Laplace transform of $F(t)$.
$\widehat{F}(s)$	Anti-Laplace transform of $F(t)$.
$\oint_P$	Cyclic integral of a periodic function.
${}_{\mathrm{qs}}\int_a^b$	Quasi-static integral from a to b.
D_{KY}	Kaplan – Yorke dimension of a nonequilibrium steady state.

Note: Upper case subscripts/superscripts indicate people. Lower case is used in most other cases. Subscripts are preferred to superscripts so as to not confuse powers with superscripts. Italics are used for algebraic initials. Nonitalics for word initials. (*e.g.,* T-mixing not T-mixing because T stands for Transient, N-particle not N-particle.)

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1
Introduction

> The instantaneous reversal of the motion of every moving particle of a system causes the system to move backwards, each particle along its path and at the same speed as before …
>
> *(Thomson, 1874)*

Until very recently, the foundations of statistical mechanics were far from satisfactory (Evans, Searles, and Williams, 2009a). Textbooks approach the derivation of the canonical distribution in one of two ways. A common approach is to *postulate* a microscopic definition for the entropy and then to show that the standard canonical distribution function can be obtained by maximizing the entropy subject to the constraints that the distribution function should be normalized and that the average energy is constant. The choice of the second constraint is completely subjective due to the fact that, at equilibrium, the average of every phase function is fixed. The choice of the microscopic expression for the entropy is also *ad hoc.* This "derivation" is therefore flawed.

The second approach begins with Boltzmann's *postulate* of equal *a priori* probability in phase space for the microcanonical ensemble and then derives an expression for the most probable distribution of states in a small subsystem within that much larger microcanonical system. A variation of this approach is to simply *postulate* a microscopic expression for the Helmholtz free energy via the partition function.

The so-called Loschmidt paradox, which so puzzled Boltzmann and his contemporaries, remained unresolved for 119 years after it was first raised. All the equations of motion in mechanics (both classical and quantum) and electrodynamics are time-reversal-symmetric. Time reversibility of the classical equations of motion is trivial to demonstrate. Consider Newton's equations of motion for the positions $\mathbf{q}_i$ of N identical particles subject to interatomic forces $\mathbf{F}_i(\mathbf{q}_1, \dots, \mathbf{q}_N)$:

$$m\frac{d^2\mathbf{q}_i(t)}{dt^2} = \mathbf{F}_i(\mathbf{q}), \quad i = 1, \dots, N \tag{1.1}$$

As Loschmidt and Kelvin (separately) noticed (Loschmidt, 1876; Thomson, 1874), time reversal $t \to -t$ leaves Eq. (1.1) unaltered since $(-1)^2 = 1$. This means that if $\mathbf{q}(t); -\tau < t < \tau$ is a solution of the equations of motion, then so too is

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$\mathbf{q}(-t)\ :\ \ -\tau < t < \tau$. Changing the direction of time inverts every velocity – as per Kelvin's quote above.

The Loschmidt Paradox can be stated quite simply. If all the laws of physics are time-reversal-symmetric, how can one prove a time-asymmetric law like the second "Law" of thermodynamics that states that the entropy of the Universe "tends to a maximum" (Clausius, 1865; Clausius, 1872). Although there have been many attempts over the last century to resolve this paradox, the matter was not really settled until the first proof of a fluctuation theorem in 1994 (Evans and Searles, 1994).

A less well-known problem concerns Clausius' inequality itself. In some ways, this is an even more fundamental problem because it concerns thermodynamics rather than statistical mechanics. Clausius' inequality for the heat Q_{th} transferred to a thermal reservoir states that the cyclic integral $\oint dQ_{\mathrm{th}}/T \geq 0$. When this inequality is, in fact, an *equality* (the process is *quasi-static*), we have the usual argument that $\int dQ_{\mathrm{th}}/T_{\mathrm{th}}$ is a state function and represents the change in the equilibrium entropy of the reservoir, S_{th} and T_{th} is the equilibrium thermodynamic temperature of that reservoir or set of reservoirs. Clausius went on to apply his inequality to the system of interest (soi) and thermal reservoir (th). Indeed, in his original papers he does not distinguish between the two systems.

Now comes the difficulty: when we have a strict inequality $\oint dQ/T > 0$, either the system of interest or the reservoir (or both) is (or are) not in true thermodynamic equilibrium (the process is not *quasi-static*). In this case, what is the temperature? Clausius only defined the temperature for quasi-static or equilibrium processes where the entropy is a state function. In the case of a strict inequality, $\int dQ/T$ is *not* a state function. It is path- and/or history-dependent.

For quasi-static processes (only!), the change in equilibrium entropies of two equilibrium states can be obtained by considering $\int dQ_{\mathrm{th}}/T_{\mathrm{th}}$ for a reversible (i.e., infinitely slow) pathway between the two equilibrium states. However, if the initial or final states are out of equilibrium or if the pathway connecting the two states is irreversible, the entropy that Clausius defined is ill-defined and so too is the temperature: $T \equiv \partial U/\partial S|_V$, where U is the internal energy, S the (undefined) entropy, and V the volume. This means that the Clausius *inequality* $\oint dQ/T > 0$ is without meaning.

Clausius is famous for his declaration:

> The energy of the Universe is constant. The entropy tends to a maximum.
>
> *(Clausius, 1865, 1872)*

He did not recognize the fact that he only defined the entropy (and temperature) for reversible processes. This particular difficulty was first discussed in the late nineteenth century by Bertrand (1887) and early in the twentieth century by Orr (1904), Orr (1905), Planck (1905), and Buckingham (1905).

"There are three things in Prof. Orr's article (Orr, 1904) which stand out as of particular importance. (1) He says in substance, though with great moderation, that all proofs of the theorem … when the integral is taken round an irreversible cycle, are rubbish." Buckingham later discusses problems with writing textbooks while being aware at the time, of some of the difficulties mentioned above. Buckingham continues: "The question how a treatise should be written is not so easily answered. … I do not know of a single book which today deserves the title of 'Treatise on Thermodynamics'." He concluded: "We must leave the question of the proper method for a treatise to the future when the difficulties which now beset us may have vanished." (Buckingham, 1905)

In 1905, Planck responded to Orr (Planck, 1905) agreeing with Orr's concerns on the definition of temperature and saying in part that: "If a process takes place so violently that one can no longer define temperature …, then the usual definition of entropy is inapplicable."

These particular difficulties were only exacerbated in 1902 with the publication (and subsequent circulation) of Gibbs' seminal treatise "Elementary Principles in Statistical Mechanics" (Gibbs, 1981). In his treatise, Gibbs showed that the microscopic expression he identified at equilibrium, as the thermodynamic entropy $S_G(t) \equiv -k_\mathrm{B} \int d\mathbf{\Gamma} f(\mathbf{\Gamma};t) \ln[f(\mathbf{\Gamma};t)]$, where $f(\mathbf{\Gamma};t)$ is the N-particle phase space distribution function at time t, is in fact a constant of the motion for autonomous Hamiltonian dynamics! If the initial distribution was not the equilibrium distribution, the Gibbs entropy did not, as Clausius claimed, increase in time until it reached its maximum and the system was effectively in equilibrium. For these systems, the Gibbs' entropy is simply a constant independent of time.

After Boltzmann's death, this distressing state of affairs was reviewed without satisfactory resolution by the Ehrenfests in 1911 (Ehrenfest and Ehrenfest, 1990). (Paul Ehrenfest was a student of Boltzmann.) Indeed ,in the Preface to the (English) Translation, Tatiana Ehrenfest confides: "At the time the article was written [1911], most physicists were still under the spell of the derivation by Clausius of the existence of an integrating factor for the … heat … it became clear to me afterwards, that the existence of an integrating factor has to do only with the differentials $dx_1, dx_2, \dots, dx_n$ of the *equilibrium* [T. Ehrenfest's italics] parameters $dx_1, dx_2, \dots, dx_n$, and is completely independent of the direction of time … Nevertheless even today [1959] many physicists are still following Clausius, and for them the second law of thermodynamics is still identical with the statement that entropy can only increase."

The Ehrenfests' article did point out that away from equilibrium entropy was problematic and that for autonomous Hamiltonian systems the entropy defined by Gibbs was indeed a constant of the motion. In Ehrenfest and Ehrenfest (1990, p. 54), they agree with Gibbs that, "From Liouville's theorem, Eqs. (26) and (26'), it follows immediately that the quantity σ [i.e., S_G above] … remains exactly constant during the mixing process." They go on to discuss Gibbs' flawed attempts to resolve the paradox by defining a coarse-grained entropy. This quantity's time dependence is determined by the grain size and is thus not an objective property of the physical system of interest.

The theory of the relaxation to equilibrium has also been fraught with difficulties (Evans, Searles, and Williams, 2009a). First, there was no mathematical definition of equilibrium! The first reasonably general approach to this problem is summarized in the Boltzmann H-theorem. Beginning with the definition of the H-function, Boltzmann proved that the Boltzmann equation for the time evolution of the single particle probability density implies, for uniform ideal gases, a monotonic decrease of the H-function in time (Boltzmann, 1872) – see the review by Lebowitz (1993) for a modern discussion of Boltzmann's ideas.

However, there are at least two problems with Boltzmann's treatment. First, the Boltzmann equation is valid only for an ideal gas. Second, and more problematic, unlike Newton's equations, Hamilton's principle, or the time-dependent Schrödinger equation, the Boltzmann equation itself is *not* time-reversal-symmetric. It is therefore completely unsurprising that the Boltzmann equation predicts a time-irreversible result, namely the Boltzmann H-theorem.

This leads to a second version of the irreversibility paradox (at least for ideal gases): how can the time-irreversible Boltzmann equation, which leads easily to the time irreversible Boltzmann H-theorem, be derived exactly for ideal gases from time-reversible Newton's equations? This issue was also discussed, without resolution, in the Ehrenfest encyclopedia article (Ehrenfest and Ehrenfest, 1990).

Since our new proof of how macroscopic irreversibility arises from time-reversible microscopic dynamics is valid for all densities, we do not need to directly answer this question in this book. We do make the comment, however, that it is thought that in the ideal gas limit, the Boltzmann equation is exact, but its detailed derivation is beyond the scope of this present book.¹⁾

The 1930s saw significant progress in ergodic theory with a proof that for a finite, autonomous Hamiltonian system, whose dynamics preserves a *mixing* microcanonical equilibrium distribution (i.e., a distribution that is uniform over the constant energy phase space hypersurface), averages of physical properties must, in the long-time limit, approach those obtained with respect to that equilibrium microcanonical distribution, regardless of the initial distribution (Sinai, 1976). Later in this book we will give a generalization of the ergodic theory proof. We consider finite systems with autonomous dynamics that are mixing with respect to some possibly thermostatted and/or barostatted equilibrium distribution that is also a solution to the dynamics considered. We show that for such systems, at sufficiently long times, averages of physical phase functions will approach, to arbitrary accuracy, the equilibrium averages taken over their mixing equilibrium distributions, irrespective of the initial distribution.

These proofs are, however, not very revealing. They tell us almost nothing of the relaxation process, only that it takes place. Relaxation is inferred rather than elucidated.

We go on to discuss a new set of theorems and results that, when taken together, provide a completely new approach to establishing the foundations of classical statistical thermodynamics and simultaneously resolving all the issues mentioned above. Each of these theorems is consistent with time-reversible,

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1) In Chapter 9, we do make some comments on the relationship between Boltzmann's assumption of molecular chaos (stosszahlansatz in German) and the axiom of causality. It is this assumption that breaks time reversal symmetry in the Boltzmann equation.

deterministic dynamics. Indeed, time reversibility of the underlying equations of motion is the key component to proving these theorems. We do comment that there are stochastic and/or quantum versions of some of the theorems. Each of these theorems is exact for systems of arbitrary size: taking the thermodynamic limit is not required. The theorems are valid for arbitrary temperatures and densities. The theorems are exact arbitrarily near to, or far from, equilibrium. Assumptions about being arbitrarily close to equilibrium, so that the response of systems to external forces is linear, are not required. In the process of deriving these theorems, the so-called "Laws" of thermodynamics cease to be unprovable "Laws" and instead become mathematical theorems.

The first step toward understanding how macroscopic irreversibility arises from microscopically time-reversible dynamics came in 1993 when Evans, Cohen, and Morriss (1993) proposed the first so-called fluctuation relation. By generalizing concepts from the theory of unstable periodic orbits in low-dimensional systems, these authors proposed a heuristic, asymptotic argument for the relative probability of seeing sets of trajectories and their conjugate sets of antitrajectories in nonequilibrium steady states maintained at constant internal energy. In the following year, Evans and Searles (1994) published the first mathematical proof of a fluctuation theorem. A generalized and detailed proof of the Evans–Searles fluctuation theorem is given in Chapter 3. This proof concerns the relative probability of fluctuations in sign of a quantity now known as the time-averaged *dissipation function*. Unsurprisingly, fluctuation theorems lead to many new results. This is what the present book sets out to describe. It used to be said that there are very few exact results that are known for nonequilibrium many-body systems. This is no longer the case.

In Chapter 3, we prove the second law inequality (Searles and Evans, 2004), and the nonequilibrium partition identity (Morriss and Evans, 1985; Carberry *et al.*, 2004; Evans and Searles, 1995). These are simple mathematical consequences of the fluctuation theorem. The second law inequality is, in fact, a generalization of the second "Law" of thermodynamics that is valid for finite, even small systems, observed for finite, even short, times. Classical thermodynamics applies to only large, in principle infinite, systems either at equilibrium or in the infinitely slow, or quasi-static, limit.

Dissipation was first explicitly defined in 2000 by Searles and Evans (2000a), although it was, of course, implicit in the earlier proofs of the Evans–Searles fluctuation theorems in 1994, et seq. It is also implicit in many of Lord Kelvin's papers in the late nineteenth century. The dissipation function has many properties, but its original definition directly involved sets of trajectories and their conjugate sets of time-reversed antitrajectories. For classical N-particle systems, the specification of all the coordinates and momenta of all the atoms in the system completely describes the microstate of a classical system. We define the phase space vector $\mathbf{\Gamma} = (\mathbf{q}_1, \dots, \mathbf{q}_N, \mathbf{p}_1, \dots, \mathbf{p}_N)$ of the positions $\mathbf{q}_i$ and momenta $\mathbf{p}_i$ of the N particles. We imagine an infinitesimal set of phases inside an infinitesimal volume $dV_{\mathbf{\Gamma}}(\mathbf{\Gamma})$ in phase space. For simplicity, we assume that the system is autonomous (i.e., the equations of motion for all the particles, $\dot{\mathbf{\Gamma}}(\mathbf{\Gamma}, t)$, do not refer explicitly to time $\dot{\mathbf{\Gamma}}(\mathbf{\Gamma})$; any external fields are time-independent).

As time evolves, this set will trace out an infinitesimal tube in phase space. We follow this tube for a time interval $(0, t)$. At time t, an initial phase space vector $\mathbf{\Gamma}$ has evolved to the position $S^t\mathbf{\Gamma}$, where S^t is the phase space – time evolution operator. If we take the set of phase points inside the infinitesimal volume $dV_{\mathbf{\Gamma}}(S^t\mathbf{\Gamma})$ and reverse all the momenta leaving all the particle positions unchanged, we have the phase vector $M^T S^t\mathbf{\Gamma}$, where M^T is a time-reversal mapping: $M^T(\mathbf{q}, \mathbf{p}) = (\mathbf{q}, -\mathbf{p})$.

If we now imagine following the natural motion of this mapped set forward in time from time t to $2t$, we arrive at the phase point $S^t M^T S^t\mathbf{\Gamma}$. Because the equations of motion are time-reversal-symmetric, the final set of phase points will have the same position coordinates but the opposite momenta to the original set of time zero phases: $S^t M^T S^t\mathbf{\Gamma} = M^T\mathbf{\Gamma}$. This is the fundamental property of time-reversible dynamics discussed in Kelvin's quote at the beginning of this chapter. This time reversibility property is exploited directly in the definition of the dissipation function. We will give a more detailed description of reversibility using a more precise notation in Chapter 2 – especially in Section 2.1.

The time integral of the dissipation function is simply defined as the natural logarithm of the probability ratio of observing at time zero the conjugate sets of trajectories inside phase space volumes $\delta V_{\mathbf{\Gamma}}(\mathbf{\Gamma}),\ \ \delta V_{\mathbf{\Gamma}}(M^T S^t\mathbf{\Gamma})$:

$$\lim_{\delta V_{\Gamma}\to 0} \frac{p(\delta V_{\mathbf{\Gamma}}(\mathbf{\Gamma}); 0)}{p(\delta V_{\mathbf{\Gamma}}(M^T S^t\mathbf{\Gamma}); 0)} \equiv \exp\left[\int_0^t ds\,\Omega\,(S^s\mathbf{\Gamma})\right] \tag{1.2}$$

The small phase space volume $\delta V_{\mathbf{\Gamma}}(\mathbf{\Gamma})$ defines an initial set of phase space trajectories. The volume $\delta V_{\mathbf{\Gamma}}(M^T S^t\mathbf{\Gamma})$ defines the conjugate set of the antitrajectories. Going forward in time from $\delta V_{\mathbf{\Gamma}}(M^T S^t\mathbf{\Gamma})$ is like going backward in time from $\delta V_{\mathbf{\Gamma}}(S^t\mathbf{\Gamma})$ except that all the momenta are reversed. For Eq. (1.2) to be well defined requires that the system should be *ergodically consistent*, that is, if the numerator is nonzero for initial phases inside some specified phase space domain D, then the denominator must also be nonzero. This condition ensures that the dissipation function is well defined *everywhere* inside the ostensible phase space domain, D.

As a historical remark, we can see from the definition, Eq. (1.2), that ergodic consistency guarantees the existence of (almost all) conjugate phase space trajectory/antitrajectory pairs. However, the mere existence of these pairs of trajectories by no means implies that the probability ratio of observing infinitesimal *sets* of these conjugate trajectory pairs is unity, as Loschmidt tried to imply. Once you have written down Eq. (1.2) for the relative probability of seeing a set of trajectories and its conjugate set of antitrajectories, it seems obvious that Loschmidt's assertion of both sides of Eq. (1.2) equaling unity is wrong. One must not make the mistake of discussing *individual* conjugate phase space trajectories rather than conjugate *sets* of trajectories. The probability of observing any individual phase space trajectory is precisely zero! Their rephrasing of Eq. (1.2) would have been ill defined, leading to zero divided by zero on the left-hand side.

We will see in Chapter 5 that an equilibrium state is characterized by a set of equations of motion and a phase space distribution for which the dissipation