Chapter 1

1.1 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…

W. Thomson (Lord Kelvin) 1874

Until very recently, the foundations of statistical mechanics were far from satisfactory. Textbooks approach the subject in one of two ways[1-3]. 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 maximising 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 [2-5] 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 [3] via the partition function.

The so-called Loschmidt Paradox that so puzzled Boltzmann and his contemporaries has remained unresolved in the 140 years since it was first raised. This paradox can be stated quite simply. All the laws of mechanics (both classical and quantum) are time reversal symmetric.

Time reversibility is trivial to demonstrate. Consider Newton's equations of motion for the positions $\mathbf{q}_i$ of N identical particles subject to interatomic forces $\mathbf{F}_i(\mathbf{q}_1,...,\mathbf{q}_N)$:

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

As Loschmidt and Kelvin (separately) noticed, the time reversal $t \to -t$ leaves (1.1) unaltered since $(-1)^2 = 1$. Changing the direction of time inverts every velocity – as per Kelvin's quote above.

How do we reconcile this reversibility with the manifest irreversibility of the Second Law of thermodynamics? Although there have been many attempts over the last century to resolve this paradox, the matter wasn't really settled until the first proof of a Fluctuation Theorem in 1994.

A less well-known problem concerns Clausius' Inequality. In some ways this is an even more fundamental problem because it concerns thermodynamics rather than statistical mechanics. Clausius' Inequality for the heat, Q, transferred to a thermal reservoir, states that the cyclic integral $\oint dQ/T \geq 0$ where T is the equilibrium thermodynamic temperature of that reservoir. When this inequality is in fact an *equality*, we have the usual argument that $\int dQ/T$ is a state function and represents the equilibrium change in the entropy. Clausius went on to apply his inequality to the system of interest *and* the reservoir. Indeed in his original papers he doesn't even distinguish between the two systems. He is famous for stating that the entropy of the Universe (system of interest plus the reservoir) "tends to increase".

Now comes the difficulty: when we have a strict inequality: ; $\oint dQ/T > 0$ either the system of interest or the reservoir, or both, are not in true thermodynamic equilibrium (the process is not *quasi-static*). In this case what is the temperature? It is only defined for quasi-static or equilibrium processes. This difficulty was discussed in the late 19$^{\text{th}}$ century by Orr and Buckingham.

"There are three things in Prof. Orr's article (Phil Mag S6 V8 No 46 p509 (1904)) which stand out as of particular importance. 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 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' " E. Buckingham Phil Mag S6, v9 p208(1905).

In 1905 Planck responded saying in part that: "If a process takes place so violently that one can no longer define temperature or density, then the usual definition of entropy is inapplicable". In that same year Buckingham discussed problems with writing textbooks for the average students while being aware at the time, of some of the difficulties mentioned above. He realised that some of the smarter students might recognise the logical inconsistencies in applying Clausius' *inequality* to non-equilibrium systems. Buckingham 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 Phil Mag S6 v9, p208(1905).

The theory of the relaxation of systems to equilibrium is also fraught with difficulties. 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 in the H-function [2, 4, 6] – see the review by Lebowitz [7] for a modern discussion of Boltzmann's ideas.

However, there are at least two problems with Boltzmann's treatment. Firstly the Boltzmann equation is only valid for an ideal gas. Secondly and more problematically, unlike Newton's equations, Hamilton's Principle or the time dependent Schrodinger 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?

Since our 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 that it is thought that in the ideal gas limit, the Boltzmann equation is exact, however its detailed derivation is beyond the scope of the present book.

The early 1930's saw significant progress in ergodic theory with the proof that a finite autonomous Hamiltonian system that is *mixing* must relax towards microcanonical equilibrium at long times. In 1970 Sinai proved ergodicity for a

number of different hard disc and hard sphere systems [9]. He also proved that for these systems, the equilibrium state is the usual microcanonical distribution. However it must be said that the ergodic theory of dynamical systems is highly technical and thus these results have largely been restricted to the mathematical physics community. To this day only a *very* few dynamical systems have been proved to be mixing and ergodic.

Later in this book we will give the ergodic theory proof that for finite, autonomous, mixing Hamiltonian systems, at sufficiently long times, averages of smooth phase functions are given, to arbitrary accuracy, by the usual microcanonical averages. This proof is however not very revealing and tells us almost nothing of the relaxation process but rather tells us only how to calculate the long-time average properties of the system. Relaxation is inferred rather than elucidated.

We go on to discuss a new set of theorems and results which when taken together provide a completely new approach to establishing the foundations of classical statistical thermodynamics and simultaneously resolving the issues mentioned above. Each of these theorems is consistent with time reversible deterministic dynamics. Indeed time reversibility is a key component to proving each of 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 "Laws" of thermodynamics cease to be "Laws" that are unprovable from the Laws of mechanics.

The first step towards understanding how macroscopic irreversibility arises from microscopically reversible dynamics, came in 1993 when Evans, Cohen and Morriss proposed the first so-called "fluctuation relation". Generalizing concepts from the theory of unstable periodic orbits in low dimensional systems, these authors proposed an heuristic, asymptotic argument for the relative probability of seeing sets of trajectories and the conjugate sets of antitrajectories for nonequilibrium steady states maintained at constant internal energy. In the following year Evans and Searles 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 and the Nonequilibrium Partition Identity. 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 only applies to large, in principle infinite, systems either at equilibrium or so close to equilibrium that they can be assumed at least locally, to be at equilibrium.

Dissipation was first explicitly defined in 2000, by Evans and Searles [19] although it was of course implicit in the earlier proofs of the Evans-Searles Fluctuation Theorems in 1994, *et. seq.* Prior to 1994, this quantity, the dissipation function, was unknown. It is however implicit in many of Lord Kelvin's papers in the late 19th century. The dissipation function has many properties but its original definition directly involved sets of trajectories and their conjugate sets of time reversed anti-trajectories. For classical N-particle systems the specification of all the coordinates and momenta of all the atoms in the system completely describes the micro-state of a classical system. We define the phase space vector, $\mathbf{\Gamma} = (\mathbf{q}_1,...,\mathbf{q}_N,\mathbf{p}_1,...,\mathbf{p}_N)$ of the positions $\mathbf{q}_i$ and momenta, $\mathbf{p}_i$ of the N particle*s*. We imagine an infinitesimal set of phases inside an infinitesimal volume, $dV_\Gamma(\mathbf{\Gamma})$, in phase space. For simplicity we assume 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 the initial phase space vector $\mathbf{\Gamma}$ has evolved to the position $S^t\mathbf{\Gamma}$. If we take the set of phase points inside the infinitesimal volume, $dV_\Gamma(S^t\mathbf{\Gamma})$ and reverse all the momenta leaving all the particle positions unchanged we arrive at the following phase vector: $M^T S^t\mathbf{\Gamma}$.

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: $S^t M^T S^t \mathbf{\Gamma} = \mathbf{M}^T \mathbf{\Gamma}$. This is the fundamental property of time reversible dynamics discussed in Kelvin's quote above. 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 descriptive notation in Chapter 2 – especially in §2.1.

The time integral of the dissipation function is simply defined as the exponential of the probability ratio of observing at time zero, the conjugate sets of trajectories inside phase space volumes $dV_\Gamma(\mathbf{\Gamma}), dV_\Gamma(M^T S^t \mathbf{\Gamma})$ respectively in the initial distribution of phases:

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

The infinitesmal volume $dV_\Gamma(\mathbf{\Gamma})$ defines a set of phase space trajectories. The volume $dV_\Gamma(M^T S^t \mathbf{\Gamma})$ defines the origin of the conjugate set of anti-trajectories. Going forward in time from $dV_\Gamma(M^T S^t \mathbf{\Gamma})$ is like going backwards in time from $dV_\Gamma(S^t \mathbf{\Gamma})$ except that all the momenta are reversed. [We see this illustrated in Figure 1.1.] For equation (1.2) to be well-defined requires that the system should be *ergodically consistent i.e.* if the numerator is nonzero for all 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 an historical aside, we can see from the definition (1.2) ergodic consistency guarantees the existence of (almost all) conjugate trajectory anti-trajectory pairs. However the mere existence of these pairs of trajectories by no means implies the probability ratio of observing infinitesimal sets of these conjugate trajectory pairs is unity – Loschmidt implied.

We will see in Chapter 5 that an equilibrium state is characterized by a phase space distribution in which the dissipation function is identically zero everywhere in phase space. Thus for the equilibrium states alone, the probabilities of observing trajectories and their conjugate anti trajectories is identical.

Equation (1.2) also points out the flaws in Loschmidt's argument about reversible dynamics leading to purely time reversible macroscopic results. You cannot sensibly talk about the probability of observing an individual phase space trajectory. Its probability is precisely zero! The dissipation function is defined in terms of conjugate *sets* of trajectories and antitrajectories.

Although the definition of the dissipation function may appear rather abstract and mathematical, it turns out that in the linear regime close to equilibrium the average of the dissipation function is equal to a quantity that is familiar in linear irreversible thermodynamics, namely the spontaneous entropy production. For systems that are driven by an applied dissipative field (*e.g.* an electrically conducting system being driven by an electric field), the average dissipation is equal to the average power dissipated in the system divided by the thermodynamic temperature of the surrounding thermal reservoir to which the dissipated work, on average, eventually relaxes. A notable aspect of our exposition is the fact that except at equilibrium, entropy plays almost no role.

The first theorem that referred to dissipation was the Evans-Searles Fluctuation Theorem (1994) (FT). This theorem states that for systems with time reversible dynamics where the initial distribution of phases is even in the momenta and which satisfies the condition of ergodic consistency, then taken over all states in the initial ensemble, the ratio of probabilities that the time averaged dissipation function $\bar{\Omega}_t$, takes on an arbitrary value, *A*, compared to the negative of that value, -*A*, satisfies the following equation

$$\frac{\Pr(\bar{\Omega}_t = A)}{\Pr(\bar{\Omega}_t = -A)} = e^{At} .$$

(1.3)

This shows that the probability of positive dissipation is exponentially more likely than negative dissipation and moreover the argument of the exponential is extensive in the number of particles in the system and the averaging time, *t* . Equation (1.3) has been confirmed in both molecular dynamics computer simulations and in actual laboratory experiments.

A trivial consequence of the FT is the Second Law Inequality which states that if we average the response of repeated experiments on our system with

macroscopically identical initial conditions, the so-called ensemble average of the time averaged dissipation $\langle \bar{\Omega}_t \rangle$, is non-negative

$$\langle \bar{\Omega}_t \rangle \geq 0, \forall t \tag{1.4}$$

This does not imply the instantaneous ensemble averaged dissipation is non-negative. This ensemble averaged *instantaneous* dissipation $\langle \Omega(t) \rangle$ may be positive or negative.

The Second Law Inequality also shows that

$$\Omega(\mathbf{\Gamma}) = 0 \Leftrightarrow \langle \bar{\Omega}_t \rangle = 0 \tag{1.5}$$

The proof is rather obvious. Obviously the left hand side implies the right. Does the right imply the left? Suppose the ensemble averaged time integral of the dissipation is not identically zero everywhere. Average the dissipation over some possibly short time interval (0,t). Ergodic consistency implies the existence of conjugate sets of trajectories with opposite values for the time averaged dissipation $\pm(A + dA)$. Applying the FT to each conjugate set with time averaged dissipation $\pm(A + dA)$ shows that positive dissipation is exponentially more likely than negative for each value of $|A|$ that is observed. If we now average over all possible values for $|A|$ we see that $\langle \Omega_t \rangle > 0$. The ensemble average of the time integrated dissipation must be strictly positive. So if the dissipation is nonzero anywhere in the allowed phase space and the system is ergodically consistent, the time averaged ensemble average dissipation must be strictly positive. The only states where the ensemble averaged , time averaged dissipation is zero, are equilibrium states where the instantaneous dissipation is identically zero everywhere in the allowed phase space.

Thus equation (1.5) gives statistical mechanics for the first time, a strict mathematical definition of an equilibrium distribution of phases. An equilibrium distribution function is one for which the dissipation function, calculated using the definition (1.2), is zero for all initial phases $\mathbf{\Gamma}$ in the allowed phase space.

The recently discovered Dissipation Theorem (Chapter 4) states that the ensemble average of an arbitrary integrable function of phase, $B(\mathbf{\Gamma})$ is related to the time integrals of the correlation function of the dissipation function with the phase variable

$$\langle B(t) \rangle = \langle B(0) \rangle + \int_0^t ds \langle B(s)\Omega(0) \rangle . \tag{1.6}$$

The dynamics employed for evaluating *all* functions on both sides of (1.6) employs that natural system dynamics including any external fields or thermostats. This result is valid arbitrarily far from equilibrium and for systems of arbitrary size. In systems where an externally applied field is responsible for driving the system out of equilibrium, in the weak field regime where the response to this field is linear, equation (1.5) reduces to the very well known Green-Kubo linear response equations.

Since the instantaneous dissipation is zero for equilibrium systems. Equation (1.6) shows that in the absence of external field ensemble averages of phase function never change for systems at equilibrium.

Together with the definition of dissipation a second very important definition is that of a T-mixing system. A system is said to be T-mixing if infinite time integrals of all suitably smooth, phase variables $B(\mathbf{\Gamma})$ with the dissipation function at time zero are convergent. A system of harmonic oscillators with zero friction is obviously not *T*-mixing. *T*-mixing is a stronger condition than the mixing condition met in ergodic theory. From (1.5) we see that if an autonomous system is *T*-mixing then at long times the ensemble average of smooth phase functions become time independent at long times. At long times *T*-mixing systems must therefore either form nonequilibrium *steady* states or form equilibrium states. No other possibilities exist.

The dissipation function, ergodic consistency and the T-mixing condition hold over some specified phase space domain. For example while particle momenta may be unbounded, the particle coordinates are usually only defined over a fixed region of physical space. A system is said to be ergodic over some specified phase space domain if time averages of smooth phase functions taken along almost any phase space trajectory, equal long time ensemble averages taken over the ensemble of initial states. *T*-mixing systems must be ergodic over that specified phase space domain. If they were not ergodic over the specified domain we could easily construct time correlation functions (1.1) that would never decay to zero. Any initial static correlation between the phase function and the initial dissipation would be preserved forever therefore violating the condition of T-mixing.

All systems are in fact ergodic over *some* phase space domain. It really becomes a question of specifying how large the ergodic domain actually is. In

systems that a physicist may call "non-ergodic", the ergodic domain may have a relatively small or even zero measure in the ostensibly accessible phase space.

The Equilibrium Relaxation Theorem derived in Chapter 5, states that autonomous N-particle, *T-mixing* systems that may be isolated or perhaps interact with a heat bath and whose initial distributions are even functions of the momenta, will at sufficiently long times, relax to a unique equilibrium state and that

$$\lim_{t \to \infty} \left\langle \Omega(S^t \mathbf{\Gamma}) \right\rangle = 0, \forall \mathbf{\Gamma} \in D \,. \tag{1.6}$$

For various forms of thermostat or ergostat, the mathematical forms of these equilibrium distributions can be determined explicitly using the various individual forms of the Equilibrium Relaxation Theorem.

For constant energy dynamics the equilibrium distribution is uniform over the energy hypersurface in phase space. The Equilibrium Relaxation Theorem therefore gives a mathematical proof of Boltzmann's postulate of equal *a priori* probability for constant energy systems. Unlike Boltzmann's H-theorem the Relaxation Theorem does not imply that all relaxation processes are monotonic in time. This is just as well since experience shows that most relaxation processes are *not* monotonic. For thermostatted systems where the number of particles and the volume is fixed, the unique equilibrium distribution is the well-known canonical distribution postulated by Boltzmann and Gibbs.

In Chapter 6 we discuss the Steady State Relaxation Theorem. For systems that are initially in equilibrium for the zero field dynamics, if a dissipative field is then applied to the system and it is T-mixing, the system will eventually relax to an ergodic nonequilibrium steady state. At long times, time averages of phase functions equal long time, ensemble averages. Further we show that if the initial equilibrium distribution is perturbed by some deviation function (even in the particle momenta) the final steady state is independent of the initial perturbation.

Also in Chapter 6 we discuss asymptotic steady state Fluctuation Theorems. For T-mixing systems these steady state fluctuation relations are valid even for large deviations from the mean behaviour of the system.

In Chapter 7 we discuss various experimental demonstrations of the various theorems discussed in the book. Some of these experiments are actual laboratory experiments while others are computer simulation experiments.

In Chapter 8 we discuss the Crooks Fluctuation Relations and the Jarzynski Equality. These relations show how equilibrium free energy differences can be computed from nonequilibrium path integrals of the work. Using various generalisations of these we give a mathematical proof of Clausius' Inequality. We consider a set of large thermal reservoirs at a set of temperatures. Because the reservoirs are large compared to the system of interest they can be regarded as being in thermodynamic equilibrium. We prove that for systems that respond periodically to some cyclic protocol, the ensemble average of the cyclic time integral of the heat transferred to the reservoirs divided by the corresponding reservoir temperature, is non-negative. Clausius proved his inequality by *assuming* the Second Law of Thermodynamics. Our proof makes no such assumption. Since Clausius' Inequality is often taken as the most fundamental statement of the Second Law, our proof constitutes a direct proof of this statement of the Second Law. We show that it is only true if the system responds periodically to the cyclic protocol (not all systems do this of course) and it is only true if we take the ensemble-averaged response. A single cycle for an individual system, if it is small, may not satisfy Clausius' Inequality.

We also show that if the reservoirs are small and cannot be regarded as being in thermodynamic equilibrium the ensemble average of the cyclic integral still satisfies Clausius' Inequality. Of course it only applies if the system responds periodically. At each point in the cycle the temperature appearing in Clausius' Inequality in this case is the equilibrium temperature that the entire system would relax to if at any point in the cycle the execution of the protocol is stopped and the entire system is allowed to relax to equilibrium.

An immediate consequence of this is that for the entire system (system of interest plus reservoirs) the cyclic integral of the heat transfers divided by the temperature is exactly zero. This is consistent with an observation made by Gibbs, namely that for an autonomous Hamiltonian system, the so-called fine-grained Gibbs entropy is a constant of the motion. It is the total dissipation that tends to increase and not the entropy. The constancy of the Gibbs entropy has been well known to those who know but is probably not commented on in most text books because without the concept of dissipation the text book writers could not "explain" irreversibility.

In Chapter 9 we re-visit the proof of the Evans-Searles FT and discuss the role played therein by the Axiom of Causality. We prove that in an anticausal Universe there is an anti-Second "Law" of thermodynamics and that ultimately the explanation

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for the macroscopic irreversibility we see around us is the direct result of Causality. In very few discussions of irreversibility is it realized that if you apply a time reversal mapping to a system trajectory not only do you reverse the direction of the flow of heat and work but the causal response to some time dependent field becomes anti-causal! Fluxes respond to changes in field strength *before* those changes occur!

If we watch a movie played backwards, of macroscopic machines in motion not only will we see examples of "perpetual motion machines of the second kind", but we will also see a Universe of effect *preceding* cause. The transient response to a sudden application of a cause will have the opposite sign to that observed in the forward movie but that transient response will start slightly before the application of the cause! The transient electric current will start to flow (backwards) *before* the light switch is switched to on. The light will absorb photons and heat from the ambient world and generate electricity. The transient electric current (flowing backwards), will start to fall towards zero *before* you switch the light switch off!

The assumption of causality seems so ingrained and natural to the human way of thinking that we often don't realize that it is an assumption. It is this assumption or rather the use of this Axiom in the proofs of the Evans-Searles and Crooks FTs, that breaks the symmetry of time and leads to the Second Law Inequality rather than an anti-Second Law Inequality.

The Principle of Least Action, which is completely time reversal symmetric, does not contain sufficient information to prove any Fluctuation Theorem. The equations of motion of mechanics must be supplemented with the Axiom of Causality to predict the operation of machines and engines in the real world. The Axiom is constantly applied without us even noticing, precisely because it seems so natural. Students are taught to solve differential equations involving time by integrating the equations of motion forward in time from the *initial* conditions. The response of a system (engine) at a given time is obtained by convolving the response function for the system with the time dependent driving force backwards over the past history and *not* over its future. This immediately breaks the time reversal symmetry of our analysis of the system. This is in spite of the time reversal symmetry of the underlying equations of motion.

A clear example of the unrecognised application of the Axiom of Causality is in the Mori-Zwanzig projection operator formalism. This formalism leads in the linear response limit, to an exact reformulation of Newton's equations of motion in

the form of a frequency and wavevector dependent generalised Langevin equation. In the time domain, the memory kernel associated with the generalised friction coefficient, is convolved *backwards* in time with the time dependent driving force. This breaks the time reversal symmetry inherent in the equations of motion themselves. The spatial convolution is over all space. The temporal convolution is over the half space that describes history rather than future. The spatial convolution is over all physical space to $\pm\infty$.

The Axiom of Causality is also met in electrodynamics where the Maxwell's Equations permit two solutions for the vector potential: the advanced and the retarded vector potential. In a well-known textbook they state with little fanfare: "We can now neglect the term V_2' ... for it would make the effect appear before the cause". P445 Corson and Lorrain "Electromagnetic Fields and Waves (1962). Panofsky and Phillips are a little more equivocal on the subject: "but only the minus sign appears to have physical significance"; "the advanced potential…. appears to violate elementary notions of causality".

It is interesting to re-examine the Boltzmann equation in the light of these observations. In writing the collision integral in the Boltzmann equation it is assumed that *before* collisions of ideal gas atoms the positions and momenta are uncorrelated. After the collision there is correlation. This is the assumption of molecular chaos. If one assumes that the positions and momenta are uncorrelated *after* the collisions then one forms an anti-Boltzmann equation and the signs of all the transport coefficients (*e.g.* shear viscosity or thermal conductivity etc.) computed using the anti-Boltzmann equation are opposite to those predicted from the Boltzmann equation. This was first understood by Cohen and Berlin in 1965.

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