Chapter 1

Introduction

In the late 19th Century there was a public debate between several well known scientists: Loschmidt, Boltzmann, Maxwell and others. This debate, known as Loschmidt's paradox, centered on finding the link between Newton's equations of motion for individual molecules (part of the pioneering work by Boltzmann in statistical mechanics) and the irreversible equations in thermodynamics. Loschmidt pointed out that Newton's equations of motion could be solved in both a time-forward and time-reverse direction from an initial set of time-reversible conditions. That is, starting at state 1 the equations of motion can be solved from time $s = 0$ to some arbitrary time t later in state 2, producing a certain amount of entropy. But as the equations of motion are time-reversible it is equally possible to start at state 2 at $s = 0$ and proceed back to state 1 over the same period of time "consuming" entropy. This is in "violation" of the second law of thermodynamics. The second law of thermodynamics states that the entropy of a closed system must increase, and these time-reversed paths clearly disobey this law. In order to overcome this paradox, and referring to the second law, Boltzmann stated "as soon as one looks at bodies of such small dimension that they contain only very few molecules, the validity of this theorem must cease" [1].

In 1903 Einstein published a paper that also attempted to determine the link between Newton's equations of motion for single molecules and thermodynamics [2], however his proof was based on an incorrect assumption [3]. Einstein wrote "We will have to assume that more probable distributions will always follow less probable ones, that is, S always increases until the distribution becomes constant and S

has reached a maximum."[1] [2] The variable S is the thermodynamic probability, originally derived by Boltzmann to relate the entropy of the system, S, to the number of microstates in the system, $S = k_B \ln \mathcal{W}$. Einstein's assumption then becomes: if S is in a low probability state then a higher probability state must follow. Einstein effectively assumes second law irreversibility, and does not allow for time-reversible paths or for the surroundings to do work on the system. "It appears that Einstein was unaware of Loschmidt's paradox." [3] Einstein published a second derivation in 1904, also based on this same assumption [4]. Einstein's assumption was questioned by Hertz in 1910, and Einstein did not provide any proof of this assumption.

Loschmidt's paradox was finally overcome in 1993 when Evans, Cohen and Morriss [5] published the first paper on the Fluctuation Theorem (FT). This paper provided the link between the reversible equations of motion for individual molecules and thermodynamics that Einstein, Boltzmann, Loschmidt and others had attempted to find. The paper provided a heuristic proof of what is now known as the Steady State Fluctuation Theorem. In 1994 Evans and Searles [6] provided a formal proof for the FT. In this paper Evans and Searles describe how a thermostatted equilibrium system can be perturbed by an external field. Evans and Searles calculated the probability of observing energy being *dissipated to* the surroundings and compared this to the probability of observing energy being *absorbed from* the surroundings. This energy absorption is exactly what Loschmidt was trying to address in his paradox. The FT states that the probability of observing these trajectories that absorb energy from the surroundings decreases exponentially as time and/or the system size increases. In this way the FT recovers the second law of thermodynamics. Several simulations were performed following this paper to test the FT [7, 8].

The Kawasaki Identity, a function closely related to the FT, has also been derived recently [9, 10, 11]. Morriss and Evans derived the Kawasaki function in 1985 [9] and the Kawasaki Identity (KI) in 1990 [10]. However, it was not until Evans and Searles' 1995 paper [11] that the KI, finite sampling and time reversibility were understood. Evans and Searles did not explore the relationship between the KI and the FT at this time, but rather explored the use of the KI as a phase space normalising term. Currently no experiments have been carried out to test the KI or to see if this can

[1] The original notation used by Einstein used W rather than S. The notation has been changed so as to prevent confusion between W used by Einstein and the number of microstates available to a thermodynamic system used by Boltzmann, $\mathcal{W}$.

be used when testing the FT.

In 2002 Wang *et al* [12] performed the first FT experiment, demonstrating an integrated form of the FT. Using Optical Tweezers Wang *et al* slowly dragged a colloidal particle through an aqueous solution and measured the particle's position as it moved with and against the flow field. In their experiment Wang *et al* demonstrated that work can be done by the system on a particle for time periods out to approximately 2 seconds in an apparent "violation of the second law". They showed that the probability of observing "second-law violating trajectories" decreases exponentially with time. In the long time limit Wang *et al* only observed "second law abiding trajectories", thus recovering the expected second law behaviour.

1.1 Thesis Goals

The experiments presented in this thesis use Optical Tweezers, a device that enables energies that are a fraction of thermal energy (k_BT) to be measured. In this energy regime there is a distinct probability of observing the surroundings performing work on the system and, as such, Optical Tweezers are an ideal tool to test the FT. The primary goal of this thesis is to experimentally investigate the FT and associated relations with Optical Tweezers, obtaining results that can be analysed without ambiguity. The FT needs to be experimentally demonstrated to determine whether the assumptions made in its derivation are applicable to a real system. The second goal is to explore whether the FT applies only for systems that can be modelled using deterministic or stochastic equations, or whether it can be applied to a wider range of systems. Finally, the third goal is to demonstrate the KI in an experiment and investigate its relationship with the FT.

1.2 References

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