# FLUCTUATION THEOREMS AND THE FOUNDATIONS OF STATISTICAL MECHANICS

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In 1993 Evans, Cohen and Morriss described the first Fluctuation Theorem[1]. Fluctuation theorems describe the statistics of time averages of a generalized entropy production, namely the dissipation function. Close to equilibrium the average dissipation function is the average purely irreversible entropy production. However far from equilibrium where the entropy production cannot be defined, the dissipation function remains a precisely defined mathematical quantity. In words, the time average dissipation function $\bar{\Omega}_t$, is the irreversible work performed on a system divided by the ambient thermodynamic temperature. Because the microscopic equations of motion (either classical or quantum mechanical) are always time reversal symmetric, the dissipation function like the entropy production may be positive or negative. The Evans-Searles[2] transient fluctuation theorem states that it is exponentially more likely that the time average dissipation function will be positive rather than negative:

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

Since the dissipation function is extensive for macroscopic systems it is essentially impossible to observe instances of negative dissipation.

In nano-systems this is not the case and we see that as thermodynamic engines are made smaller and smaller they operate differently from their macroscopic counterparts. Weak nano-engines inescapably run thermodynamically in reverse for a fraction of the time.

The Fluctuation Theorem (FT) is an exact result arbitrarily far from or close to, equilibrium.

The FT leads to a number of interesting corollaries among them the nonequilibrium partition identity[2]: $\langle \bar{\Omega}_t \rangle \geq 0$ (*i.e.* the ensemble average of the time averaged dissipation function cannot be negative). The instantaneous dissipation function may be negative.

Recently we have derived two new theorems that are consequences of the FT. The Dissipation Theorem[3] shows that arbitrarily far from equilibrium, the linear and nonlinear response of systems is controlled by time integrals of transient time correlation functions of the instantaneous dissipation function:

$$\langle B(t) \rangle_{f(\Gamma,0)} = \langle B(0) \rangle_{f(\Gamma,0)} + \int_0^t ds \langle \Omega(0) B(s) \rangle_{f(\Gamma,0)}$$

The Relaxation Theorem (RT) proves that for systems where the initial phase space distribution is even in the momenta and which satisfies the t-mixing condition, $\lim_{t\to\infty} \langle \Omega(0) B(t) \rangle = 0$, then arbitrary initial microscopic phase space distribution functions will, at sufficiently long times, relax to equilibrium: microcanonical equilibrium for constant energy systems[4] and to the Maxwell Boltzmann distribution[5] for systems in contact with a heat bath. The relaxation process is not monotonic in general. Systems satisfying these conditions are also ergodic.

The derivation of the RT for constant energy systems constitutes the first mathematical proof of Boltzmann's *postulate* of equal *a priori* probability.

The RT also proves that for equilibrium systems the dissipation function is identically zero everywhere in phase space:

$$\lim_{t\to\infty}\Omega(\mathbf{G}(0),0)=0,\ \forall f(\mathbf{G}(0),0)\mathbf{G}(0).$$

We will now show computer simulation results for a model system based on a colloidal particle in water that is at equilibrium at time zero when the spring constant is suddenly changed from one value to another.

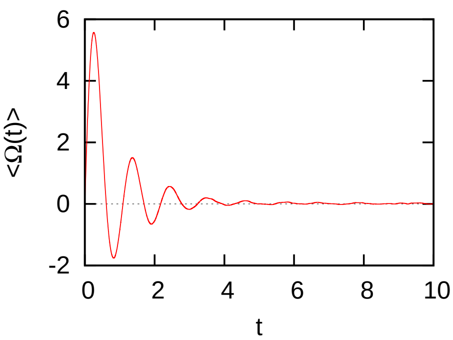


**Figure 1:** Plot of the ensemble average dissipation vs time for our model system, showing non-monotonic relaxation. Note that the total dissipation is always greater than zero.

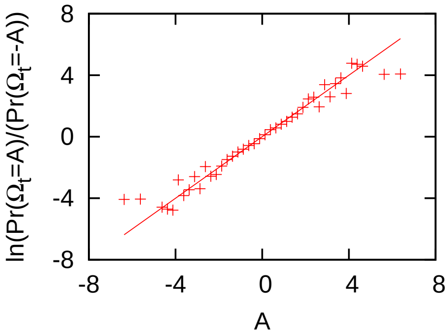


**Figure 2**: Plot of the Evans-Searles transient fluctuation theorem for the model system at the first maxima (t=0.256). The linear behaviour demonstrates that this relation is obeyed for this system while it is still out of equilibrium.

## References

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