



# LIQUID STATE CHEMICAL PHYSICS

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Our research interests include nonequilibrium statistical mechanics and thermodynamics. We have been involved in the development of nearly all of the computer simulation algorithms used for the calculation of transport properties of classical atomic, molecular and short-chain polymeric fluids and lubricants. Algorithms that we have proposed are used to compute the viscosities, thermal conductivities, and diffusion coefficients for molecular fluids and fluid mixtures.

These practical applications are based on the theory of nonequilibrium steady states, also developed by our group. Our theory of such systems provides a framework within which exact relationships between nonequilibrium fluctuations and measurable thermophysical properties have been proved.

We derived the first exact, practical link between the theory of chaos, dynamical systems theory, and thermophysical properties. This link shows that a transport coefficient, like shear viscosity, is related in a direct, quantitative way to the stability of molecular trajectories. Later we derived the so-called Fluctuation Theorem (FT). This remarkable theorem gives an analytic expression for the probability that in a nonequilibrium system of finite size, observed for a finite time, the dissipative flux flows in the reverse direction to that required by the Second Law of Thermodynamics. Close to equilibrium the FT can be used to derive both Einstein and Green-Kubo relations for transport coefficients. In collaboration with members of the Polymers and Soft Condensed Matter Group, the FT has been verified experimentally.

## Unified Description of Recent Theorems in Nonequilibrium Statistical Mechanics

The understanding of thermodynamics is largely confined to equilibrium states. The field of "nonequilibrium thermodynamics" represents an extension of the 19th century concepts of equilibrium thermodynamics to systems that are close to, or at equilibrium. Moreover, these traditional concepts are limited in application to large systems; this restriction is referred to as the "thermodynamic limit". However, in the last decade, two new theorems have revolutionised the field of thermodynamics and its application to modern systems. These new theorems firstly, lift the restriction of the thermodynamic limit, allowing thermodynamic concepts to be applied to small systems, and secondly, apply to systems that may be far-from-equilibrium. The first of these theorems, the Fluctuation Theorem (FT) generalises the Second Law of Thermodynamics so that it applies to small systems, including those far from equilibrium. The second, the Work Relation (WR) (also known as the Jarzynski equality or the nonequilibrium free energy theorem), provides a method of predicting equilibrium free energy differences from experimental trajectories along far-from-equilibrium paths. Previously the FT and WR have been treated as independent theorems. However, in 2005, we proved that these theorems, when expressed as general relations of thermodynamic systems, are related by an additional fluctuation theorem, which we have named the conjugate Fluctuation Theorem (cFT). Each of these theorems describes the distribution of energies along nonequilibrium trajectories. *(With J C Reid, E M Sevick)*



## Experimental Confirmation of Fluctuation Theorems and Nonequilibrium Work Theorems

Associate Professor Sevick and Professor Evans have a joint ARC research grant to work on this subject. See the research summary by Associate Professor Sevick for a description of all the experimental work in this area. *(With E M Sevick, D C Carberry, G Wang, and D J Searles [Griffith U])*

### Gallavotti–Cohen Fluctuation Theorem (FT)

Work has continued on our proof that the so-called Gallavotti–Cohen FT (which only applies to steady states), in fact applies only to constant energy steady states. We now understand why changing from ergostatted to thermostatted dynamics has such a profound effect on the Gallavotti–Cohen FT and the Sinai–Ruelle–Bowen measure. The corresponding Evans–Searles theorems are valid for all kinds of thermostat or ergostat. *(With D J Searles [Griffith U], L Rondoni [Turin Polytechnic])*

### Deterministic Fluctuation Theorem (FT) Applied to Glassy Systems

We applied the FT to glassy systems. Our work on the Gallavotti–Cohen FT has provided a theoretical basis for understanding the limits to the linear response regime in thermal systems. It has been claimed in the past that as the glass transition is approached both the Fluctuation Dissipation Theorem (due to Einstein) and the Evans–Searles Fluctuation Theorem (ESFT) break down. We have shown that these claims are false. Using a combination of theory and nonequilibrium molecular dynamics simulations we have shown that the Fluctuation Dissipation Theorem (FDT) does not fail, but rather as the glass transition is approached the range of field strengths over which linear response can be expected, shrinks to zero. Inside the linear response domain the FDT always works. Outside this domain the FDT does not apply. The previous claims that the ESFT fails as the glass transition is approached was simply due to sampling problems as the glass transition is approached. When sampling is carried out with sufficient care the ESFT always works – as expected from theory.

### Second Law Inequality in Viscoelastic Materials

Linear irreversible thermodynamics asserts that the instantaneous local spontaneous entropy production must always be non-negative. However for a viscoelastic fluid this is not always the case. Given the fundamental status of the Second Law, this presents a problem. Recently we have derived the Second Law Inequality from first principles *via* the Fluctuation Theorem. This derivation proves that the time average of the entropy production is non-negative. The distinction between time averages and instantaneous values has not previously been appreciated. This provides the first known macroscopic consequence of the Fluctuation Theorem. We present a new derivation of the Second Law Inequality from the nonequilibrium Work Relation which has a different domain of validity than that from the Fluctuation Theorem derivation. We tested the Second Law Inequality using molecular dynamics simulations of oscillatory shear in the linear regime. After the decay of the initial transients the Second Law Inequality is valid for time averaged entropy production. We observe that the instantaneous entropy production is negative for various ranges of times.

<http://rsc.anu.edu.au/research/evans.php>