



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 steady state 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.

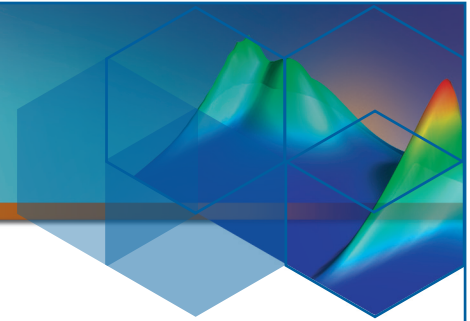
Fluctuation Theorem (FT)

Work has continued on our proof that the so-called Gallavotti-Cohen FT (which only applies to steady states), in fact only applies to constant energy steady states. We are still exploring 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 Thermostats

We have demonstrated how the FT remains independent of thermostating details for an infinite class of fictitious time-reversible deterministic thermostats. We have shown this theoretically and provided an explicit numerical demonstration firmly establishing how the fictitious thermostat is a convenient but ultimately irrelevant mathematical device. This is important because the derivation of the FT uses fictitious thermostats. Until now, thought (gedanken) experiments have been used to argue that the theory is also directly relevant to laboratory experiments, where the temperature is controlled by a large heat reservoir.

In other work we have discovered that the class of thermostats that Hoover and Evans invented in 1982, is unique. These thermostats which can be derived from Gauss' Principle of Least Constraint applied to fix the kinetic energy of the system, are the only thermostats which permit an equilibrium state. In finite sized systems, if we use non-Gaussian methods to constraint the kinetic energy or we use Gauss' Principle to constrain other moments of the kinetic energy, then the thermostats so derived cannot support an equilibrium state. They are auto-dissipative. This discovery was quite surprising. When the number of degrees of freedom employed in the thermostat becomes infinite, this auto-dissipative aspect of non-Gaussian thermostats can vanish. *(With D J Searles [Griffith U])*



Deterministic Fluctuation Theorem (FT) Applied to Glassy Systems

Work has begun on the application of the FT to glassy systems. Nonequilibrium molecular dynamics simulations are used to provide a realistic model glassy system. The FT provides theoretical expressions, which may be used to probe the distribution function of a glassy system in the absence of an external field. Applying the theory to glassy systems, which dominantly exhibit elastic storage on the simulation time scale, can give very different results to equilibrium fluids, which predominantly exhibit viscous dissipation on the simulation time scale.

Kawasaki Identity

We showed that the Kawasaki Identity can be proved in three lines of simple algebra from the Evans-Searles FT. We have conducted the first experimental tests of the so-called Kawasaki Identity. This identity is a useful diagnostic check on optical tweezers apparatus. *(With E M Sevick)*

Second Law Inequality

We have derived an inequality for the dissipation function that appears in the Evans-Searles FT. We have proved that if we start from the specified initial state, then time integrals of the ensemble average of the dissipation function *cannot* be negative. In thermostatted steady states the ensemble average of the dissipation function is equal to the entropy production. Thus, we have proved that time averages of the entropy production are non-negative. This is in contradistinction to the usual (erroneous) statement of irreversible thermodynamics that says that the entropy production is always positive. This usual statement is wrong as any simple consideration of viscoelastic systems reveals. Our proof of the Second Law Inequality shows that time averages of the entropy production are always non-negative. This is an exact consequence of the Evans-Searles FT. *(With D J Searles [Griffith U])*

Experimental Confirmation of the Transient FT

Two years ago we conducted the first experimental test of an Evans-Searles FT. However, experimental difficulties meant that we could only test the integrated form of the theorem. This year we conducted the first experimental verification of the distinct version of the Evans-Searles Transient FT. The experiment involved a stationary optical trap in which the trap strength was suddenly changed. The FT was tested for the transient relaxation of the system to its new equilibrium state. *(With E M Sevick, and D J Searles [Griffith U])*

Stochastic Derivation of a Transient Fluctuation Theorem

It has been known for some time that the dissipation function defined deterministically in the Evans-Searles FT, also obeys the Fluctuation Relation when the dynamics are stochastic. We have now given the first completely stochastic derivation of the FT. This work shows that for some stochastic systems the dissipation function that satisfies a Fluctuation Relation is not unique. *(With E M Sevick, and D J Searles [Griffith U])*

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