Liquid State Chemical Physics
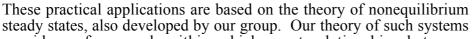
Professor Denis Evans

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 in the calculation of transport properties of classical atomic, molecular, 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 established.

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

Further progress was made towards gaining a better understanding of the FT. Constructs used in the Evans-Searles proof of the FT were used to derive a formula for the difference in free energies of two *equilibrium* states by summing over all possible *nonequilibrium* paths that can connect those states. Previously it was thought that equilibrium free energy differences could only be computed from quasi-static (*i.e.* equilibrium) path integrals. Late in the year we proved 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. The corresponding Evans-Searles theorems are valid for all kinds of thermostat or ergostat.

The Conjugate Pairing Rule

Lyapunov exponents characterise the stability of phase space trajectories of molecular systems. For systems of N atoms there are ~6N Lyapunov exponents – a huge number! The conjugate pairing rule (CPR), says that these exponents pair in such a way that transport coefficients of certain nonequilibrium steady state processes can be computed from any conjugate pair of Lyapunov exponents. This reduces the problem of computing transport coefficients from one involving Avogadro's number of exponents to one involving just 2. CPR holds exactly for Hamiltonian systems that are thermostatted homogeneously using Gaussian type thermostats. In this work we are studying the validity of CPR to nonequilibrium systems in the weak dissipative field limit (weak shear flow or colour field) but which are thermostatted in a way that the CPR should fail. There is some evidence that CPR is universal in the weak field limit.

Transport Properties of Molten Salts

We investigated the transport properties of molten salts, such as shear viscosity and electrical conductivity in dc and ac fields using non-equilibrium molecular dynamics. In particular, we investigated the influence of the thermostat used in simulation on the results in strong external fields. Molten salts were shown to have a larger Newtonian region of shear viscosity than simple liquids, and the choice of thermostatting method had little influence on the results for the investigated range of shear rates. In an electric field, dependence of the results on thermostat becomes apparent only at extremely high fields (greater than 0.5×10^9 V/m). For this range of fields, quantitative differences of unexpected size can be seen in the melt. In the supercritical fluid, different thermostats predict qualitatively very different behaviour and structure. While the kinetic-type thermostats predict increased association of ions in the field, configurational thermostat predicts enhanced dissociation. In an alternating field, the response is linear for high frequencies, whereas for low frequencies it contains higher harmonics of the field. The time-dependent shape of the response can be deduced from the knowledge of currents in dc fields. Only the first harmonic of this current contributes to the dissipation. *(with J. Delhomelle [U. Henri Poincaré, France])*

Non-equilibrium Simulations of a Hard Sphere Fluid

Analytic solutions for free trajectories and collisions of a hard sphere fluid under shear and in a constant colour field with a Gauss kinetic thermostat have been found. In both systems, the solutions provided surprising insights into the mechanical aspects of thermostatting a system in an external field. For the sheared fluid, the equivalence of constant temperature and constant energy ensembles in the thermodynamic limit in equilibrium, the conditions for the nature of heat exchange with the environment, and the condition for appearance of the artificial string phase followed from the solution. The colour field solution permitted us to perform the first non-equilibrium hard sphere simulation using the analytic form of curved trajectories, in order to inverstigate the conditions for the breakdown of ergodicity in this system. *(with O.G. Jepps, [Griffith U.])*

Soft Condensed Matter

We continue to investigate the application of small angle neutron scattering to problems of interest to members of the group. Experiments carried out at ANSTO (Australian Nuclear Science and Technology Organisation) include studies of the adsorption of organic long chain molecules on a clay mineral surface and a very speculative investigation of the scattering and velocity distribution of neutrons passed though a fluid.

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