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 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, and are presently being used in thermophysical data correlation packages provided to the chemical industry by the National Institute of Standards and Technology (NIST), Boulder, Colorado.

These practical applications are based on the theory of nonequilibrium steady states, also developed by this group. Our work on the theory of thermostatted nonequilibrium 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 a collaboration with members of the *Polymers and Soft Condensed Matter Group*, the FT has been verified experimentally.

Fluctuation Theorem

Considerable progress was made in understanding the basis of the Fluctuation Theorem. A major review was published late in the year in Advances in Physics. During the year we proposed a version of the FT, that applies to thermostatted dissipative systems which respond to time dependent dissipative fields. In testing the time dependent Fluctuation Theorem we provided for the first time, convincing evidence that sets of trajectories with conjugate values for the time integrated entropy production, ($\pm A \pm dA$), are indeed, time reversed images of one another. "*The famous problem, the creation of anti-events from events has no solution. Although, using simple instructions, the [solution] may be put into words: reverse the instantaneous velocities of all of the atoms in the Universe*" - Loschmidt, 1876. For an ensemble of experiments we now know that we can observe conjugate pairs of time reversed responses without intervening and actually reversing particle velocities. All one has to do is to sort the ensemble of responses on the basis of their time integrated dissipation functions (entropy production in thermostatted systems), and to compare those responses with complementary values of total dissipation. These responses will be time reversed mappings of each other. The ratio of probabilities of observing these complementary time integrated values of dissipation are given by the Fluctuation Theorem, with Second Law satisfying responses being exponentially dominant.

Configurational Temperature

Work continued towards understanding how to measure and how to control the temperature of a system through purely configurational means - with no knowledge of, or changes to, molecular velocities. The emphasis in this work has moved to molecular rather than atomic systems. *(with J. Delhomelle [U. Henri Poincaré, France])*

Transient Time Correlation Function

Work was completed on a demonstration of the utility of the Transient Time Correlation Function formalism for calculating transport coefficients over an extremely wide range of external field strengths. *(with I. Borzsak, [Hungarian Academy Sc], P. Cummings, [Oak Ridge Nat. Lab. and Vanderbilt USA.])*

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¥109 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. The anomalous behaviour of "configurational" temperature helped us gain new insights into its physical meaning. *(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 comment on the similarities and differences between an ionic and a "coloured" liquid. In this case, the first non-equilibrium hard sphere simulation with curved trajectories was performed in order to verify the analytic predictions. *(with O.G. Jepps, [Griffith U.])*

Soft Condensed Matter

This project continues a collaboration between the RSC, The Australian Nuclear Science and Technology Organisation (ANSTO) and the National Institute of Standards and Technology (NIST), USA. The objective is to understand better the relationship between the properties of a system and its structure. Soft condensed

disordered systems are emphasised - for example: gels, precipitates in petroleum fluids, polymeric solutions and melts, micelles and macromolecules in solutions, and inorganic/organic complexes. The project has promoted and encouraged the use of the small angle neutron scattering instruments at the ANSTO facility and the NIST Center for Neutron Research, under an agreement between ANSTO and NIST. *(with H.J.M. Hanley)*

http://www.rsc.anu.edu.au/evans.html