Polymers and Soft Condensed Matter — Dr Edith Sevick

In the past decade, Atomic Force Microscopy (AFM) and Optical Tweezers (OT) have revolutionised molecular science by measuring picoNewton forces over lengthscales from 1 to 10^4 Å. In our laboratory, we have an Optical Tweezer Apparatus which has been extensively modified for our force measurement experiments in polymer and colloids science. The apparatus consists of an optical trap that weakly "holds" a micron-sized bead. The trap is formed by a focused laser beam that is refracted through the transparent bead. The refracted rays differ in intensity over the volume of the colloidal bead and exert a force on the bead, drawing it towards the region of highest light intensity. The optical trap is harmonic near the focal point: the optical force acting on a colloidal particle positioned at x from the trap centre is F_{opt}=-kx, where k is the trapping constant which can be tuned by adjusting the laser power. In this way, the optical trap generated by the OT serves to both localise a colloidal particle and to measure the small, sub-picoNewton scale forces acting on the particle. With substantial modifications, our OT apparatus probes forces at small lengthscales and over small timescales that are necessary in studies of nonequilibrium statistical mechanics and polymer/biopolymer science.

Probing Thermodynamics of Small Systems over Small Timescales Using Optical Tweezers

The puzzle of how time-irreversible microscopic equations of mechanics lead to the time-irreversible macroscopic equations of thermodynamics has been a paradox since the days of Boltzmann. Boltzmann simply side-stepped this enigma by stating "as soon as one looks at bodies of such small dimension that they contain only very few molecules, the validity of this theorem [the Second Law of Thermodynamics and its description of irreversibility] must cease." Today we can state that the Fluctuation Theorem (FT), first proposed by Denis Evans and colleagues in 1993, is a generalised, Second-Law-like theorem that bridges the microscopic and macroscopic domains and links the time-reversible and irreversible descriptions. The predictions of the FT should be relevant to many nanotechnological applications. Our FT-related work in 2004 had two major themes:

Experimental Demonstrations of the FT using a Colloidal Particle in a Viscoelastic Solvent

Recently the Evans and Sevick groups demonstrated experimentally the FT for the first time using a colloidal particle weakly held in a translating optical trap. This work received considerable attention in the popular press, science journals, and other media primarily because of its implications to nanotechnology. Miniature engines are not simple rescaled versions of their larger counterparts, and if the work performed during the duty cycle of any machine is comparable to thermal energy per degree of freedom, then, according to the FT, one can expect that the machine will operate "in reverse" over short time scales. However, to date the FT has been confirmed only with exceptionally simplified systems that are fully describable using deterministic or stochastic dynamics, such as a single optically-trapped colloidal particle in a Newtonian fluid, or a computational sea of Lennard-Jones particles. Our premise is that the FT holds for any general system, including more complex systems that currently defy exact description, such as biological or molecular motors. To test the application of the FT to more relevant nanosystems, we need to address systems of increasing complexity. Our approach is to increase complexity one-step-at-a-time and a strategic system to investigate is, therefore, a single colloidal bead, optically-trapped in a viscoelastic solution. While an optically-trapped particle in a Newtonian fluid is perfectly describable using Langevin dynamics, the dynamics of the same particle in a viscoelastic solution is far more difficult to describe. We have performed preliminary experiments that show that the particle's trajectories in viscoelastic solution should obey the FT. *(With M A B Baker, D M Carberry, J C Reid, G M Wang, D J Evans)*

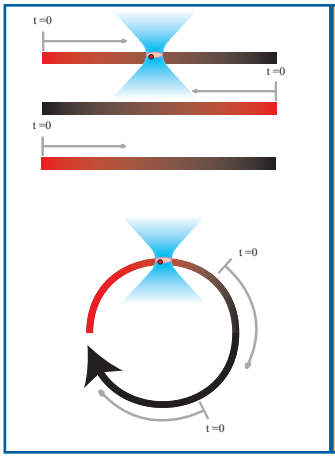

Figure: An illustration of linear (left) and circular (right) translation of an optical trap containing a colloidal particle. The trajectory of the optically-trapped colloidal particle is used to demonstrate the FT under transient and steady-state conditions. Several thousand linear translations are constructed providing transient trajectories (indicated by red portion of the translation) as well as short steady-state trajectories (indicated by black portion). In contrast, a single circular translation provides a single transient trajectory, but a very long steady-state trajectory that can be segmented into "independent" steady-state trajectories.

Application of the FT under Steady-state Conditions

While the FT has been experimentally demonstrated for systems that are perturbed from an initial equilibrium state, there are a number of studies suggesting that the theorem applies asymptotically in the long time limit to systems in a nonequilibrium steady-state. The asymptotic application of the FT to such nonequilibrium steady-states has been referred to in the literature as a separate theorem, the Steady-State Fluctuation Theorem or SSFT. In 2004, we investigated the SSFT and FT under nonequilibrium steady-states using a colloidal particle localised in a linearly-translating optical trap and in a circularly-translating trap. From these colloidal trajectories we demonstrated that the FT holds under nonequilibrium steady-states for all time, and not just in the long time limit, as in the SSFT. We demonstrated experimentally and theoretically that the SSFT holds asymptotically in the long time limit when the argument of the FT, the dissipation function, is derived approximately. However, when the dissipation function is derived exactly, the FT holds for all time, including short times. This suggests that the asymptotic limit in the SSFT is simply due to approximations in the argument of the theorem, and that when the argument of the theorem is derived exactly, the FT is operative over all time. *(With J C Reid, D M Carberry, G M Wang, D J Evans)*

Using Optical Tweezers to Characterise Viscoelasticity of Polymer Solutions

The optical tweezers can also be used as a micro-rheometer to experimentally determine the viscous and elastic response of polymer solutions. By recording the colloidal particle's position in a stationary optical trap over frequencies ranging from 10^{-1} to 10^{4} Hz, we are able to determine viscoelastic properties of the small fluid volume containing the colloidal particle. As the colloidal particle is micron-sized, the volume of fluid probed is very small, in the order of a pico-litre. This year our OT rheometer was used primarily in conjunction with FT experiments. *(With G M Wang)*

Optical Tweezers for Biopolymer Studies

By attaching specially-coated latex beads to the ends of modified DNA, we are able to use an optical trap and micropipette to stretch a single bead-DNA-bead assembly and to construct a force versus extension profiles of several DNA systems. These force profiles are used to study the effect of different salts and the interactions of specific binding proteins on DNA. In conjunction with the Protein Synthesis and Evolution Group headed by Nick Dixon, we focused upon different end-tethering techniques so that we can efficiently stretch double-stranded DNA where one strand is linked to the beads, and where both strands are linked to the beads. *(With G M Wang, D M Carberry, N E Dixon)*

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