



# POLYMERS AND SOFT CONDENSED MATTER

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In the last 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. Our research focuses upon experiments using the technique of OT, but we are also involved in theory and simulation that is complementary to these OT measurements. The OT apparatus is based upon a focused laser beam that is refracted through a micron-sized, 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  $F_{\text{opt}} = -kx$ , 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. These measurements are central to our overall aim to probe and develop new understandings of the energetics and dynamics of small systems, including polymers and colloids.

## Design and Construction of a New Holographic Optical Tweezers Apparatus

With funding from ARC-LIEF and ANU-MEC, we designed and constructed a flexible optical tweezers apparatus that provides a wider range of manipulations on small objects. Using a single light beam passing through a hologram (which is effectively a phase-only diffractive beam splitter), it is possible to construct an array of traps in 2 or 3 dimensions. Depending upon the hologram, traps can be generated with different trapping characteristics, e.g. a combination of forces and twist-like torques. If the hologram is replaced with a computer-addressed SLM or spatial light modulator, a component that dynamically controls the phase-shift and intensity at individual pixel elements, then we create an array of traps that can move or "dance" in 2 or 3 dimensions and dynamically alter the trapping characteristics of each trap. These advances can potentially make difficult OT force measurements far simpler; but more importantly, they also increase the vista of explorations available. This new apparatus will be used to study the stretching of synthetic and biological single polymer chains, to investigate colloidal interactions, to measure the micro-rheology of various solutions, and to demonstrate new theorems in nonequilibrium physics. *(With G M Wang, D M Carberry, D J Evans, and T J Senden, D R M Williams [RSPHYSSE, ANU], H R Brown, G M Spinks [U Wollongong])*

## Demonstrations of the Fluctuation Theorem using Complex Systems

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 sidestepped 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, and our experimental demonstration of the FT in 2002 received considerable attention in the popular press, science journals, and other media primarily because of its implications to nanotechnology. 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. Our experiments demonstrate that the particle's trajectories in viscoelastic solution obey the FT. *(With D M Carberry, G M Wang, D J Evans)*

### Experimental Demonstrations and Stochastic Description of the Work Relation using a Colloidal Particle in an Optical Trap

The Work Relation (WR) predicts that the free energy difference between two equilibrium systems can be determined by measuring the work done along dynamical paths that connect the two states. These paths may be traversed at arbitrary rates, so that the intervening path may not be in true thermodynamic equilibrium. This is a complete anathema to our understanding of conventional thermodynamics: conventional thermodynamics states that the free energy difference is the work done along a path that is traversed so slowly that the intermediate states are all in thermodynamic equilibrium, *i.e.*, a "quasi-static" pathway. The potential importance of the WR has both theoretical and practical aspects. One could theoretically calculate the free energy difference between states using fictitious paths that "morph" between two states on a computationally convenient (not necessarily realistic) energy surface. On the practical side, the WR suggests that measuring work on small microscopic processes could yield thermodynamic quantities that are traditionally inferred from bulk calorimetric measurements. This is particularly interesting, as measurements of the work done by small colloidal/polymeric/biological systems are possible with techniques such as OT, and the WR then translates these nonequilibrium measurements into thermodynamic information. We investigated both theoretically and experimentally, the work done along the trajectory of a single colloidal particle weakly held by an optical trap whose strength was changed. *(With G M Wang, D M Carberry, J C Reid, P Ranganathan, D J Evans)*

### Collapse Dynamics of Semi-flexible Polymer Chains using Brownian Simulations with Hydrodynamic Interactions

Many linear biopolymers such as actin and DNA have backbones that are much stiffer than, say, polystyrene. These stiff polymers cannot easily bend, much like a garden hose, and are called semi-flexible. When flexible polymers are placed in a poor solvent, where strong attractive monomer-monomer interactions dominate, surface tension drives the chain into a compact, globule shape. However, for semi-flexible chains, the backbone stiffness impedes this compaction and favours conformations with minimal bending along the contour, in particular, very few tight bends. Instead of a collapsed globule, a semi-flexible chain in poor solvent folds into a torus. This toroidal configuration is often seen in experiments. To biologists the toroidal conformation is useful, as it allows one to introduce foreign pieces of compact DNA into cell nuclei. The final folded state of the chain depends sensitively upon the dynamics of the system, including the solvent that mediates forces between distant segments of the chain. However, efficient algorithms that account for hydrodynamic interactions in long polymeric chains were only recently developed. We initiated a simulation study of the dynamics of the collapse of flexible and semi-flexible chains in poor solvent. We use Brownian dynamics simulations that incorporate hydrodynamic interactions to explore and to develop a better understanding of the dynamics of the coil-to-globule transitions of single polymer chains in poor solvents. Understanding the process of single chain collapse is important in predicting the behaviour of DNA and proteins, which form folded and highly compact structures. *(With P Ranganathan, and D R M Williams [RSPHysSE, ANU])*

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