CONFORMATION CHANGES IN THE MOLECULAR STRUCTURE OF MICRO- AND NANO-SCALE FILMS ON APPLICATION OF STRESS: A COMPUTATIONAL STUDY

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Keywords: Lubricants; Chain conformations; Molecular dynamics; Temperature.

INTRODUCTION
We use computational methods to describe some of the dynamic mechanisms occurring in the developing subject of nanotribology, in which the motions of solids on an atomic scale have been observed to lead to novel and interesting phenomena [1]. Lubricant films, represented by alkyl chains C$_n$H$_{2n+1}$, containing between 12 and 24 carbon atoms (n) are simulated on atomic-scale resolution so as to occupy the space between two solid surfaces. Combinations of normal and tangential pressures applied to the surfaces and the time-evolution of the chains are studied by a combination of atomistic simulation techniques including static lattice, molecular dynamics and Monte Carlo methods.

COMPUTATIONAL METHODS
The methods employed use atomistic potentials to describe the interactions between atoms, and involve coulombic, bond-stretching, bond-angle-deformation and torsional functions. The resulting energies are then either minimised with respect to the molecular configuration or used in equations of motion to describe the dynamics of the lubricant chains [2].

RESULTS
It is found that at low normal pressures (i.e. in which the main force is perpendicular to the solid surfaces) the lubricant chains show a preference for configurations in which they are oriented with their chain backbones parallel. As found in Langmuir films, their orientation to the solid surfaces becomes close to perpendicular with increasing ‘surface coverage’. In addition the chains show a preference for conformations which, even at room temperatures, are closely all-trans but higher surface coverages (lateral pressures) and higher temperatures lead to reduced order.

Relative displacements applied to the two solid surfaces lead to a series of ‘saw-tooth’ energy profiles in which the energy initially increases smoothly but at a critical point in the displacement the energy drops sharply. Monitoring the conformation changes in the chain shows that this stick-slip effect (experimentally observed on a micrometer scale, associated with local crystallisation and melting of the chains), does indeed correspond to alternate chain disordering and reordering.

A critical point is also observed on increasing the normal pressure. Whereas the internal energy of the system first increases continuously, at a pressure of several tens of GPs the energy decreases as the molecular motions abruptly cease. At still greater pressures the energy increase resumes, but the atoms are now locked into a highly ordered lattice structure.

By monitoring the frictional force as the rate at which the total momentum of the layers are exchanged, the manner in which friction depends on the temperature, pressure and the structure of the lubricant material (length, conformation and regularity of the molecular chain) are presented.

REFERENCES