

## Special Interest Group in Non-Equilibrium Molecular Dynamics

Please see the SIG website for further details and links: <https://fluids.ac.uk/sig/NonEqmMD>

Name	Title/Subject	Start	Chair
	Coffee and welcome	09:30	
<b>Ed Smith</b>	Introduction	10:00	
	Discussion	10:15	Ed Smith
<b>Ian Ford</b>	Entropy production for non-Markovian stochastic dynamics	10:30	James Ewen
<b>Dimitrios Mathas</b>	An evaluation of Equilibrium Green-Kubo and Nonequilibrium Molecular Dynamics for viscosity simulations of lubricants at different temperatures and pressures	11:00	
<b>Sritay Mistry</b>	Charge based rejection in Boron Nitride nanotubes	11:15	
	Coffe/discussion	11:30	Fernando Bresme & Karl Travis
<b>James Ewen</b>	NEMD in Tribology - Methods and Applications	12:15	Ed Smith
<b>Mike Allen</b>	Viscosities of Smectic-A Phases	12:30	
	LUNCH + coffee	13:00	
<b>Fernando Bresme</b>	Thermal transport across soft and hard interface	14:00	Ian Ford
<b>Josep Bonet Avalos</b>	Fluctuations in Generalised Dissipative Particle Dynamics	14:30	
<b>Lev Kantorovitch</b>	Non-equilibrium MD based on Generalised Langevin Equation	14:45	
<b>Karl Travis</b>	Non-equilibrium Molecular Dynamics: A powerful tool for gaining insight into fluid behavior	15:00	
	Coffe/discussion (FORM LINK)	15:30	Daniele Dini
<b>Hongtao Zhang</b>	Effects of suspending Al nanoparticles on nucleation, microexplosion and combustion of a kerosene droplet: measurement and molecular dynamics simulation	16:15	Lev Kantorovitch
<b>Carlos Ayestarán Latorre</b>	Surfactants Interactions with Engineering Surfaces: From Density Functional Theory to Molecular Dynamics	16:30	

**Entropy production for non-Markovian stochastic dynamics**

Ian Ford, University College London

Substantial progress towards a derivation of the second law of thermodynamics from the underlying laws of mechanics has recently been made through the development of stochastic thermodynamics. The price to pay is to swap Newton for Brown or Langevin, namely to consider the mechanics of a system in the presence of environmental noise. Entropy production can now be computed for a variety of nonequilibrium processes, but often the noise is idealised as white and the dynamics Markovian. However, it is possible to consider the stochastic thermodynamics of non-Markovian systems, those subjected to environmental forces with memory, and we consider a simple illustration. It seems that to a certain extent the dynamics merely introduce a lag time in the entropy production, which seems intuitively reasonable.

**An evaluation of Equilibrium Green-Kubo and Nonequilibrium Molecular Dynamics for viscosity simulations of lubricants at different temperatures and pressures**

Dimitrios Mathas, University of Southampton

This study aimed to develop robust models to simulate and calculate various rheological properties of molecular systems, such as shear viscosity and the viscosity-pressure relation, which are of industrial interest and direct use. In order to calculate these properties, Green-Kubo equilibrium molecular dynamics (EMD-GK) and Nonequilibrium molecular dynamics (NEMD) were applied to a system of hydrogenated 1-decene dimer molecules. Although previous studies include a variety of calculations for viscosity with EMD-GK combined with NEMD, in the literature there are less results on viscosity index and pressure-viscosity coefficient calculations, a fact that may indicate that these properties can be difficult to simulate. As a result, one of the aims is to determine how much information can be extracted from theoretical simulations and if it is possible to develop a descriptor/predictor model for lubricants and additives, which will be extended in the future to include the lubricant-metal interactions. Results showed that there was good agreement with theoretical and experimental data for the investigated molecule, as optimised calculations were able to predict viscosity at different temperatures and pressures. The choice of forcefield plays a very important role in this kind of simulations. Finally, NEMD simulations of hydrogenated 1-decene dimer (PAO-2) at high pressure successfully captured shear viscosity and shear thinning behaviour. Running longer simulations, with simulation replicates, reduced standard deviation of viscosity, which is more noticeable and important at lower pressures.

**Charge based rejection in Boron Nitride nanotubes**

Sritay Mistry, University of Edinburgh

**NEMD in Tribology - Methods and Applications**

James Ewen, Imperial College London

### **Viscosities of Smectic-A Phases**

Michael Allen, University of Bristol and University of Warwick

There is a long-standing controversy over the viscosities of Smectic-A liquid crystals. Are they well defined, or do they diverge in the limit of low frequency and wavenumber, as a result of layer undulations? This talk will present the preliminary results of equilibrium and nonequilibrium simulations, intended to resolve this question. If time permits, additional simulations revealing long-time tails in time correlation functions in nematic and smectic phases will be described.

### **Thermal transport across soft and hard interface**

Fernando Bresme, Imperial College London

Thermal gradients induce a range of non-equilibrium phenomena that are of interest in energy conversion applications, analytical devices or particle transport. In the colloidal domain, the interfacial properties become important, and they determine interfacial thermal resistance, which influences the characteristic time scale for heat transport across material-fluid interfaces. Non-equilibrium simulations provide an approach to quantify the thermal resistance and the response of molecular fluids and suspensions to strong thermal fields. When these are combined with intrinsic sampling methods, which eliminate the blurring effect of capillary wave fluctuations, it is possible to gain unique microscopic insight into the interfacial structure defining the thermal resistance of fluid interfaces.

### **Fluctuations in Generalised Dissipative Particle Dynamics**

Josep Bonet Avalos, Imperial College London and Universitat Rovira i Virgili

The increasing need for coarse grained models for the study of complex systems has led to the development of density as well as temperature-dependent interparticle potentials for Dissipative Particle Dynamics [1]. This type of potentials are particularly relevant in systems with important local temperature variations, accompanied by heat transport, within the energy-conserving version of the DPD, namely DPDE [2,3]. In this talk we discuss the problem of the fluctuations of mesoscopic systems, here represented by the DPDE particles, conceived as small subsystems of many physical molecules. The appropriate fluctuation-dissipation theorems, when the interaction potentials depend upon a fluctuating 'internal' particle temperature, require the detailed consideration of the thermal fluctuations in small systems, the effect of the dependent and independent variables, as well as the impact of the different ensembles in the calculation of the relevant averages.

Fluctuations in small systems have been experimentally observed to depend upon the variables held constant [4]. The same situation occurs in the analysis of the equilibrium dynamics of complex DPDE particles. [1] J. B. Avalos, M. Lísal, J. P. Larentzos, A. D. Mackie and J. K. Brennan, *Phys. Chem. Chem. Phys.*, 21 (2019), 24891-24911 [2] J. B. Avalos and A. D. Mackie, *Europhys. Lett.*, 40 (1997) 141–146. [3] M. Lísal, J. K. Brennan and J. B. Avalos, *J. Chem. Phys.*, 135 (2011), 204105. [4] C. Bustamante, J. Liphardt and F. Ritort, *Phys. Today*, 58 (2005), 43–48.

**Non-equilibrium MD based on Generalised Langevin Equation**

Lev Kantorovitch, King's College London

We have developed a technology that enables one to consider MD simulations of an open system connected to a solid-like heat bath (or baths), e.g. crystals. The theory is based on the Generalised Langevin Equation (GLE) method and is exact. An implementation of this technique in the LAMMPS code is based on a mapping of GLE into a finite set of white noise stochastic differential equations. The method allows arbitrary simulations of the open systems (e.g. liquid), e.g. friction, under general non-equilibrium conditions.

**Non-equilibrium Molecular Dynamics: A powerful tool for gaining insight into fluid behavior**

Karl Travis, The University of Sheffield

**Effects of suspending Al nanoparticles on nucleation, microexplosion and combustion of a kerosene droplet: measurement and molecular dynamics simulation**

Hongtao Zhang, Brunel University London

The combustion characteristics of a Chinese RP-3 kerosene droplet have been investigated and compared to a nanofuel droplet of the same kerosene suspended with Al nanoparticles under different ambient pressures (0.2 bar - 1 bar). More intense puffing was observed during the burning of the nanofuel droplet compared to the RP-3 droplet. A lower ambient pressure was found to enhance the intensity of puffing for both RP-3 and RP-3/nano-Al droplets, causing microexplosion during the burning of the nanofuel droplet at 0.2 bar. On the other hand, microexplosion did not occur for the kerosene droplet at 0.2 bar. In order to understand nanoparticle effects on nucleation that initiates puffing and microexplosion, nucleation characteristics in metastable n-decane with and without Al nanoparticles have been compared using molecular dynamics (MD) simulations. Firstly, vapor-liquid-equilibrium (VLE) MD results demonstrated that the TraPPE-UA force field is able to properly predict phase transition processes. Three evolution modes of the system pressure towards a stable, metastable, or unstable state were identified. At  $\rho = 0.456 \text{ g/ml}$  and  $T = 524 \text{ K}$  (85% of n-decane's critical temperature), the metastable system became unstable with the addition of nanoparticles. At  $\rho = 0.462 \text{ g/ml}$  and  $T = 524 \text{ K}$ , nanoparticles were found to increase the nucleation rate to almost twice that of homogeneous n-decane without nanoparticles. Due to a larger van der Waals force between Al atoms and n-decane molecules than between just n-decane molecules, a density gradient was observed near the nanoparticle surface. This results in an increase in the nucleation rate and easier formation of bubbles further away from the particle surface where the density is lower than that in the homogeneous nucleation case.

**Surfactants Interactions with Engineering Surfaces: From Density Functional Theory to Molecular Dynamics**

Carlos Ayestarán Latorre, Imperial College London

The relevant outcomes of our calculations include modelling previously conjectured chemical reactions for phosphate dissociation, accurate results to benchmark previously employed FFs against and models that open the doors to new kinds of simulations.