The Second Meeting of the Non-Equilibrium Molecular Dynamics (NEMD) Special Interest Group (SIG)

6th September 2021

Name	Title/Subject	Start (BST)	Chair
Coffee and welcome		08:00	
Ed Smith	**Introduction**	08:20	
Peter Daivis	Energy and temperature in NEMD simulations	08:30	James Ewen
Billy Todd	Pumping of nano-confined water with rotating electric fields	09:00	
Jun Zhang	Molecular Dynamics and Multiscale simulation of Droplet Wetting and Evaporation	09:30	
Discussion		10:00	
Karl Travis	New Dolls tensor-based algorithm for studying liquid fragmentation and the tensile test for solids.	10:30	
Patrick Ilg	Surface rheology of polymers at the liquid-vapour interface	10:45	
Suman Chakraborty	Evaporation of Saline Aqueous Nano-Droplets: The Coffee-Ring Effect and Beyond	11:00	
Paola Carbone	Thermodynamic properties of the graphene/electrolyte interface	11:30	
Lunch		12:00	
Philip Camp	Using non-equilibrium molecular-dynamics simulations to study problems in industry	13:00	Matthew Borg
Alessio Lavino	Surface topography effects on pool boiling via non-equilibrium molecular dynamics simulations	13:30	
Ozgur Yazaydin	Concentration Gradient Driven Molecular Dynamics to Model Gas and Liquid Phase Separations in Membranes	13:45	
Jesper Hansen	On nanoscale polarization	14:00	
Discussion		14:30	
Kaihang Shi	Can we define a unique microscopic pressure in inhomogeneous fluids?	15:00	Ed Smith
Jagjeevan Bhamra	Interfacial Bonding Controls Friction in Diamond-Rock Contacts	15:30	
Dimitrios Mathas	Evaluation of methods for viscosity simulations of lubricants at different temperatures and pressures: a case study on PAO-2	15:45	
James Sprittles	Noisy Interfacial Nanoflows	16:00	
Lorenzo Botto	Graphene nanohydrodynamics: non-equilibrium MD simulation of graphene nanoplatelets suspended in sheared liquids	16:30	
Sergey Karabasov	A thermostat-consistent fully coupled molecular dynamics – generalised fluctuating hydrodynamics model for non-equilibrium flows	17:00	
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Energy and temperature in NEMD simulations

Peter Daivis

Although non-equilibrium molecular dynamics (NEMD) simulations begin with an atomistic description of the system, a clear connection to the macroscopic description is vitally important for the interpretation of the results. Temperature, entropy and internal energy and their time derivatives are vital ingredients in the macroscopic description, but the relationship between these variables and the microscopic variables is not always clear. In this presentation, I will give a brief introduction to the role of energy, entropy and temperature in non-equilibrium molecular dynamics simulations and discuss some of the subtleties of the relationship between the microscopic and macroscopic descriptions of NEMD simulations.

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Pumping of nano-confined water with rotating electric fields

Billy Todd

Electropumping is the process by which an electric field is used to transport fluids, particularly in the context of nanofluidics. In the case of water confined to planar nanochannels and carbon nanotubes, the application of a rotating electric field that couples to the permanent dipole moment of water has been shown to be an effective means of inducing a net positive flow in fluids [1-4]. In this talk, we summarise the application of this technology to water confined to planar nanochannels and systems of carbon nanotubes. We furthermore investigate the efficiency of electropumping relative to Couette and Poiseuille flows. To accomplish this, we apply a spatially uniform rotating electric field to a fluid confined in a functionalized nanochannel that couples the water's permanent dipole moment resulting in a net positive flow. We then induce a net positive flow in nanochannels for traditional Couette and Poiseuille flows, matching volume flow rates to allow a direct comparison of average power dissipation per unit volume between all flow types. We show that while electropumping is less efficient than Couette flow, it is 4 orders of magnitude more efficient than Poiseuille flow [5]. This suggests that, rather than being a mere novelty, electropumping is a far more energetically efficient means of transporting pure water compared to conventional pressure driven pumping. [1] S. De Luca, B.D. Todd, J.S. Hansen and P.J. Daivis. The Journal of Chemical Physics 138, 154712 (2013). [2] S. De Luca, B.D. Todd, J.S. Hansen and P.J. Daivis. Langmuir 30, 3095-3109 (2014). [3] D. Ostler, S.K. Kannam, P.J. Daivis, F. Frascoli and B.D. Todd. The Journal of Physical Chemistry C, 121, 28158-28165 (2017). [4] D. Ostler, S.K. Kannam, F. Frascoli, P.J. Daivis and B.D. Todd. Langmuir 35, 14742 (2019). [5] D. Ostler, S.K. Kannam, F. Frascoli, P.J. Daivis and B.D. Todd. Nano Letters 20, 3396-3402 (2020).

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Molecular Dynamics and Multiscale simulation of Droplet Wetting and Evaporation

Jun Zhang

Droplets spreading and evaporation on a solid surface are relevant for a variety of engineering applications such as coating, spray cooling, and inkjet printing. Improvements in nanotechnology and nanofabrication over the past decade mean it is now possible to generate droplets down to nanoscales. In this talk I will report our recent works in droplet wetting and evaporation using molecular dynamics and multiscale simulations. For static wetting, we assessed the applicability of the modified Young's equation to nanodroplets. The effects of the Tolman length and the position of the solid-liquid dividing interface on the measured line tension were discussed. For dynamic wetting, we developed a multiscale simulation strategy by enhancing VOF simulations using self-consistent boundary conditions derived from MD. Specifically, the boundary conditions include a particular slip model based on the molecular kinetic theory for the three-phase contact line to account for the interfacial molecular physics, the classical Navier slip model for the remaining part of the liquid–solid interface, and a new source term supplemented to the momentum equation in VOF to replace the convectional dynamic contact angle model. The simulation results demonstrate that with these new boundary conditions, the enhanced VOF simulations can provide consistent predictions with full MD simulations for the dynamic wetting of nanodroplets on both smooth and pillared surfaces. For salt water droplet evaporation, we found that there are two typical forms of salt crystals - as a clump and ring-like - are deposited on the surfaces, depending on the solid-liquid interaction strength and the evaporation rate. We demonstrated that electrowetted nanodroplets can produce various deposit patterns, which vary substantially from the original deposit that occurs when there is no electric field. These findings have potential application to fabricating nanostructures and surface coatings with desired patterns.

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New Dolls tensor-based algorithm for studying liquid fragmentation and the tensile test for solids.

Karl Travis

The Dolls tensor algorithm proposed in 1980 by Hoover and co-workers [1] is an example of a synthetic field driven simulation method in which an external field is coupled to the equations of motion enabling the simulation of arbitrary flow fields. The method is highly versatile and can be used, for example, to drive isothermal-isobaric, isothermal-isoenthalpic dynamics at equilibrium, or to obtain shear and bulk viscosities from non-equilibrium simulations. In the latter case, the Dolls tensor equations of motion can be used to derive the Green-Kubo expressions for these transport coefficients using linear response theory.

In this presentation I will demonstrate how the Dolls tensor equations of motion can be used to simulate the fragmentation of liquids, improving on an algorithm first proposed by Holian and Grady [2] - which relied on expanding boundaries alone - and a new method for simulating the tensile testing of solids.

The latter application enables the estimation of the Young's modulus, ultimate tensile strength and yield strength from atomistic simulation, free from problems associated with the application of a mechanical load. It may also be used to study adiabatic and isothermal compression of fluids.

[1] W. G. Hoover, D. J. Evans, R. B. Hickman, A. C. Ladd, W. T. Ashurst and B. Moran, "Lennard-Jones triple-point bulk and shear viscosities. Green-Kubo theory, Hamiltonian mechanics, and nonequilibrium molecular dynamics", Phys. Rev. A, 22, 1690 (1980).

[2] B. L. Holian and D. E. Grady, 'Fragmentation by Molecular Dynamics: The Microscopic "Big Bang"', Phys. Rev. Lett., 60, 1355 (1988)

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Surface rheology of polymers at the liquid-vapour interface

Patrick Ilg

The structure and surface rheology of two model symmetric triblock copolymers with different degrees of hydrophobicity but identical polymerization degree, spread at an explicit liquid/vapor interface, are investigated employing extensive equilibrium molecular dynamics and innovative nonequilibrium molecular dynamics simulations with semipermeable barriers in both the linear and nonlinear viscoelastic regimes. Results are obtained for interface microstructural and surface rheological quantities under dilatation and surface shear. A structure-rheology relationship is obtained by means of the first harmonic analysis of the surface stress and the corresponding amplitude of the microstructure signal. In-plane oscillatory shear flow simulations are performed as well. The presented approach thus renders possible a test of theoretical frameworks, which link interfacial rheological data to the surface microstructure. It is furthermore shown to provide physical insights, which can be used for the interpretation of 25 existing experimental surface rheological data.

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Evaporation of Saline Aqueous Nano-Droplets: The Coffee-Ring Effect and Beyond

Suman Chakraborty

Water containing dissolved micro ions has huge implications in multifarious applications ranging from water desalination, ion pre-concentration to the manufacturing of novel optical and electronic equipment. A particle-laden water droplet is commonly observed to leave a ring-like deposit when it dries on a solid substrate, as hallmarked by the so-called “coffee-ring” effect. The contact line at the outer rim tends to get pinned to the surface due to its natural topographical features over interfacial scales, necessitating drawing of liquid from the droplet's interior to replenish what it loses due to evaporation. The particles in the droplet are thus dragged to the outer rim. When the droplet evaporates completely, these particles form a ring-like deposit. It has been observed from previous studies that the particle deposition pattern mentioned as above may be modulated by factors beyond evaporation and contact-line pinning. However, the role of an intricate interplay of electrostatics, interfacial tension and hydrodynamics over the three-phase contact line towards modulating the same remains unexplored. Here, the speaker aims to underpin how ion-water interaction over nanometer scales may offer exclusive alterations to the drying dynamics of a particle-laden droplet in sharp contrast to similar phenomenon observed over larger physical scales. Our molecular simulation results reveal how the coupled effect of salt concentration and surface charge manifests itself with a unique change in the pinning-depinning dynamics and layering of interfacial water molecules which eventually alters the evaporation rates of the droplet in an intriguing manner. These unveil that a plethora of deposition patterns, varying from uniform to ring formation, can be easily controlled by modulating the droplet salt concentration and surface charge. Such exclusive scale effects may be harnessed in various emerging applications of nano-bio sciences and nanofabrication technology.

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Thermodynamic properties of the graphene/electrolyte interface

Paola Carbone

The understanding of the physical chemistry of the graphene and electrolyte interface underpins the development of carbon-based devices for applications in water purification and sensors. Here I'll present how thermodynamics of such interface is affected by the layering of graphene flakes, the concentration and ion types and confinement.

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Using non-equilibrium molecular-dynamics simulations to study problems in industry

Philip Camp

Several examples of how non-equilibrium molecular-dynamics (NEMD) simulations are being used to tackle industrially relevant problems will be summarised. In all cases, complex fluids containing amphiphilic molecules or functionalised polymers are studied using all-atom or united-atom force fields, so that important chemical details are preserved. The specific applications include NEMD simulations of rheology (viscosity) and thermal conductivity in bulk solution, and tribology (friction) at solid-liquid interfaces, complemented by equilibrium simulations as appropriate. A recurring theme is the formation of self-assembled structures at equilibrium, and the response of these structures to external perturbations. It will be shown how subtle chemical details can significantly affect material properties, and how these are manifested in experiments and industrial applications.

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Surface topography effects on pool boiling via non-equilibrium molecular dynamics simulations

Alessio Lavino

Pool boiling is a complex and out of equilibrium process and key phenomena take place at different scales. Molecular interactions are particularly important as they strongly affect the resulting nano-bubble nucleation as a result of the combined effect of wettability, wall superheat and surface roughness. The interplay of these parameters is here investigated at the nanometre scale through non-equilibrium molecular dynamics simulations for a Lennard-Jones system. A rectangular cavity is considered as nucleation spot and its width-to-depth ratio is taken as a measure of the defect size effects. Heat is uniformly provided from the bottom through a tethered solid wall. Nucleation times are directly extracted from the MD data and fitted to a classical nucleation theory-based model, resulting in a good agreement. The systematic analysis of the effect of all the aforementioned parameters is summarized in a phase diagram and interesting insights into the boiling process are achieved by analysing the heat flux and temperature fields inside the nucleation spot. The conducted analysis shows a promising way to link the molecular scale to higher-scale models in a more general multiscale framework.

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Concentration Gradient Driven Molecular Dynamics to Model Gas and Liquid Phase Separations in Membranes

Ozgur Yazaydin

In this presentation, I will talk about the development of the concentration gradient driven molecular dynamics (CGD-MD) method and its application for gas and liquid phase separations in porous membranes (Chem Sci 8 (5), 3858-3865, 2017). CGD-MD is a non-equilibrium molecular dynamics simulation method which works by applying bidirectional bias forces to maintain the concentration of molecules in designated control volumes. By maintaining a higher concentration at the inlet of a membrane (feed), and lower concentration at the outlet of a membrane (permeate), aconcentration gradient is created which drives the diffusion of molecules through the membrane. Using the CGD-MD approach allows computing the steady-state flux of molecules and membrane selectivity directly. I will then talk about the application of the CGD-MD method to study multicomponent transport and separation of gases and liquids in porous membranes (DOI:10.26434/chemrxiv.14049719.v1; Chemistry of Materials, 2020, 32, 1288-1296.; Advanced Theory and Simulations, 2019, 1900120.)

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On nanoscale polarization

Jesper Hansen

In the first part of the talk I present molecular dynamics simulation results for the polarization of water at both equilibrium and non-equilibrium. First, it is observed that the dispersion relation for the polarization relaxation is linear with respect to wave-vector squared indicating an underlying diffusive process. Secondly, the dielectric respond to an external field is found to be reduced for small wave-lengths. In the second part of the talk I will derive the dynamical equation for the polarization, and it is shown that the observed reduced dielectric response is due to diffusion of polarization. The inclusion of the diffusion is therefore important when modeling the dielectric response on small length scales.

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Can we define a unique microscopic pressure in inhomogeneous fluids?

Kaihang Shi

The estimation of the microscopic pressure tensor in an adsorbed thin film on a planar surface remains a challenge in both experiment and theory. While the normal pressure is well-defined for a planar surface, the tangential pressure parallel to the surface at a point is not uniquely defined at the nanoscale. We will talk about the origin of this non-uniqueness from both hydrodynamics and thermodynamics perspective. We will show that by integrating the local tangential pressure over a small region of space, roughly the range of the intermolecular forces, it is possible to define a coarse-grained tangential pressure that is unique and free from ambiguities in the definition of the 'virial-route' local pressure tensor. This unequivocal definition of the microscopic pressure provides further insights into the pressure enhancement phenomenon inside the pore for strongly wetting systems and will help bridge the gap between experiment and theory in comparing microscopic properties.

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Interfacial Bonding Controls Friction in Diamond-Rock Contacts

Jagjeevan Bhamra

Harder rocks usually are usually more difficult to drill; however, poor performance is often observed for polycrystalline diamond compact (PDC) bits on soft calcite-containing rocks, such as limestone. Using macroscale tribometer experiments with a diamond tip, we show that soft limestone rock (mostly calcite) gives much higher friction coefficients compared to hard granite (mostly quartz) in both humid air and aqueous environments. To uncover the physicochemical mechanisms that lead to higher kinetic friction at the diamond-calcite interface, we employ nonequilibrium molecular dynamics simulations (NEMD) with newly developed Reactive Force Field (ReaxFF) parameters. In the NEMD simulations, higher friction is observed for calcite than quartz when water molecules are included at the diamond-rock interface. When the tips are immersed in water, the friction coefficients obtained from the nanoscale simulations and macroscale experiments are in good agreement for both the quartz- and calcite-containing rocks. The NEMD simulations show that the higher friction for calcite than for quartz is due to increased interfacial bonding. For calcite, the interfacial bonds mostly form through chemisorbed water molecules trapped between the tip and the substrate, while quartz forms mainly direct tip-surface bonds. For both rock types, the rate of interfacial bond formation increases exponentially with pressure, which is indicative of a stress-augmented thermally activated process. The mean friction force is shown to be linearly dependant on the mean number of interfacial bonds during steady-state sliding. The agreement between the friction coefficients obtained from the NEMD simulations and tribometer experiments suggests that interfacial bonding could also control diamond-rock friction at the macroscale.

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Evaluation of methods for viscosity simulations of lubricants at different temperatures and pressures: a case study on PAO-2

Dimitrios Mathas

The behavior of lubricants at operational conditions, such as at high pressures, is a topic of great industrial interest. In particular, viscosity and the viscosity-pressure relation are especially important for applications and their determination by computational simulations is very desirable. In this study we evaluate methods to compute these quantities based on fully atomistic molecular dynamics simulations which are computationally demanding but also have the potential to be most accurate. We used the 9,10-dimethyloctadecane molecule, main component of PAO-2 base oil as the lubricant for our tests. The methods used for the viscosity simulations are the Green-Kubo equilibrium molecular dynamics (EMD-GK) and non-equilibrium molecular dynamics (NEMD), at pressures of up to 1.0 GPa and various temperatures (40-150 degrees Celsius). We present the theory behind these methods and investigate how the simulation parameters affect the results obtained, to ensure viscosity convergence with respect to the simulation intervals and all other parameters. We show that by using each method in its regime of applicability, we can achieve good agreement between simulated and measured values. NEMD simulations at high pressures captured zero shear viscosity successfully, while at 40 degrees Celsius EMD-GK is only applicable to pressures up to 0.3 GPa, where the viscosity is lower. In NEMD, longer and multiply repeated simulations improve the confidence interval of viscosity, which is essential at lower pressures. Another aspect of these methods is the choice of the utilized force field for the atomic interactions. This was investigated by selecting two different commonly used force fields.

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Noisy Interfacial Nanoflows

James Sprittles

At the nanoscale, the classical Navier-Stokes paradigm no longer provides an accurate description of the flow physics; however, microscopic models such as molecular dynamics (MD) are often computationally intractable for flows of practical interest. In this talk I will consider the influence of thermal fluctuations, which we will see are key to understanding counter-intuitive phenomena in nanoscale interfacial flows.   A `top down’ framework that incorporates thermal noise is provided by fluctuating hydrodynamics and we shall use this model to gain insight into interfacial nanoflows such as drop coalescence, jet breakup and thin film rupture, using MD as a benchmark.

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Graphene nanohydrodynamics: non-equilibrium MD simulation of graphene nanoplatelets suspended in sheared liquids

Lorenzo Botto

We use a combination of analytical theory, boundary integral equations, and non-equilibrium molecular dynamics simulations to examine the rotational dynamics of graphene nanoplatelets freely suspended in sheared liquids. Examining simulations of graphene in simple shear flow of water by MD, we found a very puzzling effect: the platelet does not rotate with the fluid vorticity vector, rather it attains a stable orientation. This observation goes against all observation made so far with plate-like colloids and the century-old analytical theory of Jeffery. The behaviour seem not to be specific to water as solvent, rather to the extremely small thickness of the particle. The talk will summarise the work we have done in the past 3-4 years to understand this important phenomenon, which could have ramification in graphene processing, rheology and tribology of graphene-based lubricants.

References:

C. Kamal, S. Gravelle, L. Botto "Effect of hydrodynamic slip on the rotational dynamics of a thin Brownian platelet in a shear flow" J. Fluid. Mech., 919, 2021

S. Gravelle, C. Kamal, L. Botto "Violations of Jeffery's theory in the dynamics of nanographene in shear flow" Physical Review Fluids, 6.3 , 2021

C. Kamal, S. Gravelle, L. Botto. "Hydrodynamic slip can align thin nanoplatelets in shear flow." Nature communications 11.1, 1-10, 2020

S. Gravelle, C. Kamal, L. Botto "Liquid exfoliation of multilayer graphene: a molecular dynamics investigation", The Journal of Chemical Physics, 152, 104701, 2020

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A thermostat-consistent fully coupled molecular dynamics – generalised fluctuating hydrodynamics model for non-equilibrium flows

Sergey Karabasov

The thermostat-consistent fully coupled molecular dynamics – generalised fluctuating hydrodynamics method is developed for non-equilibrium water flow simulations. The model allows for strong coupling between the atomistic and the continuum hydrodynamics representations of water and shows an improved stability in comparison with the previous formulations of similar multiscale methods. Numerical results are demonstrated for a periodic nano-scale Poiseuille flow problem with SPC/E water. The computed time-averaged velocity profiles are compared with the analytical solution, and the thermal velocity fluctuations are well reproduced in comparison with the Equilibrium Molecular Dynamics (EMD) simulation. Several options to account for the long-range electrostatics interactions available in GROMACS are incorporated in the model and compared. It is demonstrated that the suggested non-equilibrium multiscale model is a factor of 4 to 18 faster in comparison with the standard all-atom equilibrium molecular dynamics model for the same computational domain size.

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