Joint CCP5-RSC Workshop:

Advances in Theory and Simulation of non-Equilibrium Systems

Imperial College London

26th June – 27th June, 2013

Imperial College London

RSC | Advancing the Chemical Sciences

Statistical Mechanics & Thermodynamics Group

CCP5

NATIONAL NUCLEAR LABORATORY

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Dear Delegate,

Non-equilibrium phenomena are ubiquitous in both the natural world and within the domain of applied science and engineering. Advances in understanding the non-equilibrium response of materials to changes in the mechanical and thermodynamic fields, including thermal, electric, magnetic and pressure gradients, is of significant pedagogical and practical importance, but also very challenging. Materials design and processing, energy recovery and energy conversion are just a few examples of obvious industrial relevance.

Significant developments in statistical mechanics, most notably the Mayers' contribution to the virial equation of state and Green and Kubo's (linear response theory), coupled with the rapid development of simple, deterministic algorithms for simulating non-equilibrium systems, has opened the door to a tractable non-equilibrium thermodynamic theory applicable beyond the linear regime.

Simulation is at its most useful and powerful when providing pseudo-experimental data to test these new theories. Atomistic simulation, for example is more usefully employed in suggesting new constitutive equations; recent work has suggested ways in which to handle the treatment of shockwaves and viscous flow in ultra thin films by going beyond Newton's law of viscosity and Fourier's law of heat conduction.

New fluctuation theorems and formulae have been expounded and tested using fairly simple computer simulation algorithms. Many systems of interest involve a multitude of length and timescales and there is therefore a need for new algorithms capable of bridging these.

We would like to thank CCP5, the Statistical Mechanics and Thermodynamic Group of the RSC and the National Nuclear Laboratory for sponsoring the Workshop.

We hope everyone enjoys what promises to be a fantastic meeting and that you leave buzzing with fresh ideas and that new collaborations are born.

Karl Travis and Fernando Bresme

June 2013

Conference Information

Registration

Registration will take place in Department of Chemistry, Lecture Theatre D, Imperial College London, South Kensington Campus, from 08.30-09.15 on Wednesday 26th June.

Lunch and Coffee Breaks

They will take place in the Chemistry Senior Common Room.

Web Access

The web can be accessed through the eduroam network.

Evening reception on Thursday

This event is a social mixer. A selection of canapés, wine and soft drinks will be served. It will take place at 58 Prince's Gate

(http://www3.imperial.ac.uk/conferenceandevents/venues/southkensingtonvenues/58pg)**.**

Please ensure you have your name badge with you.

Joint CCP5-RSC Workshop on Advances in Theory and Simulation of non-Equilibrium Systems

June 26th-27th 2013

Department of Chemistry, Lecture Theatre D, Imperial College London, South Kensington Campus

WEDNESDAY 26TH JUNE	
08:30-09:15	**Registration,** *Lecture Theatre D*
09:15-09:20	**Welcome**: Karl Travis & Fernando Bresme, Lecture Theatre D.
Morning Session 1, Lecture theatre D **Chair: Denis Evans**	
09:20-10:00	**P.T. Cummings:** *Non-equilibrium molecular dynamics of nanoconfined fluids and nanostructured materials*
10:00-10:20	**J. Muscatello:** *Non-equilibrium molecular dynamics study of transport diffusivity in nanoporous graphene*
10:20-10:40	**E. Smith:** *The control volume formulation applied to molecular dynamics*
10:40-11:10	**COFFEE BREAK, Chemistry Senior Common Room**
Morning Session 2 , Lecture theatre D **Chair: Miguel Rubi**	
11:10-11:50	**B. Rousseau:** *Thermal Diffusion of simple liquid mixtures: what have we learnt from molecular dynamics simulations?*
11:50-12:10	**A. Masters:** *Orientation of particles under thermal gradient – a kinetic theory study*
12:10-12-30	**C. Braga:** *Non equilibrium molecular dynamics simulations of solute transport in biphasic mixtures*
12:30-13:30	**LUNCH BREAK, Chemistry Senior Common Room**
Afternoon session 1, Lecture Theatre D **Chair: Peter Daivis**	
13:30-14:10	**B. Todd:** *The determination of slip for highly confined fluids: methods and applications*
14:10-14:50	**C. McCabe:** *Novel Lubrication Schemes for Silicon-Based Microelectromechanical Devices*

14:50-15:10	**J. Miller:** *Viscosity Calculation Methods For Borosilicate Glasses*
15:10-15:40	**COFFEE BREAK, Chemistry Senior Common Room**
	Afternoon session 2, Lecture Theatre D **Chair: Dick Bedeaux**
15:40-16:20	**D. Heyes:** *Non Equilibrium molecular dynamics (NEMD) Simulation of Confined Liquids under shear and normal load: Traction and Non-equilibrium phase behaviour*
16:20-16:40	**C. Gattinoni:** *Non-Equilibrium molecular dynamics simulations of confined liquids under shear and high pressure*
16:40-17:00	**H. Frentrup:** *Transport diffusion of confined fluids from equilibrium and boundary driven non-equilibrium molecular dynamics*
17:00-17:20	**D. Ross:** *Multi-Scale Simulation of the Transport of hydrocarbons in Porous Engine Deposits*
18:00-19:30	**EVENING RECEPTION AT 58 PRINCE'S GATE** **Sponsored by NNL**

	THURSDAY 27TH JUNE

	THURSDAY 27TH JUNE
	Morning Session 1 , Lecture theatre D **Chair: Peter Cummings**
09:00-09:40	**D. Evans:** *Dissipation and the foundations of statistical Thermodynamics*
09:40-10:20	**P. Daivis:** *Confined flows of binary solutions*
10:20-10:40	**I .Ford:** *Stochastic entropy production in thermal conduction*
10:40-11:10	**COFFEE BREAK, Chemistry Senior Common Room**
	Morning Session 2 , Lecture theatre D **Chair: David Heyes**
11:10-11:50	**D. Bedeaux:** *Exploring the property of local equilibrium for the Gibbs surface in two-phase multi-component mixtures*
11:50-12:10	**J. Armstrong:** *On the reversal of the thermo-polarisation of water*
12:10-12-30	**L. Stella:** *The Generalised Langevin Equation: an efficient approach to non-equilibrium molecular dynamics of open systems*
12:30-13:30	**LUNCH BREAK, Chemistry Senior Common Room**

	Afternoon session 1, Lecture Theatre D **Chair: Billy Todd**
13:30-14:10	**T. Spencer:** *Application of lattice Boltzmann method to modeling multicomponent flows and devices*
14:10-14:50	**M. Rubi:** *Carbon nanotube-based motor driven by a thermal gradient*
14:50-15:10	**H. Ness:** *Non-equilibrium steady state properties of single-molecule nanodevices*
15:10-15:30	**A. Lervik:** *Non equilibrium thermodynamics approach to quantify the thermodynamic efficiency of molecular machines*
15:30-16:00	**COFFEE BREAK, Chemistry Senior Common Room**
	Afternoon session 2, Lecture Theatre D **Chair: Claire McCabe**
16:00-16:40	**I. Nezbeda:** *Simulation of aqueous solutions in an external field: Molecular picture of NanoSpider technology*
16:40-17:00	**H. Okumura:** *Non-equilibrium molecular dynamics simulations of a bubble in a simple liquid and biomolecular system*
17:00-17:20	**H. Hijar:** *Tracking control of colloidal particles under stationary non-homogeneous flow conditions*
17:20-17:40	**W. Plazinski:** *Carbohydrate ring puckering: transition path sampling analysis*
17:40-17:50	**CLOSING:** Fernando Bresme & Karl Travis

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Presentation Abstracts

In Order of Schedule

Non-Equilibrium and Equilibrium Molecular Dynamics of Nanoconfined Fluids and Nanostructured Materials

Peter T. Cummings [1]

[1] CDepartment of Chemical and Biomolecular Engineering, Vanderbilt University, USA, and Center for Nanophase Materials Sciences, Oak Rifge National Laboratory, USA

Abstract

In this talk, we describe our research using non-equilibrium molecular dynamics (NEMD) to understand and resolve conflicting experimental studies on the viscosity of nanoconfined fluids, which led to using simulation to understand phase transitions in nanoconfined fluids.

Non-equilibrium molecular dynamics study of transport diffusivity in nanoporous graphene

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Abstract

With the advent of large-scale fabrication of nanostructured carbon such as graphene and carbon nanotubes has come increased interest in the potential of these structures for use as membrane materials. Recent reports suggest that such structures are selective to the permeation of water molecules in particular [1,2]. It has been proposed that this property may endow nanoporous graphene and graphene sheets as candidates for desalination membranes. The process of diffusion through such membranes is expected to be mediated by adsorption mechanisms and confinement effects at the nanoscale. Computer simulation is an ideal tool for detailed study of the microscopic mechanism of diffusion in such systems. In this work we use steady-state Non-Equilibrium Molecular Dynamics simulations to study the diffusion of water through nanoporous graphene and layered functionalised graphene sheets. This method allows us to systematically investigate the selectivity of these materials and effectively evaluate their potential as reverse osmosis membranes.

References

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The Control Volume Formulation applied to Molecular Dynamics

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Abstract

The control volume is an invaluable tool for the study of fluid mechanics – a highly non-equilibrium subject. When expressed in this form, the flow equations are exactly conservative for mass and energy, and ensure the balance of momentum between adjacent Eulerian regions of space. However, there are many cases of fluid mechanical interest where the continuum assumption fails and a molecular-scale description is required [1]. The aim of this work [2] is to apply the Control Volume formulation to these discrete molecular scales.

The current derivation has its starting point in the work of Irving and Kirkwood [3]. We present a rigorous mathematical formulation that transcribes the equations of motion for a discrete system in a conservative, Eulerian form. The final equations are the time evolution for mass, momentum and energy in a control volume (figure 1a), expressed entirely in terms of the surface fluxes (figure 1b) and forces (figure 1c). Within this formalism, we also derive the discrete equivalents of Reynolds' Transport [4] and Gauss' (divergence) theorems.

(a) Schematic of the molecules within an Eulerian control volume (b) Schematic of the molecular flux over two surfaces of an Eularian control volume (c) Schematic of molecular forces acting inside and through the Eularian control volume
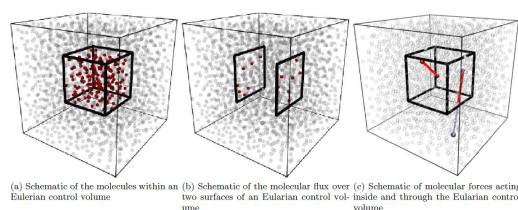
Figure 1: The CV function and its derivative applied to a system of molecules. The figures were generated using the VMD visualisation package [5].

An important issue that is resolved with the current approach relates to the appropriate expression of the pressure tensor - a matter that has received significant attention and been the source of lively debate in the literature. Following on naturally from our previous work [6], which links the Volume Average (VA) [7] and Method of Planes (MOP) [8] stresses, the current work provides a rigorous link between the two expressions and the formal definition of Cauchy stress. The final form of the evolution equations exactly relates these stresses to the time evolution of momentum.

In this presentation we give an overview of the mathematical treatment, outline the key steps in deriving the Eulerian equivalent of the equations of motions for a discrete system, and show the various forms of stress and the link between them. The final evolution equations are exactly conservative, a property we demonstrate numerically using Molecular Dynamics simulation. The formulation has a wide range of applications which we discuss with examples from equilibrium and non-equilibrium molecular dynamics simulations along with hybrid continuum to molecular dynamic coupling schemes.

References

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Thermal diffusion in simple liquid mixtures: what have we learnt from molecular dynamics simulations?

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Abstract

When a fluid mixture is subjected to a thermal gradient, it responds with concentration gradients: some species enrich at the cold side of the cell, while some others enrich at the hot side [1,2]. In binary liquid mixtures of chemically homologous molecules, heavier molecules usually go to the cold side. However, this simple rule is very fragile: a given species will flow in a certain direction according to its peculiar properties but also to temperature, pressure and most importantly, to the mixture composition! A typical example concerns water-ethanol fluid mixtures where water goes to the cold side at low concentration and to the hot side at high concentration. Recent experimental works have shown that thermal diffusion process is in many cases sensitive to molecular interactions *between different species* [3,4]. This was suspected from original works on transport properties and this partly explains why thermal diffusion phenomenon is so difficult to predict.

In this talk, we review what molecular dynamics has brought to the understanding of the thermal diffusion effect in simple fluid mixtures. We describe the various methods that have been developed by the community during the last decades to study this non-equilibrium phenomenon [5,6,7,8]. We present how these methods have been used to quantitatively predict transport coefficients. Finally, in the light of important advances in experimental setup that have brought accurate and reliable data in this area, we assess how molecular simulations contribute to the understanding of molecular mechanisms of the thermal diffusion effect and the elaboration of accurate macroscopic models.

References

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Orientation of particles under a thermal gradient – a kinetic theory study

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Abstract

In a recent series of papers [1-4], Bresme et al. reported the discovery that particles can orient in response to a temperature gradient. The flux-force relationships describing this phenomenon were then derived using the techniques of irreversible thermodynamics. For hetero-nuclear diatomics, this orientational effect was correlated to the Soret coefficients for the two types of atoms in the dimer. To date, though, there is no fully microscopic explanation of this orientational effect and this is the issue we wish to address here.

In order to make initial progress, we have solved the linearised Boltzmann equation for a dilute mixture of asymmetric hard rods and spheres. We have also looked at the torque on a single, fixed rod in a fluid of hard spheres subjected to a temperature gradient – an angular version of the well-known thermophoretic effect. Both studies require the calculation of collision integrals for non-spherical, hard particles [5], but these can be carried out analytically for the models considered. The calculations show that the rods orient in the presence of a temperature gradient and we obtain explicit expressions for how the orientation depends on the rod mass distribution. Furthermore we obtain expressions for the Soret coefficients for this system and thus we may formally link the microscopic roots of these two, related effects.

In addition, we have derived Green-Kubo relations for the transport coefficient describing the orientational order. This allows one to pursue mode-coupling approaches for calculating the coefficients at high density for interaction potentials that are not hard-body and we report some early results that have been forthcoming.

References

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Non Equilibrium Molecular Dynamics Simulations of Solute Transport in Biphasic Mixtures

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26th June 2013

Abstract

Knowledge of the partition coefficient of a solute, which describes its distribution between two immiscible phases, typically water and octanol, is a key component in the thermodynamic description of biochemical, pharmaceutical and environmental processes [1]. Although the practice in industry is to employ empirical correlations, it is self-evident that a description of the system from a molecular standpoint is essential. Some examples are available in the literature [2, 3]. In particular, several studies have been performed to predict the solute properties in an immiscible biphasic system where one of the phases is polar while the other is not [3-5]. The rationale behind this is that it is often assumed that the partitioning of a solute between a polar aqueous environment and a nonpolar organic environment is the rate limiting step in many chemical and biochemical processes [3].

The evaluation of partition coefficients and corresponding free energies of transfer has been performed previously using perturbation theory [2], configurational-bias Monte Carlo simulations in the Gibbs ensemble [3], umbrella sampling [4] and thermodynamic integration [6]. Although free energy differences are an indication of the tendency of a solute to migrate from one phase to another, they provide no information on the underlying thermodynamics of the process and on the interfacial properties of the solute. We address these factors by a

non equilibrium analysis of both the free energy profile and diffusion properties along the direction normal to the interfacial surface [7-10]. Within it a particular molecule in the bulk fluid is "pulled" through a two phase equilibrium system by means of an external force. The analysis of its trajectory at steady state and the extrapolation to the limit of zero force give us an indication of the effective permeability of the molecule and the corresponding partition coefficient. The methodology is described with a simple test benchmark case.

References

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The determination of slip for highly confined fluids: methods and applications

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Abstract

Slip is a very important phenomenon for fluids confined to nano- and micro-scale dimensions. Large degrees of slip are responsible for very large flow enhancements of fluids such as water confined to carbon nanotubes, as reported in experimental and simulation literature. However, the extent of this flow enhancement is hotly debated, with experimental and simulation studies conflicting by as much as several orders of magnitude. In order to help provide solutions to such discrepancies, and hence clarity in this important application of fluid transport at the nano-scale, we present a derivation to predict the slip velocity for a system of fluid molecules confined by atomistic walls. Even though flow is an inherently non-equilibrium phenomenon, our derivation is based in equilibrium statistical mechanics, and is seen to remain valid for experimentally accessible flow rates. Our formalism involves computing time correlation functions of relevant measurable fluid properties. These correlation functions are formed for fine-grained slabs of fluid immediately adjacent to the walls. By computing the various correlation functions at equilibrium we are able to extract the slab friction coefficient adjacent to the wall for a limiting slab width, and hence the slip velocity for a highly confined fluid, to extremely high accuracy. We present numerical results from non-equilibrium molecular dynamics (NEMD) simulations of water and methane confined to graphene sheets to verify our theoretical predictions and discuss the advantages and limitations of the current model. We then apply our method to cylindrically confined systems, such as carbon nanotubes (CNTs), and predict flow rate enhancements for water and methane flowing in CNTs of various diameters. Our results are compared with other simulation and experimental data and provide some of the most accurate results available. We furthermore show the limitations of NEMD simulations for high-slip systems and demonstrate that for such systems our equilibrium method is more accurate and computationally far less expensive. Finally, we demonstrate a novel application of the insight gained from manipulating slip boundary conditions for highly confined fluid systems, in which we apply a rotating electric field to generate non-mechanical unidirectional pumping of a polar fluid such as water, providing a novel means of fluid actuation for miniaturised nanofluidic devices.

Novel Lubrication Schemes for Silicon-Based Microelectromechanical Devices

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Abstract

The adhesion and friction properties of the native amorphous silicon oxide layer in silicon-based micro- and nano-electromechanical devices (MEMS/NEMS) has a strong influence on device control, performance, and durability. To improve the friction and adhesion properties surfaces coated with alkylsilanes have been proposed and shown to reduce the friction forces as the chain length of the alkylsilanes increases. In an effort to develop surfaces with enhanced durability and optimal frictional forces we have performed extensive molecular dynamics simulations and experimental studies on a variety of alkylsilane systems. In particular, we have explored both pure and mixed monolayers composed of hydrocarbon and fluorocarbon chains, finding that mixed fluorocarbon/hydrocarbon monolayers out-perform both pure fluorocarbon and pure hydrocarbon monolayers. Furthermore, the simulations suggest that when chains of differing length are used a liquid-like layer is formed by the longer chains that protrude above the shorter chains and aids in friction reduction. Surface coverage is also found to have a significant effect on the performance of all systems tested, with higher surface coverage resulting in lower coefficients of friction. Alkylsilanes with hydroxyl terminal groups have also been studied and, as expected, exhibit higher frictional forces than the corresponding akylsilane surfaces, while surfaces coated with mixtures of alkylsilanes and hydroxyalkylsilanes show behavior dependent on the composition of the surfaces.

Viscosity Calculation Methods For Borosilicate Glasses

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Abstract

The United Kingdom nuclear industry produces over 60,000m^3 of high level radioactive waste a year. Safe treatment of this material requires a clear understanding of its properties, with viscosity being an important process parameter for nuclear waste vitrification in a stable glassy matrix. It is difficult to collect viscometry data for the full range of compositions and temperatures for radiounclei-loaded glass, so mathematical modelling is used to help augment and extrapolate experimental studies.

In this presentation we consider the techniques of both equilibrium and non-equilibrium molecular dynamics methods which can be used to calculate viscosities. Green-Kubo, SLLOD, and sinusoidal transverse force techniques are all demonstrated for a model WCA system. Then we consider the application to alkali borate and alkali borosilicate glasses. As non-equilibrium materials with strongly nonlinear property trends, such glasses present a number of basic difficulties for molecular dynamics simulation. We review the various theoretical and semi-empirical treatments of glass viscosity, and test the available forcefields for reproducing glassy networks. Finally, we present preliminary results on calculated viscosities for basic nuclear waste glass frits.

Non-equilibrium Molecular Dynamics (NEMD) Simulation of Confined Liquids under Shear and Normal Load: Traction and Non-equilibrium phase behaviour

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Abstract

The technique of Non-Equilibrium Molecular Dynamics (NEMD) is ideally suited to explore the fundamental origins of the flow behavior of liquids very close to a wall. Control and investigation of the effects of the key variable parameters can be made more systematic than typically is the case in experiments. Boundary conditions emerge naturally rather than being decided upon in advance as is often the case in other branches of theory. NEMD can be used to establish an improved understanding of the flow pattern and physical behavior of the liquid next to a wall, and thereby to help develop better-founded theories of the phenomena. In fact, this is an old application of Molecular Dynamics, dating back to the 1970s and pioneered by Ashurst and Hoover [1]. In more recent years, the Department of Mechanical Engineering, Imperial College has developed a growing capability in this area.

This talk will present the results of NEMD simulations of boundary-driven flow, with an emphasis on computing traction coefficients, stress profiles [2] and the non-equilibrium phase behaviour in the presence of shear flow. The technical aspects of our work will be discussed, such as how the walls are constructed and how they interact with the liquid molecules. Also the procedures by which both temperature and pressure controls are prescribed will be covered. A non-equilibrium phase diagram for a confined sheared liquid under pressure is proposed [3].

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Non-equilibrium Molecular Dynamics simulations of confined liquids under shear and high pressure

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Abstract

The understanding of the physical and mechanical properties of lubricants is a central problem in engineering, since most mechanical components rely on lubricants to reduce wear and improve energy efficiency. In recent years, the focus on reducing energy consumption has increased the pressure to produce new, better performing lubricants and to understand the physical and mechanical properties of existing ones. Non-equilibrium molecular dynamics (NEMD) simulations are a powerful tool in this investigation, as they provide the possibility of describing in detail microscopic molecular motion and self-assembly at length scales unattainable from experiments.

This work presents a systematic approach to the study of confined Lennard-Jones (LJ) liquids of variable wetability, for a wide range of velocities and pressures which builds on and is complementary to the work presented in Ref. [1].

A systematic study of simple systems in non-equilibrium conditions is fundamental as a precursor for more complex studies as it gives the possibility to optimise variables and parameters which might be neglected otherwise, as well as providing a benchmark for phenomena and molecular behaviour which can then be further explored in more complex systems.

The systems, studied using the LAMMPS package [2], show a variety of phase transitions under shear confinement and their sensitivity to the choices of externally-applied conditions is highlighted. The traction curves produced in this study revealed the non-Newtonian behaviour of these liquids at high temperature and pressures, and the causes have been investigated.

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Transport diffusion of confined fluids from equilibrium and boundary-driven non-equilibrium Molecular Dynamics

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Abstract

Transport properties of confined fluids are pivotal for engineering applications of catalytic or selective purposes, e.g. fluid flow through polymeric membrane materials, transport of gases and crudes through oil reservoirs, transport of pharmaceuticals through biological membranes. Under these conditions, fluids exhibit a highly complex behaviour. Tractable theories for the prediction of mass transport properties in microporous media are an active field of research, which is plagued by a number of controversies [1]. The distinction between diffusive and convective mass transport as well as a competition between the phenomenological description and a fully molecular understanding of mass transport [2] give rise to several unanswered questions with respect to fluid transport in porous media. Transport processes in porous materials are influenced by structural and thermodynamic effects and the effects are often superimposed which makes a clear distinction very difficult [3, 4].

It is common to characterise transport properties of confined fluids via the self-diffusion coefficient based on the Einstein diffusion model. The validity of this approach is very limited and it fails to capture important factors [5]. We showcase these limits for a popular reference case, a Lennard-Jones fluid confined in structured slit pores. The influence of the repulsive and attractive fluid-pore interactions, pore loading as well as steric confinement effects on transport is presented. Self-diffusion and collective diffusion coefficients from Equilibrium Molecular Dynamics (EMD), based on the Green-Kubo relations [6], and the thermodynamically related Fickian diffusivities, were calculated. A recently proposed boundary-driven Non-Equilibrium Molecular Dynamics (NEMD) algorithm was employed to calculate corresponding effective diffusion coefficients [7]. In an attempt to paint a holistic picture of single-component diffusion under confinement, we draw a direct comparison between transport diffusion coefficients calculated from EMD and effective diffusivities from NEMD for a range of pore loading and sizes, as well as varying fluid-pore interactions. These results are put in contrast to theoretical models of mass transport in porous materials such as the Knudsen diffusion approach [1] and predictions from hydrodynamics on the molecular level [8], where limitations of these theories become apparent.

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Multi-scale Simulation of the Transport of Hydrocarbons in Porous Engine Deposits

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Abstract

Engine deposits are complex carbonaceous material accumulating on the inner surfaces of car engines that can act as a "sponge" and adsorb fuel components [1]. The presence of these deposits lead to adverse engine performance such as power loss, slow acceleration, poor drivability, a poor cold start and increased emissions. The mechanisms of which strongly depend on the porous nature of the deposits and may or may not depend on the surface roughness of pores. A previous study found that the equilibrium adsorption capacity is certainly sufficient to perturb the combustion process [1], however a method is needed for finding credible adsorption within a realistic time frame, i.e. that of an engine cycle (circa 1 ms).

We use non-equilibrium molecular dynamics simulations as a first step for modeling adsorption in intake valve deposits in order to understand the transport of adsorbed species in the heterogeneous porous structure. As a starting point, we confirm the results of Stukan et. al. for the spontaneous imbibition in nanopores of different roughness and wettability [2]. We observe that the rate of imbibition increases with decreasing roughness and increasing wettability. Simulations are performed using a coarse grained Martini forcefield implemented in GROMACS [3]. Initially pores are modeled as perfectly smooth cylinders with equal atomic spacing between carbon atoms laying along the circumference. The meniscus location is calculated as a function of time as well as the evolution of the contact angle. Later a more random arrangement is used with a decreasing atom density moving radially towards the centre of the pores, thereby giving a rough internal surface to the pore.

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Dissipation and the Foundations of Statistical Thermodynamics

By Denis J Evans, Debra J. Searles and S.R. Williams

Abstract

The argument of the Evans Searles Fluctuation Theorem [1], namely the dissipation function [2] is also the key quantity in all linear and nonlinear response theory [3]. It is also the key quantity in the proof of the newly discovered equilibrium relaxation theorems. For the first time we have, subject to certain simple assumptions, a proof of thermal relaxation to the canonical distribution function [4] postulated by J. Willard Gibbs.

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Confined flows of binary solutions

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Abstract

Flows of highly confined single component fluids have previously been studied in detail using non-equilibrium molecular dynamics methods by several authors (e.g. [1-3]). These studies have shown that for channels wider than approximately 10 molecular diameters and for sufficiently slow flows, the velocity profile is successfully predicted by the Navier-Stokes equations, and the viscous heating is so small that the temperature is essentially constant. As the driving field is increased, a non-uniform temperature profile begins to emerge. For sufficiently wide channels, the solution of the heat equation with Fourier's law of thermal conductivity shows that this temperature profile should be quartic. However, for the relatively narrow channel widths that have commonly been investigated (less than about 80 molecular diameters), it has been found that the temperature profile has a quadratic component due to coupling of the heat flux to the gradient of the strain rate. This coupling is non-linear, but it results in a term in the heat equation that is of the same order in the driving field as the viscous heating and therefore cannot be neglected [3]. Confined flows of binary solutions are even more complicated. In this case, we also have to consider the effects of thermal diffusion, the concentration gradient and concentration and temperature dependence of the transport properties [4]. In this presentation, we will discuss the simplest level of phenomenological theory that can be used to model heat and mass transport in highly confined binary solutions, and show that a strain rate coupling term strongly affects both the concentration and temperature profiles [5]. This has important consequences for separation technologies.

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Stochastic entropy production in thermal conduction

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Abstract

Irreversibility is an intrinsic feature of stochastic thermodynamics. There are random, dissipative forces in the dynamics that do not readily allow a trajectory of a system to be reversed when externally imposed protocols of driving forces are reversed. The likelihood of deviation when making such an attempt is measured by the so-called stochastic entropy production associated with an individual trajectory. We have linked this quantity to thermodynamic entropy production for systems described in full phase space, such that microscopic coordinates include both positions and momenta [1], and examined its separation into three components that reflect different sources of irreversibility. The approach is used to study thermal conduction in simple discrete [2] and continuous systems [3], demonstrating that two of the components of entropy production satisfy certain fluctuation relations, giving them a non-negative mean over all possible realisations of the process, while the third does not.

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Exploring the property of local equilibrium for the Gibbs surface in two-phase multi-component mixtures

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Abstract

Interfaces possess interesting thermodynamic properties that do not exist in bulk phases. A typical interfacial effect with many observable consequences is the surface tension of a liquid-gas interface. Can the concept of surface tension be generalized from equilibrium to nonequilibrium situations? Since we would expect the surface tension to depend on temperature, what kind of temperature shall we assign to interfaces in nonequilibrium situations? Interestingly, interfaces possess thermodynamic properties that do not coincide with the corresponding properties in the surrounding bulk phases. In this regard, the most important thermodynamic property characterizing the state of an interface in a pure two-phase system is its temperature, which may not even lie between the temperatures of the adjacent bulk phases [1,2].

The classical approach to describe equilibrium interfacial thermodynamics in phase coexistence relies on the arguments of Gibbs [3], who considers the interface as a separate 2D thermodynamic system which can be characterized in terms of excess densities. A nonequilibrium thermodynamic description of interfaces based on Gibbs' approach has been developed by Bedeaux and coworkers [4]. The main challenge is to generalize the concept of local equilibrium, which is known to be a key ingredient to the nonequilibrium thermodynamics of bulk systems to interfaces. Even when in contact with nonequilibrium bulk phases, interfaces quickly relax to states that can locally be described by the same set of variables as equilibrium interfaces, with the same thermodynamic relations between these variables. Several studies have investigated the validity of the local equilibrium hypothesis. For instance, the hypothesis has been supported by nonequilibrium molecular dynamics simulations [5] and by the van der Waals square-gradient model [1,2]. Excess densities are

known to depend on the precise choice for the location of the interface. How can we deal with this ambiguity in going from global to local equilibrium? Is there a unique or convincing way to implement local equilibrium? What are the observable consequences of local equilibrium?

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Thermo-orientation in polar fluids: Towards an understanding of the microscopic origin

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Abstract

The theory of non-equilibrium thermodynamics predicts that polar systems may show orientational order when subjected to a thermal gradient. Recently this has been validated by simulation for the modified central force model of water and the linear scaling of the effect as a function of applied thermal gradient has been confirmed [1,2]. Thermo-orientation effects have also been observed in non-polar systems, involving fluid dumbbells to which a source of asymmetry is added via either a difference in the mass, or short-range interaction between the two atoms. In particular it is established that the resultant thermo-orientation is intimately linked to the Soret effect [3].
We attempt to explore some of the microscopic details influencing the magnitude of the thermo-orientation effect and also look at the effect of thermodynamic state. In particular we observe a non-monotonicity in the magnitude of the effect as a function of temperature and show that the volume occupied by hydrogen sites plays a large role in determining the extent of the effect.
The hope is that this work shall pave the way for a microscopic interpretation of planned experimental work on the subject. Such experiments will take advantage of techniques capable of observing to a high accuracy, the spatially variation of the dielectric constant which should arise due to the induced polarisation of the medium.
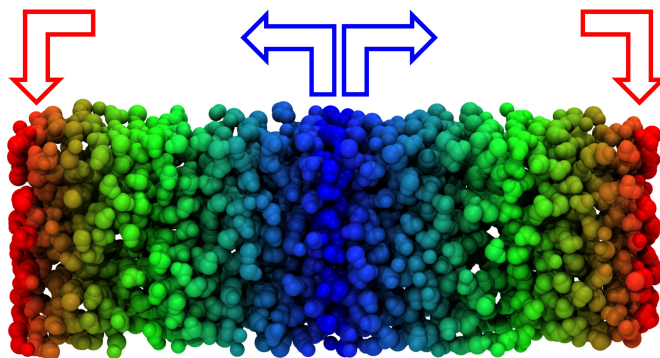
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The Generalised Langevin Equation: an efficient approach to non-equilibrium molecular dynamics of open systems

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Abstract

The Generalised Langevin Equation (GLE) has been recently suggested to simulate the evolution of solids [1] and molecular systems [2] coupled to a realistic dissipative environment, e.g., displaying non-markovian correlations. In fact, the GLE formalism is mathematically sound and it has already found promising applications, e.g., in nanotribology [3]. Besides, it also provides a very efficient thermostat for classical molecular dynamics [2,4]. However, efficient algorithms to solve the GLE for practical memory kernels are highly non-trivial, especially if the kernels decay non-exponentially [5]. In this contribution, we present a simple, yet efficient, algorithm to solve the GLE for practical memory kernels and we demonstrate its capability in two paradigmatic examples: (a) the exactly solvable case of a harmonic oscillator coupled to a Debye bath and (b) a simple bistable system whose transition rate is studied as a function of the kernel parameters [6]. Finally, the extension of the GLE to the quantum case is discussed within the same numerical framework of the classical case.

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Application of lattice Boltzmann method to modelling multi-component flows and devices

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Abstract

The lattice Boltzmann method (LBM) for computational fluid dynamics benefits from a simple, explicit, completely local computational algorithm making it highly efficient. In this presentation we detail some extensions of the LBM to recover the hydrodynamics of multi-component immiscible fluids that maintains a local and explicit algorithm. The local nature of the algorithm makes the method highly scalable when using high performance parallel-computing.

Such methods will eventually be used to help investigate the emergent macroscopic constitutive laws of complex suspensions and emulsions found in engineering, industry and biological sciences. Initial demonstrations of the algorithm towards complex suspensions were done by modelling a fluid containing a large number of individually tunable immiscible drops [1,2]. Comparisons are made of the emergent non-Newtonian behaviour with a power-law fluid. Further extension to suspensions of vesicles [3] within the LBM framework is discussed through the use of an appropriate free energy functional which enhances the application regime still further (eg. blood flows).
We have also applied the LBM recently to some industry applications such as the characterisation and design optimisation of a novel liquid crystal display device [4] and bioreactor [5] design. Results of such investigations are illustrated.

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Carbon Nanotube-Based Motor Driven by a Thermal Gradient

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Abstract

We present a model describing the dynamics of a nano-electromechanical device activated thermally. The nanosystem consists of two coaxial carbon nanotubes of disparate lengths. The presence of strong thermal inhomogeneities induces motion of the shorter nanotube along the track of the longer nanotube. A model which combines the action of frictional, van der Waals and thermal forces and the effects of noise is proposed and used to reproduce the motions observed in experiments and simulations. The dynamics of the nanomotor reveals the existence of a rich variety of dynamical behaviors and a high sensitivity to noise and initial conditions.

Non-equilibrium steady state properties of single-molecule nanodevices

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Abstract

The understanding of irreversible phenomena including non-equilibrium (NE) steady state is a longstanding problem of statistical mechanics. One of such phenomena is thermo-electronic transport through single-molecule nanodevices, which exhibits many important new features in comparison with conduction through macroscopic systems. This leads to promising new applications in nanotechnology.

In this presentation, we show some applications of a quantum field theory approach, namely the non-equilibrium Green's functions technique, to calculate the non-linear transport properties in the presence of electron-vibration interaction. Examples for model systems as well as for realistic molecular systems are considered. We show how the electron-vibration interaction affect the transport properties in the steady state [1], and how both the electronic and vibronic properties of real molecules could be used to obtain functionality in nanodevices [2].

We also present recent developments concerning the extension to the NE conditions of the properties of the single-molecule devices, such as NE charge susceptibility versus dynamical conductance [3], NE fluctuation-dissipation relations [4] and NE distribution functions [5]. Finally we discuss the application of such new concepts to the modelling of realistic molecular systems.

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Non-equilibrium thermodynamics approach to quantify the thermodynamic efficiency of molecular machines

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Abstract

Experimental studies have shown that the activity of the reconstituted molecular pump Ca^{2+}-ATPase strongly depends on the thickness of the supporting bilayer. It is thus expected that the bilayer structure will have an impact on the thermodynamic efficiency of this nanomachine. Here, we introduce a non-equilibrium thermodynamics theoretical approach to estimate the thermodynamic efficiency of the Ca^{2+}-ATPase from analysis of available experimental data about ATP hydrolysis and Ca^{2+}-transport. We find that the entropy production, i.e., the heat released to the surroundings under working conditions, is approximately constant for bilayers containing phospholipids with hydrocarbon chains of 18–22 carbon atoms. Our estimates for the heat released during the pump operation agree with results obtained from separate calorimetric experiments on the Ca^{2+}-ATPase derived from sarcoplasmic reticulum. We show that the thermodynamic efficiency of the reconstituted Ca^{2+}-ATPase reaches a maximum for bilayer thicknesses corresponding to maximum activity. Surprisingly, the estimated thermodynamic efficiency is very low, 12%. We discuss the significance of this result as representative of the efficiency of other nanomachines, and we address the influence of the experimental set-up on such a low efficiency. Overall, our approach provides a general route to estimate thermodynamic efficiencies and heat dissipation in experimental studies of nanomachines.

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Polymer Solutions in an External Field: Molecular Understanding of Electrospinning

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Abstract

Nanospider technology is a method to produce nanofibers by electrospinning from the free surface of polymer solutions. Due to the lack of understanding of the process on the molecular level, the actual setup of the process (strength of the electric field, composition of the solution, temperature, etc.) has been based so far on the trial-and-error.

In the presentation the process will be briefly described, the main problems identified, and the role of molecular simulations (i) to understand what is going on in the system during the spinning and (ii) to reveal relations between various molecular and/or thermodynamic properties affecting the process detailed.

We report first simulation results focussing on the interplay between the ions, electric field and water molecules, and on the onset of the surface waves and the origin of the Taylor cones. Furthermore, of a particular interest is the orientational arrangement of the water molecules in the interphase layer because this arrangement seems to be responsible for all the observed phenomena. All these results provide the necessary input information into semiempirical and theoretical macroscopic methods leading to improved efficiency of the production.

Finally, the relations between the conformational behavior of the polymer and its impact of the final product is briefly discussed.

Non-equilibrium molecular dynamics simulations of a bubble in a simple liquid and biomolecular system

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Abstract

Investigating a bubble dynamics has been one of the interesting targets of non-equilibrium molecular dynamics simulation. First, Molecular dynamics simulations of a bubble in a simple liquid were performed when liquids were locally heated [1]. We observed that the heated atoms scatter the neighboring non-heated atoms and make a bubble, and then the bubble is cooled and compressed by the surrounding liquids. The bubble dynamics in this process agrees with the results of the Rayleigh-Plesset equation which describes the dynamics of a bubble in terms of macroscopic hydrodynamics.

Next target was a bubble in a biomolecular system. We performed non-equilibrium MD simulations of an Amyloid-b oligomer in explicit water to study cavitation around the oligomer and the oligomer destruction by the bubbles. Cavitation is caused by negative pressure of the supersonic wave. When the pressure was decreased to a negative value of -100 MPa from a room pressure, a bubble formation was observed around the C-terminal region, the amino acid residues of which were hydrophobic. Even after the bubble size increased, the secondary structures of the oligomer were maintained. When the pressure was decreased to -500 MPa, we observed multiple bubble formation. In this case, the oligomer was destroyed as the bubble grew.

References

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Tracking control of colloidal particles under stationary non-homogeneous flow Conditions

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Abstract

In the present work we consider the problem of controlling the trajectory of a micro-sized particle immersed in a fluid under stationary homogeneous as well as non-homogeneous flow conditions. We restrict our analysis to flows with small Reynolds numbers and consider a Langevin-type equation in order to describe the motion of the particle. In our model, the friction force on the particle is assumed to be described by the Faxén's Theorem for the force on a sphere immersed in a stationary flow. We propose an explicit control force to be applied on the particle such that it will asymptotically follow any given desired trajectory starting from an arbitrary initial condition. In order to test the validity of our model, we implement hybrid simulations using Molecular Dynamics in order to approximate the motion of the suspended particle at the microscopic time-scale, and Multi-Particle Collision Dynamics in order to simulate the motion of the surrounded fluid and to incorporate hydrodynamic effects and thermal fluctuations. Firstly, we perform simulations in a fluid at rest, where the proposed control force is applied on the particle in order force to follow diverse trajectories. Then, we consider the tracking control of the particle in simulations in fluids with a homogeneous shear rate. We find that the simulations reproduce very well the predictions of the model. Thus, we confirm that the proposed force allows for effectively controlling the trajectory of the microsized particle. Finally, we estimate the ranges for the parameters characterizing the problem for which the present model is valid.

Carbohydrate ring puckering: transition path sampling analysis

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Abstract

The structure of saccharides is defined by two dynamic conformational determinants: glycosidic linkage geometry and pyranose ring conformation (pucker). The dynamics of conformational transition within the ring remains enigmatic as exchange between chair ($^4C_1$) and inverse chair ($^4C_1$) conformations occurs on microsecond timescales, which is problematic for experiments and simulations. We applied the transition path sampling (TPS) method [1] to the conformational investigation of carbohydrate ring puckering. TPS allows for significantly enhanced sampling of the unbiased 'reactive' trajectories, connecting the two predefined basins of attraction in the free energy landscape, i.e. the minima corresponding to the $^4C_1$ and $^4C_1$ chair conformations of the a-D- and b-D-glucose molecules. These 'reactive' trajectories are used to describe the dynamical features of the $^1C_4 \leftrightarrow {}^4C_1$ transition including all the intermediate stages (e.g. boat, twisted boat, etc.). The problem of the transition states and the optimal model of the $^4C_1 \rightarrow {}^4C_1$ reaction coordinate is discussed in terms of the likelihood maximization approach [2]. Additionally, the comparison of the efficacy of two TPS algorithms ('shooting point bias' vs. 'unbiased shooting') is performed for the case of b-D-glucose.

References

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