Computational nanofluidics

Workshop report

Background

Materials at the nanoscale often have properties that can be substantially different from those of the corresponding bulk phases. In particular, the surface characteristics and fluid flow properties in pores or channels of nanoscale dimension can deviate strongly from macroscopic expectations. Nanoscale systems are difficult to probe experimentally. However, the small dimensions often make them accessible to molecular simulation, providing theory and simulation an opportunity for the discovery of new phenomena.

There is also a considerable interest in applications of nanoscale flow. Advances in molecular biology, human genetics, and functional genomics continue to produce increasing numbers of molecular targets available for therapeutic intervention. This, coupled with major increases in compound collections produced by combinatorial technologies, is driving innovation in high throughput screening (HTS) and towards ultra fast and ultra sensitive HTS based on nanoscale components.

The interactions between the fluid and the conduit are central to the description of nanoscale flows. While there has been significant progress in our understanding of equilibrium wetting behaviour of nanopatterned/nanostructured surfaces, our knowledge of the dynamics of wetting and flows over such surfaces is still poor. Yet it is clear that dynamical processes are vital to technical applications. There is an extensive literature on the wetting dynamics of homogeneous surfaces and some progress has been made for structured surfaces, part of which we will be able to exploit in developing models for nanofluidics.

Nevertheless, the precise relationship between molecular and nanoscale surface structure, surface friction and flow is not yet established. ,Some progress has been made by extending Maxwell's model, intended originally for gas flows. Different molecular dynamics techniques produce different answers for accommodation coefficients since they sample different aspects of the fluid/surface region. For multiscale physics determining this relationship is central to the prediction of boundary conditions within Navier Stokes hydrodynamic theories.

The workshop addressed the central questions of the construction of model systems to study nanoscale fluid flow and of relevant simulation methodologies, including equilibrium and non-equilibrium methods. The workshop also explored the results obtained for flow at the nanoscale, and the methodologies developed to describe the multi-scale physics of nanoflow, including boundary conditions and hydrodynamic models.

The location of the workshop

The workshop was organised at the EPFL (Lausanne) where the CECAM headquarters recently relocated. The local staff and the director ad interim, Mauro Ferrario, made all efforts to ensure that the workshop run smoothly. From the local staff the programme secretary, Emilie Bernard, and computer system manager, Jordi Brusa, were very helpful in solving many complex technical problems including broadcasting Professor Quirke's talk over the internet, urgently arranged due to a cancelled flight from the UK. The organisers

would like to thank the host organisation, CECAM, and its staff for their competent and efficient help.

The format of the workshop

The workshop was a small and informal meeting with about 20 participants from Europe, Asia, Australia, and America, having truly international and interdisciplinary character. All speakers were allocated 35 min slots and additional 10 min were given for questions and discussion, which appears to work well. Long discussions with many questions were a typical feature of each presentation. In some cases, when discussion required more time, it continued over the coffee and lunch breaks.

Subjects covered and methods discussed on the workshop

The contributions covered many aspects of the nanofluidics, and a number of different approaches for simulation of fluid flow including traditional particle and field theory methods (hydrodynamics), and newer fluid particle methods have been discussed.

In the first talk, Dennis Rapaport (Bar-Ilan University, Israel) discussed the molecular mechanisms of swimming (self-propelled motion) of microscopic bodies motivated by biological and microrobotic design. He showed that efficiencies of mechanisms vary significantly, which needs to be taken into account when practical nanofluidic applications are designed. He further considered Rayleigh-Benard convection in a thin layer and Taylor-Couette vortex formation in an annular container, where quantitative agreement between continuum theory and simulation was obtained.

In the second talk, Billy Todd (Swinburne University, Australia) discussed the problem of estimating shear viscosity in fluids confined to nanoscale dimensions and demonstrated that apart from simple cases with constant or linear shear rate (Couette and Poiseuille flow), viscosity cannot be computed in local approximation. He demonstrated further how to compute the nonlocal viscosity kernel within the framework of generalised hydrodynamics from equilibrium molecular dynamics of homogeneous fluid at equivalent thermodynamic state.

After the break, Roland Winkler (IFF, Jülich, Germany) presented the results of mesoscale simulations of micro- and nanochannel low-Reynolds-number flow of polymers using multiparticle collision dynamics (the Malevanets-Kapral method).

Dónal Mac Kernan (UCD, Ireland) concluded the first day by discussing the mechanisms of dispersion-aggregation of single-walled carbon nanotubes (SWCNTs) in a polar solvent. SWCNTs usually come in ropes, or bundles, which is the main obstacle to its exploitation. The rate of the bundling process is determined by the free energy landscape, which requires enormous computational resources for its estimation since the solvent plays an important role in this process. In his talk, Dónal presented results of extensive molecular dynamics studies of this problem in case of highly polar solvent. He showed how the solvent between the nanotubes undergoes the order-disorder transitions as nanotubes approach each other.

On the next day, the first speaker was Lydéric Bocquet (Université Claude Bernard, Lyon, France), who discussed the nanoscale fluid flow in the presence of charged interfaces. He presented a detailed study of the nanoscale effects on transport phenomena that occur within the Debye layer and discussed the consequences of the breakdown of the classical no-slip boundary conditions for such systems. He concluded by discussing the impact of

nano- and micro- textures on the surfaces, showing that massive flow amplification can be achieved in experimentally realisable superhydrophobic channels.

Juergen Koefinger (University of Vienna, Austria) moved to important topic of water structure in carbon nanotube pores. He focused on consequences of the orientational defects on the hydrogen-bonded network in the pore. He described new lattice model developed to accurately describe the energetics of defects and the fragmentation of the hydrogen-bonded chains formed along the pore axis. This model allows them to study the size dependence of the orientational order using advanced Monte-Carlo techniques, and they found that as the tube length increases the water system remains predominantly ordered up to a length of 0.1mm, thereby allowing fast long-range proton transport.

Gerhard Hummer (NIH, Maryland, USA) discussed how water, protons, and ions behave in the weakly polar pores and cavities that occur inside carbon nanotubes, fullerenes, and proteins. He presented results for the unusual thermodynamic and transport properties of these nano-confined fluids and discussed their implications on protein function and design of nanofluidics.

In the first talk after the lunch, Monte Pettitt (Univeristy of Houston, USA) gave a thorough investigation of transport theories of simple fluids over a wide range of thermodynamic parameters. He discussed recent simulation results obtained in his group used to validate the theories and compared them with the projections from their biochip simulations in order to derive a suggestions for the design of the next generation of nanofluidic and surface mounted technologies.

In the next talk, Graham Macpherson (University of Strathclyde, UK) described a new and versatile MD code developed at Strathclyde, which is based on free, open-source OpenFOAM CFD toolbox. He in particular described to enabling components: parallel generation of initial molecular configurations in arbitrary geometries, and calculation of intermolecular pair forces between molecules that lie on mesh portions assigned to different, and possibly non-neighbouring processors. He demonstrated the capabilities of the code on a case study of flow in realistic nanoscale mixing channel where the geometry is drawn and meshed in engineering CAD tools.

The next talk, given by Marcus Müller (Georg-August Univeristät, Göttingen, Germany), was dedicated to structural changes near the surface to which polymers are grafted and how these changes can be parameterized by a type of hydrodynamic boundary conditions. He showed that individual, unentangled chains in the dense brush exhibit cyclic, tumbling motion and that non-Gaussian fluctuations of their molecular orientations are similar to that of isolated tethered chains in shear flow. Using a molecular dynamics simulation of a coarse-grained model and dynamic Single-Chain-in-Mean-Field simulations they observed the inversion of the flow direction in the vicinity of the brush-coated surface. Finally, by comparing their results with those obtained for near-surface flow of a polymer melts at a corrugated solvophilic surface they were able to extract the effective interface position and the slip length.

Vladimir Lobaskin (UCD, Dublin, Ireland) discussed hydrodynamic lift forces induced on a solute particle when flowing close to a modified solid-liquid interface and originated by excluded volume effects. By solving numerically the flow equations in a nanotubes forest they show that excluded volume interactions between the solute particles and the posts lead to a residual lift effect, which varies with the flow direction, shear rate and particle size. By varying the shear rate or driving pressure they were able to “switch” the lift force to the

opposite direction. He concluded by discussing the applications of this effect to particle sorting devices.

A very welcome contribution from Zuzanna Siwy (University of California, Irvine, USA) gave an introduction to emerging field of nanofluidic electronic, describing her recent experiments on nanofluidic diodes and transistors. She then showed how the ion current oscillations could be induced in conical nanopores by tuning the concentration of divalent ions in buffered monovalent ionic solution.

Vlad Sokhan (NPL, Teddington, UK) discussed the problem of slip flow in nanoscale channels and presented a new analytic result for the slip coefficient that requires only two material parameters: shear viscosity, which can be taken from the bulk equation of state for the viscosity, and characteristic relaxation time that describes the dissipation processes in the fluid and can be estimated from the collective velocity autocorrelation function of the fluid. He demonstrated the accuracy of the result by comparing its prediction with the results of non-equilibrium MD simulation. Both the theory and the simulation results, that agree well, show that for a slit pore in contact with the reservoir of a fluid, the slip coefficient scales as the pore width for small pores and for wider pores, above 20 molecular diameters, reaches a plateau. This effect should be taken into account when calculating fluxes and could be responsible for some discrepancies between experimental and theoretical values of slip coefficients.

Andrey Milchev (IPC, Sofia, Bulgaria) gave on overview of recent simulation results of forced imbibition of simple fluids in polymer brush-coated capillaries. They found a significant (by a factor of four) increase in the suction force when the brush width approaches the tube radius and a similar effect was found with increased density of brush coating. They speculate that the fluid in vertical brush-coated capillaries can be raised to much higher levels than in an equivalent capillary with bare walls. He then presented the results of spreading of tracer particles transported by the uptaking fluid with regard to the grafting density and the length of the polymer. They observed asymmetric concentration profiles of the tracers and the evolution is interpreted in terms of a drift-diffusion equation with a reflecting boundary, which moves with the fluid front.

Nick Quirke (UCD, Dublin, Ireland), who was unable to attend physically the workshop due to cancelled flight, delivered his talk over the internet using skype. This experiment proved the viability of remote broadcasting and showed that nothing is impossible with good hosts. Nick Quirke presented the extensive results of combined experimental and simulation study of slip boundary conditions in various pores and fluids. He presented new results for the flow enhancement factor due to wall slip as a function of chemical composition (water, ethanol, decane), pore geometry (slit, tube), and pore dimensions. He then discussed the nature of differences between the theoretical results and experimental measurements.

Petros Koumoutsakos (ETH Zurich, Switzerland) discussed the problems of multiscale simulations of liquids using partices. He started from redefining the concept of a particle and presented the recent advances in his group in the coupling of multiscale particle descriptions of liquids using control algorithms. He discussed possible applications to problems involving flow on nanoscale structures embedded in aqueous environment.

Matthew Borg (University of Strathclyde, UK) completed the day by presenting a hybrid molecular-continuum model for nanofluid mechanics.

Scientific outcome

The lectures were of very good quality and presented various aspects of the nanofluidics and the underlying theory. Several new approaches presented at the workshop attracted high interest; they initiated lively discussions during the breaks and evenings, and several potential collaborations between the participants emerged. Two discussion sessions, one on applications, experiments, and prospects, and another on theory, algorithms, challenges, and the outlook were organised on 4 September and 5 September, respectively, both stimulating lively and productive exchanges.

Recommendations

Simulation, as a bridge between the experiment and the theory, can significantly facilitate application and technology development, saving industry precious time and efforts needed. The industrial areas immediately related to nanofluidics include biomedical applications, *e.g*. a recognition element that kills the bacteria on the outside, drug delivery, treatment of cancer. There are other topics, such as detection and elimination of health hazards (toxicity of nanoparticles, nanotubes penetrating cell membranes), which require simulation for better understanding and reducing the health impact. One of the *real* problems that Australia and parts of Africa are facing, and where the nanofluidics can be helpful, is desalination.

One of the problems, which is of rather general nature and was identified at the workshop too, is to find a common language with experimentalists. There are very few experiments to compare (slip length, fluxes) and the main reason is that experiments are complex and difficult to conduct. Examples of possible experiments would be nanolithography, water droplets on graphite surface, kinetic measurements, interfacial viscosity, desalination. Experimentalists want a simple set of parameters and therefore theory at all levels needs to be refined. This is a major problem due to the complexity of the nanofluidic systems and multiscale nature of the basic phenomena spanning many orders of magnitude in spatial and temporal domain. The main question remains: how the equations can be generalized.

Many more specific problems also have been identified and discussed at the workshop. Thus, most of the existing forcefields have difficulties in describing kinetics, as was emphasized by Monte Pettitt, and it is not clear how to parameterize the kinetic properties. This problem is largely ignored at present by assuming the local equilibrium and there is clear need for a better solution. The forcefields need to be refined to consistently include effects of polarizability: an abiding problem that is even more acute for ionic systems. In studying nonequilibrium processes a steady state is achieved by using a uniform thermostat, which is a problem for anisotropic and spatially inhomogeneous systems typical for nanofluidics and improperly used can give wrong results. Thermal transport is important for nanofluidics, but very few groups in the world currently working on it, and there are many unsolved problems here including the basic question of how to set up the temperature gradient in a simulation.

To solve these questions various approaches and methods are being developed as was demonstrated at the workshop. Thus, Petros Koumoutsakos is developing multiscale synthetic approach. Surface-force apparatus measurements can be used as a reference as was demonstrated by the work of Lydéric Bocquet. To alleviate the multiscale problems, simulation can be arranged in two stages, where the results of the former are used as input for the latter. The slip problem in the nanoscale fluid flow is actively investigated and the ways to determine the slip from fundamental properties are emerging.