

RISING TO THE CHALLENGE OF THERMODYNAMIC NON-EQUILIBRIUM IN ENGINEERING FLOW PROBLEMS

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ABSTRACT

Micro- and nano-scale fluid systems can behave very differently from their macro-scale counterparts. Remarkably, there is no sufficiently accurate, computationally efficient, and — most importantly — generally agreed fluid dynamic model that encapsulates all of this important behaviour. The only thing that researchers can agree on is that the conventional Navier-Stokes fluid equations are unable to capture the unique complexity of these often locally non-thermodynamic-equilibrium flows. Here, we outline recent work on developing and exploring new models for these flows, highlighting, in particular, slip flow as a quintessential non-equilibrium (or sub-continuum) phenomenon. We describe the successes and failures of various hydrodynamic and molecular models in capturing the non-equilibrium flow physics in current test applications in micro and nano engineering, including the aerodynamic drag of a sphere in a rarefied gas, and the flow of water along carbon nanotubes.

Key Words: *Thermodynamic Non-Equilibrium, Sub-Continuum Fluid Dynamics, Microfluidics, Nanofluidics.*

1. INTRODUCTION

The set of Navier-Stokes-Fourier (NSF) equations, with no-velocity-slip and no-temperature-jump conditions at bounding surfaces, is the traditional model for the transfer of heat and momentum in fluid flows. While it has proven successful for flows ranging from liquids in capillaries to the atmosphere of planets, remarkably it can be a poor predictor when the flow system is either very small (i.e. in micro/nano devices) or very low pressure (e.g. high-altitude air vehicles, spacecraft re-entry), or if the process depends on interactions at the molecular level (e.g. protein folding). This is despite the flows being very typically laminar in such conditions, so simpler in a conventional sense. For example, measured gas flow rates in micro channels are typically a factor of two larger than expected, and drag on a micro sphere is a similar factor smaller [1]. At the nano scale, surface effects such as hydrophobicity, wetting and electrokinetics dominate, and lead to unexpectedly high liquid transport rates in, e.g., carbon nanotubes that different experimental groups not only cannot fully explain but also fail to agree on.

These predictive failures arise from a limiting assumption underlying conventional fluid mechanics: scale-separation — macroscopic flow behaviour is assumed to be independent of the microscopic dynamics of the fluid material [2]. The conventional fluid mechanical model of near-instantaneous local equilibration of heat and momentum throughout the fluid follows from this, and provides a powerful tool for treating most macro scale flows. However, scale-separation is not always guaranteed in micro and nano scale flows: in these cases we often need to account for the effect of the fluid's molecular nature on the overall (macro) flowfield. Micro- and millisecond effects are important for micro and nano scale flows, but depend on the outcome of pico- or nanosecond molecular processes [3,4]. The design of future technologies that exploit micro and nano scale flow components will require the ability to resolve phenomena across scales of at least 8 orders of magnitude in space, and 10 orders of magnitude in time — a formidable multiscale problem.

In this paper we describe some of our most recent computational and theoretical tools we are bringing to bear on this problem. We examine slip flows in microscale gas and nanoscale liquid applications as quintessential non-equilibrium or sub-continuum phenomena that are still not properly understood. We tackle gas and liquid flows alternately in this paper, because we wish to highlight the interesting commonalities between non-equilibrium gas and sub-continuum liquid flows at these small scales.

2. THERMODYNAMIC NON-EQUILIBRIUM IN GASES

In dilute gas flows, molecules travel in free-flight between brief (binary) collisions with each other or bounding surfaces. The Knudsen number, Kn , indicates the degree of scale independence; in terms of the molecular mean-free-path, λ , and a characteristic length scale, L , of the system (or the local gradient of a relevant flow quantity, Q):

$$Kn = \frac{\lambda}{L} \cong \frac{\lambda}{Q} \left| \frac{dQ}{dl} \right|.$$

If $Kn > 0.01$, physical scales are no longer clearly separated, and non-local-equilibrium flow behaviour arises: the flow velocity at a surface takes on a finite “slip” value, and the temperature of the gas near the surface also differs from the surface temperature. At higher Kn the linear NSF constitutive relations themselves become inappropriate. Air flowing at atmospheric pressures in a device with a characteristic length scale of 1 μm has $Kn \approx 0.1$ and will show these non-equilibrium (rarefaction) effects. Gas flows in, e.g., micro-pumps or micro-turbines of complex geometry will have a range of Kn : the NSF equations cannot, therefore, be expected to be generally applicable to these flows.

While a molecular-level description of the gas is available through the classical Boltzmann equation — or other kinetic models, such as BGK or ES-BGK — direct solution is computationally expensive. Even the cost of indirect methods, such as the direct simulation Monte Carlo (DSMC) technique, makes complex 3D full-field flow simulation impractical: to resolve micro flow velocities of the order of 0.01 m/s in DSMC, we need roughly 500 million statistical samples of the flowfield at any point [2]. However, variance reduction techniques can be applied to conventional DSMC to create a powerful and more economical method for generating molecular distributions at the most critical points in a flow.

A computationally-efficient gas flow method, but one which has had only modest success to date, is to establish either a Kn -series or a Hermite polynomial approximation to the distribution function in the Boltzmann equation. To first order, i.e. for near-equilibrium flows, both approaches yield the NSF set, but the solution methods can be continued to second and higher orders to incorporate more and more of the salient characteristics of a non-equilibrium flow. Specifying the additional boundary conditions required for the derived higher-moment and higher-order extended hydrodynamic equation sets remains a critical problem. In any case, the complexity of most of the models (Burnett, Grad 13-moment, R13, R26, etc.) is overwhelming, particularly when considering the only modest improvement in accuracy they provide. While they have particular difficulty in resolving strong non-equilibrium phenomena, e.g. the Knudsen layer close to bounding surfaces [5,6], they may have some use in the “near near-equilibrium” regime [7,8].

3. THERMODYNAMIC NON-EQUILIBRIUM IN LIQUIDS

Non-equilibrium phenomena analogous to that in gases (i.e. slip and non-linear constitutive behaviour) dominate liquid flows at the nanoscale. But identifying and modelling non-equilibrium in liquids is significantly more difficult than for gases: a Knudsen number cannot be ascribed

because liquid molecules are constantly moving within each others' potentials, and the length scale for equilibrium breakdown is similar to that at which the continuum-fluid model itself fails. The complexity of material-dependent effects at interfaces cannot be treated by simple phenomenological parameters or by "equivalent fluxes" [9]. Direct molecular simulation of the liquid, however, can simultaneously model these phenomena with minimal simplifying assumptions, and some recent results will be presented below.

Molecular dynamics (MD) simulations calculate the intermolecular forces between molecules (based on their configuration in space) and then integrate the classical equations of motion using the net force on each molecule. Intermolecular force models can be empirically fitted to experimental data, or derived from first principles. The dynamics of real molecules in collision with real surfaces can then be investigated by accumulating the properties of individual molecules colliding with a (rough) surface lattice of molecules. The major problem again is that, like DSMC, MD is computationally very intensive. For example, to simulate 1 μ s of water flow in a $10 \times 20 \times 100$ nm channel would require up to 10 years on a modern PC. However, much of this time is spent in calculating unnecessary molecular detail in parts of the flow that are near to equilibrium [10]. Ultimately, a hybrid framework is called for, which dynamically couples the efficient NSF model in near-equilibrium regions to the detailed molecular dynamics model elsewhere.

4. RESULTS

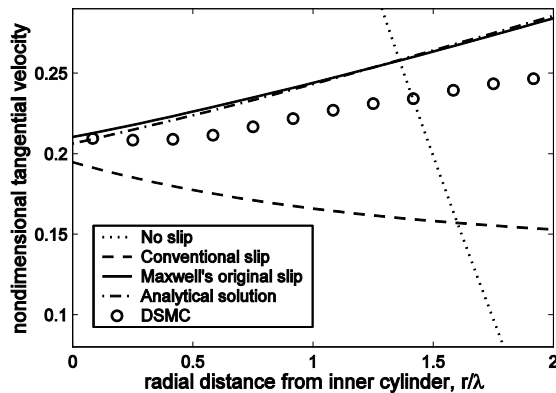


FIGURE 1. Cylindrical Couette flow ($Kn = 0.5$, argon gas, momentum accommodation coefficient is 0.1), non-dimensional velocity radial profiles. Note the inverted velocity profile, captured by DSMC and an analytical kinetic theory [11].

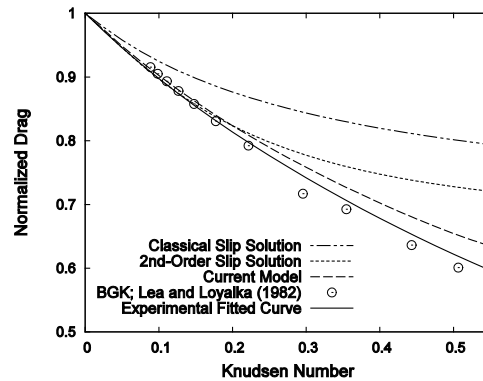


FIGURE 2. Normalized drag force on a sphere at various Kn , comparing predictions using the model of [1] with, as noted, Basset's classical slip solution, Cercignani's 2nd-order slip solution, BGK kinetic theory results, and experimental data.

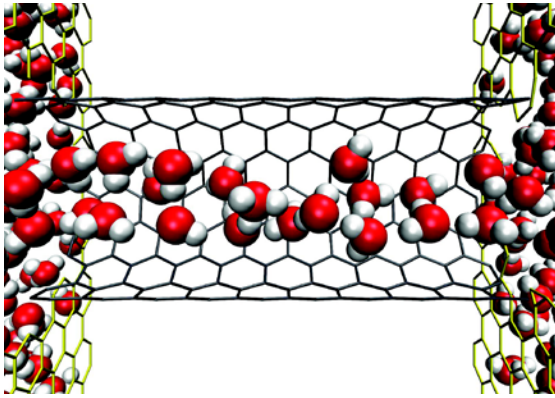


FIGURE 3. Molecular dynamics simulation of water molecules (red and white) transported through a short carbon nanotube (green lines), shown in cutaway, that is fixed between two graphene membranes (thin gold lines). The water is moving from an upstream to a downstream reservoir.

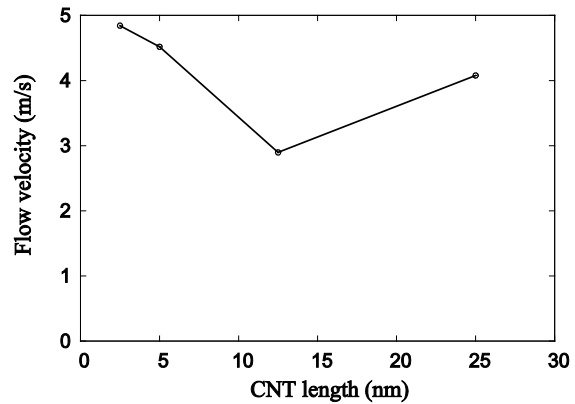


FIGURE 4. Variation of water flow velocity with CNT length under 200 MPa pressure difference. The flow enhancement factors (relative to continuum expectations) are 71, 126, and 353 for the 5nm, 12.5nm and the 25nm lengths, respectively.

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