3rd Polish Congress of Mechanics

21st International Conference on Computer Methods in Mechanics

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Short Papers

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Cover design
Dawid Białowąs
bialowasdawid@gmail.com

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Nanoscale challenges of fluid mechanics

Tomasz A. Kowalewski[1]
Paweł Nakielski[2], **Filippo Pierini**[3], **Krzysztof Zembrzycki**[4], **Sylwia Pawłowska**[5]
[1,2,3,4,5]*Institute of Fundamental Technological Research, Polish Academy of Sciences*
Adolfa Pawinskiego 5B, 02-106 Warszawa, Poland
e-mail: tkowale@ippt.pan.pl [1]

Abstract

In this talk we would like to tackle general question of contemporary fluid dynamics, how far its assumption of a continuous, smooth medium remains useful when size and time scales start to approach molecular ones. The question is not trivial and seems to depend on several additional factors usually minored. For example, when full Navier-Stokes equations are replaced by their linear approximation we are loosing basic characteristics of convective motion, and still we use such approach. Once our fluid becomes granular matter with its own internal properties, proper interpretation of flow interactions with other molecular structures probably needs deeper physics. But still we try to convert such problem to the classical macro/micro scale description. Hence a general question arises, how small does a fluid have to be before it is not a fluid anymore?

Keywords: microfluidics, nanofluids, Brownian motion, nanofilaments

1. Introduction

It is generally understood, that the main difference between macro- and nano-scale mechanics originates from rapidly increasing surface to volume ratio along with the decreasing of object size. A total surface of one nanometre particles filling volume of a cubic centimetre is 6000 square meters! Hence, nanoscience is mainly a science of surface forces and surface interactions. It applies particularly to fluids.

The field of microfluidics is characterized by the study and manipulation of fluids at the submillimetre length scale. The fluid phenomena that dominate liquids at this length scale are measurably different from those that dominate at the macroscale. For example, the relative effect of the force produced by gravity at microscale dimensions is greatly reduced compared to its dominance at the macroscale. Conversely, surface tension and capillary forces are more dominant at the microscale. These forces can be used for a variety of tasks, such as passively pumping fluids in microchannels, precisely patterning surfaces with user-defined substrates, filtering various analytes, and forming monodisperse droplets in multiphase fluid streams for a variety of applications [1].

It is interesting to note how many valuable hints on behaviour and explanation of micro-word indicates our *mother nature*, which evolutionary optimized the best nanoscale engineering system to control living organisms. For micro-fluidics surface tension is much more crucial, as this is the surface related force. This can be actually noticed observing bugs walking on the water surface. Their small size permits them to benefit from the surface tension. Another example is nanofibre web produced from polymeric solution exhibiting strength of the similar product produced in nature by spiders. The spider web is an ideal material in terms of endurance. It can stop flying bug and still remains untouched. In macro-scale adequate web would have to stop a whole airplane without damage, which obviously is still far from the current engineering capabilities.

By far the most difficult question which nanotechnology is facing is how to effectively produce tools and systems in nano-scale. And again the nature can help engineers to solve this problem. Any type of biological system is build from cells, which form more complex structure by organizing themselves. One of current research tasks is to study self-organization mechanism for efficient building of micro-systems. The macro-scale design techniques currently in use (top-down approach) such as lithography are relatively expensive and slow. Even, if prototypes of quantum computer are built of few atoms manipulated under electron microscope, such technique is completely inefficient for mass production. Separately manipulating millions of atoms to cover micro-meter surface would take several centuries. By self-organization this process can be achieved far more rapidly, in a matter of minutes or less. Hence, fluidic techniques based on patterned shapes of mono-layers and capillary forces are used to assemble micro devices. In most cases the self-assembly requires that the components are mobile in a fluidic environment. Observing biology one obtains plethora of valuable hints how to proceed with such process [2].

Physics of nanoscale mechanics can be more or less completely described using quantum mechanics. The methods, called *ab initio*, are rigorous but limited by present-day computers to systems containing a few hundred atoms at most. To determine the properties of larger ensembles of atoms the Molecular Dynamics method is commonly used, enabling studies of billions of atoms with effective interatomic potentials. Still its practical applications are limited by time and space scales to first nanoseconds of the analysed phenomena and several nanometres in space. Hence, modelling fluid flow in micro- and nano-scales needs specific technique, which is based on assumption that fluid particle can be represented as a cluster of atoms. Effective clustering can be based on so called Voronoi tessellation, describing a special kind of decomposition of the flow domain [3]. Such coarse grained modelling is useful for general flow description, but needs predefined interactions if we approach molecular distances to interpret specific phenomenon. Hence, despite of technical and physical problems with direct, experimental analysis of nano/micro scale flows, it's the only way to validate simplified assumptions which by definition have to be incorporated to theoretical models. Some experimental examples we my gain observing the mother nature, some of them has been recently proposed using

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completely new for fluid mechanics techniques, like fluorescent microscopy, atomic force microscopy, and optical tweezers.

Most of microfluidic problems concern multiphase flow, suspensions of micro and nanoparticles, cells or macromolecules (proteins, DNA etc). Understanding and properly interpreting fluid-particle interaction is crucial for interrogating such systems. One of the basic optical tools is based on Brownian motion [4]. The local and bulk mechanical properties of a complex fluid can be obtained by analysing thermal fluctuations of probe particles embedded within it.

Thermal fluctuations generated by molecules are not only noises, it has been demonstrated that such fluctuations are fundamental to the function of biological systems. Here, several results are possible with the same probability, in contrast to a mechanical system in which the result is deterministic. In ensemble measurements, the obtained values, which are average values over many molecules, have been usually wrongly interpreted as deterministic values. However, in biological systems, the average values are not necessarily effective, but the values of individual molecules play a decisive role [5,6]. The system may spontaneously fluctuate, and one of the two states occurs alternately. Preferential binding of ligands to one of the spontaneously fluctuating structures of proteins leads to activation or deactivation. This mechanism appears essential for a long scale evolutionary development of leaving species, and at short time scale to create signalling paths for early immune response of individual cells [7]. Hence, looking at the "bottom" of our fluid mechanics, there is no place for steady, unique and predictable modelling. Rather, by analogy to quantum mechanics, we have to talk about the most probably evolution of the analysed system. As an illustration of the difficulties, in the following we cope with two intriguing problems, kinematic boundary conditions in micro and nano scales flow, and mobility of nano-objects suspended in liquids.

2. To slip or not to slip

One of the primary questions, which appeared when fluid mechanists started to play with microfluidics, concerned the interactions between liquids and solid surfaces. From the physical point of view it seems obvious that molecules of liquid cannot be arrested at the solid surface, otherwise the local thermodynamic parameters of liquid should abruptly change. This problem is of fundamental physical interest and has practical consequences in rarefied gas flows. Recently it became rediscovered for small-scale systems, including transport phenomena in biological fluids [8].

The physics of hydrodynamic slip may have different origins. Purely molecular slip is clearly relevant in case of gases. For very small channels formed by carbon nanotubes (CNT) possible drag reduction is expected due to the synchronized slippage of water molecules. It is interrelated with molecular structure of water. For constrained conditions, i.e. tube diameter below 1 nm, water forms a long single molecular chain [9]. Hence, its transport properties largely deviate from continuous understanding of fluid flow.

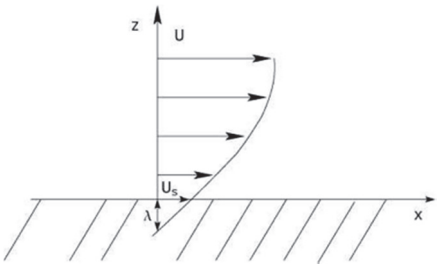

Figure 1: Schematic definition of the slip velocity U_s and the slip length λ for the fluid flow over solid wall

For dense fluids several additional factors appear to play a more or less significant role. One of them involves wetting properties of the solid surface. Molecular scale roughness allows for creation and stabilization of nanobubbles. Such trapped on the wall nanobubbles may effectively work as a gaseous slip layer, responsible for super-hydrophobic surface properties [10].

Identification of the slip appears not a simple task, both numerically as experimentally. Molecular simulations performed up to now neither confirm nor exclude possible daviation from the classical "non-slip" condition formulated by Navier in 1823. Using continuum mechanics we have to combine a grid size that copes with a nanometer while covering enough space to also include a millimetre scale flow. Experimentally, our techniques for looking at the very small objects (e.g., atomic force microscopy) are slow and cannot cope with large areas very well. The attempts to look at both these scales simultaneously show how our intuition about the relationships between nanoscale objects and macroscopic objects can fail badly.

Classical microscopy used for nanoscale observation has resolution limited by the light wavelength of about 500 nm micrometres. Evaluating diffraction disks the measured position of particle coordinates in plane perpendicular to the optical axis can be improved by order of magnitude. However, resolution in depth, along optical axis, remains very low (tenths of micrometre), and is defined solely by focal depth of the microscope lens. Total Internal Reflection Microscopy (TIRF) helps to bypass some of these limitations offering possibility to locate objects position with resolution of about 20 nm. Laser light illuminating object undergoes total internal reflection at a interface between investigated medium (liquid) and the wall (glass), and part of the light penetrates into the medium parallel to the interface with an intensity that decays exponentially with the normal distance from the interface (Fig. 2). This evanescent wave illumination has been used extensively in the life sciences. Recently it was rediscovered in microfluidics for near wall flow measurements. The main advantage of the method is possibility to reduce the depth of focus of the acquisition system [11]. Hence, it became possible to obtain images of particles, which are in the direct vicinity of the wall. In our recent study of the Brownian motion of fluorescent particles observed close to the wall, the deviation of the particle diffusion rate has been interpreted as an evidence of the slip boundary conditions.

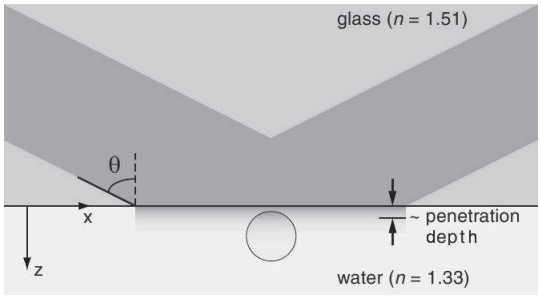

Figure 2: Evanescent wave illumination, laser light reflects at specific angle from the glass wall creating thin evanescent light beam penetrating liquid along the wall [11]

According to the theoretical model by Lauga & Squires [12] the diffusion coefficient of a single colloidal nanoparticle is directly related to the distance from the wall, and the slip velocity. In our work [11] we apply this outcome to determine the slip length from measured and calculated variations of the diffusion coefficient of particles as a function of distance from the wall. For this purpose the effect of the wall on the Brownian motion of nanoparticles suspended in water is examined experimentally and compared with numerical simulations performed by Molecular Dynamics approach.

The outcome is in the range of uncertainty found in the literature. For relatively large nanoparticle used in the experiments (300 nm diameter) the evaluated slip length measured at 170nm from the wall appears to be nearly 300nm. In the numerical analysis, for much smaller particles (24 nm) the evaluated slip length is less than 4 nm.

Difficulties arising with proper interpretation of available measurements of slip length performed by particle tracking became partly understandable if we look at inherent factors modifying mobility of nano-objects. We discuss it in the following chapter.

3. Mobility of nanoparticles

Micro and nano scale motion is coupled or sometimes mainly driven by molecular diffusion, direct effect of molecular structure of our environment. Diffusion governed by Brownian motion is an efficient transport mechanism on short time and length scales. Even a highly organized system like a living cell relies in many cases on the random Brownian motion of its constituents to fulfil complex functions. A Brownian particle will rapidly explore a heterogeneous environment that in turn strongly alters its trajectory. Thus, detailed information about the environment can be gained by analysing the particle's trajectory. For such analysis spatial resolution down to the nanometre scale is needed. High resolution is directly connected to the requirement to observe the motion on short time scales. However, at short time scales, the inertia of the particle and the surrounding fluid can no longer be neglected, and one expects to see a transition from purely diffusive to ballistic motion [13]. The effect is not negligible for transport phenomena observed in nanoscales, e.g. single-molecule reactions which are basis for transcription of encoded in DNA information. Thus, for complete understanding, an analysis of Brownian motion at very short time scales is necessary, taking effects of inertia into account.

Biochemical reactions in living systems occur in media of very high molecular concentration. In fact it is difficult to talk about diffusion of molecules, at such crowded environment the interactions between macromolecules hinder their displacements, limiting transport and signalling functions [14].

Observation of Brownian motion of micro-objects is classical basis for particles size measurements, evaluation of liquid properties (viscosity, microrheology), analysing particle – wall interactions, and many others. Nevertheless even such seemingly simple problem creates plethora of uncertainties. In all applications it is necessary to be able to maintain the colloid well dispersed and to avoid the formation of aggregates. Moreover, it is absolutely necessary to know the fluid-solid interaction in nanoscale and the hydrodynamic properties of the particles.

The equilibrium state and the hydrodynamic properties of many colloids system in aqueous medium is affected to several environmental parameters. The ionic character of water solutions needs beside analysis of hydrodynamic friction (famous Stokes formulae) evaluation of wall interactions. The evaluation of surface charges, ionic streams, creation of the electrostatic double layer theoretically is possible with help of Derjaguin-Landau-Verwey-Overbeek (DLVO) theory [15]. Practically we are far from incorporating all necessary molecular and ionic interaction to our macro hydrodynamics, hence commonly used empirical expression called "hydrodynamic diameter", effectively shadows our lack of knowledge. In several cases such simplification is sufficient for chemical-engineering; it becomes unacceptable if size of particles strongly decreases. Any ionic layer, streams of ions attaching particle, steric interactions with suspended molecules, effectively decrease particle mobility. To predict such effects is crucial for understanding transport processes at the single cell level.

Figure 3 illustrates our attempts [16] to evaluate size effect for Brownian nano particles. It is obvious that decreasing their size, the effective (hydrodynamic) diameter strongly affects their diffusion.

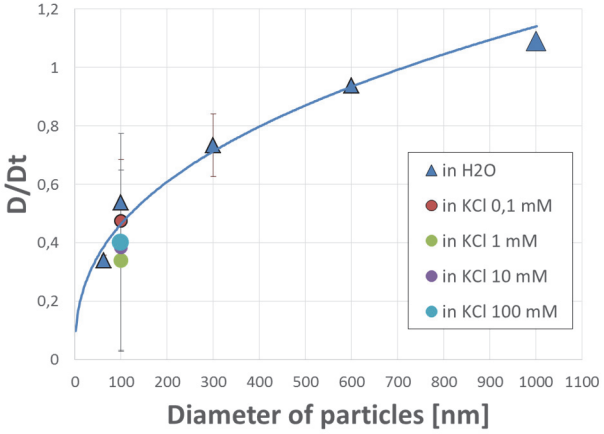

Figure 3: Relative diffusion coefficient measured for polystyrene nano spheres suspended in water and four different solutions of KCl

Detailed experimental analysis of interactions of liquid molecules and surface molecules of individual particle is very difficult. Hence, in practice more or less sophisticated hydrodynamic models are implemented to interpret observed variation of the apparent particle diameter (in fact friction coefficient). Such models used later for measuring and sorting macromolecules are in common use, despite questionable theoretical background given by fluid mechanists.

Recently, a new optical tool, so called Optical Tweezers (OT) expanded our traditional instrumentation creating possibility for undisturbed measurements of forces and position in picoNewton and nanometre scales. Dragging, towing single particle allows to perform precise analysis of forces involved by liquid environment, wall interactions, and particle-particle interactions. One of the fundamental problems of single particle mobility, namely ballistic regime and effects of inertia creating time dependent recirculation of surrounding liquid molecules, could be proven using OT [17]. Electronic way of signal analysis allows for thermal motion of particle trapped by OT to be evaluated with MHz sampling frequency and displacements below 1 nanometre. In our preliminary study [18] OT developed at IPPT have been used to analyse Brownian motion of trapped polystyrene particle. It appears that already at sampling times of 10kHz diffusion becomes influenced by ballistic regime of molecular interactions (Fig. 4).

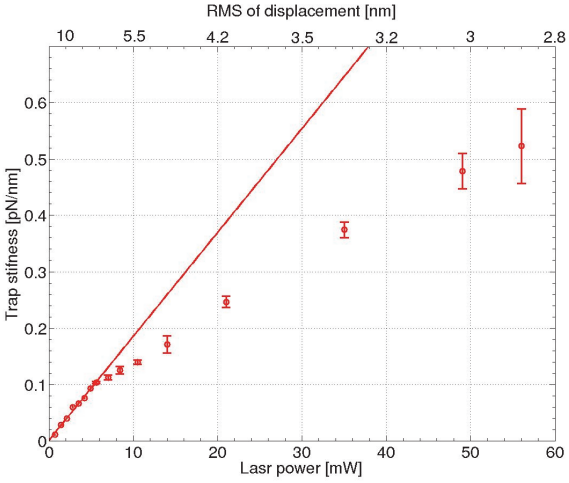

Figure 4: Stiffness of the Optical Tweezers evaluated for 1µm polystyrene particle suspended in water; particle diffusion increases as the mean Brownian displacement decreases (upper axis). Straight line - large displacements theoretical limit

4. Worm-Like Chain (WLC)

The flow of deformable objects (fibres, polymer chains) has non-Newtonian character, strongly influencing its short time response at microscopic level [19,20]. Under flow these objects are oriented, deformed, and coiled leading to a macroscopic variation of the transport properties. The microscopic structures, as well as the macroscopic response, depend on both the nature of the suspended objects and the flow configuration. Linking mechanical and microscopic properties of the suspended objects to the macroscopic response of the suspension is one of the fundamental scientific challenges of soft matter physics and remains unsolved for a large number of situations typical for intercellular transport of proteins and ligands.

Most of the biomolecules have strongly elongated form, far from idealistic ball like shape. Their penetration through the crowded cellular environment is strongly enhanced by its shape flexibility. The interplay between crowding and thermal bending allows for the controlled mobility.

For micro or nanoscale objects their natural shape deformation are induced by thermal fluctuation leading to some intriguing behaviour. For example, it has been predicted that long fibres may perform spectacular windings to form more or less stable knots, phenomenon of fundamental importance for biological macromolecules [21].

Despite the strong recent expansion of this field, it still lacks experimental investigations to validate the assumptions of the theoretical and numerical models. The lack of experimental studies is mainly due to the absence of good model systems that allow determining and controlling elasticity and geometry of analysed objects.

Observation of proteins or DNA is still mostly qualitative, limits of the optical methods permit to find out some predicted characteristics only. Therefore, to systematically investigate the influence of long molecules on their interaction with given flows and the resulting macroscopic properties, a synthetic models of flexible objects are useful. Hence, we aimed to produce flexible nanofibres to mimic behaviour of long chains of microparticles. Alas, winding of the objects predicted by simple Stokesian model could not be confirmed [22]. It was probably due too high stiffness of nanofibres used in the experiment.

Recently, we have developed new method allowing constructing highly deformable microscopic filaments with typical diameter of 100nm and contour length ranging from single micrometres to millimetres [23] (Fig. 5). Introducing them directly to microfluidic channels allowed us to observe their deformations due to the flow as well as those induced by thermal fluctuations. The last effect has additional advantage, analysis of thermal fluctuations of flexible objects is used to evaluate their *persistence length* [24], directly correlated with its mechanical properties. Typical values of persistence length obtained for our hydrogel filaments range from 5 nm to 70 nm, being very close to that reported for DNA chains (30nm).

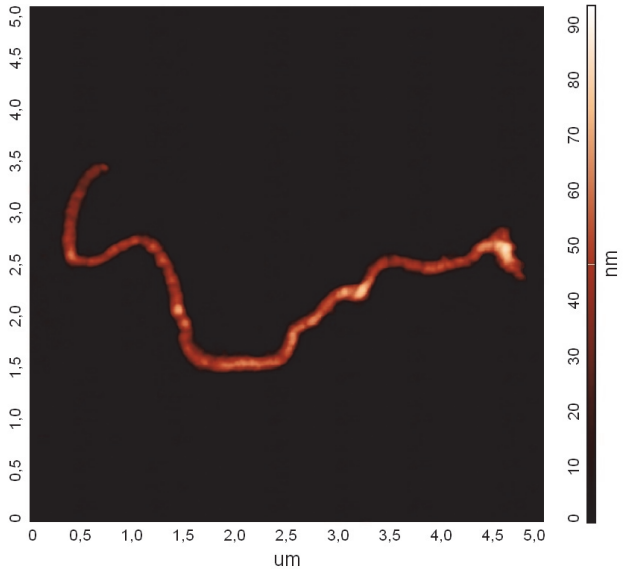

Figure 5: Hydrogel nano-filament observed under an atomic force microscope; contour length 7 µm, diameter 80nm [23]

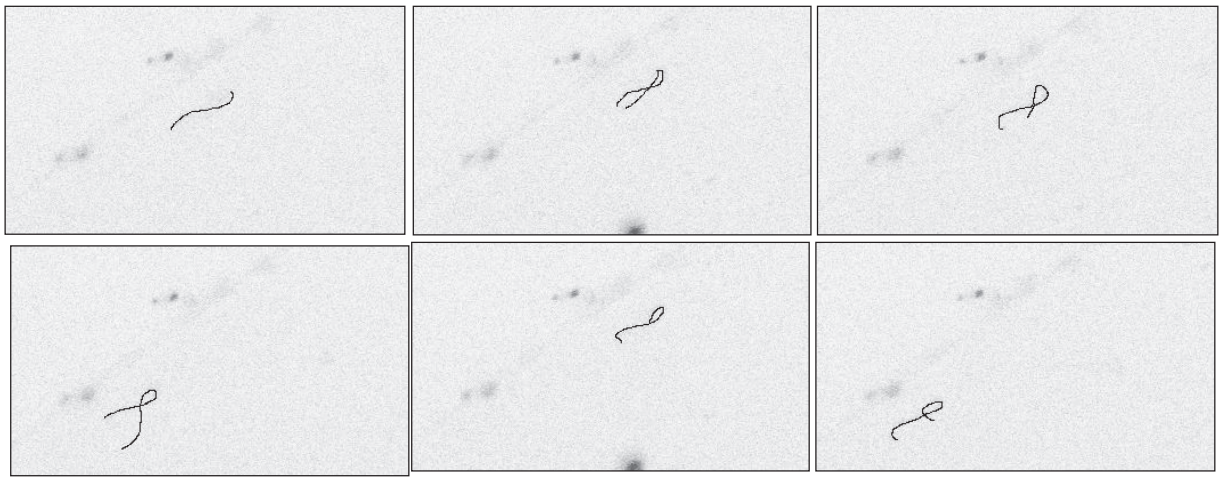

Figure 6: Single highly flexible nanofilament conveyed by Poiseuille flow in 100 μm microchannel. Filament of 100 nm diameter and contour length 25 μm. Flow Reynolds number based on the microchannel size equals $4 \cdot 10^{-3}$. Sequence of images (not ordered in time) extracted from the movie recorded under fluorescent microscope and displayed as negatives; image width ~50 μm.

Hence, we are able to validate worm-like chain models with material parametrization obtained from the experiment. This approach could in the future be used to gain further fundamental understanding of filaments dynamics under flow as a function of their complex properties as anisotropy or deformability. It is interesting to note that even for relatively low flow Reynolds number (Fig. 6) we observed typical coiling – uncoiling sequences. It is remarkable similar to WLC modelling performed with Stokesian approach [21,22]. Understanding the link between the microscopic structure of the filaments and the macroscopic flow properties opens the possibility to design nano-objects transported by body fluids for targeted drug release or local tissue regeneration.

5. Conclusions

Recent development of experimental techniques applicable to fluid mechanics of nano and microscale permits to have a closer look at applicability of existing mechanical models to small scale phenomena. In the following we have presented few selected problems characterizing nano and micro scale fluid dynamics, namely kinematic boundary condition at solid interfaces and suspension of nano scale intrusions, like nanoparticles and long, deformable filaments. In modelling of such nanoscale problems, similarly to solid mechanics science, there is still unsolved problem of merging atomistic scales with nano, micro and macro systems. In case of fluid mechanics there is additional difficulty, time stepping merging has to be performed for very short time scales. It is challenging, still not available approach. Therefore, we have to cope with simplified models, where solely experimental validation may offer background for tuning and adjustment of crucial model parameters.

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