

Nanomechanics Selected problems



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Nanofluids and Nanofibres

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Abstract: Micro- and nanofluidics is a new emerging field in fluid mechanics. It refers to the research and technologies dealing with small volumes of fluids (as small as micro-, nano-, pico- and even femtolitre of volume). On such scales the physics of fluids becomes dominated by interfacial phenomena, intermolecular and electrokinetic forces will play a significant role. Methods used by hydrodynamics on large scales often do not provide correct answer for such scales. Hence, several new research areas emerged from micro and nanoscale studies. Here, we concentrate on two of them: nanofluids concerning the behaviour of nanometre sized particles suspended in liquids, and quickly expanding research area of nanofibres – fraction of micrometre in diameter fibres produced by electrospinning.

Keywords: nanofluids, microfluidics, nanofibres, microrheology, optical tweezers.

2.1. Introduction

The beginning of nanotechnology had its unexpected origin during World War II. The development of radar provided a need for semiconductors. Miniaturisation of electronic devices created technologies used by nanotechnology now. However, some aspects of nanotechnology were used without understanding for centuries. An example is the technique of colouring window glass by adding metal nanoparticles, commonly used in the Middle Ages. Only at the end of the 20th century science advanced enough to help understand and control such phenomena. Hence, the official beginning of nanotechnology is commonly marked as 1959, when Richard Feymann presented in his famous lecture a visionary description of the 21st century micro- and nanomachines. As we now are in the 21st century, indeed it seems that nanotechnology, and biotechnology closely interconnected, are the major challenges for current engineering.

The progress of nanotechnology in its early years was very slow and the next milestone was achieved a decade later, in 1970 with the development of the first microprocessor. The official beginning, however, is marked 1981, when K. E. Drexler proposed the protein design as a pathway to molecular manufacturing [1]. Since that time nanotechnology has turned out to be one of the most rapidly expanding fields in engineering science. Nanotechnology in the 20th century restricted itself mainly to electronics and solid state physics. A series of important successful technologies were obtained enabling electronics boom and also improving design of materials. Especially the discovery of carbon nanotubes led to the design of strong materials with embedded nanostructure, now used even in the production of tennis rackets. The end of the 20th century and beginning of the 21st century moved the focus of nanotechnology research from solid state physics into the domain of fluids and fluid-solid interaction on nanoscale.

The main difference between macro- and nanoscale mechanics originates from the rapidly increasing surface to volume ratio along with a decrease of the object's size. The total surface of one nanometre particles filling the volume of a cubic centimetre is 6000 square metres! Hence, nanoscience is mainly a science of surface forces and surface interactions. It applies particularly to fluids. For micro- and nanofluidics the capillary action changes the way in which fluids pass microscale channels. In addition, there are unknown factors involved, especially concerning microscale heat transfer and mass transfer, the nature of which only further research can reveal.

The field of microfluidics is characterised by the study and manipulation of fluids on the submillimetre length scale. The fluid phenomena that dominate liquids on this length scale are measurably different from those that dominate on the macroscale. For example, the relative effect of the force produced by gravity in microscale dimensions is greatly reduced compared to its dominance on the macroscale. Conversely, surface tension and capillary forces are more dominant on the microscale. These forces can be used for a variety of tasks, such as passively pumping fluids in microchannels, precise patterning surfaces with user-defined substrates, filtering various analytes, and forming monodisperse droplets in multiphase fluid streams for a variety of applications [2].

When the dimensions of a device or system reach a certain size, the particles of fluid, or particles suspended in the fluid become comparable in size with the apparatus itself. This dramatically alters its behaviour. Another important difference between the macro- and micro- world is that most of tools or systems in macro-scale have a large number of moving parts (e.g. turbines, engines). In the micro-world this is not possible due to difficulties of manufacturing and also due to strong surface interaction between the moving parts. Hence, any micro-system is basically very simple, using basic physical principles. A micro-pump can be built by having a bubble in the channel and heating and cooling it. Expanding and collapsing the micro-bubble would block or unblock the channel and this causes the pump to work. This is a very different approach from complex mechanical pumps on a large scale. Similarly, other micro devices such as sensors, propellers, and engines are very simple designs.

Microfluidic systems have diverse and widespread potential applications. The idea of microfluidics is that fluids can be precisely manipulated using a microscale device built with technologies first developed by the semiconductor industry and later expanded by the micro-electromechanical systems (MEMS) field. These devices, commonly referred to as miniaturized total analysis systems (µTAS) or lab-on-a-chip (LoC) technologies, could be applied to biology research to streamline complex assay protocols. Some examples of systems and processes that might employ this technology include inkiet printers, blood-cell-separation equipment, biochemical assays, chemical synthesis, genetic analysis, drug screening and delivery, electrochromatography, surface micromachining, laser ablation, and mechanical micromilling. Not surprisingly, the medical industry has shown keen interest in microfluidics technology. The advance of the small scale allows performing analysis in minutes, while for a macro-scale a similar analysis can take hours or days. Also, the small scale allows implementing some devices into the patients' bodies, delivering drugs to specific organs or performing local surgery. Currently, several groups in the world are working on the drug delivery systems which may specifically target cancer cells. Such systems would be built by specially designed nanoparticles transported by blood flow and activated at the targeted place. For example, simple clustering of such particles can be used to stop blood perfusion in the vicinity of cancer cells. Such treatment will be much less invasive than currently used chemotherapy, which basically kills all cells, not just only cancer cells. Nanofluidics helps in understanding, controlling and modelling transport mechanisms of such nanoparticles. Hence, it has become an important part of nanomedicine, the new explosively growing application field of nanotechnology.

It is interesting to note how many valuable hints on the behaviour and explanation of micro-word indicates our mother nature, which evolutionarily 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 the 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 a flying bug and still remains untouched. On macro-scale the corresponding web would have to stop the whole aeroplane without damage, which obviously is still far from the current engineering capabilities. In our group we focus on applying nanofibres in materials science and tissue engineering [3].

Modelling fluid flow on micro- and nanoscales needs specific technique, which is based on the assumption that a fluid particle can be represented as a cluster of atoms. Effective clustering is based on the so-called Voronoi tessellation, describing a special kind of decomposition of the flow domain [4]. Our mother nature discovered this type of space decomposition a long time ago, for example assembling cells in a plant tissue.

Looking more carefully around us we find striking similarities between life and nanoengineering. Scientists are building micro-robots: flying like bugs, crawling like snails or walking on the ceiling like a gecko lizard. The lizard's foot has hundreds of fibres, and by controlling the distance between them, it can stick to any surface implementing use of van der Waals forces on the macro-scale. Full understanding of this process will help engineers to build better materials, glues and in the future probably allow humans and robots to walk on any surfaces.

By far the most difficult question which nanotechnology is facing is how to effectively produce tools and systems in nanoscale. And again the nature can help engineers to solve this problem. Any type of biological system is built from cells which form a more complex structure by organizing themselves. One of the current research tasks is to study the 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 an electron microscope, such technique is completely inefficient for mass production. Separately manipulating millions of atoms to cover a micro-metre 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 a plethora of valuable hints how to proceed with such process [5].

2.2. Experimental

The specific needs of nanotechnology forced the development of several new tools and methods to record and analyse specific phenomena. Some of these tools came from electronics (production of microsystems), some from materials science (X-ray and electron microscopy), but most of them were adopted from biology, where imaging and biophysical analysis in microscale is an everyday task. Fluid flow analysis has specific needs, like an accurate evaluation of velocity, temperature and pressure fields. In microscale such measurements have to be done not only with high spatial resolution, but also with high temporal resolution. If we imagine any micro- or even nanoobject under a microscope its relative speed appears magnified proportionally to the magnification factor of the system. Hence, high-speed imaging is inevitable in most of the microfluidic studies.

The need to get detailed and accurate measurements in micro-scale devices enforces the application of new experimental techniques, unusual in the classical fluid mechanics. One of them is micro-PIV, full field microscopic velocity measurement using fluorescent tracers with the dimension of only several nanometres [6]. The technique refers to the application of Particle Image Velocimetry [7] to measure velocity fields of fluid motion with length scales of the order of 100 micrometres, and with the spatial resolution of individual velocity measurements of the order of 1–10 micrometres. Due to the small dimensions light sheet technique, typical for macroscale PIV, cannot be applied for flow illumination, and the whole investigated volume is flooded with light. Images of individual tracers, necessary for PIV evaluation, are obtained by taking advantage of fluorescence, removing by appropriate filters diffused light originating from the bulk illumination. The emphasis of contemporary micro-PIV is placed on its ability to measure accurately and reliably two-dimensional velocity fields with the spatial resolution below limits imposed by optical diffraction.

The fundamentals of the micro-PIV method were established by Santiago et al. [8], over one decade ago. Currently using a microscope, an image intensified CCD camera, pulsed laser light, and narrow wavelength optical filter one may obtain discrete images of the fluorescent tracers with spatial resolution of fraction of micrometre and temporal resolution of dozen of nanosecond. Figure 1 shows a typical micro-PIV system used at IPPT PAN for micro-fluidic studies. Correlation analysis is applied to the particle image field, producing a regularly spaced velocity field. The velocity measurements in the form of two-dimensional vector field allow a detailed analysis of microflow structures [9,10].

Scaling down a micro-PIV system is limited by optical resolution. Nevertheless, if the concentration of tracers is low enough, localisation of Airy diffusion disk centre appears sufficient to identify the position of nanoparticles. In such case nanotracers may additionally play the role of local thermometers. Their Brownian motion overlapping flow induced translation can be separately evaluated and used to obtain an important thermal field difficult to measure in micro-scale [11].

A similar optical configuration is used for particle tracking, where long sequences of images are collected to analyse their displacements. In this way the Brownian motion of fluorescent nanoparticles is used to evaluate fluid properties (microrheology) and particle properties (hydrodynamic diameter, shape). The tracking of single tracer particles or even single, labelled molecules has become a standard tool to probe the dynamics of tracers in living biological cells or other microscopic systems. Single particle tracking has become a tool of choice to investigate the effect of molecular crowding, the superdense environment present in the cytoplasm of living biological

cells. In fact, the observed motion of freely diffusing molecules and tracers in living cells exhibits significant deviations from the linear time dependence of the mean squared displacement characteristic of the Brownian motion [12,13].



Fig. 1. Typical micro-PIV system using double-pulsed laser and epifluorescent microscope; excitation and emission wavelengths matched with Rodamine based micro-tracers [9]

Classical microscopy used for nanoscale observation has a resolution limited by the light wavelength of about 0.5 micrometres limits. Evaluating diffraction disks position particle coordinates in plane perpendicular to the optical axis can be improved by an order of magnitude. However, the resolution in depth, along the optical axis remains very low (tenths of micrometre), defined solely by the focal depth of the microscope lens. Total Internal Reflection Microscopy (TIRF) helps to bypass some of these limitations offering the possibility to locate objects' position with the resolution of about 20 nm. Laser light illuminating an object undergoes total internal reflection at the 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 [14]. The main advantage of the method is the possibility to reduce the depth of focus of the system below 100nm. Hence, it became possible to obtain images of particles which are in direct vicinity of the wall. All other particles suspended in the liquid stay out of the illuminating sheet and are practically invisible to the acquisition system.

The TIRF system can be used to analyse particle wall interactions, specifically to elucidate problem of wall slip condition for the adjacent flow field. In our study of the Brownian motion of fluorescent particles observed close to the wall, the deviation of the particle diffusion rate could be interpreted as evidence of the flow slip boundary conditions [14].

Another optical tool useful for 3-D nanofluids study is confocal microscopy, laser scanning illumination system developed primarily for life sciences. Confocal microscopy makes use of coherent (laser) light property allowing focusing it to a tiny pinhole, and this way rejecting the light out of focal plane of the lens. It permits obtaining vertical resolution of fraction of micrometre, hence comparable to the in plane optical resolution of the microscope. Tracking nanoparticles with such a tool is possible, however, the laser scanning time limits the temporal resolution of such 3-D imaging. Nonetheless, it was successfully applied to visualise the Brownian motion of deformable fibres, where imaging the out of plane motion becomes necessary to evaluate the rotation and deformation of the tracked object [15].



Fig. 2. Evanescent wave illumination, laser light reflects at a specific angle from the glass wall creating thin evanescent light beam penetrating liquid along the wall. Particle distance from the wall can be measured from the scattered evanescent light intensity

Manipulating micro and nanoobjects became possible with two other nanoscale methods: Atomic Force Microscope (AFM) and Optical Tweezers (OT). AFM resembles the principle of piezoelectric gramophone head. Sharp needle (cantilever) with a tip radius of curvature of few nanometres moves along the interrogated surface and its deflection is measured using laser beam reflection. High sensitivity of nowadays electronic systems allows measuring deflections of the order of a fraction of nanometre, hence detecting forces on the molecular scale. AFM appears to be a useful tool for elucidating the origin of the particle-wall and interparticle interactions, evaluating changes of the particle surface to the ionic and steric interactions [16]. It is also used to obtain mechanical data about deformability of long polymeric chains, DNA or nanofibres. Specific extension of AFM nanoscale manipulator offers Optical Tweezers (OT), laser systems allowing trapping of nanoobjects within a focused light waist and measuring exerted forces with piconewton sensitivity. Despite complicated setup systems based on OT the principle became more and more commonly used to manipulate biological molecules, DNA, or to evaluate the Brownian motion of nanoparticles [17].

2.3. Micro- and Nanofluidics

In microfluidics, the flow is predominantly laminar, creating challenges in the design of actuators such as mixers and sorters. The extremely low Reynolds numbers associated with microfluidic flows mean that inertial effects cannot be used to sort particles, yet the ability to select and sort both colloidal and biological matter in a fast and efficient manner related to its physical properties is a key requirement in this environment. Extensive investigations have been conducted in order to trap and sort cells and particles using innovative active techniques, such as dielectrophoresis, magnetophoresis, acoustophoresis, and optical tweezers.

In practice most microfluidic problems concern the 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 tools is based on the Brownian motion, analysed using optical methods [18]. It gives a basis for new tools of probing properties of complex fluids called microrheology of nanofluids. The local and bulk mechanical properties of a complex fluid are extracted from the motion of probe particles embedded within it. Particles are forced by thermal fluctuations and probing their concentration or position, statistical parameters are extracted to be used for generalized Smoluchowski-Einstein molecular diffusion model [19,20]. The importance of the Brownian motion was rediscovered after nearly two hundred years of the first observations [21]. Not only is it a tool for studying thermal fluctuations of nanoparticles, but is also used as an important stochastic methodology driving the development of mathematical models for areas far from physics, such as the development of financial markets [22].

Thermal fluctuations are not only noises, it has been demonstrated that fluctuations are fundamental to the function of biological systems. Here, several results are possible with some 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 usually been 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 [23,24]. 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 living species, and on a short time scale to create signalling paths for an early immune response of individual cells [25].

The displacement of a particle undergoing the Brownian motion is obtained by solving the diffusion equation under appropriate boundary conditions [20]. It shows that the displacement varies as the square root of the time. However, on very short time scales, the motion of a particle is dominated by its inertia and its displacement will be linearly dependent on time. Recently, the instantaneous velocity of a Brownian particle (a glass microsphere trapped in air with Optical Tweezers) was measured successfully

[26]. The velocity data verified the Maxwell-Boltzmann velocity distribution, and the equipartition theorem for a Brownian particle.

The studies of Li et al. [26] demonstrated the ballistic motion of particles in the air. Huang et al. [27] used water as a medium. The Optical Trap with a fast position sensitive detector allowed observing for 1 μ m particles the transition from ballistic motion to diffusive motion. It was found to take place on time scales below 0.1 μ s. It is worth of note that in their experiments the resulting single displacements of particles observed for the time of 0.02 μ s are of the atomic scale (0.3Å)! The experiment confirmed previous hints from computer simulations, suggesting quite complex transition from the ballistic to diffusive regime. In particular, hydrodynamic vortices in the liquid created by the particle's motion lead to memory effects, and the particle's velocity decays much more slowly than exponentially, exhibiting a "long-time-tail" [28]. These observations, besides the fundamental meaning for physics of fluids, have also practical potential. Extending measurements to the ballistic Brownian motion in confined regions should help understand the details of prediffusive motion over subnanometre distances, relevant to microbiological processes [29].

As we scale down the size of suspended objects their behaviour starts to depend not only on hydrodynamic forces but also (or mainly) on complex molecular and electrostatic interactions. Additional complications arise due to the local heterogeneity, amplified if the size of the suspended object approaches molecular dimensions. Analysing the diffusion of macromolecules should take into account their biological localisation, sizes and shapes, and positions in three dimensional space. Intermolecular interactions (both specific and nonspecific, repulsive and attractive) should also be included. Ideally, the modelling of such systems should be performed at atomic resolution. However, due to the micrometre size of an average cell and a large number of components occupying its volume, reductionist (coarse-grained) approaches are unavoidable [30]. Although the hydrodynamic approach is valid only on scales of length and time much larger than these characteristics at the molecular level, it is possible to show the gap between the microscopic and macroscopic definitions by phenomenological extrapolation of hydrodynamic results. If we concern the hydrodynamic regime, where the local properties of the fluid vary slowly on microscopic scales of time and space, there exist the conserved microscopic variables that satisfy the continuity equation and constitutive relations between fluxes and gradients (e.g. momentum and pressure). To obtain such expression it is necessary to evaluate the hydrodynamic limit for the appropriate time-correlation function.

On small scales it becomes obvious that the average bulk fluid main property, namely density, is spatially varying due to atomic or suspended particle fluctuations. Nonhomogeneous situations appear at the interfaces due to the surface tension. Interaction of liquid molecules at walls is responsible for strong variation of surface energy, wetting or repulsion. Fluids confined on microscale by walls containing nanopores locally exhibit granular properties, e.g. biological cells membrane. In this context we may expect severe deviations from the classical understanding of particlefluid interactions based purely on simple hydrodynamic interactions. Hydrodynamic interactions are forces between suspended particles that are transmitted by fluid motion. When analysing the Brownian motion they are usually approximated as a dissipative force given by Stokes formulae for a sphere moving in fluid. However, it has to be underlined that Stokes formulae are based on hypothetical assumptions linearizing momentum transfer given by Newtonian mechanics. Hence, any deviation from the ideal case is corrected using any arbitrary definition of the so-called "hydrodynamic diameter", which is the phenomenological dissipation coefficient which appears to depend on a large number of factors. It results in the observed deviations of the measured diffusion constant D and expected theoretical value D_t , based on the physical size of sphere (cf. Figs 3, 4).



Fig. 3. The evaluated effective hydrodynamic diameter of nanoparticles represented as diffusion ratio depends on ionic strength of the medium and its steric interactions. Brownian diffusion of single fluorescent particles changes with their surface area

In dilute solutions, their sizes, shapes, temperature, and solvent viscosity determine the diffusional properties of molecules treated as rigid bodies. The complete information required to describe translational and rotational motions of Brownian particles in dilute solutions is contained in their diffusion tensors. The translational diffusion coefficient is an average over the diagonal terms of the tensor. For a spherical molecule, diffusion is isotropic, the diffusion tensor is diagonal, and the molecule can be described with a single translational and a single rotational diffusion coefficient. The translational diffusion coefficient determines the time dependence of the diffusion of the particle's centre of mass. In a biological setup, solutes interact with their environments and other molecules, which affects their Brownian motion, thus single-particle diffusion tensors are no longer the unique determinants of diffusion. Nevertheless, the relation between the mean square displacements and time (not necessarily linear) can still be used to measure the apparent translational diffusion of molecules.

The influence of environments on the diffusion of macromolecules is manifested

through the intermolecular and electrostatic forces acting on individual particles. The types and functional forms of interactions vary depending on the level of detail used to describe the studied systems. The DLVO (Derjaguin-Landau-Verwey-Overbeek) model [31] is commonly applied to include electrostatic effects to describe electrostatic effects. Non-specific interactions between molecules can be described with the Lennard-Jones type functions that are commonly used in molecular dynamics simulations to compute the van der Waals interactions between atoms [32].



Fig. 4. The effective hydrodynamic diameter of nanoparticles depends on the ionic strength of surrounding fluid (left) and steric interactions with surfactant molecules (right). Thickness of these layers may vary from several nanometres to fractions of micrometer

A further complication of nanofluids description appears when flexible molecules are analysed. They are usually described in a reduced way with spherical subunits (e. g., as in the case of model spherical proteins or bead-models of flexible polymers). The distances over which biological molecules and their complexes can operate range from a few nanometres, in the case of folded structures, to millimetres, for example, during chromosome organization. The level of theoretical description of macromolecules dynamics depends on the length scales, which vary from 0.1nm for chemical bonds to over 1000nm for hydrodynamic interactions. In most models it is assumed that in the case of DNA chains the persistence length scale beyond 150 bp \approx 50 nm suffices to treat dsDNA as a stiff elastic filament without explicitly modelling the base-pairs [33].

Describing the phenomena that cover such diverse length, and also time scales, requires models that capture the underlying physics for the particular length scale of interest. Theoretical ideas, in particular, concepts from polymer physics, have guided the development of coarse-grained models to study folding of DNA, RNA and proteins. More recently, such models and their variants have been applied to the functions of biological nanomachines. Simulations using coarse-grained models are now ready to address a wide range of problems in biology.

In fluid mechanics insights into many phenomena involving an immersed body have emerged from analytic theories of models based on the mechanical approach. However, complex problems in biology such as protein and RNA folding and functions of macromolecules, have resisted solutions using purely mechanical methods. Additionally, small-scale transport phenomena appeared to be qualitatively and quantitatively different from the simple models assuming constant viscosity of base fluid. It becomes obvious that the necessary assumptions made to construct the multiscaled numerical models covering all these effects need experimental validation [34].

One of the most intriguing phenomena associated with long molecules dynamics is the loop formation, an elementary process in the self-assembly of DNA, RNA and proteins. The problem of loop cyclization seems to be relevant in controlling gene expression and DNA condensation, hence its understanding plays an important role in molecular biology. An important role in this mechanism is played by thermal fluctuations [35]. Replication and passage of genetic information to daughter cells, major events in cell reproduction, are likely driven by complex and well-orchestrated thermal fluctuations of tightly confined polymer chains. DNA is an unusually stiff, highly charged polymer. The stiffness is due mainly to base stacking and the double helical structure, whereas most of the charge is accounted for by the phosphate backbone. These remarkable physical properties are vital to biology; for example, proteins exploit them to transcribe, package, regulate, and repair the information encoded in the sequence of nucleotides that comprises the DNA.

Deformability and elasticity of long DNA chains resemble the properties of long polymer nanofibres. There are several attempts to describe fibre suspension using simple Stokesian fluid dynamics. Recently the bead-spring model [36] developed at IPPT, applied to simulate the dynamic behaviour of fibres in Poiseuille flow, surprising replicated some coiling-uncoiling sequences only due to the hydrodynamic interactions.



Fig. 5. Definition of slip velocity Us and slip length λ for fluid flow over solid wall

The classical no-slip hypothesis for the tangential velocity of the liquid adjacent to the solid surface became questioned for the flow in micro- and nanofluidic devices. The topic is of fundamental interest and has potential practical consequences in many areas of applied sciences. For small-scale geometries this slip can be significant permitting nearly frictionless flow in 2nm carbon nanotubes [37]. Hence, several experimental and numerical studies have been performed to demonstrate and explain the presence of the molecular-scale slip at the fluid-solid interface (see the reviews by Neto et al. [38], Lauga

et al. [39]). The key factor is that the continuum fluid dynamics still holds within the interior of the liquid and the slip is due entirely to discontinuity in the speed between the wall and adjacent liquid layer. The slip is usually viewed from the averaged flow properties over all liquid molecules near the solid boundary and expressed as slip length, which is determined by extrapolating the velocity profile beyond the channel wall (Fig. 5). The amount of the slip is quantified in terms of the shear rate and local flow velocity. The slip condition in the case of channel walls has a relatively simple interpretation and possibility to validate its value experimentally [14]. The slip boundary condition has to be accounted for suspended nanoparticles as well, modifying the description of the particle surface – fluid interactions. These combined with electrostatic effects (ionic double-layer) or/and steric effects (attached surface active molecules) makes the proper description of nanoparticle mobility really challenging.

2.4. Nanofluids

The term nanofluids became reserved for specific suspensions of nanoparticles, namely those where enhanced heat conduction is expected. The term was proposed in 1995 by Choi of the Argonne National Laboratory [40], who described nanofluids as the next-generation heat transfer fluids offering exciting new possibilities to enhance heat transfer performance. The suspensions of nanoparticles appeared to have superior properties compared to conventional heat transfer fluids, as well as fluids containing micro-sized metallic particles. The plausible interpretation of the effect is based on much larger relative surface area of nanoparticles compared to those of conventional particles. This should not only significantly improve heat transfer capabilities, but also increase the stability of the suspensions. Successful employment of nanofluids should support the current trend toward component miniaturization by enabling the design of smaller and lighter heat exchanger systems. Keblinski et al. [41] made an interesting simple review to discuss the properties of nanofluids and future challenges. Later on an avalanche of publications appeared confirming or partly confirming the existence of such heat transfer enhancement.

The theoretical considerations are based on the Maxwell evaluation of effective medium thermal conductivity for solid suspensions. However, this macroscale model shows only a slight linear variation of the thermal conductivity of dilute solid suspensions as the volume concentration of particles increases. It completely fails to predict reported significant change of the thermal conductivity of typical nanofluids (usually nanoparticles of metallic oxides in water or oil). Hence, it was suggested that the Brownian motion of nanoparticles could somehow enhance mixing and improve overall heat transfer in nanofluids. Another possible explanation is based on the effective increase of the nanoparticle size by aggregated molecules of the base fluid. Such process in fact increases the hydrodynamic diameter of the particle, but it effectively decreases its Brownian diffusivity, acting in the opposite direction. Hence, looking at typical thermal properties of liquids and metals (Table 1), and the effective change of thermal conductivity of selected nanofluids, one may have doubts, if any significant improvement of thermal conductivity is present. One has to remember an unavoidable increase of apparent viscosity of such suspensions; hence the cooling efficiency of nanofluids is additionally degraded by increased pumping work.

Table 1

Material	Thermal Conductivity (W/M.K) (at 300K)	Source
Alumina (A2O3)	40	Sarit K. Das et al. [42]
Water	0.613	Sarit K. Das et al. [42]
Alumina in water 4% vol.	0.647	Sarit K. Das et al. [42], Fig. 3.20
Polyalphaolefins oil (PAO)	0.161	Boungiorno et al. [43], Table VI
Alumina nanorods 80nm x 10nm in water 1% vol	0.627	Boungiorno et al. [43], Table VI
Alumina nanoparticles 10nm in PAO + surfactant 1%vol	0.162	Boungiorno et al. [43], Table VI
Alumina nanoparticles 10nm in PAO + surfactant 3%vol	0.174	Boungiorno et al. [43], Table VI

Thermal conductivities of liquid, particle components of nanofluids and selected nanofluids

Experimental confirmation of these mechanisms is weak. It stimulated Buongiorno and his colleagues [43] to perform an international benchmark, offering several group samples of nanofluids to be experimentally tested to find out possible improvement of the thermal conductivity. The conclusion is disappointing; the summary of experimental data from 34 organizations suggests no anomalous enhancement of thermal conductivity. But nanofluids research still continues.

2.5. Nanofibres

Nanoparticles and nanofibres belong to the same family of small dimension objects used in nanotechnology. Whereas nanoparticles are commonly used in medicine for diagnostics, polymeric nanofibres appear to be a very promising material for tissue engineering, tissue protection, and drug delivery.

Instability of the liquid column and mechanical fracture of the fibre are the main limitations of the process. In the absence of external forces, the resulting radius of the jet depends on the orifice diameter only. Due to surface tension and interfacial forces at the orifice it is impossible to directly generate very thin jets in the micrometre range, so that stretching appears as the only alternative to bypass this limit. However, due to the capillary instability and aerodynamic forces, the length of liquid filaments obtained in such a way is limited to a few hundreds diameters only. Hence, using the mechanical spinning technique it is possible to obtain filaments of a few micrometres only. Further improvement of the process makes the electric field possible. The electrostatic forces may lead to new ways for farther elongation of the material. The charged liquid jet experiences bending instability and executes spiralling motion when accelerated towards the collector. For solidifying polymers, the looping instability results in extreme elongation values [3]. The axial tension of a fibre, provided by electrostatic forces, leads to elongation ratios of 10000 and more without breaking the thread. The resulting nanofibre is often collected as an interconnected web of thin filaments (fibre mat) on the surface of a grounded target.

Currently, the most common methods for making nanofibres use either an electrostatic charge (electrospinning) or external air jets [44,45]. The versatility and simplicity of electrospinning makes it particularly interesting [46]. It has already been applied to more than 20 different polymer types including PA, PP, PE, PAN, PEO, Nylon-6, polyaniline and aramids [47-49].

Despite the simplicity of the electrospinning technology industrial applications of electrospinning are still relatively rare, mainly due to the unresolved problem of the very low fibre throughput for the existing devices. Collection of experimental data and their confrontation with simple physical models appears to be an effective approach towards the development of practical tools for controlling and optimising the electrospinning process.

A simplified physical description of the main phenomena involves charge density, electric field geometry, mass and charge flow rate, variation of fluid parameters and initial conditions. The model proposed by Reneker et al. [50,51] we used [3] to perform a sequence of simulations varying few of the control parameters and analysing shape of fibre tracks produced by the model. According to the model, the jet dynamics is governed by a set of three equations representing the Maxwellian model of stretching the viscoelastic segment, mass and momentum conservation for the electrically charged jet segments. In our computer simulation a set of electrostatic charges coupled by viscoelastic one-dimensional elements subjected to surface tension effects evolves within a static electric field. The electrostatic field is modelled by a sphere-plane capacitor configuration, where the spherical electrode represents the injector and the infinite plane electrode represents the collector. The fibre-induced field is in turn approximated by considering only short range electric interactions.

Due to its simplicity the model described above is far from the realistic configuration. It assumes the fibre as an ideal insulator of constant physical properties and induced charges moving in vacuum. To simplify the analysis we neglect very important for polymers effects of solidification. The fibre is represented as a chain of one dimensional dumbbells, hence the capillary instability is absent. Despite these limitations some characteristics of the simulated fibre paths can be related to the observations (Fig. 6). It was possible to evaluate the effects of surface tension, elastic modulus, conductivity, and electrostatic potential on the jet stability and its bending amplitude [3, 52].

Most of the current applications of nanofibres concentrate on biomedicine. The nanofibrous mats produced from biodegradable polymers by collecting nanofibres on specially designed targets (rotating disks, drums, or water surface) are used for scaffolds in tissue engineering, wounds protective material, and to construct drug delivery systems. It is due to their high porosity allowing cell migration, nanometre structure, which resembles extracellular matrix, and the ability to also use natural materials (proteins) as the nanofibrous material. Such materials as collagen, elastin, keratin, silk, fibrin clot, BSA, and chitosan are successfully applied for nanofibrous scaffold fabrication.



Fig. 6. Electrospinning of nanofibres: experiment (left) and numerical model (right) [3,52]

Nanofibrous mats used for drug delivery need several modifications to fulfil not only biocompatibility of the material but also the possibility to bind specific drug, and what is even more challenging, to control its release. The desired release time may be of the order of days or weeks, and it is crucial to keep constant, controlled over this period of time. Several techniques are used to insert drugs into electrospun material, besides simple mixing, producing core shell materials with drug solution encapsulated within the fibre core, or two-phase composition of basic polymeric material with suspended emulsion containing the drug solution. Each of the approaches depends on the drug properties, solubility, and hydrophobicity.

Recently, successful application of nanofibrous mats has been demonstrated as effective and controllable delivery of therapeutic agents for neurosurgery [53,54]. The main advantage of nanofibrous mats in that context, namely their structural similarity to extracellular collagen matrix, appeared to have a positive effect for tissue regeneration [55]. The flexibility of composing polymer mixtures offers the possibility of employing nanofibrous mats for drug delivery systems [56]. The material composition or fibre arrangement can be adjusted to modify the release process. Engineering of the material with desired porosity and fibre morphology affects the diffusion transport and therefore opens the possibility for controlling the dynamics of drug release from the material. Depending on hydrophobic or hydrophilic properties of the released drug,

the composition of the serum substitute is based on the chemistry of released drug. Usually the release of hydrophobic drugs is conducted in a dilute solution of sodium dodecyl sulphate (SDS) that contains micelles capable of absorbing drug molecules. Hydrophilic drugs are released in phosphate buffered saline (PBS), which provides a physiological pH. The aliquots collected after the predetermined time intervals are analysed to provide quantitative data of the released drug (or its fluorescent analogue). Our experimental and numerical investigations [57, 58] allowed building a system for evaluating drug release profiles for selected nanofibrous materials, their structure, composition or morphology (cf. Fig. 7). The characterization includes determination of burst release, time of reaching release plateau and its values.



Fig. 7. Structure of nanofibres mat observed under electron microscope (left), and its Finite Element representation used for numerical simulations of drug release process (right) [57,58]

2.6. Conclusions

We hope that this short introduction has elucidated a few fundamental issues prominent for micro and nanoscale fluid mechanics, absent or neglected for the classical flow description. For the microflow regime the characteristic dimension, defined by a channel or suspended particles geometry, imposes the consideration of molecular, electrostatic, and surface forces dominating locally over mass the forces present in macroscales. In addition, on nanoscales the number of molecules involved in the flow becomes an issue, confirmation changes of molecules and scholastic character of interactions leads to severe deviations from the averaged description offered by continuum mechanics. New tools, both in experiments as well as in computational simulations, are necessary to have a better insight into the rules governing on such scales.

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