Brownian motion in confined geometries

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Abstract. In a great number of technologically and biologically relevant cases, transport of micro- or nanosized objects is governed by both omnipresent thermal fluctuations and confining walls or constrictions limiting the available phase space. The present Topical Issue covers the most recent applications and theoretical findings devoted to studies of Brownian motion under confinement of channel-like geometries.

Diffusion is a universal phenomenon controlling a wide variety of physical, chemical, and biochemical processes. A deep understanding of the diffusion mechanisms of nano- and micro-sized objects serves as a sound footing for creating the methods of an efficient control of mass and charge transport. Diffusion under strong confinement is typically encountered in biological cells, zeolites, catalytic reactions occurring on templates or in porous media, separation techniques of size-dispersed particles, and many other systems of Nature and technology. Interestingly, the restrictions of the phase space resulting from geometrical boundaries are able to change the transport characteristics significantly, sometimes bringing about quite counter-intuitive results.

Variations of the geometrical constriction along the direction of motion imply changes in the number of accessible states of the particles, which, at one-dimensional description, result in spatial variations of entropy. Consequently, bottlenecks and other geometrical obstacles lead to entropic barriers. These entropy variations are hindering or promoting particle transport to certain regions (for a minireview see [1]). Along with the progress in experimental techniques, theoretical methods to investigate the kinetics of entropic transport were developed. Studies by Jacobs [2] and Zwanzig [3] stimulated the theoretical efforts to further analyze an important approximate description of diffusion in corrugated channels – the so-called Fick-Jacobs approach. This approximation was revisited by Reguera and Rubi in 2001 [4] and, in the following decade, advanced with respect to (i) extremely corrugated straight channels [5, 6], (ii) to channels with curved midline [7], (iii) to forced diffusion [8], (iv) to the impact of inertia [9, 10], (v) to the presence of a hydrodynamic flow field

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Fig. 1. A corrugated channel confining the overdamped motion of point-like Brownian particles with a unit cell marked by the separating dashed lines. The field lines depict a typical external force field acting on the particles. It results from a competition of a constant bias and an oppositely oriented divergence-free force from a pressure driven solvent [11].

[11], and (vi) to the effect of particle-particle repulsion [12], to name but a few. In general, in the spirit of the Fick-Jacobs approach, spatial variations of the confinement are taken into account by means of not only an effective entropic potential contribution, i.e. the potential of mean force, but also an effective, coordinate-dependent diffusion coefficient. The transport through periodic two- and three-dimensional channels exhibits characteristic and peculiar phenomena [1]: besides of certain scaling laws, the mobility increases with decreasing temperature and an enhancement of diffusion may take place [13]. Beyond the applicability of the Fick-Jacobs approach [14], i.e. in the limit of septate periodic channels, different approaches are necessary [15, 16]. Nevertheless, the Fick-Jacobs approach succeeded – at least qualitatively – in explaining the particle transport through arrays of cylindrical obstacles arranged in a square lattice [17, 18]. Furthermore, it can be applied to the case of time-dependent forcing and closed geometries as demonstrated by the entropic stochastic resonance [19]. It was also shown that in the presence of time-dependent forcing, channels with broken reflection symmetry are capable to separate particles of different sizes [20]. Theoretical advancements come along with new experimental techniques such as microfabricated devices [21] which will allow one to test the theoretical predictions.

In addition to potential technological applications in the developing field of micro- and nanofluidics, understanding the physics of diffusion under conditions of strong confinement is crucially important for a number of biological problems. In many respects these transport phenomena can be regarded as diverse manifestations of geometrically constrained Brownian dynamics in one or higher dimensions.

Though the progress in theoretical understanding of Brownian motion in confined geometries is quite impressive and, by now, has been expanded to include hydrodynamic effects (see Fig. 1) and finite size particles, the complexity of real systems, especially in biology, presents a huge challenge. Indeed, as a biological cell is a very crowded place, the natural confinement in the cell changes equilibria and kinetics of intermolecular reactions, leading to unexplored and often unexpected anomalous behaviors. Moreover, additional complications stem from the fact that a significant fraction of transport processes in the cell is about transport of polymers, either within cells and organelles or across their membranes. Modern research demonstrates that beta-barrel membrane channels are able to serve as conduits for peptide polymer

Fig. 2. A cartoon of translocation of alpha-synuclein (a neuronal water-soluble protein 140-amino acid long involved in the etiology of Parkinson disease) through the alpha-hemolysin channel beta-barrel pore [22]. The highly negatively charged C-terminal tail of the alpha-syn molecule (red solid line) enters the channel from the trans-side and goes past the channel constriction by length x .

transport [22] across cellular and organelle membranes (see Fig. 2). It is clear that polymer molecules can hardly be represented by mathematical points or even finite size spherical particles, which necessitates the extension of the theoretical approaches to particles with more elaborate structures. In particular, the entropy effects coming from the restrictions on the number of structural conformations available for translocating polymers [23] should be incorporated into the future approaches.

The present topical issue concentrates on both the theory and experiment of mass and charge transport in artificial and natural micro- and nano-structures, with the goal to present the current understanding of the diffusive mechanisms in confined geometries. The theoretical findings come along with new experimental observations in biological channels, porous materials, and newly developed artificial nano-pores with tuned particle-pore interactions.

The idea of this topical issue is a result of the workshop devoted to the Brownian motion in confined geometries. It was hosted by the Max Planck Institute for the Physics of Complex Systems in Dresden, Germany, in March of 2014. The workshop was attended by many world leading scientists in theory, experiment, and mathematics of confined diffusion, with most of them agreeing to contribute reviews and original articles.

The state of the art of the theory of Brownian motion in various geometries is presented in the first contributions. In a comprehensive review Kalinay [24] discusses reduction methods for mapping 2D or 3D transport in corrugated channels onto the longitudinal coordinate. Pineda et al. [25] introduce the Fick-Jacobs formalism focusing on the different proposals for the effective position-dependent diffusion coefficient which appears in the reduced dynamics. The applications and limitations of the concept of entropy potentials arising in the one-dimensional description of transport of ions and molecules are discussed by Berezhkovskii and Bezrukov [26].

Reguera and Rubi [27] concentrate on a control problem with the goal of optimizing the shape of the confining tube. In the article by Martens et al. [28] it is shown that hydrodynamic flows through thin channels can induce unexpected effects in transport of tracer particles. Application of the functional density theory to the problem of diffusion of strongly interacting Brownian particles is discussed in the contribution by Löwen and Heinen [29].

The three following contributions give a critical analysis of specific experimental approaches representing the state of the art in the field. Sturm et al. [30] present a

theory of dynamic force spectroscopy that unifies the limits of slow and fast loading. In the contribution by Pagliara et al. [31] a detailed guideline for the fabrication and manipulation of micron-scaled channels on microfluidic chips is given. Their experimental setup serves as a scaled-up model for diffusion in biological membrane channels. Krause et al. [32] concentrate on fluctuation phenomena in electrochemical signals from nanoscale detection devices.

A number of articles are devoted to biological macromolecules. Dorfman et al. [33] analyze behavior of worm-like chains such as DNA confined in a slit or a channel using experiments, numerics, and theory. Relaxation of a polymer, either flexible or semi-flexible, initially wrapped around a rigid rod is investigated by Walter et al. [34]. Problems of active motion have been treated in the two articles by Klein et al. [35] and Ao et al. [36]. The first article reports on fluctuation-induced bidirectional motion in the tug of war model, the second one studies the properties of stochastic self-propelled particles in a narrow channel. Becker et al. [37] investigate adsorption and desorption kinetics of interacting particles moving on a one-dimensional lattice where the confinement is created by the limitation on the number of particles allowed to occupy a lattice site.

The aspects of the exit problems resulting from the clustered geometry have been discussed in Burch et al. [38]. In their review Guerrier and Holcman [39] apply first passage time techniques and report on recent progress in quantifying the search time for Brownian particles to find small targets hidden in cusp-like pockets. The contribution of Metzler et al. [40] considers a single file diffusion model as a basic model of transport of particles in narrow channels under excluded volume conditions. Margaretti et al. [41] work out an energetic analysis of the so called cooperative rectification mechanism. To this purpose the review gives basic ideas of the effective performance and applies them to a two-state ratchet model for directed motion in confined geometries.

Among the main attempts and, hopefully, achievements of the workshop was to bridge the still existing disconnect between the scientists who work on the theory of Brownian motion of confined particles and those who perform experimental work on transport of biological metabolites and polymers, such as proteins, DNA, and RNA in confining media and in newly designed model systems. As witnessed by a great number of responses received by the workshop organizers, the participants from both theory and experiment have found the meeting truly rewarding and constructively different from large-format conferences. A lot of questions were asked by younger participants, suggesting that the atmosphere of the workshop was friendly and conducive to general discussions.

We hope that this Special Topics EPJ issue convincingly demonstrates that the topic of Brownian Motion in Confined Geometries is an exciting and rapidly developing scientific area, and that publication of the present compilation is timely, because it reflects the healthy growth of the field. We expect that the articles, addressing many interesting subtopics of diffusion under strong confinement, will further stimulate this promising direction of research.

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