Particle transport in asymmetrically modulated pores

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Abstract. Brownian motion plays an important role in the separation of small particles and molecules, but generally leads to undirected motion or intermixing by diffusion. Matthias and Müller (2003 Nature 424 53–7) reported on the experimental realization of a drift ratchet, a microfluidic particle transport mechanism that utilizes random fluctuations instead, i.e. a Brownian motor. Here, we offer a new interpretation of this previously published work on the drift ratchet. New experiments, which allow us to distinguish between particles of different sizes, as well as a re-examination of the original work, lead to the conclusion that the measured particle transport does not result from a ratchet effect. We demonstrate that the transport is caused by convection instead. While our result challenges one specific type of experiment, we do not assess the feasibility of a drift ratchet in principle. Instead, we identify the experimental conditions that need to be fulfilled for the successful separation of particles.

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Contents

1. Introduction 2
2. Overview of the experimental setup 2
3. Investigation of particle transport 3
4. Evidence for particle transport by convective movement 5
5. Conclusion 8
Appendix. Methods 10
References 10

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1. Introduction

The separation of mesoscopic particles has numerous applications in industry, medicine and biology [2]–[4]. Brownian motion generally hinders the mechanical sorting of particles because it leads to intermixing by diffusion [5, 6]. In microfabricated lab-on-a-chip applications, this problem can be overcome by increasing the velocity of the flow and the immersed particles that are to be separated, so that the role of Brownian noise becomes comparatively small, i.e. by driving the system into a regime of high Péclet numbers [4, 7]. However, this method is limited to larger particles (e.g. biological cells), since the noise increases with decreasing particle size.

Kettner et al [8] predict a particle transport mechanism—the drift ratchet effect—that utilizes random fluctuations: particles are immersed in water, which oscillates through a microchannel with a periodically and asymmetrically modulated diameter and no-slip walls. The parabolic flow profile of incompressible laminar Poiseuille flow is established. The particles experience Stokes’ drag, Brownian motion, and they interact with the pore walls. Although there is no net transport of water, their movement is not symmetrical; on average, they can move in a preferential direction. Thus the drift ratchet constitutes the prime example of a Brownian ratchet [9, 10]. Due to the stochastic nature of the Brownian motion, a massively parallel array of microchannels is needed to transport the particles. The transport direction is predicted to depend strongly on the size of the particles; that is, different sized particles could be transported into opposing directions and therefore be separated [8, 11].

Matthias and Müller [1] experimentally observed the transport of particles and the dependence of the transport direction not on the particle size but on the applied hydrodynamic pressure; they concluded to have evidence for the ratchet effect. The imperfect reproducibility of their results was attributed to particle agglomeration and impurities in water.

The aim of further experiments on the drift ratchet was to improve the reproducibility, to quantify the results and primarily to demonstrate the separation of spherical particles of different sizes, i.e. to transport particles of different sizes in opposite directions.

In this paper, we show that these new experiments with simultaneously measured particles of different diameters as well as a repetition of the previously conducted control experiments lead to the conclusion that the measured particle transport cannot be interpreted as due to a ratchet effect. We describe further experiments that lead to a new explanation: convection instead causes the particle transport.

2. Overview of the experimental setup

The experimental setup is largely identical to the one used in the original work [1]. It consists of two basins filled with water and dispersed polystyrene beads (see figure 1). A membrane of macroporous silicon with 900 000 110 µm long pores separates the basins; the pore diameter is modulated from 2.0 to 3.8 µm in 12 modulations. 40 Hz-pressure oscillations are applied to the lower basin in cycles of 120 s. The number of particles in the upper basin is measured via the intensity of their photoluminescence (PL). The particles are polystyrene spheres marked with fluorescent dyes with different emission wavelengths corresponding to the beads’ diameters. They all show efficient luminescence when excited with a single wavelength and allow the simultaneous measurement of the transport of differently sized particles, which was not possible in the previous experiments. The light was detected with a monochromator equipped with a CCD camera.

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3. Investigation of particle transport

The PL evolution for a suspension of particles with diameters of 100, 300 and 500 nm is shown in figure 2. The ‘on’ phases of the 40 Hz-pressure oscillations are highlighted in grey. In analogy to [1], the pressure is given as the root mean square (rms) of the fundamental frequency of the pressure. The PL intensity of each type of particles shows the same characteristic properties as in the original work: the intensity increases during the ‘on’ phases and decreases when the oscillations are switched off; this basic result is reproduced. The increase was originally interpreted as particle transport out of the membrane into the upper basin due to the ratchet effect, and the decrease during ‘off’ phases was explained by a back-diffusion of particles into the membrane caused by an increasing gradient of the particle concentration above the membrane in the upper basin.

However, the intensities depicted in figure 2 show an unexpected characteristic: differences in the PL evolutions of particles of different diameters are not detected; they show the same behaviour independently of their size. This seems to contradict theoretical work, in which a strong dependence of the transport direction on particle size is predicted [8, 11]. The absence
of any change in the PL characteristics holds true even for very small particles: in an additional experiment, in which dye molecules (Alexa 488, diameter approximately 1 nm) were used instead of larger particles, the same evolution of the PL signal is detected (see figure 3). No transport at all is expected for these small molecules due to their strong diffusion.

In the original work, several additional control experiments seemingly support the interpretation of the PL signal as a ratchet effect: no change in the PL signal was measured for membranes with straight, cylindrical pores; and if the membranes were reversed, a decrease was measured with otherwise unchanged experimental parameters. Also, in an experiment in which the oscillation pressure was not kept constant but increased with every ‘on’ phase, a reversal of the drift direction was observed for 100 nm particles at an rms pressure of 3000 Pa; that is, the PL was observed to decrease during ‘on’ phases at pressures above 3000 Pa.

We could not reproduce the results of the control experiments of the earlier work. Figure 4 shows the simultaneously measured PL signals of three different particle types for varied parameters. In figures 4(a) and (b), the amplitude of the pressure oscillation is increased with every phase from 400 to 6000 Pa. The same porous membrane was used for the two experiments but their orientation was changed in between the measurements. No change in PL can be observed for small pressures, but for both orientations the intensity always increases for rms pressures above 600 Pa, and a PL decrease is not seen in any ‘on’ phase. In figure 4(c), a membrane with cylindrical channels was used; and in figure 4(d), a measurement for a membrane with a geometry of much smaller pores is shown (average diameter 800 nm instead of 2500 nm). In our new experiments, the detailed evolution of the PL signal shows some fluctuations from experiment to experiment, but the essential characteristics—PL increase during ‘on’ phases and decrease during ‘off’ phases—are always detected with reliable reproducibility. They are independent of particle size, pore shape, membrane orientation and amplitude of the pressure oscillation.

By definition, the ratchet effect must depend on the orientation of the asymmetric pores. Therefore, these results lead to the conclusion that the PL evolution cannot be explained by the ratchet effect.

Figure 3. Comparison of simultaneously measured particles with diameters of 600 nm, 300 nm (polystyrene beads) and 1 nm (Alexa 488 dye molecules).
Figure 4. The simultaneously measured PL evolution of 100, 300 and 500 nm sized particles for different types of porous membranes. (a) Measurement with different oscillation pressures for a membrane with asymmetrically modulated channels. (b) Measurement with the same membrane in reversed orientation. (c) A membrane with straight, cylindrical channels was used. (d) A membrane with asymmetrical pores with an average diameter of 800 nm instead of 2500 nm was used.

4. Evidence for particle transport by convective movement

This finding that the measured PL is not caused by a ratchet effect then raises the question about the origin of the observed signal.

Several possible origins can be ruled out: the sedimentation of particles (density $1.05 \text{ g cm}^{-3}$) is slow compared to the timescale of one PL measurement. Particle–particle interactions are negligible due to the low concentration of 1:25 000 corresponding to approximately one 300 nm sized particle per channel. Laser heating cannot be the source of the particle transport because it is independent of light intensity. Electrokinetic effects do exist but do not influence the PL curves, which are unchanged when the water is replaced with a buffer solution that decreases the streaming current across the porous membrane by a factor of 20. The membranes were subjected to wet organic cleaning before every measurement; no fouling or particle agglomeration was observed.

In general, all possible effects that are dependent on particle size are unlikely to have a dominating influence on the transport, since beads with diameters ranging over three orders of magnitude...
Figure 5. Spectra of particles detected in the upper basin. The increase in PL due to injecting a measured amount of particle-containing solution (red curves) is compared with the increase over time due to pressure oscillations (black curves). This increase in PL intensity is caused by six phases of pressure oscillations of 40 Hz and 2800 Pa in a time of 6 min.

magnitude show the same behaviour. This is also the case for diffusion: according to Fick’s law, the diffusion current is inversely proportional to the particles’ diameter.

To improve our understanding of the source of the observed particle transport, further experiments were conducted. In a first step, we quantitatively measured the number of particles corresponding to the increase in PL. Only particles inside the membrane can contribute to the ratchet effect; therefore a comparatively small change in PL is expected. However, after 6 min of pressure oscillations (40 Hz, 2800 Pa), the increase in PL intensity in the upper basin corresponds to a quantity of particles that is approximately 100 times larger than the number of particles in the membrane (see figure 5).

The only possible source of the particles causing the large increase in PL is the lower reservoir. To understand how transport from the lower into the upper basin could take place, a closer look at the exact starting conditions for the experiments is necessary: a difficulty in the experimental setup lies in the signal-to-noise ratio of the PL due to a large background intensity. To prevent lateral inhomogeneities of the flow above the membrane, a large upper basin of 300 µl was chosen; its hydraulic resistance is negligible compared to the membrane. This volume is approximately 500 times larger than the volume of all the pores in the membrane (0.6 µl). If the experiment were started in an equilibrium particle distribution, a strong background intensity would prevent the detection of a comparatively small particle transport. Therefore the upper basin is purged with water before every measurement. Nonetheless, the particle distribution was originally assumed to be in effective equilibrium, since a small particle-containing layer should remain directly above the membrane, and the particle movement out of and back into the pores should be reversible due to the laminarity of the flow.

Despite this consideration, a combination of two effects could lead to the observed transport of particles from one reservoir into the other towards an equilibrium particle distribution: (i) the displaced volume of each pressure modulation is much larger than expected.
Figure 6. The capacitively measured oscillating volume of water as a function of the pressure applied to the lower reservoir. The red line indicates the membrane volume of 0.6 µl. The pressure is modulated at a frequency of 40 Hz.

If the displacement does not encompass a small fraction of the membrane volume (i.e. 2–3 unit cells of ratchet modulations for 12 modulation across the membrane) but the whole volume instead, all particles inside the membrane are transported in and out of it 40 times per second. (ii) The reversibility of the particle movement in the upper basin is broken. This is the case if the streamlines of the water are not symmetrical in time. A number of particles would move out of the membrane into the upper basin but only a small fraction would follow the water back into the pores when the pressure is reversed. Both of these effects—a strong particle oscillation in combination with an irreversible movement at the membrane surface—could lead to the measured transport between the reservoirs.

The magnitude of the water oscillation was monitored by a capacitive measurement: The water–air meniscus in the upper basin is moving between two electrodes; the change in capacitance was measured with a Boonton 7200 and a lock-in amplifier. The dependence of the displaced volume on the applied pressure is shown in figure 6. At a pressure of 2800 Pa, the displaced volume of water of one oscillation is as large as the entire volume of the membrane of 600 nl and therefore large enough to account for a macroscopic particle transport. This measurement is also in good agreement with the law of Hagen–Poiseuille, which gives the pressure drop as a function of the displacement and the hydraulic resistance.

To check for an additional irreversible particle movement in the upper basin, a highly concentrated solution of particles was injected into a small part of the upper basin. To observe and visualize their movement, the whole basin was then illuminated with the excitation wavelength and photographed spatially resolved with a CCD camera (see figure 7; the movement can be seen much better in the movies in the Supplementary information (online supplementary data available from stacks.iop.org/NJP/13/033038/mmedia)). This measurement reveals a strong convection current in the upper basin with a velocity of approximately 100 µm s⁻¹ at the membrane surface, which is fast enough to transport the particles away from
Figure 7. Fluorescent photograph of particles injected into the upper basin of the setup. The particle distribution changes over time due to a convective flow. The green colour is a background PL from the measurement setup and is not related to the particles.

the membrane. This convection is most likely caused by evaporative heat loss at the air–water meniscus in the basin.

The combination of this convective streaming and the large oscillating volume is therefore responsible for a strong transport or mixing of particles from the lower basin into the upper one towards an equilibrium particle distribution.

The additional convection in the upper basin can also give an explanation for the decrease of the PL intensity in the ‘off’ phases of the pressure oscillation: in a typical experiment both the excitation and the detection focus are limited to a small part of the upper basin in order to increase the signal-to-noise ratio of the measurement. In the ‘off’ phases, the particles are then convectively transported out of the detection focus and the intensity decreases. When both foci are widened to encompass the whole basin instead, the decrease in PL intensity disappears (see figure 8).

5. Conclusion

We conclude that while we confirm the basic result of the earlier experiment, i.e. increase and decrease in PL intensity when pressure oscillations are switched on and off, the increase cannot be explained by a ratchet effect. It is caused by convective transport of particles from the lower
Figure 8. Comparison of the decrease in PL intensity during ‘off’ phases for different detection foci. (a) The detection volume is limited to a small area of the basin. (b) Both the excitation and the detection focus encompass the whole upper basin.

to the upper basin towards an equilibrium particle distribution. For a strong oscillation, particles are moved from one basin to the other with every stroke of the pressure oscillator. In the upper basin, the particles are transported laterally above the surface of the membrane; in spite of the flow’s laminarity, the reversibility of the particle movement is broken and the particles stay in the upper basin. Stokes’ drag is the only dominant force acting on the particles; diffusion plays only a negligible role.

This understanding of the particle movement now allows us to speculate about the low reproducibility and the control experiments in the original publication whose results we cannot confirm. To achieve a high reproducibility, a thorough purging of the upper basin as well as a stable unchanged position of the detection focus is necessary. If a large number of particles remain above the membrane, any change in particle concentration is lost in a strong background PL. Depending on the initial particle distribution and the position of the detection focus, a continuous convective transport of particles out of the detection area is also possible. These effects could be an explanation for the originally reported control experiments in which no change in PL or only a decrease in PL was detected.

Let us mention specifically that we do not conclude that a ratchet effect does not exist in principle, but for the given setup other effects dominate the particle transport. Requirements for a successful measurement are lower pressures and a system in which an additional convection plays no role. This could be achieved either by a complete suppression of the convection in the upper basin or by greatly reducing the volume of the basin; then it could be possible to extend the detection to the whole volume and measure with an equilibrium particle distribution as the starting condition that is not compromised by a low signal-to-noise ratio. An alternative approach would be the direct detection of the particles inside the membrane, which is not possible for nontransparent silicon. Particle transport has been observed in transparent ratcheted polydimethylsiloxane microchannels [12], but generally other material systems do not allow for the averaging over millions of parallel pores.
Appendix. Methods

The same experimental setup as in the original work was used for sample fabrication. Also, 0.3 cm$^2$ size macroporous silicon membranes with a thickness of 110 µm and an interpore distance of 6 µm were used.

The setup for the transport measurements is improved. The particles are TransFluoSpheres carboxylated polystyrene spheres with Excitation/Emission wavelengths of (505/515) nm, (488/605) nm, (488/685) nm and Alexa Fluor 488 dye provided by Invitrogen. Excitation is done with 473 nm light from a solid-state laser. The PL is detected using a Spex 270M monochromator equipped with a Jobin Yvon Symphony 1024 × 256 Thermoelectric Open Electrode CCD Detector.

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