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Fluidic delivery of homogeneous solutions through carbon tube bundles

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Abstract
A wide array of technological applications requires localized high-rate delivery of dissolved compounds (in particular, biological ones), which can be achieved by forcing the solutions or suspensions of such compounds through nano or microtubes and their bundled assemblies. Using a water-soluble compound, the fluorescent dye Rhodamine 610 chloride, frequently used as a model drug release compound, it is shown that deposit buildup on the inner walls of the delivery channels and its adverse consequences pose a severe challenge to implementing pressure-driven long-term fluidic delivery through nano and microcapillaries, even in the case of such homogeneous solutions. Pressure-driven delivery (3–6 bar) of homogeneous dye solutions through macroscopically-long (~1 cm) carbon nano and microtubes with inner diameters in the range 100 nm–1 μm and their bundled parallel assemblies is studied experimentally and theoretically. It is shown that the flow delivery gradually shifts from fast convection-dominated (unobstructed) to slow jammed convection, and ultimately to diffusion-limited transport through a porous deposit. The jamming/clogging phenomena appear to be rather generic: they were observed in a wide concentration range for two fluorescent dyes in carbon nano and microtubes, as well as in comparable transparent glass microcapillaries. The aim of the present work is to study the physics of jamming, rather than the chemical reasons for the affinity of dye molecules to the tube walls.

(Some figures in this article are in colour only in the electronic version)

1. Introduction
A number of applications require localized delivery of biological compounds within seconds or minutes; see recent reviews [1–3] and the references cited therein. Such applications include DNA and protein analysis, drug development, screening and delivery, biotechnological and forensic analysis, cell manipulation, lab-on-chip technologies, mass-limited chemical analysis and the development of new materials in highly confined spaces. Such technologies rely on microfluidic principles and can benefit significantly from further miniaturization [4–10]. Consequently, fluid transport inside carbon nanotubes with diameters of the order of 100 nm has attracted increased attention in the past 3–4 years [11, 12].

In these recent studies, the flows were driven by capillary or thermal forces.

Pressure-driven flows through aligned, densely-packed carbon nanotube membranes have also been considered [13, 14] for nanotubes with diameters close to the molecular scale, i.e., well below 10 nm. These pore sizes, however, are much more suited to separation technologies than microfluidic delivery. Both of the above studies [13, 14] employed only pure liquids (including water) and demonstrated dramatically enhanced flow through the nanotube cores compared with conventional fluid flow theory. This phenomenon, however, seems to be limited to very small pore sizes and has not been confirmed for pore diameters above 10 nm [15]. More recently, macroscopically-long (~1 cm) carbon tube bundles with diameters of the order of 300 nm–1 μm were fabricated [9, 10] to achieve high-rate delivery of low-viscosity pure liquids.
(\sim 1 \text{n} \text{l s}^{-1})$ and gases ($\sim 30 \text{n} \text{l s}^{-1}$), as well of bi-layers of liquid and gas moving in parallel. The measurements reported in [9, 10] demonstrated the ability to sustain well-controlled laminar flows through long carbon tube bundles and elucidated the main transport features, which were consistent with the Poiseuille law. A novel procedure was also formulated therein for recovering the inner-diameter distribution of the flow-carrying tubes from the measured dependence of the fluid volumetric or mass flow rate on the imposed pressure drop [9]. Also, it was demonstrated that bi-layer flows of liquid and gas can result in an over-limiting regime [10]. In such a regime, a higher flow rate of liquid can be achieved than that of the case when the same liquid flows through the same tube subjected to the same pressure drop but occupying the whole bore. Therefore it is possible to release more liquid than predicted by the Poiseuille law, even though, in the bi-layer flow, the liquid does not occupy the whole cross-section. This phenomenon stems from the fact that the less viscous gas layer can flow much faster than the underlying liquid layer and entrain the latter via a significant shear stress.

No liquid solutions or suspensions, which are more relevant to biotechnological applications [16], were considered in [9, 10]. In fact, nearly all of the limited studies that have been completed to-date on pressure-driven flows through nanotubes with diameters over 10 nm (or their packed assemblies) have concentrated on pure fluids. Thus, it appears that the pressure-driven flow of solutions or nanoparticle suspensions through single or multiple nanotubes has been overlooked and, consequently, fundamental knowledge in this high-priority area of fluid transport is lacking.

Methods relying on mechanisms other than diffusion have been targeted for infusing drugs directly into tissue at sufficiently high rates, as, for example, in microfabricated prostheses delivering chemical agents to precisely defined regions of tissue or even to the interior of cells [17]. The importance of microfluidic devices for high-rate fluid delivery seems to be well recognized [18]. It is noted that electrically-driven flows [2, 4] are typically out of the scope of most biomedical applications, as the effects of electrical charges on bioactive compounds remain controversial.

The present study examines high-rate long-term fluidic release of aqueous solutions of a model substance (fluorescent dye) through carbon tube bundles similar to those employed in [9]. Fluorescent dye Rhodamine 610 chloride is a model compound routinely used in controlled release experiments, where it reveals the characteristic features of drug/protein release, as, for example, in the following two recent works [19, 20]. The results show that this specific dye has an affinity to deposit on the walls of the present tubes, which range in diameter from 100 nm to 1 \mu m. The dye delivery rates through tube bundles dispensing dye solution into an aqueous pool are measured experimentally via fluorescence, and reveal interesting trends, which are attributed to jamming/clogging. A theoretical analysis of deposit buildup on the inner tube walls is presented as a feasible mechanism clogging this system. It is emphasized that we tackle the physical aspects of the jamming phenomenon, rather than chemical details of the dye/carbon interaction.

2. Experimental methods

The carbon tubes employed in the fluidic experiments of the present work were made by co-electrospinning the core–shell poly(methylmethacrylate)–polyacrylonitrile (PMMA–PAN) fibers with subsequent thermal treatment, following the procedure described in [9, 21]. The PMMA had $M_w = 960$ kDa and was dissolved at 15 wt\% in 60/40 dimethyl formamide (DMF)/acetone, while the PAN had $M_w = 150$ kDa and was dissolved at 12 wt\% in pure DMF. Parallel bundles of tens of thousands of such carbon tubes with cross-sectional diameters of the order of 1 \mu m have already been used in fluidic experiments [9] where air, as well as a pure liquid (n-decane), was released under the action of an applied pressure gradient. The experiments in [9] demonstrated that only a low percentage of the carbon tubes were open along their entire length and could carry throughput. Some of the carbon tube bundles used in the present work were produced following the carbonization procedure of [9]. Namely, heat treatment of core–shell PMMA–PAN nanofibers at 250°C for 0.5 h in air, and then at 750°C in nitrogen. The fibers were kept at 750°C for 1 h and then gradually cooled down in a nitrogen atmosphere. As shown in [9], this procedure resulted in bundles with several hundred carbon tubes open to throughput. In addition, with the goal of increasing the number of open carbon tubes in the bundles, a new procedure was introduced in the present work. Namely, the heat treatment of the core–shell PMMA–PAN fibers occurred at 350°C for 3.5 h in air, and then at 750°C in nitrogen. The fibers were kept at 750°C for 1 h and then gradually cooled down in a nitrogen atmosphere. This new heat treatment protocol created bundles with much more open carbon tubes delivering an order of magnitude higher volumetric air flow rates at the same pressure drop, as compared with those of [9].

This outcome confirmed that the PMMA core in the co-electrospun core–shell polymer fibers produced by the new carbonization procedure was eliminated more effectively (as compared to the fibers in [9]). Both types of bundle contained carbon tubes of diameters in the range 100 nm–1 \mu m. A portion of one of the carbon tubes produced using the new heat treatment protocol is depicted in the transmission electron micrograph of figure 1(a); this tube was separated from a carbonized bundle and shows a hollow structure with walls of uneven thickness. Figure 1(b) shows the corresponding bundle cross-section. It is emphasized that our procedure results in turbostratic carbon, rather than in ordered graphene structures seen in ordinary carbon nanotubes, which can emerge at much higher temperatures. All the bundles were initially tested by releasing air into water through them (as in [9]). Such preliminary tests demonstrated that all the bundles initially have a number of tubes fully open to flow throughout their whole length (which cannot be fully established by any TEM image similar to that of figure 1(a) spanning a length of only about several microns).

For the fluidic experiments the present work uses the experimental setup employed in [9], where air or pure n-decane were released into water. A sketch of the experimental setup is shown in figure 2. A typical hollow fiber bundle was about 10 mm long and 0.2 mm in diameter. It was inserted
into the tip of a glass capillary and secured there by epoxy cement. Briefly, the fluid supply system consisted of two standard syringes of volumes 10 and 1 ml, a 7 ml plastic air chamber and two stopcocks. All the parts of this apparatus were connected by thin silicon tubing. After pressurizing the chamber by means of the 10 ml syringe (on the left in figure 2), the one-way stopcock was closed. The pressurized chamber could sustain nearly constant pressure during long-term flow delivery tests. The second syringe (vertical in figure 2), which was connected directly to the three-way stopcock, was used to fill the silicon pipe leading to the glass capillary with the dye solution. The tip of the glass capillary with a carbon tube bundle secured at the end was immersed in a shallow pool of water and observed under a microscope (figure 2). Flow in the carbon tube bundles was driven by a pressure difference of the order of 3–5 bar applied to the tubes, and the release of a model compound, in the form of a fluorescent dye, was studied. Rhodamine 610 chloride was used to prepare an aqueous solution with a concentration of about 5 mg g\(^{-1}\) (dye in water). This compound was chosen because of its well-known fluorescent properties, which make quantifying its release rates possible, as is done, for example, during dye release from polymer nanofiber mats [19]. Prior to the fluidic experiments, the dye solution was subjected to sonication for 30 min to disintegrate any large clusters of dye molecules and assure uniform dispersion. It is important to note that the dye aqueous solutions were released through the carbon tube bundles just as pure n-decane was released [9]. The solutions were released in a 2 ml cylindrical vessel of 2.5 cm diameter containing only DI water initially. The estimates show that water evaporation from the vessel proceeds at a rate of the order of 10 mg h\(^{-1}\). Therefore, water losses due to evaporation could be neglected compared to the 2 g of water contained in the vessel in a typical experiment lasting about 2 h. Samples of 100 \(\mu\)l of the resulting aqueous dye solution from the vessel were pipetted into a 96-well plate at predetermined time intervals for measuring fluorescence using a GEMINI SPECTRAMAX spectrofluorometer. Solutions with precisely known dissolved amounts of dye molecules were formed to determine the

\[
\Delta p_{\text{osm}} = \frac{RTN_{\text{mol}}}{V_s}\]  

where \(R\) is the absolute ideal gas constant, \(T\) is the absolute temperature, \(N_{\text{mol}}\) is the number of dye moles, and \(V_s\) is the volume of the dye solution in the syringe (figure 2). For a partial dye density (concentration) in the solution of \(c_\infty = 0.005\ g\ cm^{-3}\) and \(V_s = 1\ cm^3\), the dye mass is \(M = 0.005\ g\). The dye molecular weight is \(M_w = 479\ g\ mol^{-1}\). Therefore, \(N_{\text{mol}} = M/M_w = 1.04 \times 10^{-5}\ mol\). With \(R = 8.32 \times 10^7\ g\ cm^2/(s^2 K \ mol)\) and \(T = 300\ K\), it is \(\Delta p_{\text{osm}} = 0.26\ bar\). This pressure is much lower than the typical values of \(\Delta p \sim 3-5\ bar\), which are applied to the dye solutions to create an essentially reverse osmosis flow. Therefore, \(\Delta p_{\text{osm}}\) can be neglected compared to \(\Delta p\). Consequently, all results in this work are presented below versus \(\Delta p\) (without accounting for \(\Delta p_{\text{osm}}\)).

The dye aqueous solutions were released through the carbon tube bundles just as pure n-decane was released in [9]. The solutions were released in a 2 ml cylindrical vessel of 2.5 cm diameter containing only DI water initially. The estimates show that water evaporation from the vessel proceeds at a rate of the order of 10 mg h\(^{-1}\). Therefore, water losses due to evaporation could be neglected compared to the 2 g of water contained in the vessel in a typical experiment lasting about 2 h. Samples of 100 \(\mu\)l of the resulting aqueous dye solution from the vessel were pipetted into a 96-well plate at predetermined time intervals for measuring fluorescence using a GEMINI SPECTRAMAX spectrofluorometer. Solutions with precisely known dissolved amounts of dye molecules were formed to determine the
Figure 3. Mass $m$ of Rhodamine 610 dye released in DI water using two different carbon tube bundles produced using two different heat treatment protocols. For the bundle in (a), the pressure drop along the tubes was practically constant at $\Delta p = 3.78$ bar, while for the one in (b) $\Delta p = 3.34$ bar. The error bars reflect inaccuracies in the measurement procedures, such as Rhodamine 610 fluorescence-mass calibration, mass measurement, etc. It is apparent that in each case the rate of release of dye mass ($\dot{m}$) remains nearly constant, an outcome that is consistent with a constant driving pressure $\Delta p$.

3. Experimental results

The results for the amount of dye released as a function of time for two separate cases are shown in figure 3. In figure 3(a), the carbon tube bundles were produced following the carbonization protocol of [9] (with hundreds of the initially fully open tubes), whereas in figure 3(b) the tube bundles were produced following the new protocol (with thousands of the initially open tubes). The two bundles contained different numbers of tubes with an unknown percentage of them open (available for throughflow) from tip to end.

The results depicted in figure 3 show a practically linear increase of mass $m$ of the released dye. Thus in subsequent experiments the observations of the dye release process were reduced to 0.5 h at any pressure drop. An average slope in the dependences $m(t)$ up to 0.5 h of release was used to characterize the rate of dye mass release. It is presented in figures 4(a) and (b) for different carbon bundles, each containing a different number of tubes with an unknown percentage of open tubes available for fluidic delivery. Measurements were done at different pressure drops.
in the range 3–6 bar. In particular, a nanotube bundle was initially subjected to the lowest pressure drop $\Delta p$ from this range for half an hour, and the average slope of $m(t)$ produced $\dot{m}$ for this $\Delta p$. Then, the pressure drop was increased, and a new slope was recorded for 0.5 h for this new $\Delta p$, with the same cycle repeated subsequently at a new pressure, and so on. This procedure produced the data points in figure 4, and in figures 6 and 8 subsequently. It is emphasized that the carbon nanotubes in the bundles used for figures 3(a) and 4(a) were produced following the carbonization procedure of [9]. This procedure resulted in bundles with several hundred carbon tubes open to throughflow. On the other hand, the new heat treatment protocol was used to produce the bundles in figures 3(b), 4(b), 6 and 8. As mentioned earlier, the newer heat treatment procedure created bundles with a larger percentage of open tubes available for throughflow. The fact that the bundles were different with unknown percentages of open tubes precludes meaningful direct comparisons of the measured dye mass release rates $\dot{m}$. However, all dependences of $\dot{m}$ on pressure drop in figure 4 reveal a striking result; there is no trace of linear growth of the release rate with pressure drop, as would be expected for Poiseuille flow (confirmed for pure liquids in [9]). The results in figure 4 suggest that the measured mass release rates do not scale with $\Delta p$; in fact, they seem practically independent of the pressure drop, i.e., not dominated by ordinary convective transfer. The suspicion that dye solution delivery was hindered by deposition of the dye on the inner tube walls was evaluated by a series of tests.

Filtration of the same dye solution (5 mg g$^{-1}$ in water) through a two-stage filter (Cole Parmer) with pore sizes of 0.45 $\mu$m (1st stage) and 0.2 $\mu$m (2nd filter stage) was attempted as a means to remove large dye clusters in an effort to homogenize the dye solution as much as possible for the subsequent flow of the filtrate through the carbon tubes. This measure, however, resulted in rapidly diminishing dye delivery rates through the filters, and a clear indication that the porous filters jammed (figures 5(a) and (b)). The filtrate released through the filters was passed through the carbon tube bundles at different pressure drops, thus producing the results shown in figure 6, which are very similar to those shown in figure 4. Namely, the filtrate flow rate through the carbon tubes remained practically independent of the pressure drop, i.e., it was unrelated to ordinary convective transport.

It is emphasized that the carbon tube bundles used in the experiments corresponding to figures 4 and 6 were all different, i.e., they each contained a different number of tubes of different diameters and diameter distributions. In addition, the percentage of tubes open for throughflow was also known only by an order of magnitude. Because of these reasons, the release rates depicted in these figures could not be compared with one another with any meaningful outcome. Nonetheless, the relative independence of dye delivery rate on pressure, combined with the fact that the delivery experiments were performed with the same tube bundles at low pressures and then at gradually higher pressures, indicates a jamming mechanism driven by dye deposition on the inner walls of the carbon tubes. Since jamming is an instability-related process (see section 4), it might result in unrepeatable deposit patterns inside the tubes, which in turn, prevent any clear trends in the release rate variation with pressure (see figures 4(a), (b) and 6).

After the completion of the dye delivery experiments, some carbon tube bundles were broken in the middle and the bundle cross-sections were observed using scanning electron microscopy. Figure 7 shows two details ((a) and (b)) from such broken cross-sections. In each section, fully and
partially jammed/clogged tubes can be seen, which is in drastic contrast to the tubes prior to dye solution flow in figure 1(b). Other tubes, which seem to be open in these cross-sections (figures 7(a) and (b)), could be jammed elsewhere along their lengths. The exit cross-section of the bundle is densely covered by precipitated dye (figure 7(c)). This observation is critical and supports the hypothesis that dye deposition on the inner tube walls is responsible for the reduced delivery rates at increased pressures.

In an additional experiment, the possibility of controlling the jamming rate by reducing the dye concentration in the released solution was examined. A carbon tube bundle, produced according to the new heat treatment protocol, was used initially for DI water release at $\Delta p = 3–5$ bar. Release was sustained for two days with no interruption, and the amount of pure water released during that period was in good agreement with the Poiseuille law (unhindered delivery). Subsequently, the same tube bundle was used to release dye solution at the reduced concentration of 1 mg g$^{-1}$ dye in water, a five-fold reduction compared to the experiments in figures 3–7. The results obtained from the corresponding dye solution delivery experiments are presented in figure 8(a). The reduced-concentration dye delivery rates in figure 8(a) reveal a consistent, roughly linear dependence on $\Delta p$, contrary to the results obtained when using the high-concentration solutions (figure 4). However, the slope of this dependence is lower than that expected for Poiseuille flow, thus indicating that even with reduced dye concentrations, buildup of wall deposits affects the flow. Subsequently, the same carbon tube bundle was used to release dye solution of an intermediate concentration of 3 mg g$^{-1}$ dye in water. Pressure-driven enhancement was seen in the release rate (figure 8(b)), however at a much lower delivery rate compared to that of figure 8(a), even though the dye concentration was tripled. These results indicate that the reduced dye concentrations have indeed increased the dependence on $\Delta p$, as would be expected for unhindered or partially hindered Poiseuille delivery. However, the measured dependence on $\Delta p$ is weaker than the theoretical predictions, thus pointing to wall deposit buildup even at the reduced dye concentrations of 1 mg g$^{-1}$. Nonetheless, semi-jammed tubes can still sustain diminished convective flows until complete jamming occurs (after which only diffusion-driven release would be possible). Unfortunately, release experiments with dye concentrations lower than 1 mg g$^{-1}$ were not possible, as these concentrations resulted in undetectable fluorescence in the water pool even after very prolonged release times. To demonstrate a feasible explanation for the trends shown in figure 8, a sketch of a semi-jammed tube with dye deposits on the walls is depicted in figure 9. Although dye wall deposits form obstacles to the flow, convective delivery is still possible.
Figure 8. Dye mass release rate $\dot{m}$ versus imposed pressure drop $\Delta p$ for reduced dye concentrations, compared to that (5 mg g\(^{-1}\) dye in water) used in figures 3 and 4: (a) 1 mg g\(^{-1}\), (b) 3 mg g\(^{-1}\).

but along a very tortuous path, as sketched by the dashed line in figure 9. For a fixed pressure drop, such tortuosity results in a dramatic decrease in the effective pressure gradient, and thus in the corresponding convective release rate (compare figure 8(b) to (a)). This would explain the drastically reduced delivery rates of figure 8(b) (higher dye concentration, more blockage) compared to those of figure 8(a). Essentially, the delivery mode in figure 8 (semi-jammed state) is intermediate between unhindered (Poiseuille) flow and diffusive release through jammed tubes.

It is emphasized that direct observation of multiple dye deposits along the carbon tubes in the bundles is impossible even with TEM. However, optical observations in slightly bigger transparent glass capillaries (with tapering of about 5\(^\circ\)) demonstrated jamming after a while, and revealed dye deposit patterns on the walls (figure 10) reminiscent of the sketch in figure 9. In the experiments with a glass micropipette an extremely dilute dye solution (less than 0.1 mg g\(^{-1}\)) was prepared and passed twice through a Cole Parmer filter (0.2 \(\mu\)m) to eliminate any significant clusters. The resulting clear and homogeneous filtrate was used in the experiments depicted in figure 10. Not only a different tube material (glass instead of carbon) was used in these experiments, but also a different fluorescent dye (Rhodamine 6G instead of Rhodamine 610 chloride). The outcome—jamming/clogging—is however the same, which shows the generic nature of our observations.

4. Discussion and interpretation of results

The experimental results shown in section 3 suggest that jamming/clogging of carbon tubes by dye deposits on the inner tube walls could affect the dye release kinetics. In the present section the characteristic time of jamming is estimated and the mechanism of dye delivery is elucidated.

The deposition process may become unstable, namely, perturbations of the deposit thickness at the wall may be enhanced by the deposition process itself. The term jamming/clogging is applied to such instability-related processes. Since the convective flow in these carbon tubes is rather weak [9] (the Reynolds number, $Re = 0.6 \times 10^{-2}$), we may neglect it in the interest of first approximation estimates. If the perturbation wavelengths $\lambda$ are sufficiently small compared to the tube radius $a$, the diffusion problem can be considered as planar (cf [26]), namely the diffusion equation takes the form

$$\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} = 0 \quad (1)$$

where $x$ and $y$ are the longitudinal and normal coordinates at the tube wall, respectively, and $c$ is the dye concentration (mass dye/volume of solution) in the solution. Solutions of equation (1) are subject to the following boundary conditions

$$y = \delta(x, t) \quad c = c_w; \quad y = a \quad c = c_\infty \quad (2)$$

where $\delta(x, t)$ is a small perturbation ($\delta \ll a$); $c_w$ is the dye concentration in solution near the wall (the concentration of the free dye molecules near the wall); $a$ is the inner tube radius. If $c_w = 0$, all dye molecules that come in contact with the wall precipitate on it. If $c_w$ is less than $c_\infty$ but non-zero, the dye only partially precipitates on the wall. It is emphasized that in elliptic problems such as the present diffusion problem, if the flux (the derivative of the concentration) is given, the near-wall value of the concentration $c_w$ should be found. However,
in the present case it is the flux that is to be found. Then, inevitably the near-surface concentration $c_w$ must be given. That is precisely how similar problems on evaporation are solved: vapor concentration near the surface is given, so the evaporation rate (the vapor flux) is found and the well-known $d^2$-law established (e.g. cf [27]). An additional example of this type is the classical Lifshitz–Slyozov–Wagner theory of the Ostwald ripening (cf [28]) where the boundary condition for the concentration is imposed in a similar way to the present work, or some other theories dealing with the Kelvin effect (e.g. [26]). Note that such near-wall concentration might be related to some additional parameters. In evaporation problems, near-wall concentration is determined via the temperature using the Clausius–Clapeyron relation or the Antoine equation [27], instead of considering the detailed chemical mechanism of dye–wall interaction is unknown and is not aimed at by the present work. Therefore, it is not worth changing one unknown ($c_w$) for another (the coefficient of restitution). The numerical estimate below in fact implies that most of the dye molecules coming to the wall, stick there and $c_w \approx 0$. This corresponds to the observations in the experiments that jamming by this dye is a rather ‘efficient’ process.

Since for small perturbations linearization can be applied, the wall perturbation can be represented by a Fourier mode, \( \delta(x,t) = \delta_0(t) \exp(ikx) \), where the wavenumber \( k = 2\pi/\lambda \), \( \delta_0 \) is the roughness amplitude, \( \lambda \) is the wavelength, and \( i \) is the imaginary unit. Then the linearized solution of the problem expressed by equations (1) and (2) is given by

\[
c = (c_\infty - c_w) \frac{y}{a} + (c_w - c_\infty) \frac{\delta_0}{a} \exp(ikx) \times \frac{\cosh ka}{\sinh ky} - \cosh ky.
\]  

(3)

The latter expression allows one to calculate the diffusion mass flux at the rough wall as \(-D(\partial c/\partial y)\) in estimates of the jamming time \( t \). The mass balance at the wall reads

\[
\frac{\partial \rho_d H}{\partial t} = D \frac{\partial c}{\partial y} \bigg|_{y=\delta}.
\]  

(4)

where the deposit thickness \( H = h + \delta_0 \exp(ikx) \), with \( h \) being the average thickness of the deposit; \( \rho_d \) is the deposit density. Substituting equation (3) in (4), we find

\[
h = h_0 + \frac{D(c_\infty - c_w)}{\alpha \rho_d} t
\]  

(5)

(with \( h_0 \) being the initial value of the wall deposit) and the roughness amplitude as

\[
\delta_0 = \delta_{0,\text{init}} \exp \left[ \frac{Dk(c_\infty - c_w) \cosh ka}{\alpha \rho_d \sinh ka} \right].
\]  

(6)

The initial perturbation amplitude is denoted by \( \delta_{0,\text{init}} \).

Equation (6) shows that the deposition process leads to an exponential growth of roughness amplitude. Therefore, perturbations grow and the deposition process is unstable. Moreover, the exponential growth of roughness allows one to disregard the linear growth of the uniform deposit (cf equation (5)) in estimates of the jamming time \( t \). The latter is determined in the linear approximation by the following condition: \( \delta_0 = a \) at \( t = t_0 \). Therefore, using equation (6), we obtain

\[
t_0 = \frac{\alpha \rho_d \exp(\alpha/\delta_{0,\text{init}})}{Dk(c_\infty - c_w) \tanh ka}.
\]  

(7)
Using the following values of the parameters: \( a = 10^{-4} \) cm, \( \rho_d = 1 \text{ g cm}^{-3} \), \( c_\infty - c_w = 0.005 \text{g cm}^{-3} \text{ s}^{-1} \), and considering the case \( \lambda \sim a \), we obtain \( t_j \sim 0.072 \) s. On the other hand, for longer wavelengths \( \lambda \sim L, t_j \sim 0.46 \) s (in both cases, we assumed that \( a/\delta_{0,\text{init}} = 10 \)). Note that according to [9], the average flow velocity in the tubes under fully convective conditions is about \( U = 0.3 \text{ cm s}^{-1} \). Taking the tube length \( L = 1 \) cm, the residence time is about \( \tau = 3 \) s. This corresponds to lateral diffusion in the tubes for a distance \( \ell \sim (Dr)^{1/2} = 5 \times 10^{-3} \) cm \( \gg a = 10^{-4} \) cm. This estimate supports the assumption on the diffusion-dominated situation underlying equation (7).

It is emphasized that the theory allows for an estimate of the jamming/clogging rate. Also, if an initial roughness profile at the wall should be known (it is practically never known), it can be expanded in a series of Fourier modes. The solutions found above for each of them would then provide a description of the roughness profile at the moment of jamming/clogging, and thus a detailed prediction of the clogging cross-section (which is practically never necessary).

In the experiments where the same tube bundle was subjected to different increasing pressure drops (figures 4, 6 and 8), according to the estimates of \( t_j \), partial jamming could occur very rapidly even at the lowest value of the pressure drop. Further pressure rise (in a 0.5 h interval) could probably re-establish some convective flow, which would then jam the tubes again very rapidly. Therefore, the theoretical estimates indicate that the situations at different values of the pressure drop were essentially identical: the tubes were semi-jammed practically from the very beginning. Lower dye concentrations certainly extend duration of the jamming process according to equation (7). However, jamming is still inevitable, although it would occur after longer times under reduced dye concentrations (as corroborated by the data in figure 8). It is also important to emphasize that the linear theory considered herein may not adequately describe the non-linear process leading to the jamming pattern shown in figure 9. Nevertheless, the main trends of the linear theory agree with the experimental result that reduced dye concentrations delay jamming.

### 4.1. Diffusion-driven release

The estimates in the previous subsection showed that convective-driven dye release will ultimately be replaced by dye diffusion through a completely jammed bore. The convective mass flux of dye through a carbon tube bundle free of wall deposit is estimated as

\[
\frac{dM_{\text{conv}}}{dt} = c_\infty Q, \tag{8}
\]

where \( Q \) is the volumetric rate of the solution. On the other hand, the diffusion-driven mechanism in the ultimate, completely jammed case yields

\[
\frac{dM_{\text{dif}}}{dt} = \frac{D c_\infty S}{L} \tag{9}
\]

where \( S \) is the overall cross-section area of the carbon tubes in a bundle, which is of the order of \( 10^{-5} \) cm² for a bundle with about 100 tubes open for throughflow. Then,

\[
\frac{dM_{\text{conv}}}{dt} \frac{dM_{\text{dif}}}{dt} = \frac{Q L}{DS}, \tag{10}
\]

This ratio is of the order of \( 10^4 \), indicating that the ultimate diffusion-driven release is much slower than its convective counterpart. Using equation (9), one can estimate the duration of the complete release of the dye by diffusion \( t_{\text{complete}} \) from a syringe of volume \( V_s \) as

\[
t_{\text{complete}} = \frac{V_s L}{DS}. \tag{11}
\]

Using the parameter values listed above, and the estimate \( V_s = 1 \text{ cm}^3 \), we deduce \( t_{\text{complete}} = 320 \) years. This means that slow diffusion-driven release will continue indefinitely as long as a complete blockage of all the tubes does not happen. The corresponding diffusion-driven release rates would thus be independent of the pressure drop \( \Delta \rho \) applied to the bundle, as equation (9) suggests.

### 5. Practical significance

The results reported herein have important ramifications for fluidic applications relying on long-term high-rate delivery of solutions through submicron diameter tubes. The model solute utilized in this work (Rhodamine 610 chloride) demonstrated an affinity to deposit on the walls of the present tubes (100 nm to 1 \( \mu \)m dia.), eventually jamming the delivery conduits. In fact, this standard fluorescent dye frequently used for flow visualization or as a model compound in controlled release experiments appeared to be a good model material to study the jamming/clogging phenomena. The results show the vulnerability of high-rate fluidic delivery systems that release solutes that can form deposits on the inner walls of the conduits carrying their solutions. The results indicate that jamming occurs gradually as solute molecules build up on the wall, eventually causing jamming which disrupts the delivery, shifting it from convection-dominated to diffusion-based. Reduced solute concentration in the feed solution delays the jamming rate, but also reduces the rate of solute delivery to the target. Since the jamming mechanism is non-linear, optimal solute delivery requires a complex optimization strategy that is not required for pure fluids.

### 6. Conclusion

The present work employed macroscopically-long parallel bundles of carbon tubes, made via co-electrospinning and subsequent carbonization, to deliver aqueous solutions of a model substance (Rhodamine 610 dye) in long-term, high-rate release experiments with pressures up to 6 bar. The strong indication that flows of homogeneous solutions of low molecular weight compounds result in relatively rapid jamming/clogging of nano and microtubes unveils a surprising vulnerability of potential nano and microfluidic devices.
for biomedical and other applications where the delivered compounds can deposit on the tube walls. This might be an acute problem for many proteins and macromolecules whose affinity to the channel walls might be even higher than that of the dye to carbon. The present results suggest that a prolonged controlled delivery might be improbable in many cases. An optimal solute concentration appears to be necessary to maximize the release mass. The jamming/clogging phenomena were observed in a wide concentration range for two fluorescent dyes in carbon nano and microtubes and glass microcapillaries.

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References

[9] Bazilevsky A V, Yarin A L and Megaridis C M 2008 Lab Chip 7 152–60