Nanofluidic transport and formation of nano-emulsions

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The focus of this research is to study fluidic transport through carbon nanotubes. The nanotubes studied were formed by electrospinning Polycaprolactone (PCL) nanofibers and then using them as channel templates in colyacrylamide blocks which were carbonized. A pressure driven flow is initiated through the nanochannels and the rate of emulsion formation is recorded with a CCD camera. Theoretical calculations are conducted for nanochannels because in many experiments, the nanochannels studied have two-phase flows, which make direct application of Poiseuille law impossible. The model used for the calculations is a slit with two fluid layers in between. In particular, in many experiments, decane-air system is of interest. The calculations are carried out using the Navier-Stokes equations. The results of the model are used to evaluate experimental volumetric flow rates and find the distribution of air and decane in the nanochannels.

Introduction

Nanochannel development has the potential to improve the efficacy of several commercial applications that exist today. These applications include DNA and protein analysis.\(^1,2\) In the fields of protein and DNA analysis, many researchers are interested in segmenting the longer chains and analyzing individual molecules. The integration of nanochannels in this field has the potential to help researchers gain a deeper insight into the physical properties of DNA and protein segments. One of the developing methods for this research is to segment the strands and have the segments flow through the nanochannels. The time it takes for the protein and DNA strands to travel through the nanochannels provides researchers with clues as to how long the strands are. The nanochannels will also cause the strands to unwind. This method for untangling the strands will make protein and DNA analysis much more feasible than current methods, which consists of doping the strands with fluorescent dyes.

The nanochannels are formed by electrospinning template nanofibers, and casting them in a polycyclonitrile matrix. The latter is carbonized while the template nanofibers are eliminated. The diameter of the nanochannels is indirectly found by observing the size and rate of emulsions exiting the nanochannels. However, in many of the experiments a two-phase flow is present in the nanochannels. This condition necessitates the creation of a two-phase model to characterize the volumetric flow rates and velocity profiles of the fluids traveling through the nanochannels. The model made is a slit with two fluids in between. The calculations for the model are carried out using the Navier-Stokes equations.\(^3,4\) The model is expected to show that the presence of air in the nanochannels does influence the volumetric flow of liquids. Because air is much less viscous than the liquids, it causes the liquid being studied to move at an accelerated rate. The results of the model are then used to analyze earlier experimental results and find the distribution of decane and air in the nanochannels.

Experimental Procedure

Preparation of PCL Nanofibers

The nanofluidics study begins with the synthesis of the nanofibers through electrospinning. The procedure for electrospinning involves the use of a polymer, PCL. The concentration of PCL used in the experiments is 12\% wt. Once the correct weight of PCL is obtained, it is stored in the 20 mL vial. Another 20 mL vial is used to mix the solvents of PCL, N-Dimethyl Formamide (DMF) and Dichloro Methane (MC). The ratio of DMF: MC is 60:40, respectively. When the DMF and MC are mixed in the vial, a magnetic stirrer is added. The magnetic stirrer must be rinsed in DMF before use to avoid any contamination. The final step in the procedure is the addition of PCL to the 20 mL vial with the DMF, MC and magnetic stirrer. Once all of the components are added, seal the vial and place it on a magnetic plate.

Electrospinning

The PCL is then transferred to a 5 mL plastic syringe. The syringe is loaded onto a syringe pump. The optimal flow rate of the pump varies according to the concentration of the PCL. For a value of 12\% wt. PCL, the optimal flow rate through the syringe is \(0.8 \frac{mL}{hr}\).

In order for the electrospinning to occur, an electric field must be applied to the polymer when it exits the syringe. For the experiments conducted, a DC generator was used to create the electric field. For a flow rate of
0.8 $\frac{mL}{hr}$ of PCL and a 12% wt. concentration, the optimal voltage was approximately 13 kV. The electrodes of the generator were attached to the tip of the syringe and to the base of the rotating disk collector. When the PCL emerges from the tip of the syringe, the polymer stretches out and begins to form a jet. This jet occurs from the electric field supplied the generator. A sketch of the electrospinning process is illustrated in Figure 1. The PCL is collected on the edge of the rotating disk. To make collection of the nanofibers more feasible, aluminum strips were attached on two areas of the rotating disk. The location of the aluminum strips is meant to cover the areas of the rotating disk that have gaps. The strips will have rectangular slots cut out in their centers to ensure that the gaps in the rotating blade remain exposed during the electrospinning process. A sketch of the rotating disk collector with the aluminum strips on it is shown in Figure 2.

![FIG. 1: Sketch of the electrospinning process. The polymer exits the base of the syringe, located at the top of the diagram. The jet formed from the process is illustrated by the spiral pattern between the syringe and the rotating disk collector. The jet eventually collects on the edge of the rotating disk collector, as the disk spins in a counterclockwise motion.](image1)

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**Formation of poly-acrylonitrile (PAN) blocks**

The aluminum strips are removed from the rotating disk collector and placed on top of a glass slide. The nanofiber covered aluminum strips are then coated with PAN. The PAN should cover only the area identified as the rectangular slots. This will make sure that only the nanofibers are exposed to PAN and that no aluminum remains in the future analysis of the samples. The samples are then allowed to dry for several hours. Once the coating of PAN has hardened, the samples are cut into several equal pieces.

**Heat treatment**

The PAN block segments are heated to 350°C for 3 hours. The samples are later heated to 750°C for 1 hour in nitrogen. This heating procedure will cause the PCL nanofibers to evaporate, leaving only a hollowed out channel through the PAN segments. The nanochannels are then mounted on top of a needle and the tip of the needle is sealed with epoxy. The samples are then allowed to dry for 3 - 4 hours. It is essential that not all the nanochannel be exposed to the epoxy. If the entire nanochannel comes into contact with the epoxy, then the pressure-driven flows through the nanochannels will not work.

**Pressure-driven flows**

Once the epoxy has dried, the needle is attached to the end of silicon plastic tubing. The needle is located in the same place the glass capillary is located in the fluid supply system of Figure 3. The fluid supply of the experimental apparatus was done through two syringes, one 1mL syringe and one 10 mL syringe. The 1 mL syringe was used to deliver decane to the system; the 1 mL syringe was added to the system where the three-way stopcock is located in Figure 3. The 10 mL syringe was used to pressurize the fluid supply system. The 10 mL syringe was attached to the system where the one-way stopcock is located. An air chamber and pressure gauge were also incorporated into the system. The pressure gauge was used to monitor the pressure of the fluid flow while the air chamber was used.
to keep fluid flow in the system at a constant pressure. To pressurize the system, the 10 mL syringe would pressurize the air chamber and the one-way stopcock would then be closed. To reach higher pressures, this procedure would be repeated several times. To record the fluid flow out of the nanochannel, a CCD camera was used to record the development of decane emulsions in a water bath prepared under a microscope.

Results

Several trials, consisting of two-phase flows, were examined. In the trials being studied, the initial intention was to observe decane emulsions in a water surrounding. Instead, the observations of the experiments revealed an air emulsion trapped inside of a decane emulsion, as seen in Figure 4.

The air, in the experiments, was observed to be a dark sphere in the center of a larger, lighter colored sphere at the tip of the nanochannel being studied. The analysis of the trials revealed that the total, decane, and air volumetric flows followed linear behavior, as seen in Figures 5 and 6.

The trend of these graphs was close to the behavior one would expect with a pure flow system. The air, decane, and total volumetric flow rates in the four trials examined all exhibit linear behavior. However, all of the trials observed consisted of two-phase flows. Poiseuille’s law, the equation used to find channel diameter for pure flows, cannot be used to find the nanochannel diameters. In order to understand the interactions that occur in the nanochannels, a two-phase model is needed. The two-phase model to be used will be a slit with two-fluid layers between it. A sketch of this system is seen in Figure 7.

Discussion

Many of the experiments conducted had a two-phase flow in them. Formulas, such as Poiseuille’s law, could not be used to find the channel diameter. To find an accurate estimate for the distribution of decane and air in the nanochannel, it would be necessary to construct a two-phase flow model. The model for the system is
The next step in the calculations was to calculate flow rates of decane and air. This was achieved by multiplying the velocity profiles by the differential area; the differential area being \(dx\) multiplied by a unit value in the \(z\) direction, and integrating over the height of each fluid.

\[
V_{\text{decane}} = \int_0^h \left( \frac{dP}{dx} \right) \left( \frac{y^2}{2\mu_1} \right) + C_1 y \, dy
\]  

\[
V_{\text{air}} = \int_h^H \left( \frac{dP}{dx} \right) \left( \frac{y^2}{2\mu_2} \right) + C_3 y + C_4 \, dy
\]

The volumetric profiles of the decane and air are listed in the following equations:

\[
\dot{V}_{\text{decane}} = \left( \frac{dP}{dx} \right) \left( \frac{h^3}{6\mu_1} - \frac{h^4\mu_1 - h^3\mu_2 - H^2h^2\mu_1}{4h\mu_1\mu_2 - 4h\mu_2^2 + 4H\mu_1^2} \right)
\]

\[
\dot{V}_{\text{air}} = \left( \frac{dP}{dx} \right) \left( \frac{-2H^3 - h^3 + 3H^2h}{6\mu_2} + \frac{H^2h^2\mu_2 + H^4\mu_1 - h^3\mu_1 + h^3\mu_2}{4h\mu_1\mu_2 + 4H\mu_1\mu_2} + \frac{Hh^3\mu_1 - H^3\mu_2 - H^3h\mu_1}{2h\mu_2^2 - 2h\mu_1\mu_2 + 2H\mu_1\mu_2} \right)
\]

To have the volumetric profiles as a function of \(\frac{dP}{dx}\) and \(\frac{\mu}{\mu_1}\), the volumetric profiles of the decane and air need to be divided out by the pure decane volumetric flow and pure air volumetric flow, respectively. Equations 19 and 20 are the final, dimensionless equations of the volumetric profiles.

\[
\dot{V}_{\text{pure decane}} = \frac{-H^3}{12\mu_1} \left( \frac{dP}{dx} \right)
\]

\[
\dot{V}_{\text{pure air}} = \frac{-H^3}{12\mu_2} \left( \frac{dP}{dx} \right)
\]

\[
h_1 = \frac{h}{H}
\]

\[
\mu^* = \frac{\mu_1}{\mu_2}
\]

\[
\frac{\dot{V}_{\text{decane}}}{\dot{V}_{\text{pure decane}}} = -2h_1^3 + \frac{-3(h_1^4 - h_2^2 - h_1^4\mu^*)}{h_1\mu^* - h_1 + 1}
\]

\[
\frac{\dot{V}_{\text{air}}}{\dot{V}_{\text{pure air}}} = -2(-2h_1^3+3h_1) + \frac{-3(h_1^2\mu^* - h_1^2 + h_1^4)\mu^*}{h_1\mu^* - h_1 + 1}
\]
The next step in the analysis was to plot the behavior of the decane and air volumetric flow rates in the nanochannels. Figure 8 and 9 are the plots for the dimensionless volumetric flow rates as a function of the dimensionless height \( \frac{y}{H} \) in the nanochannel.

The decane flow is not the ideal parabola that we observe with the airflow in Figure 9. The decane exceeds the maximum volumetric flow rate because of the interaction it has with the air. The air moves much faster than the decane in the nanochannels. Because of the interfacial condition stating that the decane and air must have equal velocities at the interphase, the decane will have its highest velocity and volumetric flow at the interphase. This condition is what causes the massive overshoot to occur with the decane flow rate. The air volumetric flow does not exhibit this behavior because of the massive difference in viscosities between the air and decane being studied. Since the decane is much more viscous than the air, the interaction the air has with the slower moving decane would be similar to the interaction the air has with a stationary plate.

The effect of the air on the decane exists so long as there is a clear two-phase system. As the air phase decreases, the velocity of the air also decreases. This causes the interphase velocity to decrease, and is also the source of the decrease of the decane volumetric flow rate. As the nanochannel reaches a pure decane flow, the volumetric flow rate returns to a value of 1. However, this occurrence exists only when the decane interphase increases to a height \( \frac{y}{H} \) of 0.9.

Figure 10 is a plot of the total volumetric flow of decane in the nanochannels. The plot displays the correct asymptotic behavior for volumetric flow behavior in the nanochannels. This behavior helps support the applicability of the two-phase model for the nanochannels with decane and air. Also, the inflection point in Figure 10 occurs between \( \frac{y}{H} = 0.2 \) and \( \frac{y}{H} = 0.4 \). This does not follow the trend of a pure flow, which would have the inflection point at \( \frac{y}{H} = 0.5 \). This behavior helps outline the differences between the two-phase system and the one-phase system that would directly follow Poiseuille’s law.

In order to support the volumetric flows of Figures 8 and 9, the velocity profiles for the decane and air were plotted in Figure 11 and 12. If all of the boundary conditions are satisfied, the air’s velocity will increase at a much faster rate than the decane, and the velocity of the two fluids will be equal at the interphase.

The velocity profiles in the nanochannels did help validate the results drawn from the volumetric flow rates in Figures 8 and 9. Figure 11 was the velocity profile normalized with the maximum velocity of decane in a pure decane flow. Figure 12 was normalized with the average velocity of decane in a pure decane flow. Based on Figure 11 and 12, it can be concluded that all boundary conditions are satisfied and that the conclusions drawn from Figures 8 and 9 are accurate. In Figure 11, the interphase is located at halfway through the nanochannel. The velocity of the decane is approximately 200% of the maximum decane velocity. This overshoot supports the idea that the volumetric flow of decane is due to the air moving much faster than the decane in the nanochannel.
Simulations were also conducted with different liquid phases. These simulations were designed to support the findings with air and decane and further explore the behavior of the two-phase model. Eight different liquids were used in these simulations. Air was used in all experiments as the gas phase. A list of these liquids and their viscosities are on Table I.

The graphs in Figures 13 and 14 outline the behavior of the two-phase model with different liquid phases. Figure 13 shows how the volumetric flow rate of the liquid phase changes with the different liquids, and Figure 14 outlines how the volumetric flow rate of the air changes with the different liquids used.

The liquid phase changes the location of its maxima with the different liquids used. As the viscosity of the liquid increases, the location of the maxima shifts to the right. Also, the magnitude of the maxima increases with increasing viscosity.

The air volumetric flow rates seem to remain unchanged with the different liquids used. All of the graphs of the air flow rate follow the same parabolic curve very closely. There are minor deviations in the plots with the different viscosity ratios. However, these deviations are considered to be insignificant.

The final portion of the analysis involved using the two-phase model to estimate the distribution of air and decane in the nanochannels. The distribution of air and decane in the nanochannels was found by analyzing Fig-

<table>
<thead>
<tr>
<th>Fluid</th>
<th>Viscosity (cP)</th>
<th>( \frac{\text{Max}}{\text{Max}_{\text{air}}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>0.306</td>
<td>0.058823529</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.604</td>
<td>0.029801325</td>
</tr>
<tr>
<td>Water</td>
<td>0.894</td>
<td>0.020134</td>
</tr>
<tr>
<td>Decane</td>
<td>0.92</td>
<td>0.019565</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>1.863</td>
<td>0.009661836</td>
</tr>
<tr>
<td>Ethylene Glycol</td>
<td>16.1</td>
<td>0.001118012</td>
</tr>
<tr>
<td>Sulfuric Acid</td>
<td>24.2</td>
<td>0.000743802</td>
</tr>
<tr>
<td>Olive Oil</td>
<td>81</td>
<td>0.000222222</td>
</tr>
<tr>
<td>Vegetable Oil</td>
<td>120</td>
<td>0.00015</td>
</tr>
</tbody>
</table>

FIG. 13: Volumetric flow rate simulations with different liquids

FIG. 14: Air volumetric flow rate for simulations with different liquid flows through nanochannels
TABLE II: Distribution of decane (h) for the nanochannels that produced two-phase flows of decane and air.

| Pressure (Pa) | 49200 | 48400 | 121000 | 54400 |
| Length of Channel (cm) | 1 | 1 | 1 | 1 |
| Air Vol. Flow (nL/s) | 0.1324 | 0.1075 | 1.3531 | 0.3 |
| Decane Vol. Flow (nL/s) | 1.584 | 2.342 | 7.886 | 2.969 |
| Total Flow (nL/s) | 1.716 | 2.450 | 9.239 | 3.269 |
| Decane Flow (%) | 92.290 | 95.612 | 85.354 | 90.801 |
| $\frac{h}{H}$ | 0.57 | 0.63 | 0.49 | 0.55 |
| H (µm) | 1 | 1 | 1 | 1 |
| h (nm) | 569 | 630 | 494 | 549 |

The two-phase model developed does yield estimates of nanochannel diameters that are consistent with the expectations one would have for the decane emulsions formed. The velocity profiles formed in Figures 11 and 12 help support the conclusions drawn from the volumetric flow rates in Figures 8 and 9. The simulations conducted with the different liquids in Figures 13 and 14 reveal that the trend of the decane and air are reproducible with other liquids. The distributions of decane (h) in the nanochannels with two-phase flows were found and listed in Table II.

Further development over controlling the size of the nanochannels, along with controlling the size of the emulsions generated from the nanochannels, will allow for further insight into fluid flow through nanochannels. This research will help improve the efficiency of such technologies as DNA and protein analysis.

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