MRI Quantification of Interstitial Water Transport and Diffusion in Novel Water Purification Systems

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Objectives (I)

- Hydrogel-bridged nanofluidic polycarbonate membranes (previous presentation)
  ⇒ Use NMR to measure hydration levels and states, and transport properties in PEG and HEMA hydrogels

- Scale-up of microfluidic reactors will require microchannel networks (to distribute influent)
  ⇒ Use MRI to measure velocity and concentration
Objectives (II)

- Meso-scale Taylor-Couette-Poiseuille reactor, e.g. continuous freeze distillation desalination unit, emulsion liquid membrane process, or membrane bioreactors
  ⇒ Use MRI to obtain information on flow and mass transport inside the reactor
Outline

• Brief introduction to Magnetic Resonance Imaging
• NMR characterization of the bulk transport properties of hydrogels: PEG, HEMA (preliminary results)
• Structure and velocity MRI acquisition in a microchannel network (hydraulic diameter ~ 1.2 mm)
• MRI velocity reconstruction in the Stationary Helical Vortex mode in a Taylor-Couette-Poiseuille reactor
• Numerical simulations of particle transport in the Taylor-Couette-Poiseuille reactor
• Conclusions and future work
Magnetic Resonance Imaging

- **Tomographic non-invasive** imaging technique
- **Provides** spectroscopic information and **3-D visualization** of spatial density, velocity, and temperature fields of certain molecules, …
- **MRI** is based on the **Nuclear Magnetic Resonance** phenomenon
- **Signal localization** is achieved by synchronizing radio-frequency pulses with linear magnetic gradients

- **Water** is an ideal fluid for MRI
  - Protons (H\(^1\)) are the principle isotope of hydrogen
  - Protons have high magnetic moment

⇒ Here use H\(^1\) MRI
Contrast Mechanisms in MRI/NMR

• Two characteristic relaxation times indicative of water states:
  T1 (spin-lattice) and T2 (spin-spin)
  For pure water, T1 ~ 3 seconds and T2 ~ 2 seconds

• **T1 measurement**: inversion-recovery sequence
  
  \[ S(t) = S_0 \left[ 1 - 2 \exp(- t / T1) \right] \] for one water state
  
  \[ S(t) = S_0 \sum_{i=1,2} x_i \left[ 1 - 2 \exp(- t / T1,i) \right] \] for two water states (free and bound) in hydrogels

• **T2 measurement**: CPMG sequence
  
  \[ S(t) = S_0 \exp(- t / T2) \] for one water state
  
  \[ S(t) = S_0 \sum_{i=1,2} x_i \exp(- t / T2,i) \] for two water states (free and bound)

• **Pulsed field gradient NMR**
  
  – Provides spatial distribution of spin displacements in a selected volume after a specified flow evolution time
  
  – Measures effective diffusion coefficient
Contrast Mechanisms in MRI/NMR

• **Diffusion (tensor) imaging**
  – Use diffusion-encoding magnetic gradients in combination with standard 2D imaging sequence
  – Obtain 2D distribution of apparent diffusion coefficient along encoding gradient direction

• **Spin tagging MRI velocimetry**
  – **Amplitude method**
  – Tag spins in grids or slices and allow to evolve in the flow
  – Observe displacement, distortion, and rotation of tagged spins

• **Phase contrast MRI velocimetry**
  – **Phase method**: use phase of transverse magnetization as an effective molecular label
  – Provides direct point-wise velocity measurement in slice plane
NMR Characterization of Hydrogels
Characterization of PEG

- PEG = poly(ethylene glycol): transparent hydrogel, large swelling ratios
- Synthesis using a crosslinker:
  - Mixture of monomer (PEG mono(methyl ether methacrylate) or mPEGMA), crosslinker (PEG dimethacrylate or PEGDMA), and water
  - Polymerization is initiated in a nitrogen environment by the addition of solutions of ammonium persulfate and tetramethylethylene diamine
  - After mixing, gelling process continues in a nitrogen environment
- Samples are prepared for fixed proportions of monomer / crosslinker (here 95/5) and increasing amounts of water (from 50% to 90% of the total mass) in 25 ml vials (filled to 75-80% capacity)
- NMR is used to measure the T1 and T2 relaxation times, water diffusion coefficient D to characterize the water state(s) inside PEG
Characterization of PEG

The PEG vials were thermally insulated and placed inside a DOTY receiver/transmitter RF coil and inserted in a 4.7 Tesla MRI scanner (resonance frequency = 200 MHz).

Extrapolated values for pure (deionized) water match the expected values:

\[ T_1(x=0) = 2.82 \text{ s} \]
\[ T_2(x=0) = 2.15 \text{ s} \]
Characterization of PEG

The apparent water diffusion coefficient in the PEG samples varies linearly with polymer mass fraction.

Extrapolated values for pure (deionized) water diffusion match the expected value:

\[ D(x=0) = 2.42 \times 10^{-5} \text{ cm}^2/\text{s} \]

From the T1, T2 and diffusion NMR measurements, the water inside PEG appears to be in a single state (free water), since data reduction assuming two water states (free water and bound water) was either inconsistent or reduced to a single state.
Characterization of HEMA

HEMA (2-hydroxyethyl methacrylate) samples were prepared in a similar fashion as the PEG samples with 50% water and increasing amounts of crosslinker (PEGDMA), from 4% to 24% (mass fraction).

Low measured values of T2 (< 14 ms) ⇒ spin density and diffusion MRI measurements are very noisy (signal proportional to \( \exp(-TE/T2) \), \( TE \sim 10 \) to 50 ms)

⇒ Water inside HEMA appears to be in a “solid state” if w.c. < 60% (which confirms Shaurya Prakash’s SEM observations)
MRI Investigation of a PDMS Microchannel Network
PDMS Microchannel Network

- **Material:** Polydimethylsiloxane (PDMS)
- **Capillary Network:** 2.0 mm deep inter-connecting channels forming a 10 x 8 periodic array
PDMS Microchannel Network

- **Velocity measurements using phase contrast spin-echo velocimetry:**

  water doped with CuSO₄, Re = 1, TR = 3 T1 (T1 = 1 s), TE = 45 ms

  5 x 6.5 cm FOV, 256 x 512 encoding, resolution ~100 x 100 microns
PDMS Microchannel Network

- **Virtual mask**: a mask accounting for partial volume effects is numerically computed to facilitate data analysis.

(Work in progress)
MRI Investigation of the Stationary Helical Vortex mode in the Taylor-Couette-Poiseuille System
TCP Experimental Set-Up

Radii ratio: $\eta = 0.5$

Aspect ratio: $\Gamma = 16$

ID = 19.05 mm
OD = 38.10 mm

Water Reservoir
Pump
RF coil
Test Section
To Variable Speed Motor

4.7 T Superconducting Magnet

Metering Valves

Water Reservoir
Pump
The velocity components are extracted from the nodal displacements of the tagged grid (initial grid shown in red).

Moser, Raguin, Georgiadis, PRE 64, 2001
SHV 3-D Flow Topology

2 counter-rotating stationary helical vortices

3-D cat’s eyes pattern

Raguin & Georgiadis JFM 2004
SHV 2-D Flow Topology

(C_I) and (C_{II}): 2 counter-rotating vortices

(P_I) and (P_{II}): annular regions populated by periodic orbits

h: hyperbolic point (saddle)

e: elliptic point or

p: parabolic point or

Raguin & Georgiadis JFM 2004
Numerical Simulation of the SHV mode (with Dr. Holdych)

A Lattice Boltzmann method is employed to simulate the Navier-Stokes equations, assuming a periodic flow with axial wavelength (= experimental), and using the analytical velocity field obtained via data assimilation as initial guess.

Grid resolution: 58 points in r-direction, 120 for one axial wavelength.

Good agreement: the steady-state numerical solution agrees with the data assimilation results within 10% for the velocity components and 7% for the stream function (rms normalized by max).

Raguin & Georgiadis JFM 2004
Transport of Passive Solid Particles in the SHV Flow with Time-Periodic Hamiltonian Perturbations
Time-Periodic Hamiltonian Perturbations

Fluid Elements

- Perturbation frequency: 0.16 Hz, 0.32 Hz, 0.80 Hz
- Perturbation amplitude = 0.1

Heavy Particles

Contraction of phase space
Conclusions and Future Work

• MRI used to measure hydration levels and states, and transport properties in HEMA and PEG hydrogels used by Prof. Shannon’s group (hydrogel-bridged nanofluidic polycarbonate membranes)
  ⇒ Collect complete set of data for gel characterization and selection
  ⇒ NMR or spectroscopic MRI study of prototype membranes

• Microchannel network: MRI resolves the individual channels and 2D velocity was measured
  ⇒ Systematic study for different flow rates and fluids (non-Newtonian)

• Meso-scale Taylor-Couette-Poiseuille reactor: MRI was used to reconstruct the 3D velocity field, and allowed numerical simulation of solid particles in the flow
  ⇒ Perform experiments in a more realistic prototype of the reactor (for continuous freeze distillation process, emulsion liquid membranes)
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