Open Single-File Channel Persistence Length in Crystalline Dipeptide Nanochannels

Navid M. Mirnazi,1 Hirshi Bhase,2 Muslim Dvoyashkin,2 Clifford R. Bowers2

1Department of Chemical Engineering, University of Florida, Gainesville, FL, 32611
2Department of Chemistry, University of Florida, Gainesville, FL, 32611

Introduction: Single-File Diffusion

Single-file diffusion (SFD) is a universal phenomenon observed in systems of classical one-dimensional channels. L-AlanLY-L-Valine (AV), with an internal diameter of 5.1 Å, is an ideal system to study SFD of xenon atoms (4.36 Å), and has been shown to exhibit SFD [1].

As a consequence of the inability of the particles to pass one another in such channels, the mean squared displacement along the channel axis deviates from Normal Fickian Diffusion (ND) and becomes proportional to the square root of the observation time, i.e. \( \langle \Delta z(t)^2 \rangle = 2t \theta^2 \) [4-6], where \( \theta \) is the single-file mobility factor and \( \theta \) is the fractional occupancy.

Study Objective

The goal of this study was to calculate and verify the persistent channel length in samples of AV with different particle sizes. To accomplish this task, two different samples of AV were analyzed using hyperpolarized tracer exchange NMR (HTE-NMR) technique. Fitting the process data to the analytical model allowed us to estimate an average channel persistence length.

Relevant Equations

Analytical models for SFD and ND for the HTE-NMR tracer exchange function, normalized to the steady state adsorbed gas signal, are as follows [1]:

SFD:

\[ \text{SFD: Eqn. } 1 \]

ND:

\[ \text{ND: Eqn. } 2 \]

Sample Preparation and Packing

Two different samples of AV were used in this study. The "normal AV" sample had no particle processing, whereas the "pulverizer AV" was mechanically ground to yield smaller particles conforming to the channel size of AV nanotubes. These nanotubes were packed loosely into the NMR sample holder at a pressure of 3.0 bar, enabling the evaluation of a new parameter, the channel persistence length, which is defined as the size of the smallest size of particles that can pass through the channel.

Meersmann et al. [2] performed the first tracer exchange studies using hyperpolarized \(^{129}\text{Xe}\) to study single-file diffusion in the TPP nanotube system.

In HTE-NMR, exchange of hyperpolarized molecules in the gas phase with unpolared molecules within the channels is observed under conditions of sorption equilibrium. Because exchange is predicated on transport to the channel openings, the build-up of labeled molecules (blue) contains information about the time-scaling of the root mean-squared displacement within the channels.

Continuous-Flow NMR Setup

Continuous-flow nuclear magnetic resonance (NMR) spectroscopy is a powerful tool for analyzing samples in situ. The setup involved the use of a hyperpolarized xenon gas at a pressure of 8 bar and a flow rate of 750 cm\(^3\) min\(^{-1}\) for the NMR probe and the pumping cell. The latter operated at a wavelength of 850 nm.

Results and Discussion

Hyperpolarized tracer exchange NMR data for 3 bar xenon in normal AV (left) and pulverized AV (right). Dashed and solid lines show the analytical expression for SFD and Fickian Diffusion, respectively. Blue symbols represent the normalized gas phase signal and are related to the scales on the right side (shown in blue) of the plots. Insets show the same data in a log-log plot.

The HTE-NMR results for both samples yielded SFD. As can be seen in Fig. 6, both samples fit to the dotted line (Eqn. 1) very well. Assuming SFD, and setting \( C_s \) as a fitting parameter, we determined \( C_s \) to be 0.0095 ± 0.00008 and 0.0713 ± 0.0005 for normal AV and pulverized AV, respectively. From Fig. 7, we were able to determine the ratio of channel-adsothed to gaseous Xe atoms \( \left( n_{\text{ads}} / n_{\text{gas}} \right) \).

Values utilizing these along with \( F = 6 \times 10^{-11} \) mol \( \cdot \) s \(^{-1} \) (the previous PFG-NMR data [3]) were used to calculate consistent channel lengths of 40 ± 3 μm and 5.2 ± 0.7 μm for normal AV and pulverized AV, respectively.

Conclusion and Future Work

Using hyperpolarized \(^{129}\text{Xe}\), we can achieve a large signal enhancement of the NMR spectra. Through HTE-NMR we can measure and model diffusion of xenon through AV nanotubes, and, by fitting the experimental data we can derive the open persistent channel length of samples.

Future work will include isolating samples with different size distributions of particles and analyzing them using the HTE-NMR technique to derive channel length.

References


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