

## Self-Diffusion of Water in Compressed Hexagonal Phases: Experimental and Simulated Results.

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### 1. Introduction

Lytotropic liquid crystal materials consist of self-assembled ordered structures of amphiphilic molecules in the presence of a solvent [1]. Typically the samples consist of a powder distribution of director orientations, but certain mesophases (i.e., hexagonal and lamellar) may be macroscopically aligned with external fields such as mechanical or magnetic [2; 3]. Polymerised lyotropic liquid crystal phases can be made using, for example, polymerisable surfactants (e.g., Ref. [4]). These materials are attractive for applications like anisotropic ion conductors, templating nanoporous materials and nanoparticles, drug delivery systems, nanofiltration membranes, gas separation membranes and selective vapour barriers [5].

As most of these applications involve the transport of molecules, studying the diffusion of molecules in these environments is important. Pulsed gradient spin-echo (PGSE) NMR is a non-invasive technique that is well suited to measuring self-diffusion [6]. Self-diffusion in a lyotropic liquid crystal system is well documented (e.g., Refs. [6-8]). Self-diffusion in hexagonal phases has been simulated using Cellular Automata with fixed cylinder radii and a large number of diffusing molecules; and agrees well with PGSE NMR results [9; 10]. Here we have used simple simulations of single molecule random walks in hexagonal arrays of cylinders (Fig. 1) to predict the diffusion ellipsoids for these systems for comparison with experimental results. We are particularly interested in simulating the self-diffusion and effects of imperfections and fluctuations (e.g., radii and position) in macroscopically aligned hexagonal phases with uniaxial compression/tension and comparing this to the experimentally measured self-diffusion; which is not only pertinent for some of the above applications, but also for potentially new applications of these materials.

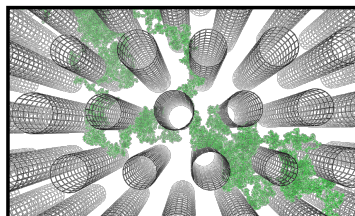


Fig. 1: A simulated random walk (green line) of a particle in the spaces around reflecting cylinders in a hexagonal array.

### 2. Model and Simulations

Briefly, the cylinders are assumed to be reflecting and impenetrable with fixed positions. Cylinder radii are random within a given tolerance or have a fixed value. The particle radius is simply added to the cylinder radius. The step size is chosen to be much

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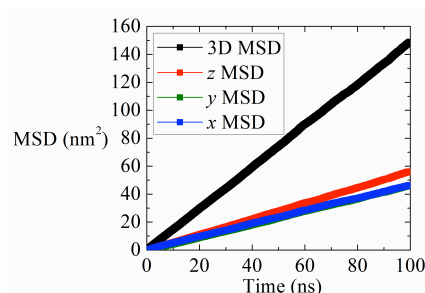


Fig. 2: MSD of a particle diffusing in a hexagonal array of reflecting cylinders with no compression.  $D_{\text{Particle}} = 2.792 \times 10^{-10} \text{ m}^2\text{s}^{-1}$ , max step size  $\pm 0.1 \text{ nm}$ , total steps = 16720 repeated 10000 times, hexagonal lattice parameter = 5.77 nm, cylinder radius = 1.35 nm with a random variation of up to  $-15\%$ , particle radius = 0.14 nm, z-axis is parallel to the cylinder axes. The x MSD is overlapping the y MSD in the figure.

simulations may be useful for studying the effects of compression on macroscopically aligned hexagonal phase materials. For such cases the orientation of the array before compression may also need to be averaged in the simulations, while for simulations of uncompressed phases the array orientation has little effect on the  $x$  and  $y$  MSD. These simulations may be altered to include other boundary conditions (such as surface binding and permeability), undulations along the cylinder axis and random variation in position within a tolerance.

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smaller than the cylinder radius/separation. The number of steps is chosen based on the desired overall mean squared displacement (MSD). The MSD is calculated for each step in the walk and this is averaged for a large number of walks (Fig. 2). For compression, the array is altered accordingly with or without cylinder compression. The resulting MSD's are compared to the experimental diffusion ellipsoids. Undulations in the cylinder axes may be account for by averaging the results over the undulations.

### 3. Conclusion

The simulated results for the uncompressed hexagonal phase match well with the experimental diffusion ellipsoids measured with PGSE NMR. These types of