



Molecular Dynamics Simulation to Study Phase Separation of a Cellulose Acetate Membrane Induced by a Non-Solvent

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ABSTRACT

Symmetrical membranes are structures with a homogeneous composition and characteristics throughout their thickness. This homogeneity makes symmetrical membranes easier to manufacture and study than their asymmetrical counterparts, which have layers with distinct properties.

The aim of the study is to understand how the phase inversion mechanism occurs in the coagulation bath, using molecular dynamics simulation. The system studied is cellulose acetate (CA) and N,N-dimethylformamide (DMF) with water as non-solvent. Packmol package was used in this work to create an initial point for molecular dynamics simulations. In this work, we have shown that molecular displacement is governed by Fick's diffusion laws.

Keywords: molecular dynamics simulation, cellulose acetate membrane, phase separation

1. Introduction

Membranes with symmetrical features possess a consistent composition and uniform properties across their entire depth. This consistency simplifies the production and examination of symmetrical membranes in contrast to asymmetrical ones, which are composed of layers with varying characteristics.

The technique of phase separation is commonly employed in industrial manufacturing to create a diverse array of products, ranging from fundamental metals to complex polymer solutions. The fabrication of polymer membranes represents a key area of interest within this domain. For the past forty years, significant research efforts have been dedicated to understanding the processes involved in the formation of polymer films, with the aim of achieving precise control over their ultimate structural morphology.

Beginning with a uniform polymer solution where the polymer is dissolved in an effective solvent, the process of thermodynamic phase separation is triggered by either a temperature shift (known as Temperature-Induced Phase Separation or TIPS) or the addition of a non-solvent for the polymer (referred to as Non-Solvent Induced Phase Separation or NIPS) [1-3].

The NIPS method, which involves immersion precipitation, is a straightforward technique for creating polymeric membrane materials. This method facilitates the alteration of both the membrane and its structure. The architecture of the membrane pores is categorized into three types: annular pores, sponge-like pores, and finger-like pores, each with distinct structural features.

Thus, mastering the complete architecture of the membrane is essential for optimizing its functionality. Yet, achieving this mastery is challenging due to the intricate nature of the membrane formation process, which is notoriously complex to model and forecast. The phenomenon of phase separation is theoretically modeled using the Cahn-Hilliard equations in polymer systems. These equations account for the system's free energy of mixing, which is based on the Flory-Huggins theory, and necessitate a distinct equation to accurately characterize the mobility aspect.

The aim of this research is to study the process of penetration of water molecules into the polymer/solvent layer and to establish Diffusion profiles. To this end, and to clarify scientifically the phenomenon of water penetration into the polymer solution, we used molecular dynamics (MD).

2-Simulation Methodology

Atomistic molecular dynamics simulations [4] have been carried out for cellulose acetate and DMF as solvent and water as an immiscible solvent. For generating multi-component cellulose acetate membrane configurations for MD simulations, Packmol package [5] was used in this work to create an initial point for molecular dynamics simulations by packing molecules in defined regions of space and Cellulose acetate, DMF and water are described by OPLS force field (OPLS/AA optimized potentials for liquid simulations / all-atom) [6]. In our work we used LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) to study the temperature effect on the formation of the member (NIPS). For simulated system, after the preparation of the initial state, energy minimization using the steepest gradient descent method is performed, followed by a short 100 ps pre-equilibration

run at constant volume at temperature $T = 300$ K. After that, the pressure in the system is equilibrated to 1 bar using anisotropic Berendsen barostat [7]. Then, two successive equilibration simulations were conducted: the first one in the NVT ensemble for 100 ps, and the second in the NPT ensemble for 750 ps. After equilibration, the production run was conducted in the NPT ensemble. MD simulations produce trajectories depicting the motions of atoms over a specified simulation time.

The simulation boxes were periodic in x- and y-directions while in the z direction, we have created an empty space above and below the region occupied by the molecules to avoid interactions with its periodic images. The system consists of two regions, the first of which is occupied by water molecules forming an aqueous layer above another region containing molecules of cellulose acetate and DMF.

An MD simulation model containing a polymer solution of cellulose acetate and DMF (solvent), and water (no-solvent) was built, as shown in Fig. 1 software, lammps, was used to progress the simulation work.

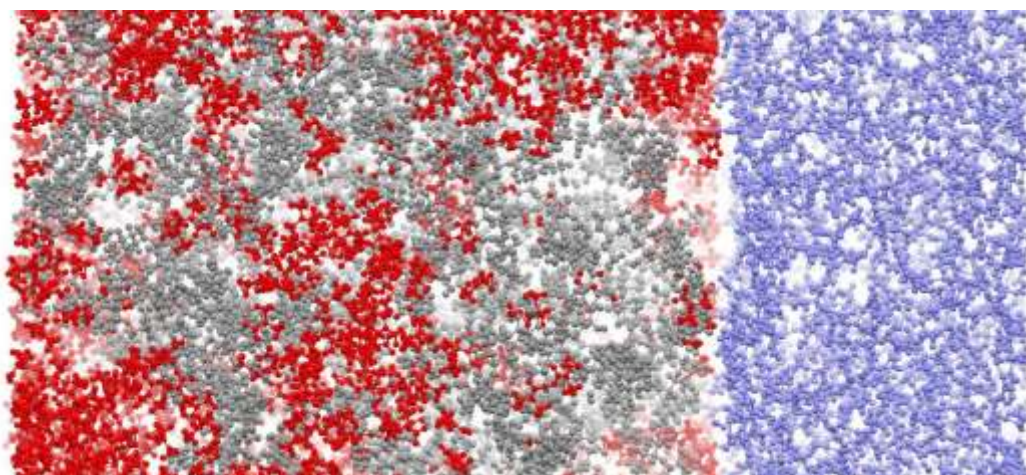
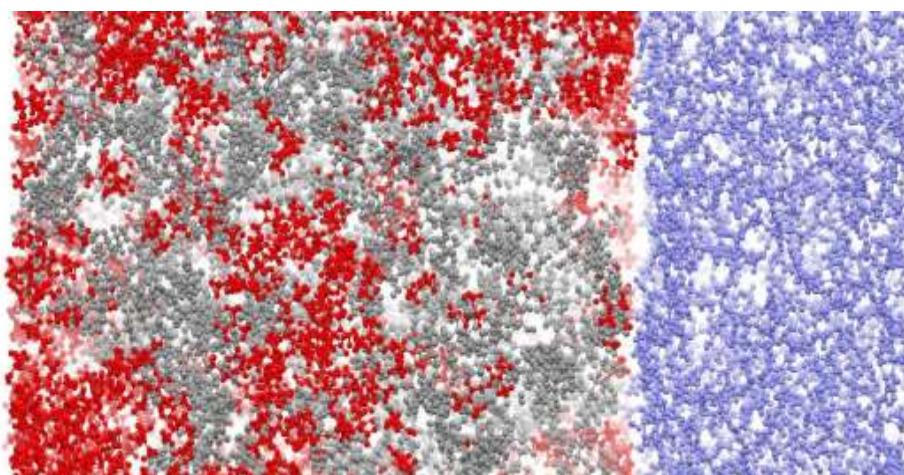


Fig. 1: Molecular configuration and boundary conditions of the MD model. Assigned colors to the atoms in the figure: blue: water molecule, red: DMF molecule, gray: CA

The upper block containing water molecules, subjected to compression, in contact with the lower block and diffusion occurred at the interface, followed by penetration of the water molecules into the polymer layer.

3-Results and Discussions

The molecular distribution profiles obtained after different calculation times show diffusion of the water molecules in the polymer layer (fig.2). Atomic configuration and boundary conditions of the MD model. Assigned colours to the molecules in the figure: red: DMF molecules, blue: water molecules and gray: cellulose acetate molecule



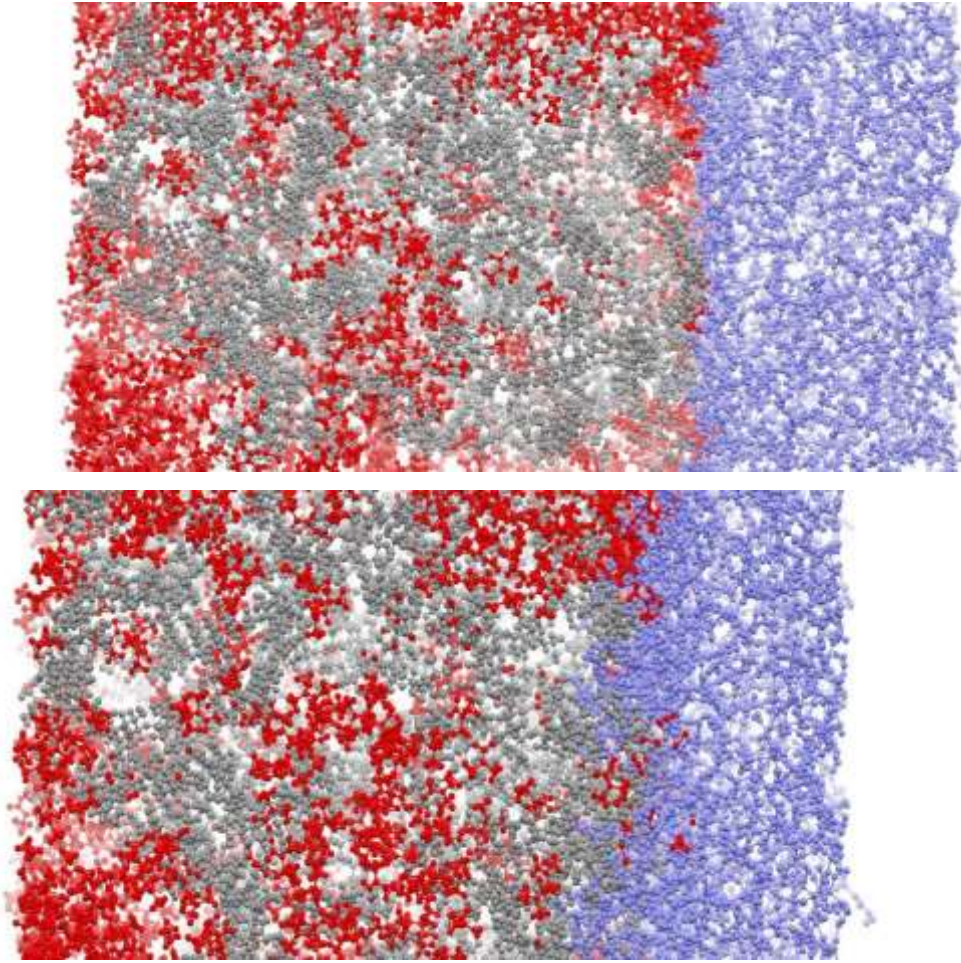


Fig. 2: Schematic of the interfacial penetrations of water, DMF, and CA at different contact times: (a) 0 ps, (b) 400 ps, and (c) 1200 ps. Assigned colours to the molecules in the figure: blue: water molecule, red: DMF molecule, gray: CA

The density profile of the water molecules shows a steep profile at the interface at the start of the simulation, followed by bell-shaped profiles during diffusion. This behaviour reflects the accumulation of water molecules at the interface and diffusion within the polymer layer (fig 2, 3).

In what follows, we will treat these diffusion profiles using the Fick formalism. This formalism describes flux as a linear function of the concentration gradient. Diffusion can be induced by the concentration gradient of the element. It implies a wider distribution which tends to an uniform concentration over depth. The driving force corresponds to a chemical potential gradient in the sample and causes the entire distribution to move towards the surface.

$$J = -D \frac{dC(z)}{dz} \quad (\text{Unit: } D: \text{cm}^2/\text{sec}; J: \text{number}/\text{cm}^2/\text{sec})$$

Infinite integration of the Fick's second law:

$$\frac{\partial C(z)}{\partial t} = D \frac{\partial^2 C(z)}{\partial z^2}$$

$$C(z,t) = \frac{\alpha}{\sqrt{t}} e^{-\frac{z^2}{4Dt}}$$

We have :

Fick's first law describes diffusive flux as a linear function of the concentration gradient.

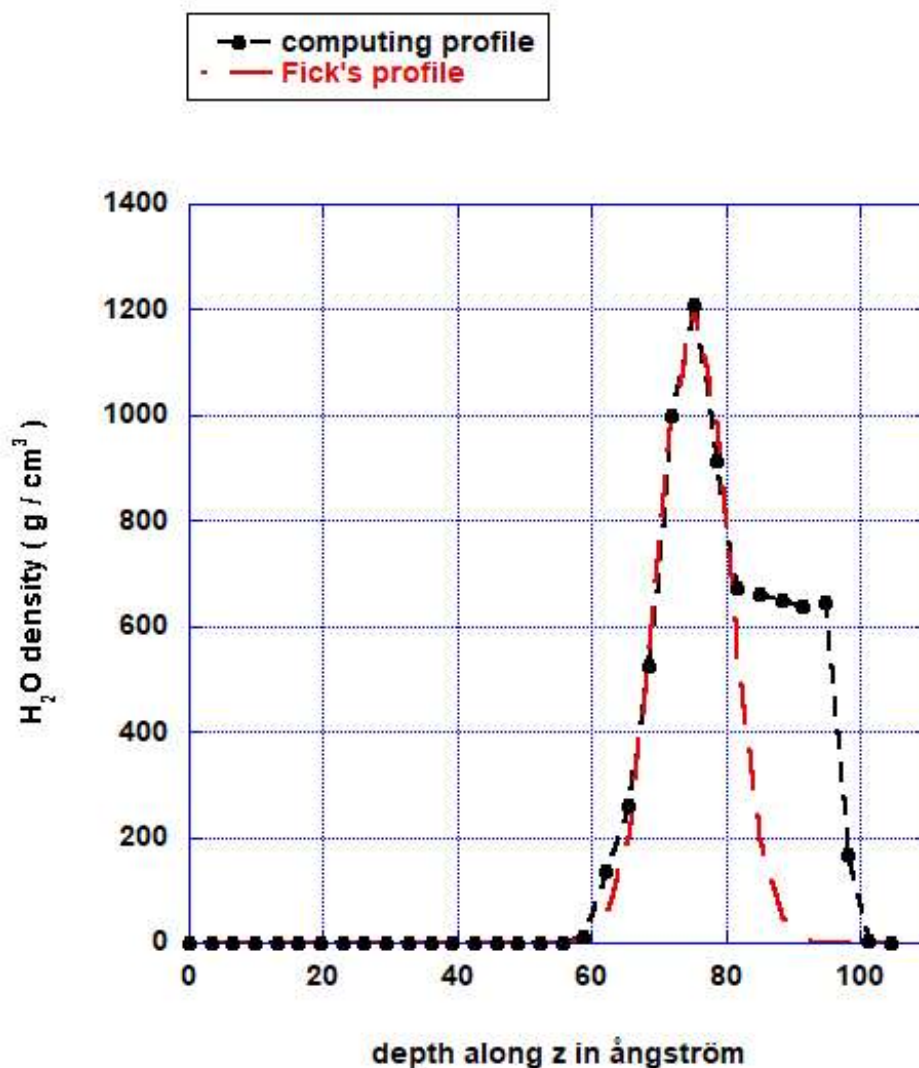


Fig. 3: Comparison between the water diffusion profile in the polymer/solvent layer calculated from molecular dynamics and that calculated from the Fick law at 1200 ps time.

Figure 3 shows that displacement of water molecules is governed by Fick's diffusion laws (fig 3). This means that the diffusion of water in the polymer solution follows an ideal behaviour.

Conclusion

Symmetrical membranes are uniform structures that maintain consistent composition and attributes across their entire depth. Their uniformity simplifies both the production process and research compared to asymmetrical membranes, which are composed of layers with varying characteristics.

The study's objective is to decipher the phase inversion process within the coagulation bath through molecular dynamics simulations (Lammps code). The focus is on the interaction between cellulose acetate (CA), DMF (the solvent), and water (the non-solvent). The Packmol package facilitated the generation of a starting configuration for the molecular dynamics simulations. The results of this study confirm that the movement of the molecules conforms to Fick's diffusion laws, indicating that the diffusion of water in the polymer solution exhibits ideal behaviour.

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