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# Modeling phase inversion using Cahn-Hilliard equations – Influence of the mobility on the pattern formation dynamics

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## HIGHLIGHTS

- Phase-field simulations for polymer/solvent system.
- Significant influence of the mobility model on the pattern evolution.
- Growth laws close to $L_c \sim t^{1/3}$ whatever the quenching conditions for constant mobility.
- Growth laws between $L_c \sim t^{1/5}$ and $L_c \sim t^{1/3}$ for non-constant mobilities, depending on the quenching conditions.
- Pattern analysis using the Minkowski descriptors.

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## ABSTRACT

This paper presents a phase-field simulation of phase separation for a polymer/solvent system and aims at investigating in a systematic way the influence of the mobility model on the simulation results. In 2D geometry, the Flory-Huggins theory was used to describe the thermodynamics of the PMMA/cyclohexanol system and four mobility models were tested: a constant model, a slow model, a fast model and a mobility model based on the free-volume theory of Vrentas. The simulated patterns were analyzed by Fourier transform and using Minkowski descriptors. Growth laws deduced from a Fourier Transform of the patterns exhibited that the power laws were ranged between 1/5 and 1/3 depending on the quenching conditions ($T$ and initial composition) and the mobility model. Using the Vrentas mobility model, growth laws of $L_c \sim t^{1/5}$, $L_c \sim t^{1/4}$ and $L_c \sim t^{1/3}$ were found for initial compositions in the range $\phi_{init} = 0.075, 0.140$ and $0.200$, respectively, whereas due to faster phase inversion dynamics, a growth law close to $L_c \sim t^{1/3}$ was simulated for the constant mobility model whatever the quenching conditions ($T$ and initial composition), thus demonstrating the importance to choose an appropriate mobility model for simulating the phase separation of polymer/solvent system.

## 1. Introduction

The formation of porous polymeric membranes is usually induced by a phase separation (PS) method: a homogeneous solution of polymer/solvent is quenched into the two-phase region and then segregates into two spatial domains where the rich-polymer region will constitute the membrane structure while the lean-polymer phase will constitute the pores after solvent extraction. Three methods are mostly used to prepare polymeric membranes: (i) the Temperature Induced Phase Separation (TIPS), (ii) dry casting method, or Non-solvent Induced Phase Separation (NIPS), including the immersion precipitation process or Liquid Induced Phase Separation process (LIPS) and the Vapor Induced Phase Separation process (VIPS). Those processes involve liquid/liquid demixing, and sometimes solid/liquid demixing, coupled with heat and/or mass transfers. Modeling and simulating the phase separation dynamics is thus a huge task, which explains why the industrial fabrication of polymeric membranes is still mostly conducted through trial and error processes. However, some modeling efforts have been made in two directions: (i) modeling the transport of low molecular weight species in a homogeneous polymeric system, i.e. prior to phase inversion and (ii) modeling the dynamics of phase separation for mostly binary systems. The first papers dealing with the description of the diffusion of small species (solvent, non-solvent) within a polymeric matrix have been published by Anderson and Ullman (1973) to describe the dry casting process. It was rapidly followed by more complex models, which aimed

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at taking into account more precisely the boundary effects, the diffusion formalism and the coupling between mass and heat transfer (Castellari and Ottani, 1981; Krantz et al., 1986; Tsay and McHugh, 1991; Shojaie et al., 1994a,b; Matsuyama et al., 1997; Altinkaya et al., 2005; Li et al., 2006). Modeling VIPS process was described latter (Matsuyama et al., 1999; Yip and McHugh, 2006; Bouyer and Pochat-Bohatier, 2013; Bouyer et al., 2017) and the description of the diffusion formalism progressively gained in complexity to better simulate the transport of the solvent and/or non-solvent species in a ternary system. Based on the first paper of Bearman (1961), the diffusion phenomena have been described using mutual diffusion formalism for binary, then ternary systems. Later, the description of the self-diffusion proposed by Vrentas and Duda (1977) and Vrentas and Vrentas (1993) has been used in most of the studies until today (Barton et al., 1998; Zielinski and Hanley, 1999; Alsoy and Duda, 1999; Price and Romdhane, 2003; Mino et al., 2015), and hence, the modeling of small species (solvent, non-solvent) in a polymeric matrix prior demixing has been studied for the whole phase separation processes, including TIPS (Li et al., 2006).

In parallel, modeling the dynamics of phase separation has been investigated in various fields such as metallurgy or polymeric materials. Cahn and Hilliard proposed the first phase-field (PF) model (Cahn and Hilliard, 1958) to describe the spinodal decomposition of a binary system. The phase field model was later generalized to take into account non-linear effects (Langer et al., 1975) and hydrodynamics (Siggia, 1979; Kawasaki and Ohta, 1983; Furukawa, 1985). Other interesting methods have appeared in recent years like Dissipative Particules Dynamics (DPD) as suggested by referee (Tang et al., 2015; Mai et al., 2016).

Phase field models were also promptly adapted to capture the phase separation dynamics of polymer blends (Gennes, 1980; Binder, 1983, 1987; Chakrabarti et al., 1993), binary polymer/solvent system (Caneba and Soong, 1985; Barton et al., 1998; Mino et al., 2015) or more recently ternary system (Barton and McHugh, 1999; Zhou and Powell, 2006). In those phase field models which describe the dynamics of the phase separation a mobility dependence has to be assumed. In a first approach, a constant mobility was chosen for binary systems (Langer et al. (1975), B model in Hohenberg and Halperin (1977), Caneba and Soong (1985), and Toral et al. (1988)) but further approaches assumed that the mobility term depends on the temperature and the polymer concentration (Novick-Cohen and Segel, 1984; Zhang et al., 1995; Cahn et al., 1996; Puri et al., 1997; Nauman and He, 2001) which was obviously more realistic.

Consequently, three non-constant mobility models have been developed, based on different local mutual diffusion assumptions: the fast model (Kramer et al., 1984), the slow model (Gennes, 1980; Pincus, 1981; Brochard et al., 1983; Binder, 1983, 1987) and the Vrentas model (Vrentas and Vrentas, 1993). In the fast model, the mutual mobility is dominated by the self-diffusion of the faster components of the system whereas for the slow model the mutual mobility is dominated by the self-diffusion of the slowest one. Both models have been mostly applied for simulating the phase separation of polymer blends, meaning that the self-diffusion of both species were of the same order of magnitude. A binary system composed of a polymer dissolved in a solvent represents a more complex problem since the self-diffusion of both components are expected to be very different. In this respect, the Vrentas model was developed to describe the phase separation of polymer/solvent systems and was based on free volume theory of Vrentas and coworkers(Vrentas and Duda, 1977; Vrentas et al., 1985; Vrentas and Vrentas, 1993). Free volume theory was used to determine the self-diffusion coefficients of small species in a polymer matrix, and later to describe the diffusion of small species (solvent, non-solvent) in ternary systems. In the last decades, it has been largely used for polymer/solvent and polymer/solvent/non-solvent systems when the degree of polymerization of the polymer was large (Barton et al., 1998; Mino et al., 2015). Nevertheless, even in the most recent papers dealing with the modeling of phase separation in the field of membrane formation, the role and the influence of the mobility models was not investigated, even though this parameter controls the dynamics of demixion.

In this paper, we aim at investigating the influence of the mobility model choice on the phase separation dynamics for binary polymer/solvent system, in 2D geometry. Four different mobility models were tested in this work: constant, slow model, fast model and mobility based on the Vrentas free volume theory. The simulation of phase separation was performed for the PMMA/cyclohexanol system since this system was previously studied in literature in TIPS process (Graham et al., 1997; Vandeweerdt et al., 1991). Different quenching points in the diphasic region of the phase diagram were tested, at different initial compositions and different quenching temperatures for the Vrentas model. The simulation results (phase separation patterns) were analyzed by Fourier Transform in order to estimate the growth law of the characteristic length. This analysis was completed by an original analysis of patterns using the Minkowski descriptors that allows quantifying the morphology differences observed in the simulated pattern(Mecke and Sofonea, 1997). To the best of our knowledge, such analysis of polymer-solvent phase separation using Minkowski descriptors has never been reported before.

## 2. Theory

### 2.1. The governing equation

The phase field dynamic that describes the phase separation is a modified time-dependent Ginzburg-Landau theory for conserved order parameter, without thermal fluctuations Eq. (1)

$$\frac{\partial \phi(\vec{r},t)}{\partial t} = -\nabla \cdot \vec{J}(\vec{r},t) = \nabla \cdot \int \frac{\Lambda(\vec{r},\vec{r}')}{k_B T} \nabla' \mu(\vec{r}',t) d\vec{r} \qquad (1)$$

where $\phi$ is the volume fraction of the polymer, proportional to the ratio of the polymer concentration $c$ over the polymer density $\rho_p(\sim c/\rho_p)$, $k_B$ is the Boltzmann constant, $T$ the temperature of the system. $\vec{J}(\vec{r},t)$ is the current associated with the mass transport which is connected to the thermodynamic force $\nabla\mu$ though a non-local relation via the mobility coefficient $\Lambda(\vec{r},\vec{r}')$ (Gennes, 1980; Binder, 1983; Kawasaki and Sekimoto, 1987; Maurits and Fraaije, 1997; Reister et al., 2001; Müller and Smith, 2005). If the molecules connectivity is neglected for a spatial resolution larger than the chain scale, a local mobility coefficient is considered to simplify the numerical resolution:

$$\vec{J}(\vec{r},t) = -\frac{\Lambda(\vec{r},t)}{k_B T} \nabla \mu(\vec{r},t) \qquad (2)$$

The chemical potential can thus be expressed as a functional derivative of the system free energy (Cahn and Hilliard, 1958) Eq. (3)

$$\mu = \frac{\delta F}{\delta \phi} = \frac{\delta}{\delta \phi} \int d\vec{r} \left( f(\phi) + \frac{1}{2} C(\phi) \mid \nabla \phi|^2 \right) \qquad (3)$$

where $f(\phi)$ is the free energy of mixing per lattice site for polymer solutions described by the Flory-Huggins theory Eq. (4)

$$f(\phi) = k_B T \left[ \frac{\phi}{N} \ln \phi + (1-\phi)\ln(1-\phi) + \chi \phi (1-\phi) \right] \qquad (4)$$

where $N$ is the degree of polymerization of the polymer and $\chi$ is the interaction parameter that depends on the temperature $T$.