GEORG-AUGUST-UNIVERSITÄT
GÖTTINGEN

Einführung ins wissenschatliche Arbeiten

Teilchensimulationen von Polymermischungen in begrenzten Geometrien mit zeitabhängigen Randbedingungen

Particle simulations of polymer mixtures in confined geometries with time dependent boundary conditions

prepared by

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Contents

Nomenclature

Lateinische Buchstaben

Variable	Bedeutung	Einheit
A	Querschnittsfl"ache	m^2
c	Geschwindigkeit	$\mathrm{m/s}$

Griechische Buchstaben

Variable	Bedeutung	Einheit
α	Winkel	$°; -$
ϱ	Dichte	$\mathrm{kg/m^3}$

Indizes

Index	Bedeutung
m	Meridian
r	Radial

Abk"urzungen

Abk"urzung	Bedeutung
2D	zweidimensional
3D	dreidimensional

Abk"urzung	Bedeutung
max	maximal

1. Introduction

2. Theory

2.1. Polymeric mixtures

Polymer mixtures consist of two or more chemically different polymer types. The mechanical and thermodynamic properties can vary greatly with several factors such as composition, molecular weight and interactions between the polymers. This makes them desirable for manufacturing materials with tailored properties.

If the composition is uniform everywhere, then the mixture is called homogeneous. In this case the properties do not change throughout the mixture. In a heterogeneous mixture, in contrast, the composition is non-uniform, leading to visible boundaries which may have very different properties. This phenomenon is also called macro-phaseseparation. From an entropic viewpoint, mixing is always favored. However, energetic interactions between polymers can either favor or suppress mixing. Whether a mixture is homogeneous or heterogeneous therefore depends on the balance between entropy and energy [4, S. 137].

2.1.1. Flory Huggins Theory

Whether mixing or phase-separation will be favored can be predicted by determining the free energy change associated with mixing the components. This free energy change can be computed within the lattice model developed by Flory and Huggins [3]. Within the Flory-Huggins framework, no volume change is assumed upon mixing. With this assumption, it is convenient to represent the system on a lattice. The lattice site volume v_0 corresponds to the smallest molecular unit and every macromolecule takes up one or multiple lattice sites. Consider a binary mixture with n_A polymers of species A and chain length N_A and n_B polymers of species B and chain length N_B. The free energy of mixing per lattice site ΔF_{mix} is then given by the Flory-Huggins equation of polymer solutions [4, S. 143]:

$$\frac{\Delta F_{mix}}{k_B T} = \frac{\phi}{N_A} \ln \phi + \frac{1 - \phi}{N_B} \ln(1 - \phi) + \chi \phi (1 - \phi) \,. \tag{2.1}$$

Here, $\phi = \frac{n_A N_A}{n_A N_A + n_B N_B}$ is the monomer fraction of species A, k_B is the Boltzmann constant, T is the system temperature and χ is the Flory interaction parameter which characterizes the interaction between different polymer species and can be obtained from experiments. A positive value of χ opposes mixing while a negative value promotes it, knowing the value of χ therefore allows a qualitative prediction of the phase separation behaviour. Let ρ_0 be monomer density in the system. The total free energy of mixing is then:

$$\frac{F[\phi]}{k_B T} = \rho_0 \int \mathrm{d}^3 \mathbf{r} \Delta F_{mix} \,. \tag{2.2}$$

2.2. Collective diffusion of homopolymers

Consider a binary mixture of homopolymers with $N_A = N_B = N$ and $\chi = 0$. Since the number of monomers in the system is constant, the continuity equation holds:

$$\frac{\partial \phi}{\partial t} + \nabla \mathbf{J} = 0 \,. \tag{2.3}$$

Here, $\mathbf{J}$ is the local current of species A. Near equilibrium, one postulates a linear relation between $\mathbf{J}$ and the local chemical potential difference μ [2]:

$$\mathbf{J}(\mathbf{r}) = - \int_V \frac{\Lambda(\mathbf{r}, \mathbf{r}')}{k_B T} \nabla' \mu(\mathbf{r}') \mathrm{d}\mathbf{r}' \,. \tag{2.4}$$

The Onsager coefficient $\Lambda(\mathbf{r}, \mathbf{r}')$ relates the force acting on a monomer at position $\mathbf{r}'$ due to the gradient of chemical potential to the density at position $\mathbf{r}$. It therefore determines the dynamics of the system. For a symmetric mixture with $N_A = N_B = N$, in the simplest case, the current is coupled only locally to the local chemical potential gradient. The Onsager coefficient then takes the simple form [1, 2]

$$\Lambda = DN\phi(\mathbf{r}')(1 - \phi(\mathbf{r}'))\delta(\mathbf{r} - \mathbf{r}') \,. \tag{2.5}$$

Here, D is the single chain diffusion coefficient.

3. Simulation technique

Text. . .

4. Results

Text. . .

5. Discussion

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6. Summary

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A. erster Anhang

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Danksagung

Dank. . .

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Gï¿½ttingen, den March 18, 2023

(Justus Multhaup)

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