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**Modul B.Phy.407.Mp: Einführung ins
wissenschaftliche Arbeiten**

**Teilchensimulationen von
Polymermischungen in begrenzten
Geometrien mit zeitabhängigen
Randbedingungen**

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

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Nomenclature

Lateinische Buchstaben

Variable	Bedeutung	Einheit
A	Querschnittsfläche	m^2
c	Geschwindigkeit	m/s

Griechische Buchstaben

Variable	Bedeutung	Einheit
α	Winkel	$^\circ$; $-$
ϱ	Dichte	kg/m^3

Indizes

Index	Bedeutung
m	Meridian
r	Radial

Abkürzungen

Abkürzung	Bedeutung
2D	zweidimensional
3D	dreidimensional

Nomenclature

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-phase separation. 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 [6, 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 [4]. 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 . Let the total number of polymers be $n = n_A + n_B$. The free energy of mixing per lattice site ΔF_{mix} is then given by the Flory-Huggins equation of polymer solutions [6, S. 143]:

2. Theory

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

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 behavior. Note that so far, no space dependency of ϕ has been assumed. In the following discussion, a symmetric mixture with $N_A = N_B = N$ is assumed. To fully capture the complexity of the system, the Flory-Huggins model has to be extended to include spatial variations of ϕ , which gives rise to the de Gennes-Flory-Huggins free energy functional [2, 7]:

$$\frac{F[\phi]}{k_B T \sqrt{N}} = \int d^3 \mathbf{r} \left\{ \phi \ln \phi + (1-\phi) \ln(1-\phi) + \chi N \phi(1-\phi) + k(\phi) [\nabla \phi]^2 \right\}. \quad (2.2)$$

Here, $\sqrt{N} = n/V$ is the invariant degree of polymerization of the system with volume V . The term proportional to $[\nabla \phi]^2$ is added to the free energy density to ensure that unphysical, sharp changes in the local densities are penalized. The precise form of $k(\phi)$ depends on the strength of the parameter χ . For [insert chi value here] one considers the *weak segregation limit* (WSL). For [insert chi value here] the *strong segregation limit* (SSL) is considered. The prefactor k takes the form [7]:

$$k_{WSL} = \frac{R_e^2}{36\phi(1-\phi)}; \quad k_{SSL} = \frac{R_e^2}{18\phi(1-\phi)}. \quad (2.3)$$

2.2. Collective diffusion

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

$$\frac{\partial \phi}{\partial t} + \nabla \cdot \mathbf{J} = 0. \quad (2.4)$$

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]:

$$\mathbf{J}(\mathbf{r}) = - \int_V \frac{\Lambda(\mathbf{r}, \mathbf{r}')}{k_B T} \nabla' \mu(\mathbf{r}') d\mathbf{r}'. \quad (2.5)$$

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} . In the literature, this nonlocal coupling is often dropped for the sake of computational efficiency [1, 2, 5]. This leads to a simple version of the Onsager coefficient that will be derived in the following. Following the discussion in the appendix of [1], a continuity equation can be written down for each type individually:

$$\frac{\partial \phi_A}{\partial t} + \nabla \cdot \mathbf{J}_A = 0; \quad \frac{\partial \phi_B}{\partial t} + \nabla \cdot \mathbf{J}_B = 0. \quad (2.6)$$

With the additional assumption of incompressibility, e.g. $\rho(\mathbf{r}, t) \equiv \phi_A(\mathbf{r}, t) + \phi_B(\mathbf{r}, t) = 1$ everywhere for all times, the continuity equation for the total density ρ separates into two distinct equations:

$$\frac{\partial}{\partial t}(\phi_A + \phi_B) = 0; \quad \nabla \cdot (\mathbf{J}_A + \mathbf{J}_B) = 0. \quad (2.7)$$

This implies that $\mathbf{J}_A = -\mathbf{J}_B$, which simply reflects the condition of incompressibility: for a flux of type A to happen, B beads must be nearby to fill the lattice sites. The Onsager relations are then

$$\mathbf{J}_A = - \frac{\Lambda_{AA}}{k_B T} \nabla \mu_A, \quad (2.8a)$$

$$\mathbf{J}_B = - \frac{\Lambda_{BB}}{k_B T} \nabla \mu_B, \quad (2.8b)$$

where Λ_{AA} and Λ_{BB} are the diagonal elements of the matrix of Onsager coefficients, which is assumed to be diagonal. Since μ_A and μ_B are not independent variables,

2. Theory

their difference $\Delta\mu = \mu_A - \mu_B$ is considered instead. The goal is now to relate $\Delta\mu$ to the current $\mathbf{J}(\mathbf{r}, t) = \mathbf{J}_A(\mathbf{r}, t) = -\mathbf{J}_B(\mathbf{r}, t)$. From (2.8b), it is easily seen that

$$\begin{aligned}\nabla(\mu_A - \mu_B) &= -k_B T (\mathbf{J}_A \Lambda_{AA}^{-1} - \mathbf{J}_B \Lambda_{BB}^{-1}) \\ &= -k_B T (\Lambda_{AA}^{-1} + \Lambda_{BB}^{-1}) \mathbf{J}\end{aligned}\tag{2.9}$$

and therefore

$$\mathbf{J} = -\frac{1}{k_B T} (\Lambda_{AA}^{-1} + \Lambda_{BB}^{-1})^{-1} \nabla(\mu_A - \mu_B).\tag{2.10}$$

The Onsager coefficient that relates \mathbf{J} to the local chemical potential difference is identified as $\Lambda^{-1} = \Lambda_{AA}^{-1} + \Lambda_{BB}^{-1}$. By relating the currents in (2.8b) to the single chain diffusion coefficients D_A and D_B , the Onsager coefficients may be identified as $\Lambda_{AA} = N_A D_A \phi$ and $\Lambda_{BB} = N_B D_B (1 - \phi)$. For a symmetric mixture with $N_A = N_B \equiv N$ and $D_A = D_B \equiv D$, the Onsager coefficient corresponding to $\Delta\mu$ becomes

$$\Lambda = DN\phi(\mathbf{r})(1 - \phi(\mathbf{r})).\tag{2.11}$$

This result has also been derived by de Gennes [2].

It should be noted that, in the general case, the single-chain dynamics will affect the collective dynamics in a more complex way that is expressed by including the pair-correlation functions of A and B in the Onsager coefficient [7].

3. Simulation technique

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4. Collective diffusion of symmetric homopolymers

4.1. Reference system

In this section, the collective diffusion properties of noninteracting homopolymers with $N_A = N_B = N$ and $\chi = 0$ are investigated. As a reference system, a simulation box with 10000 polymers and dimensions $L_x \times L_y \times L_z = 9.25 \times 3 \times 3 R_e^3$ is considered with a spatial discretization of $\Delta L = 0.125 R_e$, so the invariant degree of polymerization is $\sqrt{N} \approx 120$. Periodic boundary conditions are applied in the lateral y and z directions, whereas impenetrable walls are applied in the x direction. Initially, the polymers are distributed homogeneously in the system. To stimulate diffusion, conversion zones are introduced close to the walls at $x < 0.25 R_e$ and $x > 9 R_e$. In each time step, if the center-of-mass coordinate \mathbf{r}_{cm} of a polymer of type A lies in the conversion zone at $x < 0.25 R_e$, it is converted to type B with probability $p(A \rightarrow B) = r\phi(\mathbf{r}_{cm})$ [3]. Analogously, conversion from B to A takes place in the conversion zone at $x > 9 R_e$ at the same rate r . The total currents \mathbf{J}_A and \mathbf{J}_B are measured by tracking the number of polymer conversions.

4.2. Collective diffusion coefficient

It should be pointed out that the system can be described effectively in one dimension due to the periodic boundary conditions in the lateral directions and the equal conversion rates. The chemical potential is obtained by taking the functional derivative $\frac{\delta F}{\delta \phi}$ of (2.2). Since $\chi = 0$, no phase separation occurs and the local density differences are entirely due to the dynamics. Assuming the WSL, the chemical potential becomes:

4. Collective diffusion of symmetric homopolymers

$$\begin{aligned} \frac{\mu}{\sqrt{N}k_B T} &= \ln \phi - \ln(1 - \phi) - \frac{R_e^2}{18\phi(1 - \phi)}\phi'' \\ &+ \left[\frac{R_e^2(1 - 2\phi)}{36\phi^2(1 - \phi)^2} \right] \phi'^2. \end{aligned} \quad (4.1)$$

Here, $\phi' = \frac{\partial \phi}{\partial x}$.

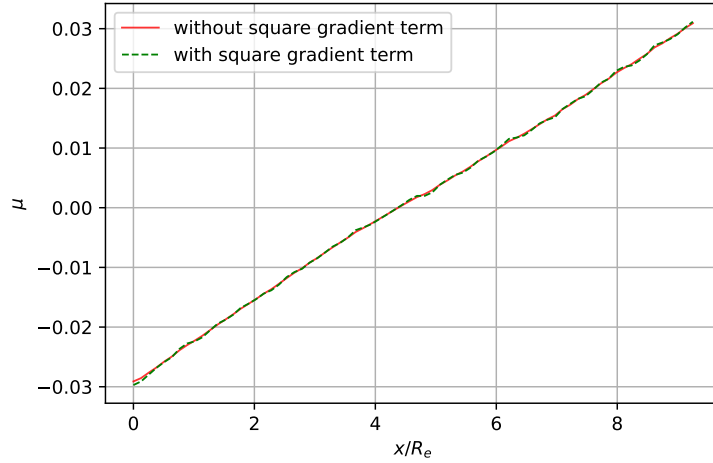


Figure 4.1.: Exchange chemical potential with and without including the square gradient term in (4.1) for $r = 0.0007$. The noise in the green curve stems from the numerical derivatives in (4.1).

In Figure 4.1, it can be seen that the terms arising from the square gradient do not contribute to the chemical potential, other than adding noise due to the numerical derivatives. Therefore, these terms prohibit an accurate numerical computation of the chemical potential gradient and thus the Onsager coefficient. In the subsequent discussion, these terms will be neglected. This approximation leads to a linear density profile, which is also consistent with the simulation results.

To verify (2.11), the Onsager coefficient may also be obtained from the simulation results using (2.5). Again assuming local coupling and making use of (4.1), while neglecting the terms arising from the square gradient, one obtains:

$$\Lambda = -\frac{J}{\sqrt{N}\phi'}\phi(1 - \phi). \quad (4.2)$$

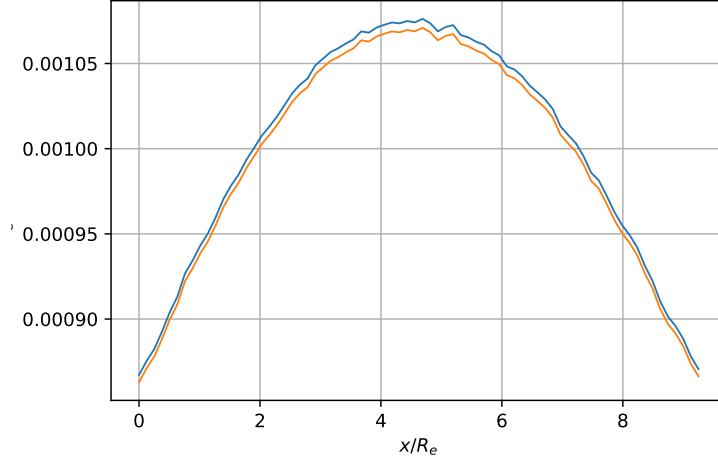


Figure 4.2.: Onsager coefficient for $r = 0.0007$. The densities are averaged over t , y and z .

Figure 4.2 shows that the Onsager coefficients obtained from (2.11) and (4.2) are in good agreement.

From (2.5), the current becomes:

$$J = -D\rho_0\phi'. \quad (4.3)$$

Here, $\rho_0 = nN/V$ is the average bead density in the system. Together with (2.4), this gives the well-known diffusion equation:

$$\frac{\partial\phi(\mathbf{r},t)}{\partial t} - D\rho_0\phi'' = 0. \quad (4.4)$$

In the steady state, this simply yields $\phi'' = 0$, so a linear density profile is obtained. The slope is given by (4.3) and the intersection is obtained from the condition that $\phi(L_x/2) = 0.5$ since the density is normalized.

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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(Justus Multhaup)