

## Generalized diffusion model for viscoelastic mixtures

Development of a theoretical model capturing both diffusion and polymer relaxation kinetics

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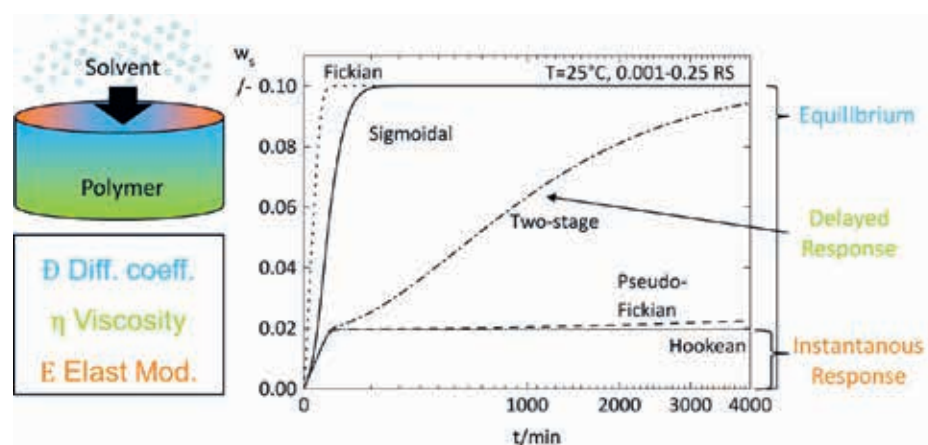
*Diffusional processes in polymeric mixtures are often governed by the structural relaxation of the macromolecular chains. Due to high molar masses, the polymeric component fails to respond instantaneously to incoming solvent molecules. In fact, the relaxation process is overlaid to translational diffusion of the absorbed species and turns out to be the rate-determining step in many cases. Ignoring this relaxation kinetic leads to concentration- and even time-dependent diffusion coefficients. This work addresses and solves this issue by incorporating the virtue of the relaxation process into the chemical potential of the solvent, enabling quantification the kinetics of both diffusion and relaxation, using established concepts for diffusion modelling.*

Polymers absorb solvent molecules from the surrounding atmosphere. During penetration, both polymer and solvent strives to establish configurational equilibrium, requiring relaxation of the polymeric chains. This turns out to be the rate-determining step of the overall diffusion process in many cases. The relaxation kinetics exhibits an instantaneous and a time-delayed contribution, depending on the relaxation time constant as the ratio of elasticity modulus and viscosity of the solvent-loaded polymer. High elasticity moduli lead to minor immediate responses whereas high viscosities cause a strong time-delayed response behavior. By incorporating elasticity moduli as well as viscosity in the expression of the chemical potential of the solvent, all observable diffusion kinetics are accessible (Fig 1).

The interplay between instantaneous and time-delayed response has extensive implications. One fundamental assumption in diffusion modelling is a boundary condition representing local thermodynamic equilibrium. Since

instantaneous changes are limited by the elasticity moduli of the polymer, even the reach for local equilibria at the phase boundary exhibits a time dependence, further slowing down the sorption of the solvent into adjoining domains. Thus, the time dependency of solvent sorption at the phase boundary has the capability to set the rate of sorption into the inner domains, determining the kinetics of the complete diffusion process in the polymer. The time evolution of the phase boundary is mainly governed by the elasticity modulus of the polymer, the viscosity of the solvent-loaded polymer and the density dependency of the thermodynamic activity of the solvent.

By considering both diffusion as well as relaxation, this work manages to display and explain all observable anomalous diffusion kinetics with only one coherent framework. Varieties in the temporal progress of the overall sorption kinetics could be traced back to model parameters reflecting physical properties, which are experimentally accessible.



**Figure 1:** Overall solvent weight fraction in the polymeric sample over time for five different relaxation time constants as the ratio of modulus and viscosity.



### Publications:

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