

471e Thermodynamic Effects on Diffusion in Thin Polymer Blend Films

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In this study, we model the diffusion behavior of a binary polymer blend system confined between two identical surfaces that have weak/strong preferential attraction for one of the components (A or B). We formulate and solve a theoretical model in terms of the gradients of the exchange chemical potential between the two components, assuming a constant self-diffusion coefficient. The exchange chemical potential function is derived from the Landau-Ginzburg expression for the total free energy in confined systems. The initial configuration is a tri-layer of ABA or BAB and the total tri-layer thickness is varied between $\sim 1-10 R_g$ (where R_g is the radius of gyration of the highest molecular weight polymer chains). The time-dependent composition profiles are fitted to an analytical solution of the diffusion equation using Fick's law. This fit assumes a constant diffusion coefficient for each time, with appropriate boundary conditions, to obtain the mutual binary diffusion coefficient (MBDC) for each concentration profile. The mutual binary diffusion coefficient is a function of the mobility coefficient, assumed constant for this study and the thermodynamic term derived from the Landau-Ginzberg expression. Our results show that, the MBDC's vary with time (by a factor of 2-3) for shorter time scales, as well as the degree of confinement when the initial distance between the surfaces and the AB interfaces are of the same order of magnitude as the radius of gyration of the polymer chains. The variation of the MBDC occurs because of the thermodynamic term that is implicit to the formulation, but not to the diffusion coefficient obtained by fitting a Fick's law type relationship. Further the composition profiles deviate significantly from Fick's behavior at longer time scales in the case of a strong surface potential, and a significant hook-like shape results near the polymer-substrate interface. The key conclusion of the work is that the thermodynamic term must be accounted for, when diffusion measurements are made in thin films systems to decouple the effect of confinement on mobility coefficient from thermodynamic effects.