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Case II diffusion and solvent-polymer films drying: a meso-scale model DIDIER LONG, CNRS/Université de Paris Sud, MIREILLE SOUCHE, Université de Paris sud — This model is based on the fact that dynamics in liquids close to the glass transition is spatially heterogeneous [Ediger2000, Souche2007], with characteristic size 3 to 4nm in van der Waals liquids. Before considering large scale diffusion experiments, we consider first the evolution of the dynamics of a layer of thickness 3 to 4nm, submitted to an arbitrary time varying activity a(t). This procedure allows in principle to calculate a constitutive relation for the dynamics of solvent- polymer mixtures, that can then be used for calculating the evolution of macroscopic samples in contact with a reservoir of solvent. We show how these constitutive relations allow for explaining case-II diffusion in glassy polymers and provide a physical interpretation for the parameters of the Thomas-Windle model. Regarding the process of film drying, we show that films up to 1 micrometer thick can be almost completely dried in an accessible experimental time, even at temperatures well below the polymer glass transition temperature. This is a consequence: 1- of the presence of the fast path 2- of the film being out equilibrium, and in a dynamical state which is must faster than the one it would have at equilibrium. When drying a thicker film, we show that a glassy crust may appear on the free surface, as has been shown experimentally. Ediger M.D., Annu. Rev. Chem., 51 (2000) 99; Souche M. and Long D., Europhys. Lett, 77 (2007) 48002

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