diffusion-fundamentals

The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application

Ultra fast processes for solvent evaporation in thin polymer films below T_g

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1.Introduction

The solvent diffusion coefficient D in a solvent-polymer system can be much larger than the ratio $a^2/□_□$, where a is one monomer length (about 0.5 nm) and $□_□$ is the dominant relaxation time measured e.g. by broadband dielectric spectroscopy [1,2]. The discrepancy can be by up to 6 orders of magnitude and more. We propose here that the solvent diffusion is dominated by path in the liquid with fast relaxation time. It allows to quantitatively explain the discrepancy between D and $□_□^{-1}$. Then, we apply this model to describe solvent evaporation of a polymer film with thickness of order a few micrometers. As a consequence of the presence of these fast paths, we show that such a film can dry within an accessible experimental time, even at temperatures well below the glass transition temperature. Our results qualitatively explain corresponding experimental results on PMMA films performed at room temperature [3].

2.Model for solvent diffusion in solvent-polymer systems close to the glass transition

The discrepancy between solvent diffusion and □-relaxation is reminiscent of other experiments in which it has been shown that the dynamics in liquids in the Williams Landel Ferry regime and down to the glass transition is strongly heterogeneous [4]. When considering the diffusion of a single fluorescent molecule in a pure liquid, such as ortho-terphenyl or a polystyrene melt, Ediger et al, Fujara et al, have shown that the diffusion coefficient is decoupled from the dominant relaxation time of the liquid, and that it is larger by up to 3 orders of magnitude as one would expect from the Stokes law. It has been proposed recently that the dynamical heterogeneities in such liquids are due to density fluctuations, which allowed to explain the amplitude of dynamical heterogeneities, the amplitude of the violation of the Stokes law, and also the shift of relaxation time in ultra-thin films as compared to the bulk [5,6]. We extend here some aspects of this model to study the solvent diffusion in polymer-solvent

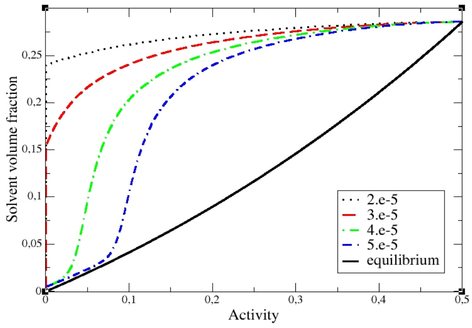

Illustration 1: Evolution of solvent volume fraction, as a function of the activity, for different values of (a/l)², at temperature T=Tg(polymer)-15K. All the solvent can evaporate even at temperatures below Tg.

mixtures.

We propose indeed that dynamical heterogeneities in solvent-polymer mixtures exist also, and that they are due to the solvent concentration fluctuations. The corresponding dominant scale is determined by considering the amplitude of these fluctuations, as a function of the considered scale, and their lifetime, which is also scale-dependent. From this and the known plasticizing effect of the solvent, we deduce the relaxation time distribution, which is significantly larger than for liquids in the bulk. In particular it allows to explain the amplitude of the ratio $Da^2/\square_{\square}$, and the fact that it can be as large as 10^6, and more when cooling the system further. Then, we consider a polymer film in equilibrium with a non-zero solvent vapor pressure, such that the system is above the glass transition. By reducing the solvent activity in the surrounding atmosphere, the solvent evaporates. The relaxation dynamics of the film is described by two coupled equation: 1- a Fokker-Planck equation, which governs the evolution of the polymer volume fraction distribution, and 2- a differential equation, which governs the overall evaporation rate of the solvent. The latter is controlled by a time scale which is the product of the fast time controlling solvent diffusion by a geometrical factor $(l/a)^2$ where l is the film thickness. Typically, for films of one micrometer thickness, this factor is of order 10^6. We show, that, by reducing the solvent activity down to zero, the solvent can totally evaporate 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 much faster than the one it would have at equilibrium. Both aspects are essential to explain the corresponding experimental features. Another striking feature of our results is that the time scale associated with solvent evaporation can be non monotonous in this kind of experiments.

3. Conclusion

We show here that dynamical heterogeneities are essential for understanding solvent diffusion close to and below T_g. The dynamical heterogeneities are even larger in polymer-solvent systems than in pure liquids. Taking them into account is essential for describing solvent evaporation from thin polymeric films [3].

References

[1] A.-C. Dubreuil, F. Doumenc, B. Guerrier, D. Johannsmann, C. Allain, Polymer, 44, 377-387 (2003)

[2] P.K. Davis, R.P. Danner, J.L. Duda, I.H. Romdhane, Macromolecules, 37, 9201-9210 (2004)

[3] F. Doumenc, B. Guerrier, C. Allain, submitted for publication (2005)

[4] Ediger M.D., Annu. Rev. Chem., 51 (2000) 99

[5] D. Long, F. Lequeux, EPJ E, 4, 371-387 (2001)

[6] S. Merabia, D. Long, EPJ E, 9, 195-207 (2002)