In the previous chapters, we have reviewed how particles pack together during the drying process and why they become deformed from their initial spherical shape. Yet, the film formation process does not stop there: an important third stage follows.

In 1958, only a few years after the theories of particle deformation were first proposed (as outlined in Chapter 4), Voyutskiĭ published his reaction to this previous work. His short paper contained some impressive insights but did not have quantitative experiments to support them. His ideas foreshadowed many of the future experimental developments that will be presented in this chapter.

Voyutskiĭ realised that particle deformation was not the final required step in latex film formation. He wrote that ‘to obtain a stable film it is necessary that the segments of chain polymers diffuse from one globule to another, thus forming a stable link’. The importance of diffusion was thus highlighted. It is worth noting that by 1958 the first measurement of a polymer self-diffusion coefficient had been reported previously for a ‘bulk’ material (Bueche, Cashin and Debye 1952). But, there were no measurements in colloidal systems. In this chapter, we shall consider the details of the crossing of polymer molecules from one particle to another and shall see that, somewhat contrary to Voyutskiĭ’s view, it takes more than a few ‘segments’ to achieve ‘a stable link’.

Calling the process ‘autohesion,’ Voyutskiĭ went on to comment on its time dependence, saying that the final strength is not achieved until ‘some length of time which is necessary for the diffusion of polymer molecules.’ In fact, the study of the dynamics of diffusion would occupy many of the most eminent polymer physicists in the later decades of the twentieth century.

A fundamental observation is that the mechanical strength of latex films is found to increase over time. In some of the early literature, the final stage of film formation was therefore called ‘further gradual coalescence’ in recognition of the fact that the process was slow (Vanderhoff 1966). The word coalescence refers here to the loss of particle boundaries to create a homogenous film, as was observed with electron microscopy in early studies. It is now fully accepted that
the strengthening of films is the result of interdiffusion – at the molecular level – across the boundaries between particles as illustrated in Fig. 5.1. We use the word interdiffusion – rather than merely diffusion – to indicate that molecules are travelling between particles rather than only within them.

Readers who have been introduced to modern soft matter physics will take the concepts of interdiffusion and interface broadening for granted. It is readily apparent why adhesion will develop between the surfaces of polymers above their glass transition temperature, $T_g$, when placed into contact. At the molecular level, the narrow gap between the initial surfaces vanishes as molecules reach across. The welding of plastic laminates and the healing of cracks through heating are just two examples of familiar processes that rely on such a diffusion process.

However, for many years after Voyutskii’s first comments, the concept of ‘autohesion’ as a third stage of latex film formation was not universally accepted (Voyutskii and Ustinova 1977). One reason for scepticism amongst scientists was because of reports of latex films in which particle identity was retained even after aging for up to two years at room temperature or after heating up to 150°C (Distler and Kanig 1978). As we shall see later in this chapter, there are good explanations for these confusing results.

An appreciation of the details at the molecular level – rather than just the macroscopic – has emerged from the theory of reptation. In this way, the subject has been shaped by some of the world’s greatest soft matter physicists. Our understanding of interdiffusion in latex films has been helped enormously by the many SANS and FRET experiments that have tested the theories and confirmed the mechanism of polymer diffusion in latex films. The principles of these techniques were described in Chapter 2.

Fig. 5.1 Molecular level view (not to scale) of the interdiffusion of molecules across particle boundaries in a latex film made up of flattened particles.