Preface

I feel privileged to be able to write the Preface for this issue of *Advances in Colloid and Interface Science*, which has been prepared 'to celebrate the 50th Anniversary of DLVO theory'. It is indeed close to 50 years after the publication in 1948 of the book 'Theory of the stability of lyophobic colloids' that Evert Verwey and I wrote in the war years and finished in 1947.

But before starting the Preface to the contents of this issue, I want to make two points.

1. The term DLVO theory was not coined by Verwey and myself, but proposed some time after the appearance of our book by Sam Levine, and it stuck.
2. The book, rather than marking the beginning of a new period, was much more a consolidation of what had been achieved in Russia by Derjaguin and Landau and, more specifically, by Verwey and several colleagues, including myself, and, of course, several other scientists contributed in building up that picture.

Let us begin with some history. The theory as presented aimed at understanding the rule of Schulze (1882, 1883) and Hardy (1900), about the very large influence of the charge number of the counterions on the respective coagulation concentrations, compared to the small influence of the chemical nature of the counterions and the particles themselves.

The early explanation of this situation was based on the assumption, proposed by Freundlich (1910), that the counterions were adsorbed by the particles, and neutralized their charge. That explanation held until Freundlich, Joachimsohn and Ettisch published a paper in 1929, in which analytical measurements clearly showed, that the assumption of discharge of the particles did not fit the facts. Shortly thereafter, Verwey, working on his doctoral thesis on the stability of AgI-sols, came to a similar conclusion. In that situation one was looking for a more subtle effect of the electric double layer surrounding the particles, and it was natural to think of the thickness (expressed as the Debye length, $1/\kappa$) of this double layer, which determines the range of the interaction, as the mechanism that governed the stability. It was perhaps no coincidence that, around that same time (1932), Kallmann and Margarethe Willstaetter drew attention to the fact, that the London-van der Waals attraction between colloid particles has a range comparable

to the size of these particles. J.H. de Boer (1936) and H.C. Hamaker (1936, 1937) took up this idea, and especially Hamaker worked this out and gave equations for the attraction between particles of various shapes *and* he constructed *potential energy curves* combining the double layer repulsion (be it in a rather primitive form) with the van der Waals attraction. He made it plausible at least, that these curves may have a sufficiently high maximum at low electrolyte concentrations. But at higher electrolyte concentrations the maximum decreases enough to allow Brownian motion to overcome it and allow the particles to make permanent contact under very strong van der Waals attraction.

It is not exaggerated to state that, with Hamaker's work, the essentials of the DLVO theory were present, although a number of important details still had to be worked out, in particular the free energy of repulsion due to the interaction of two double layers.

Unfortunately the war prevented contacts between the Russian group (Derjaguin, Landau, and others) and the Dutch group, who were both working on the same problems, between 1939 and 1945. Derjaguin and Landau published their important paper in 1941. Verwey published a few preliminary papers, some in the Dutch language, in 1940, 1942, 1944 and 1945 and Verwey and I prepared our monograph in that period.

Between 1948 and the present a great deal of work has been done in this field, and it is not astonishing, that a number of experimental data did not fit into the simple idealized DLVO theory. Just to name a few items: lyophilic colloids are not covered; actual particles are not smooth but more or less rough and the surface charge is often unevenly distributed. This has obviously a much larger effect at high electrolyte concentrations (short Debye length, $1/\kappa$) than at low concentrations. The presence of large molecules and of surfactants is interesting, but often presents theoretical complications. The chemical nature of the ions — think of the Hofmeister series — is not taken into account. Many proposals have been made to introduce 'non DLVO forces' into the simple theory. In the present issue Yaminsky and Ninham warn against the use of *ad hoc* hypotheses, without a thorough check with Gibbs surface thermodynamics, which connects surface composition with surface free energy.

It is nice to find in Churaev's paper a very complete review of the work by Derjaguin and his school with 115 references, covering the period 1934−1989, with a few papers in the nineties.

Several authors introduce dynamics into the DLVO processes. Particles in Brownian motion and in Brownian encounters cannot be quite in equilibrum, and a closer look reveals that several processes with different relaxation times play a role, and it is not easy to unravel all these effects. A preliminary conclusion seems to be, that the ζ-potential, as determined by electrophoresis, remains a satisfactory measure for colloid stability.

Unexpectedly the rate of coagulation at zero gravity was found to be faster than at normal gravity. A combination of surface roughness with convection flows caused by small temperature gradients explained the effect. Thermal fluctuations in the surface of thin films form another dynamic effect.

Some new applications of the DLVO approach are presented, such as the influence of electrostatic interactions in particle deposition, or the behaviour of foam films, stabilized by high molecular weight, non-ionic, polymeric surfactants. The great variety of subjects presented in this issue shows strikingly that after more than 50 years the DLVO theory is still considered actual and useful. A conclusion that is very satisfying to the author of this perface.

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