Advances in Colloid and Interface Science 159 (2010) 99–116

Contents lists available at ScienceDirect

Advances in Colloid and Interface Science

journal homepage: www.elsevier.com/locate/cis

Polymers at interfaces and in colloidal dispersions

Gerard J. Fleer

Laboratory of Physical Chemistry and Colloid Science, Wageningen University, 6703 HB Wageningen, The Netherlands

ARTICLE INFO

Available online 5 May 2010

Keywords:
Polymer adsorption
Polymer depletion
Scheutjens–Fleer theory
Continuum theory with finite segment size
Boundary condition in Edwards equation
Crossover from dilute to semidilute limits
Depletion thickness
Phase diagrams
Generalized free-volume theory

ABSTRACT

This review is an extended version of the Overbeek lecture 2009, given at the occasion of the 23rd Conference of ECIS (European Colloid and Interface Society) in Antalya, where I received the fifth Overbeek Gold Medal awarded by ECIS.

I first summarize the basics of numerical SF-SCF: the Scheutjens–Fleer version of Self-Consistent-Field theory for inhomogeneous systems, including polymer adsorption and depletion. The conformational statistics are taken from the (non-SCF) DiMarzio–Rubin lattice model for homopolymer adsorption, which enumerates the conformational details exactly by a discrete propagator for the endpoint distribution but does not account for polymer–solvent interaction and for the volume-filling constraint. SF-SCF corrects for this by adjusting the field such that it becomes self-consistent. The model can be generalized to more complex systems: polydispersity, brushes, random and block copolymers, polyelectrolytes, branching, surfactants, micelles, membranes, vesicles, wetting, etc. On a mean-field level the results are exact; the disadvantage is that only numerical data are obtained. Extensions to excluded-volume polymers are in progress.

Analytical approximations for simple systems are based upon solving the Edwards diffusion equation. This equation is the continuum variant of the lattice propagator, but ignores the finite segment size (analogous to the Poisson–Boltzmann equation without a Stern layer). By using the discrete propagator for segments next to the surface as the boundary condition in the continuum model, the finite segment size can be introduced into the continuum description, like the ion size in the Stern–Poisson–Boltzmann model. In most cases a ground-state approximation is needed to find analytical solutions. In this way realistic analytical approximations for simple cases can be found, including depletion effects that occur in mixtures of colloids plus non-adsorbing polymers.

In the final part of this review I discuss a generalization of the free-volume theory (FVT) for the phase behavior of colloids and non-adsorbing polymer. In FVT the polymer is considered to be ideal: the osmotic pressure Π follows the Van 't Hoff law, the depletion thickness δ equals the radius of gyration. This restricts the validity of FVT to the so-called *colloid limit* (polymer much smaller than the colloids). We have been able to find simple analytical approximations for Π and δ which account for non-ideality and include established results for the semidilute limit. So we could generalize FVT to GFVT, and can now also describe the so-called *protein limit* (polymer larger than the 'protein-like' colloids), where the binodal polymer concentrations scale in a simple way with the polymer/colloid size ratio. For an intermediate case (polymer size ≈ colloid size) we could give a quantitative description of careful experimental data.

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E-mail addresses: Gerard.Fleer@wur.nl, fleerberg@gmail.com.

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doi:10.1016/j.cis.2010.04.004

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1. Introduction

To my big surprise, I was awarded the 2009 Overbeek Gold Medal by the European Colloid and Interface Society, which acknowledges ‘excellent careers in, and inspiring contributions to, the field of colloid and interface science’. When reviewing an entire scientific career, it is unavoidable to make a selection of the topics. I decided to concentrate on four issues:

(i) the numerical Scheutjens–Fleer lattice theory which is an extension of the DiMarzio–Rubin model and may be seen as a (multicomponent and multisegment) generalization of the Flory–Huggins theory towards inhomogeneous systems,
(ii) reconciling the lattice model with continuum models based upon the Edwards equation by introducing the finite segment size into the continuum model,
(iii) finding simple expressions for the crossover between the dilute and semidilute limits of the depletion thickness and osmotic pressure for excluded-volume chains, and
(iv) applying these expressions to the phase behavior of colloids and non-adsorbing polymer.

I started my career as an experimentalist. By sheer coincidence I met in 1975, during a sabbatical year at the National Bureau of Standards (now NIST), the great polymer physicists DiMarzio and Rubin (DR), who had just developed their lattice model [1–3] accounting exactly for the conformational statistics of an ideal polymer chain next to an impenetrable interface which attracts or repels the polymer segments. Their model is discussed in Section 2. I returned to Wageningen pondering on the vague idea that it might be possible to extend the DR model (in which the chains are ideal and where the volume-filling constraint is not obeyed since there is no solvent) to more realistic situations. Then I got a brilliant undergraduate student, Jan Scheutjens. I asked him to look into the possibilities to improve on the shortcomings of the model. That is how in the late 1970s two experimentalists entered the area of polymer adsorption theory and developed what is now known as the Scheutjens–Fleer (SF) theory.

At that time two types of theories for polymer solutions (i.e., polymer and solvent) next to an interface were available in the literature. The first starts from the configurational statistics of a single adsorbed chain consisting of trains, loops, and tails. Silberberg [4] and Hoeve [5] derived approximate partition functions for one train, one loop, and one tail. Combinatorial statistics provided the partition function of an adsorbed ideal chain. In order to extend this to a chain interacting with solvent in a Flory–Huggins-type manner, additional approximations about the shape of the concentration profile were needed. The last step is to obtain the partition function of a system of many chains and solvent molecules and to maximize this to find the equilibrium situation. The overall results of Silberberg and Hoeve are rather close [6], although typical differences occur due to different approximations, amongst which the neglect of tails. These were the first reasonable (though still rather primitive) theories of polymer adsorption.

The second type of theory available in the mid-1970s was density functional theory for chains on a lattice, especially in the form proposed by Roe [7] and Helfand [8]. In these models, all the properties of the interfacial layers are expressed in the local concentrations and concentration gradients. Individual conformations are not considered, only their effect on the concentration profile is taken into account. As a consequence, the information about chain conformations is lost. In deriving the entropic part of the partition function Roe made some assumptions which boil down to the neglect of tails; also the inversion symmetry is violated. Helfand introduced so-called anisotropy factors to improve on these points, but this model is only applicable to infinitely long chains and contains an inconsistency in the normalization conditions [9].

In our attempts to extend the DR model, we had to learn about self-consistent-field (SCF) theory, where walks take place in a field which is not fixed (as in the DR lattice model) but where these walks influence the field. We also had to learn about the continuum descriptions as proposed by Edwards [10] and De Gennes [11,12]. In this continuum model the chain does not make discrete steps, as in the lattice, but is described as a continuous space curve ‘diffusing’ through a field. For simple forms of the field (which is then not self-consistent) the Edwards equation may be solved analytically but in the mid-seventies no solutions were known for polymers not only interacting with the surface but also with the solvent, taking into account the volume-filling constraint. Only after we published our first SF paper [13] Hong and Noolandi [14] came up with a real (numerical) SCF continuum solution for polymer in a monomeric solvent.

In the SF extension of the DR model, there is not one fixed field for the (one) polymeric component (as in DR) but every segment type (including the solvent) is assigned its own field, in which all the interactions and the volume-filling constraint are included. Because the interactions depend on the local concentrations, the fields are now self-consistent, unlike in the DR model. The essential steps of SF-SCF are discussed in Section 3.