

## **Book Review: *Theoretical and Mathematical Models in Polymer Research, Modern Methods in Polymer Research and Technology***

**Theoretical and Mathematical Models in Polymer Research, Modern Methods in Polymer Research and Technology.** A. Grosberg, Academic Press, San Diego, California, 1998.

In a field of science with no shortage of good books, the present editor being a coauthor of two of them, this volume was conceived as an advanced supplement covering theoretical methods used in polymer science. Though the book is oriented towards an audience of graduate students and postdoctoral investigators I believe it will be mostly enjoyed by seasoned researchers in the field who want to brush up on or restock their bag of (mathematical) tricks. The keyword is therefore “mathematical methods.” But it is also true that this book is not intended for the mathematically fainthearted.

This volume does not pretend to be exhaustive in any sense of the word. Rather it is an idiosyncratic compendium of different recent methodological advances in a field that has already made use of every useful mathematical trick invented in the context of other realms of theoretical physics. It really can not be otherwise as the current methodological repertoire of theoretical polymer physics is simply too vast and varied to be included in a single volume. This course in its turn inevitably leads to the conclusion that some people will find the book useful and other not at all, depending the readers' interests.

The first Contribution on “Statistical Mechanics of Semiflexible Chains: A Mean Field Variational Approach” by D. Thirumalai and B. Y. Ha starts off with the single chain properties in the framework of the stiff chain (Kratky-Porod) model. The difficult problem there is how to incorporate the constraint of inextensibility into a consistent formulation of statistical mechanics. Thirumalai and Ha, basing their approach on previous contributions by Bawendi and Freed as well as Lagowski *et al.* have introduced an approach that essentially exchanges the local inextensibility

constraint with a global one, with the corresponding Lagrange multiplier being estimated by variational techniques. In this respect the method bears some similarity with the  $1/d$  expansion introduced in the general context of deformable manifolds, especially membranes. I imagine that the  $1/d$  expansion framework might also allow for systemic improvement of some of the results derived by Thirumalai and Ha. The variational estimate proves especially fruitful when external fields are incorporated into the Hamiltonian for the chain. The problem of a chain under tension and a chain in a nematic field can be dealt with in the framework of this approach in a very elegant and simple way. Similarly the treatment of the chain with intersegment interactions, which is prohibitively difficult if one does not globalize the inextensibility constraint, should yield to the approach advocated here. The variational treatment of the global inextensibility constraint is introduced in a pedagogical way, is relatively easy to follow and should provide ample guidance also for applications not addressed directly by Thirumalai and Ha.

“Polymer Adsorption: Mean Field Theory and Ground State Dominance Approximation” by A. N. Semenov, J.-F. Joanny and A. Johner is a reexamination of the polymer adsorption problem. The fundamental question addressed here is the nature and the limitations of the ground state dominance ansatz in adsorption problems. Ground state dominance that correctly describes the infinite chain, does evidently not address any finite size effects. This was realized and repeatedly stressed by Scheutjens and Fleer in their version of the adsorption mean field theory. The numerical complexity of their theory precludes any evaluation of asymptotic limits and closed form results. The approach of Semenov *et al.* is thus all the more important since it deals with the limitations of the ground state dominance ansatz in a form leading to explicit limiting results in a relatively simple mathematical framework. The way this is done is to introduce an additional order parameter besides the polymer density field that is connected with finite size effects. While the polymer density field satisfies the standard ground state dominance (Schrödinger) equation the additional order parameter emerges as a solution of a separate equation that couples the external fields, the density order parameter and the ground state energy. This appears quite complicated but is nevertheless reducible to relatively simple coupled differential equations between the polymer density field and the additional order parameter. This reduction allows the authors to accomplish a straightforward analysis not only of adsorption problems but also, among other things, the analysis of interactions between adsorbing surfaces. A plethora of analytic limiting forms are derived that should complement the more arcane numerical calculations performed by Scheutjens and Fleer. This contribution too is pedagogical in

the sense that it is self contained and does not venture into mathematical realms demanding extensive consultation of any additional literature.

The chapter on “Replica field Theory Methods in Physics of Polymer Networks” by S. V. Panyukov and Y. Rabin appears as the centerfold of the volume. It is by far the most technical and comprehensive of them all. The Edwards replica trick in the physics of cross-linked networks is introduced in all its gory detail that (at least not to my knowledge) has not been available in the literature up to this point. The replica formalism is first derived and then solved at the mean field level. Homogenous and non-homogeneous solutions are analyzed separately, including replica symmetry breaking, as well as associated stability properties. This serves as a prelude to the analysis of the thermal properties of cross-linked networks and of the different correlation functions. This is a chapter that I found too difficult and too technical for a single gulp. I am nevertheless sure that the specialist will find it most valuable but it could probably not be used as an introduction to the subject.

“Winding Angle Distributions for Directed Polymers” by B. Drossel and M. Kadar deals with the winding of polymers around each other or around a rod. Though experimental realizations of this problem are not explicitly dealt with, I realized that it might be relevant for the study of collapsed single DNA phases that are currently receiving a lot of attention. The authors start with the Edwards Hamiltonian for two chains which they rewrite with the help of a conformal mapping in a form that explicitly contains the winding angle of one chain around the other one in the presence of an interaction potential. In this way they can derive the winding angle distribution in an explicit form. This distribution depends on the attractive or repulsive nature of the interaction but not on further microscopic details. The winding of confined polymers as well as winding around chiral centers is discussed at length. This article is a delight to read, is self contained and should inspire further thinking. One wanders whether the results derived here, or maybe for winding of many chains would be relevant for understanding of braided phases of semi-flexible polymers at high densities.

The last contribution to the volume “Bulk and Interfacial Polymer Reaction Kinetics” by B. O’Shaughnessy is also the only one dealing with dynamical properties of polymers. It develops the theory of reaction kinetics in the bulk and at interfaces in a systemic and comprehensive manner. I am not familiar with this subject but nevertheless found the discussion transparent and relatively easy to follow. The main results are summarized in a series of “phase diagrams” that connect the functional group reactivity with the concentration of end-functionalized chains in the bulk, or on both sides of an interface. The chapter contains a very good

introduction to the subject and a clear statement of the fundamental approximations in addition to a general map summarizing the calculations.

I imagine that the reading of this volume by any reader would be fragmentary and depend strongly on the absence or presence of topics specific to his or her own interests.

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