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Book Review: *Polymer Physics*

Polymer Physics. M. Rubinshtein and R. H. Colby, Oxford University Press, 2003.

I should start this review by bluntly stating that the book being reviewed is simply great. Judging either by its clear style, its selection of topics, or its self-contained material, it is an extremely well thought-out, thorough, and completely laudable book in every way. The audience to which this book is addressed is mainly that of upper level undergraduates and first year graduate students, but I believe it will be a delight to read even for more experienced workers in the polymer field. It has a certain beauty and acuity of presentation combined with well thought out argumentation. Only the tools of basic mathematics are used, removing one possible obstacle to understanding the polymer field. Though we have seen derivations of the basic results of polymer physics in many guises—by some extremely talented writers—books by Flory, de Gennes, Doi, and Edwards, and Grosberg and Khokhlov, this work nevertheless manages to introduce the entire field using concise language, and razor sharp arguments, while making use of only simple mathematical tools. All three features serve to distinguish this book from its predecessors and allows for a more inclusive set of potential readers.

The mathematics utilized in this book requires a knowledge of nothing more advanced than elementary integration. This feature suggests that it can be used as a text for advanced undergraduates. Even the integrals are evaluated in detail allowing the reader to focus on conceptual advances and physical arguments unimpeded by complex mathematics. Of greater importance is that none of the physics has been sacrificed. There are no gaps in derivations, and all of the arguments are self-contained. Of course this demands considerable ingenuity and a really firm command of the subject matter by the authors. In this they have succeeded quite splendidly.

All of the chapters consist of very clear and easy to follow arguments and end with a two-page summary listing the main topics covered in the chapter together with a list of the most important equations. The problems

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are listed section by section in the original chapter breakdown. There are numerous problems covering a spectrum from fairly simple ones to quite advanced ones. I hope that the authors eventually will publish a book of solutions to the problems.

The Introduction gives the reader a bird's eye view of polymer science together with the main phenomenology required to describe different polymer types as well as the fractal nature of polymer conformations. It also gives a fairly detailed discussion of the concepts underlying molar mass distributions especially as they relate to linear condensation and linear addition polymerization. The reader is also introduced to the various methods of number-averaging and weight-averaging molar mass measurements making use of the techniques of light scattering, osmometry, size-exclusion chromatography and viscometry. I should note, however, that this is not a book about polymer phenomenology. It principally develops concepts, the connections between the concepts in the form of physical laws, and the ensuing consequences.

The next two chapters introduce the subject of single chain conformations, dealing both with ideal and real chains. The first of these chapters introduces the microscopic mechanisms of chain flexibility. These include a variety of models that capture salient features of polymers: the freely rotating chain model, the wormlike chain model, the hindered rotation model, and the rotational isomeric state model. The conformation-averaged radius of gyration of the chain is then used to extract statistical properties of these various models. Expressions for distributions of the end-to-end vector is derived for the freely rotating chain model on a lattice. A knowledge of the distribution function of the end-to-end vector allows one to derive an expression for the free energy of the chain, naturally leading to the concept of chain stretching. This is followed by the the introduction of tension blobs and the scaling arguments. The inextensible freely jointed chain, whose properties are expressed in terms of the Langevin function leads to more realistic chain stretching models and to a derivation of the equation of state for semiflexible polymer stretching. The chapter ends with a detailed analysis of scattering experiments and how they allow one to estimate statistical properties of the chain. Both the Debye function and the Zimm plot are derived in detail. All of the formulas in this chapter and subsequent ones are derived in great detail, with clearly stated intermediate steps and no steps omitted in the derivation.

A description of properties of ideal chains includes a discussion of interactions between monomers, random walks with excluded volume, and self-avoiding walks. The Flory theory of excluded volume effects is dealt with first, and leads the reader to yet another application of scaling arguments. Subsequently, deformations and the concurrent equation of state for

ideal and real chains are compared, which leads to the problem of chain compression in both uniaxial and biaxial cases. Uniaxial compression in its turn, is followed by an analysis of the problem of the adsorbing chain compressed by an adsorbing potential. The logic behind all of the described developments is crisp and clear and the authors move beautifully and effortlessly from one problem to the next one. Subsequently, a scaling model of the real chain is discussed together with an introduction to the notion of the thermal blob. Later, temperature effects together with the theta temperature and second virial coefficients are introduced. The chapter concludes with a discussion of the effect of monomer interactions on the distribution of the end-to-end distance for real chains.

The following two chapters contain analyses of thermodynamic properties of blends and solutions. The first of these chapters, gives a very detailed introduction to the thermodynamics of mixing and the theory of regular solutions, particularly as applied to polymer blends. The Flory–Huggins theory is derived in all of the necessary detail, again with crisp and clear argumentation. An exposition of Flory–Huggins theory is followed by an analysis of equilibrium properties as well as aspects of the stability of the equilibrium. The ensuing phase diagrams are derived and explained together with the new vocabulary of critical temperatures, spinodals, binodals, etc. This is followed by an analysis of the limit of low volume fractions and the virial expansion of the osmotic pressure required in their analyses. Polymer melts are dealt with on the scaling level. The chapter ends with experimental techniques for investigating polymer blends and polymer solutions as well as the the associated scattering functions considered as a function of the volume fraction.

The following chapter deals solely with the equation of state, i.e., the dependence of the osmotic pressure on the volume fraction. This is done for polymer solutions at all concentrations and temperatures. It combines the knowledge of the previous three chapters to give a unified view of the behavior of polymer solutions. A first step in the analysis is to discuss the overlap concentration in terms of which one can separate semi-dilute from dilute polymer solutions. The case of a poor solvent and the subsequent collapse to the polymer globule is treated first, before proceeding to the case of a good solvent. It is first shown that the semi-dilute solution can be partitioned into space-filling correlation volumes characterized by a correlation length depending on the volume fraction of the polymer. This correlation length leads a discussion of the size of the chain, which, again, is a function of the volume fraction of the polymer. Both dependencies are derived by means of a de Gennes scaling argument, combined with the space-filling property of correlation volumes. This is followed by a discussion of the equation of state of semidilute polymer solutions away from,

and close to, the theta point, together with a description of the difference between the mean-field and scaling results. The flow of the argumentation and the logic of derivation is again flawless. The scaling arguments implied in the derivation of the equation of state of semidilute solution are then extended to Alexander–de Gennes brushes and the self-similar profile in the case of multichain adsorption. The chapter concludes by establishing the connection between theory and experiment.

The following two chapters deal with networks and gelation. First we have an introduction to the phenomenology of gelation and percolation, which is then followed by a statistical analysis of branching in polymers. The phenomenon of gelation itself is then analysed at a mean-field level. The detailed analysis is based on a placement of monomers at the sites of an infinite Bethe lattice. A derivation is then presented of the scaling model of gelation together with the definition of different characteristic exponents. It is shown that the molar mass distribution, below the gel point at different extents of reaction, can be collapsed onto a single universal scaling curve. The fractal dimension of randomly branched polymers is derived in terms of the Flory–de Gennes theory. Properties of the vulcanization transition are described on the scaling level. The chapter ends with an introduction to the experimental determination of properties of branching and gelation.

The following chapter on networks and gelation begins with a description of thermodynamic properties of rubber and rubber elasticity. The standard derivation of rubber elasticity is given for the affine-network and phantom-network model. The effect of finite chain extensibility on rubber elasticity is also examined. This leads to a discussion of entanglements and their effects on rubber elasticity. The Edwards tube-model, the Mooney–Rivlin model and constrained-fluctuation models are introduced and a description is given of their respective effects on rubber elastic moduli. In the treatment of swelling of polymer gels the previously described properties of polymer solutions are combined with the newly introduced elastic properties of gels. The theory of the swelling of polymer gels in theta, athermal, and good solvents is derived in detail. Linear viscoelasticity is introduced next, which paves the way to the two following chapters on dynamics of polymers. As in most of this book the development of the theory of viscoelasticity is again a crisp, clear and very readable account of polymer network properties.

The last two chapters of the book deal with the dynamics of polymers. First the theory for the dynamics of unentangled polymers in dilute solutions is developed. After a few preliminaries, the authors introduce the Rouse and Zimm models which furnish characteristic relaxation times and expressions for the intrinsic viscosity. The relaxation modes of both models are then treated in much greater detail, together with their stress relaxation moduli

and relevant chain sizes. Properties are derived on the scaling level for semidilute solutions, the concentration dependence of the relaxation times and the stress relaxation modulus. The Rouse and Zimm models are finally contrasted with the semiflexible chain model and its relaxational modes. The chapter concludes with a discussion of the temperature dependence of polymer dynamics and an introduction to dynamic scattering in polymers.

The final chapter of this book deals with entangled polymer dynamics, and specifically with a description of reptation dynamics. Reptation is first introduced for polymer melts and then for semidilute solutions. This allows the derivation of corresponding relaxation times, stress relaxation, and viscosity. The theoretical values all show a weaker concentration dependence than is observed in experiments. The resolution of this conundrum is sought for through a more thorough treatment of the single entangled chain dynamics and especially through reptation tube length fluctuations that give a much better correspondence between theory and experiments. The release of the constraints, i.e., those imposed by fixed obstacles, for the reptating chain leads to the consideration of many-chain effects that can substantially modify the relaxation properties of the polymers. The chapter concludes with a discussion of the role of computer simulation methods in polymer physics. A general framework for molecular dynamics and Monte Carlo simulations is developed and simulation results for a few polymer models such as those based on the standard random walk, the self-avoiding walk, unentangled chain dynamics and entangled chain dynamics are discussed in detail. This last section gives an impression of what can be accomplished by computer simulation in forming a bridge between theory and experiment. Most importantly they provide tests for validating assumptions and predictions of various theoretical models.

What I find amazing in this book are the unified arguments. All of the chapters develop their arguments with the same intensity and same level of argumentation-benchmarks of a well thought-out project. What is especially laudable with this book is its well worked out pedagogical structure. The authors present clear arguments and build and connect the various threads of the subject matter. Many times various textbook are quite weak in this respect. In short, this is a book worth reading. I am convinced that you will enjoy it as well.

Rudi Podgornik
Faculty of Mathematics and Physics
University of Ljubljana
Jadranska 19
SI-1000 Ljubljana, Slovenia
E-mail: rudolf.podgornik@finf.uni-lj.si