

Perspective

Two landmarks in polymer physics: the Edwards model and de Gennes' observation

D. Thirumalai

Institute for Physical Science and Technology, University of Maryland, College Park, MD 20742, USA

Received: 4 July 1999 / Accepted: 7 July 1999 / Published online: 17 January 2000

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Abstract. The impact of two landmark papers by Edwards and de Gennes on the field of polymer physics is highlighted.

Key words: Flory theory – Edwards model – n -vector model

A major advance in the physics of polymers occurred in 1949 when Flory [1] provided a simple but profound argument for the swelling (compared to the ideal chain size) of flexible polymer chains due to excluded-volume interactions. In essence, the Flory result for the dependence of the radius of gyration, R_g , on the degree of polymerization, N , is obtained by minimizing the elastic energy (due to chain connectivity) and the repulsive energy arising from the volume excluded by a given monomer for all other monomers. The resulting prediction for the exponent, ν , defined by $R_g \approx aN^\nu$ is remarkably accurate in all space dimensions, d . For all practical purposes the Flory result for $\nu = \frac{3}{d+2}$ may be considered exact [2]. Similarly, the Flory argument is also found to be nearly exact for describing sizes of D -dimensional objects embedded in d spatial dimensions, such as tethered membranes with $D = 2$ [3]. For polymers $D = 1$.

A fundamental understanding of the reasons for the success of the theory due to Flory is still lacking. In an attempt to derive the Flory exponent Edwards proposed a model for polymers that bears his name in 1965 [4]. This paper brought to bear, for the first time, methods of functional integrals and many-body theory on problems in polymer physics. Edwards proposed a very simple form for the short-range repulsive potential describing the interactions between the monomers. He suggested replacing the actual potential by $v\delta[r(s) - r(s')]$, where v is the strength of the excluded-volume interactions, $r(s)$ is a path of the polymer chain and s and s' are the positions of two monomers along the positions of the chain. The use of the δ function pseudopotential should

not (see later) affect the long-wavelength properties of the polymer chain. With this replacement Edwards formally showed that polymer statistics boils down to summing over all possible paths weighted by the Hamiltonian given by the sum of the “kinetic energy” (representing chain connectivity) and the pseudopotential. The resulting path integral is non-Markovian, which is a reflection of the nature of the excluded-volume interactions. The formal analogy to the path integral allowed the use of many approximations devised in the context of quantum mechanics to problems in polymers.

Several studies utilizing the Edwards model for polymers followed [5]. In addition, using enumerations of self-avoiding walks using lattice models [6] and through the ingenious use of exact relations for Ising models [7] many new results for polymer statistics were obtained; however, an understanding of the varied universal behavior of polymer solutions was lacking. This state of affairs in polymer physics was to change dramatically after the profound discovery by de Gennes, who showed a connection between polymer statistics and phase transitions in 1972 [8]. This short and lucid paper followed right at the heels of the discovery of the renormalization group in the context of second-order phase transitions. de Gennes showed that the n -vector magnetic spin problem with $n = 0$ is equivalent to the excluded-volume problem considered by Flory [1] and formalized in terms of path integral methods by Edwards [4]. The connection between the excluded-volume problem and phase transitions also clarified the reasons for the independence of the values of ν on the details of the interaction potentials as long as they are short ranged. This, in retrospect, justified the Edwards choice of delta function interaction between two monomer segments. With this profound observation the entire machinery developed for understanding critical phenomena could be imported to obtain a vast number of new results. Thus, the concept of scaling was born in polymer physics and it continues to dominate the thinking of many scientists in this area.

The marriage of the Edwards model and de Gennes' observation brought an onslaught of several field theoretical methods to derive various scaling laws describing

the static properties of dilute and semidilute polymer solutions. The Edwards model was also generalized to poor solvent conditions so that polymer collapse could be described. These developments are summarized in a beautiful monograph by des Cloizeaux and Jannink [9]. It is fair to say that these two landmarks in polymer physics have enabled us to understand many structural aspects of polymers in solution.

There still are challenges which have come about in extending the Edwards model to tethered membranes ($D = 2$) [3]. The demonstration of the renormalizability of the resulting model is a topic of current research [10]. In this context there does not appear to be an equivalent spin model which describes self-avoidance in such objects. Further extension of these models to membranes and charged species is expected to be an important problem in the general area of soft-condensed-matter physics. A perusal of the literature on these topics is sufficient to appreciate the deep influence of the two landmark papers [4, 8] on polymer physics.

Acknowledgements: I am grateful to M. E. Fisher and H. Orland for useful discussions.

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