

Supplementary Information: Molecular Dynamics Study of the Swelling and Osmotic Properties of Compact Nanogel Particles

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I. SIMILARITIES BETWEEN LINEAR CHAINS IN TWO DIMENSIONS AND NETWORK POLYMERS IN THREE-DIMENSIONS

Linear polymers embedded in two dimensions are similar to network polymers in three dimensions in the sense that high order many-body interactions can be large in magnitude^{1,2} and this greatly complicates any theoretical discussion of the configurational properties of network polymers in three dimensions and linear polymers in two dimensions under variable excluded volume conditions, both in solution and in the melt where these excluded volume interactions can be greatly modified from the case of dilute solutions. For example, these interactions in solution have the practical effect of causing the θ -point exponent ν_θ , at which the second virial coefficient vanishes, to differ significantly from polymers entirely without excluded volume interactions. The results also depend on the specific nature of these polymer-polymer interactions, i.e., universality in the exponents cannot be generally taken for granted. When the excluded volume interactions are relatively short-ranged, as in lattice calculations of linear and branched polymers where the interaction potential is normally taken to have a simple nearest-neighbor form similar to a square-well potential in off-lattice fluids, the radius of gyration exponent ν at the θ -point for linear chains in two dimensions has been argued theoretically to be exactly equal, $\nu_\theta(\text{linear}) = 4/7$, rather than the random walk value of $1/2$ ^{3,4} for linear polymer chains having no excluded volume interactions, i.e., “random walks.” Correspondingly, for self-avoiding surfaces, which are “equivalent” to network polymers in terms of their mass scaling characteristics, ν_θ has been similarly argued by Douglas to be $\nu_\theta \approx 2/5$ ⁵ based on a view of branched polymers being perforated random surfaces rather than the Zimm and Stockmayer value of $1/4$ for network polymers having no excluded volume interactions.⁶ A much early Flory estimate of the θ -point exponent $\nu_\theta = 2/5$ for randomly branched polymers in three dimensions was apparently made based on different arguments by De Gennes.^{7,8}

Interestingly, these estimates of ν_θ for linear polymers in two dimensions and branched polymers in three dimensions have both been inferred from the geometrical properties of network polymers. In particular, the “exact” linear chain exponent ν_θ was inferred from heuristic theoretical arguments identifying the fractal dimension of θ -point ring polymers with the fractal dimension of the hull of percolation clusters in two dimensions^{3,4} and based on this kernel idea Saleur and Duplantier⁴ forcefully argued that $\nu_\theta = 7/4$ for self-avoiding walks with nearest-neighbor interactions in two dimensions.^{4,9} Bradley further developed this interesting geometrical interpretation of the θ exponent for linear polymers, and this result is now widely accepted as being the “correct” θ -point exponent for linear polymer chains in two dimensions. Soon thereafter,⁵ extended this type of argument to self-attracting random surfaces, which he also recognized as being in the same “universality class” as randomly branched polymers, and he identified ν_θ for self-attracting surfaces with short-range interactions in three dimensions with the reciprocal fractal dimension of the hull of percolation clusters in three dimensions. Correspondingly, the fractal dimension for percolation clusters was estimated numerically to be very near $5/2$,^{10,11} this estimate according with the Flory estimate for this exponent.⁸ Moreover, the percolation hull dimension of percolation clusters in three dimensions was found to equal to fractal dimension of the entire percolation cluster within numerical uncertainty, prompting these authors to suggest these exponents were exactly equal.^{10,11} These arguments collectively link the θ -point exponent ν_θ of network polymers in three dimensions having short-range interactions to the fractal dimension of percolation clusters, as we have intuitively argued in our own work. Historically, the connection between randomly branched polymers at their θ -point and percolation clusters was first suggested by Domb (See Ref. 12 for a discussion). The general physical picture here is that percolation clusters can be viewed as randomly branched polymers with screened binary excluded volume interactions. Although these arguments are all very interesting, these results are not rigorously exact in a strict mathematical sense.^{13,14}

A crucial assumption in these arguments is that the interactions have a short-range nature, such the nearest-neighbor interaction of lattice model calculations mentioned before. It has been shown that the existence

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of next-nearest interactions of appreciable magnitude in spin models of phase transitions can spoil the exponent universality conventionally hypothesized for critical phenomena so that the exponents are no longer unique. This situation is a direct consequence of the emergence of multicritical phenomena associated with higher order interactions beyond binary that become relevant in linear chains in two dimensions and branched polymers in three dimensions in an interacting polymer context.^{1,2} This non-universality issue was first illuminated precisely in the context of exactly solvable Ising model with nearest-neighbor and competing next-nearest neighbor interactions by Baxter,¹⁵ Jungling and Obermair,¹⁶ Tanaka et al.,¹⁷ Anjos et al.,¹⁸ (It should be appreciated that polymer configurational properties in the good solvent limit has been related to the spin model of phase transitions in the limit of a zero component field¹⁹ and this relationship extends to the θ -point which is taken to be the “analog” of a zero component tricritical spin model, as in the case of linear polymers and ordinary critical phenomena.^{20–22} Recent work has established that the lack of universal scaling arises both in the exponents describing swollen linear polymers²³ and in linear polymers at their θ -point. Recent studies^{2,24–27} have discussed experimental evidence for exponent non-universality in both simulation and experiments and two dimensions and have introduced semi-empirical estimates the θ -point and swelling exponents of two-dimensional polymers under θ conditions based on a formal extension of renormalization group (RG) theory to describe this complex physical situation where many-body-interactions can be large in magnitude and thus exponent universality questionable. Thus, while there is some tendency for some regularity in the mass scaling exponents of linear polymers in two dimensions, especially in lattice model calculations utilizing short-range polymer-polymer interactions based on the arguments discussed above, we cannot expect the exponents to be completely universal when there are competing interactions having different interaction ranges. Exactly the same complicated situation should apply to interacting network polymers in three dimensions, thus complicating the theoretical description of swelling in these polymers. This is indicated to be the case below.

The interrelations between linear and branched polymers can be seen most clearly from the direct calculation of configurational properties of linear and branched properties through a natural extension of the classical Fixman perturbation expansion of the binary excluded volume interactions in linear polymers^{28,29} to include higher-order many-body excluded volume interaction parameters, along with the use of RG theory to extract results for limiting asymptotic behavior from these perturbative expansions. Douglas et al.² discuss an attempt to treat many-body excluded volume interactions for a linear polymer with an aim to describe the swelling of linear polymers in two dimensions and corresponding perturbative binary excluded volume and RG calculations

for network polymers have been performed by Cui and Chen^{30–32}, based on a methodology first introduced by de Gennes.³³ These calculations reproduce the results obtained for branched polymers with excluded volume interactions using the more abstract field theoretical framework of Lubensky and Isaacson.³⁴ Calculations have also been performed for the spin model “analog” of branched polymers, corresponding to the critical^{35,36} and tricritical Lifshitz points.³⁷ This alternative type of critical phenomena arise when the nearest-neighbor interaction and the next nearest-neighbor interactions have opposite signs so that the material segregates into modulated phases separated by random surface interfaces, as commonly observed in microemulsions and in mixtures of polymer blends and block copolymers under certain conditions.^{38–42} The treatment of both linear polymers in two dimensions and the tricritical Lifshitz point in three dimensions involves multiple relevant many-body interactions where the analysis is complicated by the fact that each interaction has a separate critical dimension.^{2,37} The same situation arises when considering the collapse transition in polymers.² Although the RG theory of this type of multiple interaction RG cross-over has not yet been developed for this type many-body interaction, this type of theory has been successfully developed for polymer chains with both binary excluded volume interactions and polymer surface interactions⁴³ and with binary excluded volume and hydrodynamic interactions,^{44,45} which provides a template for how such calculations might be performed for linear polymers in two dimensions and network polymers in three dimensions.

The correspondence between interacting linear polymer chains in two dimensions and network polymers in three dimensions extends to the polymer melt regime. The prevalence of many-body interactions in these systems leads to large departures from ideal polymer chain conditions that are characteristic of linear polymer in three dimensions and in branched polymer above 6 spatial dimensions.¹ In both cases, the polymers adopt nearly collapsed configurations in which the polymers exhibit relatively little interpenetration of each other’s domains.^{46–52} This remarkable phenomenon was apparently first noted in a pioneering paper by Daoud and coworkers,¹ where the significant implications of these many body effects on phase separation are also first discussed.

It is then evident that the usual argument that polymer chain excluded volume interactions become completely screened in the melt no longer applies for linear polymers in two dimensions and network polymers in three dimensions, a phenomenon with profound physical consequences.

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