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Flory exponents for generalized polymer problems

J. Isaacson and T. C. Lubensky

Department of Physics, University of Pennsylvania, Philadelphia, Pa 19104, U.S.A.

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Résumé. — On emploie l'approximation de Flory pour calculer la dimension critique d_c en dessous de laquelle la théorie de champ moyen ne s'applique plus. Ensuite, on calcule l'exposant critique ν contrôlant la variation du rayon de giration R avec le nombre de monomères N . En particulier, on étudie des polymères linéaires et ramifiés en solutions diluées avec un bon solvant et dans des phases fondues monodisperses. En plus, on étudie des polyélectrolytes linéaires et ramifiés en solution diluée. Comme nouveaux résultats, on obtient $\nu = \frac{5}{2(d+2)}$ pour des polymères ramifiés en solution diluée, $d_c = 10$ pour des polyélectrolytes ramifiés et une dérivation modifiée de Flory du résultat exact $\nu = \frac{2}{d-2}$ pour des polyélectrolytes linéaires.

Abstract. — We use Flory's approximation to calculate the upper critical dimension, d_c , below which mean field theory breaks down. We also calculate the exponent ν controlling the dependence of the radius of gyration, R , of a polymer on the degree of polymerization N . In particular, we treat linear and branched polymers in dilute good solvents and in monodisperse melts and linear and branched polyelectrolytes in dilute solutions. New results include $\nu = \frac{5}{2(d+2)}$ for dilute branched polymers, $d_c = 10$ for dilute branched polyelectrolytes, and a modified Flory derivation of the exact result $\nu = \frac{2}{d-2}$ for dilute linear polyelectrolytes.

The Flory approximation [1] for the radius of gyration, R , of a linear polymer in a good solvent gives a remarkably accurate prediction for the exponent, ν , controlling the dependence of R on the degree of polymerization, N , for spatial dimension, d , between two and four. In this approximation, competition between an elastic energy, F_{el} , tending to keep R at its free or Gaussian value, R_0 , and a repulsive energy, F_{rep} , tending to swell the polymer, lead to an optimal R . The expression for F_{el} is simply that of a Gaussian chain,

$$F_{el} \sim \frac{R^2}{R_0^2}. \tag{1}$$

(We ignore unimportant prefactors.) R_0 increases as a power of N :

$$R_0 \sim N^{\nu_0} \tag{2}$$

where $\nu_0 = \frac{1}{2}$ for linear polymers and $\frac{1}{4}$ for branched polymers [2, 3] with a fixed probability for branching. F_{rep} is determined by short range two particle encounters in good solvents. In dilute solutions, we have

$$F_{rep} \sim \frac{N^2}{R^d}. \tag{3}$$

In dense solutions or melts, the repulsive interactions are screened by other polymers [4]. The degree of screening is determined by the weight average degree of polymerization of polymers in the solution, and F_{rep} becomes

$$F_{rep} \sim \frac{N^2}{R^d} \frac{1}{N_w}. \tag{4}$$

We can use eq. (4) to treat dilute solutions with $N_w \sim 1 = N^0$, monodisperse melts with $N_w \sim N$, and some other cases to be discussed by taking

$$N_w \sim N^\rho. \tag{5}$$

It is well known that mean field theory with $R \sim R_0$ is valid for large enough d . The upper critical dimension, d_c , below which mean field theory breaks down is determined by $F_{rep}(R_0) \sim 1$. Thus, we have

$$d_c = \frac{2 - \rho}{\nu_0}. \tag{6}$$

This formula was used by de Gennes [4] to find d_c for branched polymers in dilute solutions and mono-

disperse melts and for gelation. To find ν , we minimize $F = F_{el} + F_{rep}$ with respect to R and find

$$R^{d+2} \sim R_0^2 \frac{N^2}{N_w}. \quad (7)$$

Using eqs. (2) and (5), this implies

$$\nu = \frac{2(1 + \nu_0) - \rho}{d + 2}. \quad (8)$$

We now apply eq. (7) to a number of special cases.

1. Dilute linear polymers :

$$\nu_0 = \frac{1}{2}, \quad \rho = 0, \quad d_c = 4$$

and

$$\nu = \frac{3}{d + 2}. \quad (9)$$

This is the classical Flory formula [1].

2. Dilute branched polymers :

$$\nu_0 = \frac{1}{4}, \quad \rho = 0, \quad d_c = 8$$

and

$$\nu = \frac{5}{2(d + 2)}. \quad (10)$$

For $d = 8 - \varepsilon$, this formula yields $\nu = \frac{1}{4} + \frac{\varepsilon}{40}$ instead of the exact result [5] of $\frac{1}{4} + \frac{\varepsilon}{9}$. On the other hand for $d = 2$ and 3 , it yields $\nu = \frac{5}{8}$ and $\nu = \frac{1}{2}$ in good agreement with Monte Carlo [6] and series calculations [7] yielding ν between 0.57 and 0.66 for $d = 2$ and 0.43 and 0.53 for $d = 3$.

3. Monodisperse linear melts :

$$\nu_0 = \frac{1}{2}, \quad \rho = 1, \quad d_c = 2$$

and

$$\nu = \frac{2}{d + 2}. \quad (11)$$

The observation that $d_c = 2$ for this problem was previously made by de Gennes [1].

4. Monodisperse branched melts :

$$\nu_0 = \frac{1}{4}, \quad \rho = 1, \quad d_c = 4$$

and

$$\nu = \frac{3}{2(d + 2)}. \quad (12)$$

This formula yields $\nu = \frac{3}{10}$ for $d = 3$ and $\nu = \frac{3}{8}$ for $d = 2$.

5. Gelation. — This example is somewhat more complicated than the others since N_w changes with

dimension below d_c . The concentration of polymers with N monomers, $C_p(N)$, obeys a scaling law [8, 9]

$$C_p(N) \sim N^{-\tau} f((p - p_c)^{\Delta} N) \quad (13)$$

where p is the probability that a bond has formed and p_c is the value of p at the gel point. τ and Δ are critical exponents associated with percolation [10]. $C_p(N)$ has a pronounced peak at $N = N_m \sim (p - p_c)^{-\Delta}$ corresponding to the most probable degree of polymerization. For large d the mean field theory applies and $\tau = \frac{5}{2}$ and $\Delta = 2$. Since $C_p(N)$ is normalized so that $\sum_N C_p(N) N = C =$ concentration of monomers, we have

$$N_w \sim |p - p_c|^{-1} \sim N_m^{1/2}. \quad (14)$$

Thus, $\nu_0 = \frac{1}{4}$ (since we are dealing with branched polymers), $\rho = \frac{1}{2}$ and $d_c = 6$. This is the familiar result for percolation. It was first derived in the present context by de Gennes [4]. If we assume ρ remains $\frac{1}{2}$ for $d < 6$, eq. (8) implies

$$\nu = \frac{2}{d + 2}. \quad (15)$$

This is to be compared with ν_p/Δ where ν_p is the percolation correlation length exponent. Taking values for ν_p and Δ from Stauffer's review article [8], we find $\nu_p/\Delta = 0.526$ and 0.4 for $d = 2$ and 3 compared with $\nu = 0.5$ and 0.4 from eq. (15).

We have considered common special cases of eq. (5). We note however, that it would be interesting to test experimentally the dependence of ν on ρ by preparing the appropriate polydisperse melts.

The Flory approximation can also be applied to dilute polyelectrolytes. In this case, the Coulomb potential between charged polymers is unscreened and, F_{rep} should be replaced by the Coulomb energy

$$F_c \sim \frac{N^2}{R^{d-2}}. \quad (16)$$

Setting $F_c(R_F) \sim 1$, we find

$$d_c = 2 + \frac{2}{\nu_0}. \quad (17)$$

This formula produces the well known result $d_c = 6$ for linear polyelectrolytes [11]. For branched polyelectrolytes, it yields $d_c = 10$. We have verified that an ε -expansion in $10 - \varepsilon$ dimensions is possible for this problem.

Minimizing $F = F_{el} + F_c$ with respect to R , we find for linear and branched polymers

$$\nu = 2 \frac{(1 + \nu_0)}{d}. \quad (18)$$

For linear polyelectrolytes, this yields $\nu = 3/d$ in poor agreement with the exact result [10] $\nu = \frac{2}{d - 2}$

for $4 < d < 6$. For branched polymers, it yields $\nu = 5/2 d$.

It is well known [1c] that the Flory approximation overestimates F_{rep} because it ignores correlations and overestimates F_{el} because it treats F_{el} as a function of R/R_0 rather than as a function of R/R_G where $R_G \sim N^\nu$ is the actual equilibrium radius of gyration in the presence of interactions. The two errors cancel to give a good approximation. The error in F_{rep} is difficult to treat within the context of the Flory approach. The error in F_{el} can, however be treated by replacing F_{el} by

$$F'_{\text{el}} \sim \frac{R^2}{R_G^2}. \quad (19)$$

Minimizing $F = F'_{\text{el}} + F_e$ with respect to R , we find

$$\nu = \frac{2}{d-2}. \quad (20)$$

This is the exact answer for linear polymers [12] for $4 < d < 6$. It would be interesting to see if it also is the exact answer for branched polymers for $d < 10$. At this stage we should ask why correcting one but not both of the errors in the Flory approximation should yield a much better answer for ν . The answer is that correlation effects in F_{rep} are not so important in polyelectrolytes because of the long range nature of the Coulomb force. Thus, F_{rep} is in fact correctly given by eq. (16).

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