Simplicity and scaling - size of a real polymer in three (or any) dimensions

C.P. Lowe
van ’t Hoff Institute for Molecular Science, University of Amsterdam,
Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

M.W. Dreischor
Toegepaste Industriële Procesbeheersing, Kruislaan 419, 1098 VA Amsterdam, The Netherlands

We examine the scaling of the linear dimension of the system size of a real polymer solution at constant excess free energy and in two different spacial dimensionalities, \( d = d_0 \) and \( d = d_1 \). Standard results for the functional form of the excess free energy lead to the conclusion that the scaling exponent \( \nu(d) \) satisfies \( \nu(d_0) - \nu(d_1) = d_0^{-1} - d_1^{-1} \). Taking the critical dimensionality as a point of reference \( (\nu(4) = 1/2) \) gives a scaling exponent \( \nu(d) = 1/4 + 1/d \), in agreement with the accepted result for two-dimensions \( (\nu(2) = 3/4) \) and the first term in the epsilon \( (d - 4) \) expansion. For the unsolved case of three dimensions it predicts \( \nu(3) = 7/12 \). Several simplifying features of this result are pointed out.

An amazing thing about polymers is that, although they are complex molecules, just a few parameters usually describe their macroscopic properties \([1]\). For example, the polymer size, \( L_p \), is given by the scaling relation \( L_p \sim l_0 n^{\nu(d)} \). Here, the microscopic quantities are the number of monomers \( n \), and a length \( l_0 \). The precise definition of the latter we discuss later. The scaling exponent \( \nu(d) \) generally depends on the spacial dimensionality \( d \). If the monomers do not interact the chain is “ideal” and \( L \sim bn^\nu \), independent of the dimensionality. Here \( b \) is the Kuhn length (the root mean square separation between adjacent monomers). More generally a polymer is “real”, meaning that the monomers do interact. Flory pointed out that this changes the scaling \([2]\). Using a very simple model, he postulated that if the interaction between monomers is repulsive then, \( L_p \sim l_0 n^{\nu(d)}(1 \le d < 4) \) and \( L_p \sim l_0 n^{\nu(d)}(d \ge 4) \). So, for \( d < 4 \) the real chain is expanded relative to the ideal chain. For \( d \ge 4 \) the chain scales in the same way as an ideal chain, so the interactions have no effect. In this respect Flory’s model is correct. For two dimensions it predicts \( \nu(2) = 3/4 \). Again, this is accepted as correct \([3]\). Nonetheless, it is regarded as inexact for the most important case - namely three dimensions.

The reason for this is as follows. De Gennes famously showed the equivalence of the real polymer model to the \( n = 0 \) limit of the n-vector model \([4]\). First, this shows that the real polymer problem has significance beyond the realms of polymer physics. A nice example is that modelling the universe as a real polymer resolves Olbers’ paradox without assuming an expanding universe \([5]\). Second, having identified this equivalence de Gennes could use Wilson’s method \([6]\) to show that near to the critical dimensionality \( (d = 4) \), \( L_p(\epsilon \rightarrow 0) \sim n^{1/4 + \pi \nu} \), where \( \epsilon = 4 - d \). In this limit (which we refer to as \( d = 3.99 \)), the Flory result gives \( L_p(\epsilon \rightarrow 0) \sim l_0 n^{1 + \pi \nu} \). Consequently, the prediction that for \( d = 3 \), \( L_p \sim l_0 n^{1/2} \) is approximate. Current numerical estimates are that actually \( \nu(3) = 0.5877(\pm0.0007) \). So the exact value of this fundamental exponent, almost the polymer equivalent of \( \pi \), remains unknown. Here we use the functional form of the excess free energy of a polymer solution in different spacial dimensions to argue that in three dimensions \( \nu(3) = 7/12(= 0.5833) \). We also point out a number of simplifications regarding the physics of polymers and polymer solutions that would then follow.

There are two microscopic lengths involved in the problem, \( b \) and \( l \), where \( l \) is the range of the monomer-monomer potential. For a given value of the ratio \( l/b \), the size of the chain can be written in terms of either \( l \) or \( b \). Here we take the former. Where proportionalties and similarities are used, from now on it is because we neglect constants dependent only on the dimensionality. Consider the dimensionless excess free energy of a polymer solution, \( \G^* \), where \( \G^* = G/kT \) with \( G \) the excess free energy, \( T \) the (constant) temperature, and \( k \) Boltzmann’s constant. According to scaling theory \([8]\) this takes the form \( \G^* = N_p f_d(\phi_p) \), where \( f_d \) is some dimensionally dependent function, \( N_p \) is the number of polymers in the system and \( \phi_p \) is the “polymer space fraction”

\[
\phi_p \sim \frac{N_p L_p^{d}}{L^d} \tag{1}
\]

Here \( L_p \) is the linear dimension of the polymer in the dilute limit. In the scaling \((n \rightarrow \infty)\) limit this has the form

\[
L_p(d) \sim bn^{\nu(d)} \tag{2}
\]

Equally well, we can write the dimensionless excess free energy in terms of a dimensionally dependent function \( g_d \) and the “polymer length fraction”, as \( \G^* = N_p g_d(\Phi_p) \) where

\[
\Phi_p \sim \frac{N_p^{1/d} L_p}{L} \tag{3}
\]
Because this parameter involves lengths, which can be compared in different dimensionalities, it is more convenient for our purposes here. We now consider two systems in two different dimensionalities $d_0$ and $d_1$. The Kuhn length $b$ in dimensionality $d_0$ is proportional to the Kuhn length in dimensionality $d_1$, so there is no change in the relative size of the polymers in the two dimensionalities because of a varying ratio of Kuhn lengths. We now consider how the linear dimension of the system changes as we increase the number of the polymers and/or monomers, such that the length fraction remains unchanged. That is, such that $G^*(d_0)/G(d_1)$ depends on the dimensionality but nothing else. To do this requires that

$$L(d_0) \propto N_p^{1/d_0} n^{\nu(d_0)} b$$

$$L(d_1) \propto N_p^{1/d_1} n^{\nu(d_1)} b$$

(4)

(5)

So the ratio of the system sizes in the two dimensionalities scales as

$$\frac{L(d_0)}{L(d_1)} \propto N_p^{1/d_0 - 1/d_1} n^{\nu(d_0) - \nu(d_1)}$$

(6)

The above form of the excess free energy also holds above the “overlap concentration”, $\Phi_p >> 1$, where the polymers strongly overlap and the solution looks like a monomer soup. In this limit one expects that $n$ is irrelevant and only the monomer length fraction, $\Phi_m$,

$$\Phi_m \sim N_m^{1/d_b}$$

(7)

is relevant. Here $N_m = n N_p$ is the total number of monomers in the system. In this limit the dimensionless excess free energy, in terms of a dimensionally dependent function $h_d$, then takes the form $G^* = N_m h_d(\Phi_m)$. Far above the overlap concentration, but still in the semi-dilute regime ($\Phi_p >> 1$, $\Phi_m << 1$) both functional forms of the excess free energy are valid, that is $g_d(\Phi_p) \sim n h_d(\Phi_m)$. This leads to generally accepted scaling of the free energy in this limit.

Specifically, in terms of $\Phi_m$, $G^* = N_p g_d(\Phi_m n^{\nu(d) - 1/d})$, so for the above to be true requires $G^*/N_p \sim \Phi_d^{(d_d - 1)/d}$. We should note, however, that for one dimension, where $\nu(1) = 1$, the dimensionless free energy is a function of only $\Phi_m$ so both functional forms for the excess free energy cannot be satisfied simultaneously. This is reflected in the nonsensical prediction that in one dimension the free energy is infinite.

Now we can again consider the transformation in dimensionalities $d_0$ and $d_1$ (neither of which is now unity) described above. In terms of the monomer length fraction we have

$$L(d_0) \propto (N_p n)^{1/d_0} b$$

$$L(d_1) \propto (N_p n)^{1/d_1} b$$

(8)

(9)

so the ratio of the system sizes scales as

$$\frac{L(d_0)}{L(d_1)} \propto (N_p n)^{1/d_0 - 1/d_1}$$

(10)

In the semi-dilute limit, both $a$ and $\alpha$ are true, implying that

$$\nu(d_0) - \nu(d_1) = 1/d_0 - 1/d_1$$

(11)

If we take four dimensions to define $d_0$ (that is $d_0 = 4$, $\nu(4) = 1/2$), then, because $d_1$ can be any other dimensionality $d$, we have

$$\nu(d) = \frac{1}{d} + \frac{1}{4}$$

(12)

For two dimensions this yields $\nu(2) = 3/4$, the accepted result. For three dimensions it yields $\nu(3) = 7/12$. Note that we could equally well take the two dimensional result as a point of reference. In this case we would recover the four dimensional result. According to equation (12) the excess free energy takes a particularly simple form above the overlap concentration, $G^* \sim N_p \Phi_p^d$, independent of dimensionality. We now consider a number of other simplifying features that result from equation (12).

**The monomer overlap concentration.** Returning to the more usual space fractions, the thermodynamic properties of a polymer solution above the overlap concentration are determined by the monomer concentration, $c \sim N_m / L^d$. In terms of this variable the general form of the dimensionless excess chemical potential, $\tilde{\mu}^* = G^*/N_p$, valid for all concentrations, is

$$\tilde{\mu}^* = f(c/c^*)$$

(13)

where $c^*$ is the monomer overlap concentration

$$c^* \sim \frac{L^d_p}{n} \sim n^{d_d - 1} b^d$$

(14)

According to equation (12) the monomer overlap concentration is $c^{-1} \sim (n^{1/4} b)^d$. That is, the inverse monomer overlap concentration is proportional to a length $(n^{1/4} b)$, independent of dimensionality, raised to the power of dimensionality. So, for polymer solutions the excess chemical potential, in terms of monomer concentration, takes the same form as that of a simple fluid. For the latter, the length is the range of the potential (for example, the radius of the hard spheres in a hard sphere fluid).

**The dimensional dependence of the second virial coefficient.** According to scaling theory the second virial coefficient of a polymer solution, $B_2$, is proportional to the space occupied by the polymer. That is $B_2 \propto L^2_p$. From equation (12) we then have $B_2/n \propto b^d n^{d_d/4}$ so the “second virial length” $(B_2/n)^{1/d}$ should be independent of dimensionality. In figure [2] we have plotted this quantity for the self avoiding random walk in two
and three dimensions [7]. The data for the two dimensionalities are in surprising good quantitative agreement. There is a small but statistically significant difference for smaller n, but for the largest value (n = 80000) the difference is not significant. The reason that this is surprising is because our argument only predicts that the two functions are proportional. It appears from the simulation data, at least up to n = 80000, that the constant of proportionality is also independent of the dimensionality. If the result for the exponent given here is approximate the two curves shown in the figure must diverge for higher n. This could be tested numerically.

**Hyperbranched polymers.** If an ideal chain with n monomers has m branch points, for large n and m its size is reduced by a factor of m^{1/4} [9], relative to the linear case, so

\[ L_p \sim n^{1/2} \frac{1}{m^{1/4} b} \]

For a hyperbranched chain (m \propto n) we therefore have \( L_p \sim n^{1/4} b \). For all dimensionalities between two and four the hyperbranched ideal chain is an increasingly dense object. Its size increases more slowly with increasing mass than a space filling Euclidean object. This contrasts with the linear chain, which is rarefied in that its size increases more rapidly with increasing mass. Consequently, it is generally accepted that the effect of excluded volume on a hyperbranched chain is to change the sub-Euclidean scaling to Euclidean scaling, that is \( L_p \sim n^{1/4} b \) [10]. On long length scales one expects that correlations can be neglected and that the real hyperbranched chain behaves like the equivalent hyperbranched ideal chain, but with an n dependent Kuhn length (the “uniform expansion” model). That is, \( L_p \sim n^{1/2} b_n / m^{1/4} \), with \( b_n = n^{\nu(d)} - 1/2 b \). This being the case, we have

\[ L_p \sim n^{\nu(d)} \frac{1}{m^{1/4} b} \]

For the hyperbranched chain we then have \( L_p \sim n^{\nu(d)-1/4} \), so substituting equation [12] for the exponent gives the expected Euclidean scaling, \( L_p \sim n^{1/d} b \).

To examine the roles of the microscopic parameters, we now make use of the “two parameter model” [11, 12]. From dimensional analysis, the size of a single polymer takes the form

\[ L_p \sim n^{1/4} b f(z) \]

The unknown function \( f(z) \) is a function of a dimensionless (but dimensionally dependent) quantity \( z \),

\[ z = \left( \frac{l^d}{b} \right)^{4/d} \]

Now we have lifted the restriction that we are considering a system with a given value of the ratio l/b.

**The microscopic length.** According to scaling theory [1], for large n the size has a power-law dependence on n. That is,

\[ L_p \sim b^{1-d\gamma(d)} p^{d\gamma(d)} n^{\frac{1}{d} \gamma(d) - \frac{d}{d-\nu}} \]

with \( \gamma(d) = (2\nu(d) - 1) / (4 - d) \). So, the dimensional dependence of the scaling exponent also determines the microscopic length determining the polymer size. For example, the Flory result gives \( l_0 = (d/(d+2)) b^{2/(d+2)} \). Substituting equation [12] for the exponent yields \( \gamma(d) = 1/(2d) \) meaning that

\[ L_p \sim n^{1/4} b^{2\nu(d)} \]

There is a pleasing symmetry in the fact that the two intrinsic lengths in the problem, l and b, enter with the same power. They play an equivalent role in determining the size of the polymer. The fact that \( l_0 \) is independent of dimensionality also means that, as for the ideal chain, the ratio of polymer sizes in two different dimensionalities is only a function of n.

**The excess free energy of dilute polymer solutions.** Turning to the thermodynamics of low density polymer solutions (c/c^* \ll 1), in the limit \( z \to 0 \) (where the polymer is hardly expanded) the excess free energy \( \tilde{G}^* \) is

\[ \tilde{G}^* \sim N_m c l^d \]

Thus, the system is thermodynamically equivalent to a simple fluid of monomers with size l. On the other hand, in the scaling \( (z \to \infty) \) limit the excess free energy takes the form

\[ \tilde{G}^* \sim N_m c \frac{L_p^d}{n^2} \]
In terms of the monomer concentration, using the two parameter expression for $L_p$, yields
\[ G^* \sim N_m c z (d \gamma (d) - 1) l^d \]  \hspace{1cm} (23)

Introducing the the size of the polymer relative to the ideal chain size in the dilute limit, $\alpha_0 \sim z \gamma (d)$, equation 23 becomes
\[ G^* \sim N_m c \alpha_0^{\frac{d \gamma (d) - 1}{\gamma (d)}} l^d \]  \hspace{1cm} (24)

Thus, in the scaling limit the excess free energy of a polymer solution, in terms of the monomer concentration, takes the same form as that for a simple fluid except that the interaction length is scaled by a factor related to the degree of expansion on the polymer. The dependence of this scaling on the dimensionality in turn depends on the dimensional dependence of the scaling exponent. For example, the Flory result gives $G^* \sim N_m c l^d / \alpha_0^d$, independent of dimensionality. On the other hand, using the expression for $\nu (d)$ given by equation 12 gives
\[ G^* \sim N_m c \left( \frac{l}{\alpha_0} \right)^d \]  \hspace{1cm} (25)

That is, the system is thermodynamically equivalent to a simple fluid, except that the effective size of the monomers is reduced proportionately to the degree of expansion of the chain, independent of dimensionality.

As noted above, we cannot take one dimension as a point of reference because in this case the excess free energy, above the overlap concentration, cannot be written in terms of both the polymer and monomer concentration. It is unsurprising, therefore, that equation 12 is incorrect for $d = 1$. It predicts $\nu (1) = 5/4$. From the condition of fixed contour length, $\nu (d)$ cannot exceed unity. One interpretation of this is that the expression predicts a lower critical dimensionality at $d = 4/3$ (the dimensionality for which the exponent is unity). We believe that there is tacit evidence for this from renormalization group theory (RG) calculations [13] and simulations in non-integer dimensions [14] (see figure 2). We use the word “tacit” here because ref. [13] is, to our knowledge, only published as a pre-print and the author of ref. [14] interpreted the low dimensionality behaviour as probably an error in the model because it disagreed with the Flory result (without explaining why the same model apparently worked for higher dimensionalities).

Finally we should point out the reasons for believing that the result we obtain here is not exact. First, it is outside the range of current numerical and RG estimates for the exponent in three dimensions. However, the former require extrapolation to the scaling limit and the latter the re-summation of divergent series. This makes reliably estimating the error difficult (when Nienhuis argued that $\nu (2) = 3/4$, this was outside the range of contemporaneous numerical and RG values). Second, equation 12 agrees with the epsilon expansion to first order but not to second order. Specifically, the epsilon expansion gives $\nu (\epsilon) = 1/2 [1 + \epsilon / 8 + 15/256 \epsilon^2]$, whereas equation 12 gives $\nu (\epsilon) = 1/2 [1 + \epsilon / 8 + 1/32 \epsilon^2]$. If the epsilon expansion is exact and unique to second order then, while equation 12 is correct for $d = 3.99$ and $d = 2$, it is only a very good approximation for $d = 3$. Could the epsilon expansion to second order be inexact or non-unique? It seems heresy to even suggest this, but we note that there is an added degree of subtlety in calculating the second order term in the epsilon expansion as compared to the first order term. Namely, a “magic interaction strength” is required for which corrections to scaling disappear [15]. Further, the epsilon expansion by its nature requires the concept of non-integer spacial dimensions. Are non-integer dimensions unique or just an interpolation between integer dimensions? In the analysis above we have treated $d$ as a continuous variable, but this is not actually necessary. We could equally well have restricted ourselves to integer dimensionalities. The concept of non-integer dimensionality is not required here. To summarize, there are two possibilities. The epsilon expansion is exact and unique. All the above simplifications apply in 3, 3.99 and 2 dimensions, but not quite in three. Alternatively, nature is kind and there is nothing special about three dimensions.

We would like to thank Daan Frenkel and Bela Mulder for their interest and encouragement, and participants of the Frenkel weekend for their vote of confidence.

---

References:
[1] PG de Gennes, “Scaling Concepts in Polymer Physics” (Cornell Univ. Press, Ithaca, NY, 1979).
[2] P.J. Flory, J. Chem. Phys. 17, 303 (1949).
[3] B. Nienhuis, Phys. Rev. Lett. 39, 1062 (1972).
[4] P. G. de Gennes, Phys. Lett. A38, 339 (1972).
[5] Y. Diao and A. Stasiak, Int. J. Contemp. Math. Sciences 2, 445 (2007).
[6] K. G. Wilson and M. E. Fisher, Phys. Rev. Lett. 28, 240 (1972).
[7] B. Li, N. Madras and A. D. Sokal, J. Stat. Phys. 80, 661 (1995).
[8] M. Doi and S.F. Edwards, “The Theory of Polymer Dynamics”, (Oxford Univ. Press, Oxford, 1986).
[9] B. H. Zimm and W. H. Stockmeyer, J. Chem. Phys. 17, 1301 (1949).
[10] D. Konkolewicz, R. G. Gilbert and A Gray-Weale, Phys. Rev. Lett. 98, 238301 (2007).
[11] M. K. Kosmas and K. F. Freed, J. Chem. Phys. 69, 3647 (1978).
[12] M. Muthukumar and B. G. Nickel, J. Chem. Phys. 86, 460 (1987).
[13] J. Gottker-Schnetmann, preprint ArXiv cond-mat/9909418 (1999).
[14] Z. Alexandrowicz, Phys. Rev. Lett. 50, 736 (1983).
[15] K. G. Wilson, Phys. Rev. Lett. 28, 548 (1972).