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## LETTER TO THE EDITOR

# Conformational space renormalisation group theory of 'tricritical' (theta point) exponents for a polymer chain

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**Abstract.** The marked difference between the  $n \rightarrow 0$  limit of  $O(n)$   $\phi^4$ - $\phi^6$  field theory tricritical exponents and accepted values for a polymer in  $d = 2$  are shown to persist when renormalisation is performed away from the tricritical point. The difference is removed by introducing a physically dictated renormalisation prescription for the field theoretic formulation of the polymer problem or the equivalent chain conformational space method.

The  $n \rightarrow 0$  limit of  $O(n)$   $\phi^4$  field theory has been used to describe a self-avoiding random walk, providing a model for long polymer chain above the theta temperature. This field theoretic method, as well as the formally equivalent conformation space path integral method, (Freed and Kholodenko 1983, Kholodenko and Freed 1983), provides an excellent description of the 'critical exponents', correlation functions, and cross-over behaviour of a wide variety of polymer systems. The success of the  $\phi^4$  field theory has led to the belief that field theoretic methods could also be applied to the description of the theta point ('tricritical') region, where the quartic coupling constant is small, by incorporating a  $\phi^6$  term to represent three-body interactions. Such a field theory for non-zero  $n$  is associated with the description of tricritical phenomena.

Renormalisation group calculations for the tricritical point have been given by Stephen (1975). He provides exponents like

$$\nu_s = \frac{1}{2} + \frac{1}{3} \frac{(n+2)(n+4)}{(3n+22)^2} \varepsilon^2 + O(\varepsilon^3), \quad (1)$$

for  $\varepsilon = 3 - d$  and  $d$  the dimensionality, which have recently been reproduced using field theoretic techniques by Duplantier (1983). By analogy with the  $\phi^4$  case, it has been presumed that the  $n \rightarrow 0$  limit of (1) is also relevant to polymers. The only evidence available for polymers in the theta region comes from Monte Carlo calculations, (Baumgärtner 1982, Kremer *et al* 1981) which have not yet established the  $d = 2$  theta point exponents, from crude real space renormalisation group calculations (Marqusee and Deutch 1981) which suggest that the theta point exponents are closer to the  $d = 2$  mean field predictions obtained by Flory-type arguments, and from inter-dimensional scaling arguments (Oono 1976a, b) which reproduce the Flory exponents and are quite accurate in other areas of critical phenomena (Imry *et al* 1973, Freed and Kosmas 1978). (The Flory exponent  $\nu_F$ , given below, is *substantially*

different from  $\nu_s$  for  $d = 2$ .) These  $d = 2$  theta point exponents are central quantities in the consideration of branched polymer systems where Daoud *et al* (1983) use the mean field exponents rather than (1). Hence, the strong disagreement between the results of tricritical renormalisation group calculations (Stephen 1975) and likely polymer values, which more closely resemble mean field predictions, is very troublesome. This implies that (a) either the field theory formalism becomes inapplicable to polymers in this regime or (b) some essential element of the polymer physics is omitted in the existing field theoretic formulations.

The use of the  $O(n)$  model for polymers is based on a convenient set of mathematical analogies, and care must be exercised when extending the analogies beyond their proven domain of validity. It can be shown following de Gennes (1979) that the description of a polymer chain with two- and three-body interactions can exactly be mapped into the  $n \rightarrow 0$  limit of  $O(n)$   $\phi^4$ - $\phi^6$  type field theory. The field theoretic description (Brezin *et al* 1976) of the tricritical point is based on renormalisation at the tricritical point  $T_c$ ; then the method of insertions (Amit 1978) permits calculations away from  $T_c$ . The quantity  $s = (T - T_c)/T_c$  in the field theory, with  $T$  the temperature, corresponds to a Laplace variable conjugate to the polymer chain length  $N$ . Hence, a polymer theory with  $s$  fixed corresponds to a system of polymers with an exponential distribution of chain lengths  $N$ . As we approach the tricritical point  $s \rightarrow 0$  where the effective quartic interaction vanishes, the mean value of this polymer length distribution tends toward the *physically unattainable infinite limit*. Consequently, in polymer systems the tricritical point is a physically inaccessible limit, whereas in other critical phenomena it is quite approachable from above or below.

When calculating molecular weight dependent properties of polymer systems, it is necessary to perform an inverse Laplace transform to convert from  $s$ -dependent to  $N$ -dependent quantities. The theta point is described theoretically (and empirically) as the point at which the second virial coefficient for the polymers, that is related to the inverse Laplace transformed four-vertex part, vanishes. We show below that this different choice of the renormalisation prescription for the vertex part, as dictated by the physics of polymers, leads to exponents which are close to Flory's mean field values but are distinct from (1) for  $n = 0$ . This then resolves the previous discrepancy between approximate polymer and renormalisation group exponents. We also show (Kholodenko and Freed 1984) that the massive  $O(n)$   $\phi^4$ - $\phi^6$  field theory can be renormalised, corresponding to renormalisation for  $T \neq T_c$ . This would still lead to identical tricritical exponents to those given by Stephen (1975) for the tricritical region as well as to those known in  $O(n)$   $\phi^4$  theory (Amit 1978).

Following Flory (Fisher 1968 and de Gennes 1979) the mean field free energy functional for the single chain with radius  $R$  and length  $N$  is (Isaacson and Lubensky 1983)

$$F/kT = R^2 N^{-1} + gN^2 R^{-d} + wN^3 R^{-2d}, \quad (2)$$

(with numerical constants and factors of the lattice constant omitted.) The  $R^2 N^{-1}$  term is the entropic contribution while those in  $g$  and  $w$ , respectively, are due to two- and three-body interactions. For good solvents, we may set  $w = 0$ , and the minimisation  $dF/dR = 0$  yields  $R^2 \propto N^{2\nu}$  with the Flory result  $2\nu_F = 6/(d+2)$ . Near the theta point  $g = 0$ , so the minimum free energy yields  $2\nu_F = 4/(d+1)$  which differs considerably from (1) for  $d = 2$  and  $n = 0$ .

This exponent (and others) can be reproduced more rigorously by applying renormalisation group methods to the conformational space functional integral, (Edwards

1966, Freed and Kholodenko 1983, Kholodenko and Freed 1983, 1984)

$$G_B(\mathbf{R}, N) = \int \mathcal{D}[\mathbf{c}] \exp\left(-\frac{1}{2} \int_0^{N_0} d\tau |d\mathbf{c}(\tau)/d\tau|^2 - (g_0/2!) \int_0^{N_0} \int_0^{N_0} d\tau d\tau' \delta[\mathbf{c}(\tau) - \mathbf{c}(\tau')] - (w_0/3!) \int_0^{N_0} \int_0^{N_0} \int_0^{N_0} d\tau d\tau' d\tau'' \delta[\mathbf{c}(\tau) - \mathbf{c}(\tau')] \delta[\mathbf{c}(\tau') - \mathbf{c}(\tau'')]\right) \quad (3)$$

with  $\langle \mathbf{R}^2 \rangle = \int d^d \mathbf{R} \mathbf{R}^2 G(\mathbf{R}, N) / \int d^d \mathbf{R} G(\mathbf{R}, N)$ , or to the field theoretic formulation from

$$G_B(\mathbf{R}, s) = \lim_{n \rightarrow 0} \sum_{i=1}^n n^{-1} \mathcal{N}^{-1} \int \mathcal{D}[\boldsymbol{\psi}] \psi_i(\mathbf{R}) \psi_i(0) \times \exp\left(-\frac{1}{2} \int d^d x \left[\frac{1}{2} (\nabla \boldsymbol{\psi})^2 + s \boldsymbol{\psi}^2 + (g_0/4) (\boldsymbol{\psi}^2)^2 + (w_0/24) (\boldsymbol{\psi}^2)^3\right]\right) \quad (4)$$

with  $\mathcal{N}$  the conventional normalisation factor to remove disconnected diagrams (Amit 1978). When  $w = 0$ , the renormalisation scheme for (3) is based on the relation (Kholodenko and Freed 1983)  $G(\mathbf{R}, N, uL) = ZG_B(\mathbf{R}, N_0, g_0)$ , where  $g_0 = u_0 L^{-\varepsilon/2}$ ,  $\varepsilon = 4 - d$ ,  $N = Z_2 N_0$ ,  $u_0 = Z_u u$ ,  $L$  is some length scale and the renormalisation constants are determined order-by-order. Fourier-Laplace inversion of  $G$  converts this (Kholodenko and Freed 1983) to the standard field theory form

$$G(\mathbf{k}, s, u, L) = [\tilde{Z}^{\frac{1}{2}} \mathbf{k}^2 + Z_s + \tilde{Z} \Sigma(\mathbf{k}, Z_2 s)]^{-1} \quad (5)$$

with  $\tilde{Z} \equiv ZZ_2^{-1}$  and  $\mathbf{k}$  is the Fourier variable conjugate to  $\mathbf{R}$ . The computations are then the same as for *massive, one-component*  $\phi^4$  field theory, corresponding to chains of finite length. The only difference between the polymer problem and one-component  $\phi^4$  theory lies in the combinatorial weights for individual diagrams (Kholodenko and Freed 1983). Use of (5) eliminates the need for insertions. It can be shown (Kholodenko and Freed 1984) that there is a direct correspondence between our method of renormalisation and that of field theory with insertions (Brezin *et al* 1976, Amit 1978) through the correspondence between our renormalisation constants ( $Z, \tilde{Z}, Z_u$ ) and the respective ones ( $\tilde{Z}_{\phi^2}, Z_{\phi}, Z_u$ ) of Amit's book (1978). Hence, renormalisation based on (5) yields the same exponents in the long chain  $N \rightarrow \infty$  limit as the  $n \rightarrow 0$  limit of  $\phi^4$  field theory.

The extension of the renormalisation scheme to the theta ('tricritical') region is based on (3) and the relationship

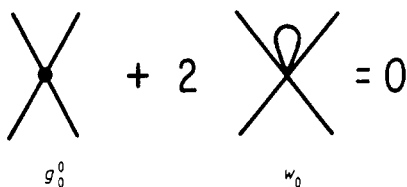
$$G(\mathbf{k}, N; g, w, L) = e^{aN} (2\pi i)^{-1} \int_C ds \exp(sN) [\frac{1}{2} \tilde{Z} \mathbf{k}^2 + Z_s + Z_a + \tilde{Z} \Sigma(\mathbf{k}, Z_2)(s+a)]^{-1}, \quad (6)$$

with  $C$  the contour for inverse Laplace transforms, and the additive renormalisation enters through  $a$  and  $Z_a$ . Paralleling the procedure for (5) it can be shown (Kholodenko and Freed 1983) that renormalisation of (4) and the portion of the right-hand side of (6) in brackets for fixed  $s$  are identical. We now proceed to show how tricritical renormalisation can be made for  $s \neq 0$ . The conventional renormalisation prescription implies the vanishing of the four-vertex part at the tricritical point (or the second virial coefficient at the theta point) for a particular quartic coupling constant  $g_0^0$ . This

condition is represented diagrammatically in figure 1 to lowest order. Within the dimensional regularisation method, the fixed  $s$  solution is obtained in lowest order as  $g_0^0 = 2w_0(2s)^{1/2}$ . In general, the solution has the form  $g_0^0 = (2s)^{1/2} \sum_{i=0}^{\infty} \sum_{j=0}^i a_{ij} w^j \epsilon^{-j}$  as follows from dimensional arguments. Hence, the vanishing of the four vertex part for  $s \neq 0$  implies

$$\Gamma^{(4)}(g_0^0, w, s) = (2s)^{1/2} \tilde{\Gamma}^{(4)}(w) = 0, \tag{7}$$

where the solution for  $g_0^0$  is substituted into the four-vertex part to obtain the coefficients  $a_{ij}$  which are dictated by dimensional analysis to be pure numbers. Consequently, our renormalisation scheme may be performed for any non-zero fixed  $s$  and leads to the same exponents as Stephen's, i.e., gives the same results as from (4) with the use of insertions (Duplantier 1983).



**Figure 1.** First-order diagrams to determine the tricritical  $g_0^0$  in  $s$ -space or the theta point  $g_0^0$  in  $N$ -space. Diagrams follow standard rules in both cases (Amit 1978, Kholodenko and Freed 1983, 1984). External legs are included in the equation for the polymer second virial coefficient, but not in the equation for the tricritical case.

In polymers,  $s$  is just a Laplace variable which cannot, in principle, be fixed. Inverse Laplace transformations of the equation in figure 1 yields the fixed  $N$ , theta point coupling constant  $g_0^0 = 4w_0(2/\pi N)^{1/2}$  in lowest order. The simple property of inverse Laplace transforms  $L^{-1}[f(s)h(s)] \neq L^{-1}[f(s)]L^{-1}[h(s)]$  for  $f$  and  $h$  arbitrary functions implies that the solutions  $\Gamma^{(4)}(g_0^0, w, s) = 0$  and  $\Gamma^{(4)}(g_0^0, w, N) = 0$  are numerically different (see comment in figure caption) and yield different cancellations for the inverse two-point propagator expansion. Therefore, finite  $N$  renormalisation produces numerically different results than renormalisation with  $s$  fixed. We have not found any simple relation between the fixed  $s$  and  $N$  renormalisation constants and exponents. In the  $N \rightarrow \infty$  limit the fixed  $N$  formalism yields  $2\nu = 1.102$  in  $d = 2$  to be compared with the Flory value of  $2\nu_F = 1.333$  or (1) for  $n \rightarrow 0$  of  $2\nu_S = 1.011$ .

Away from the theta point  $g = g_0^0 + \delta g \neq 0$ , and a full calculation yields the polymer cross-over exponent  $\Phi = \frac{1}{2} + \frac{4}{11}\epsilon$  to be compared with Stephen's (1975) tricritical  $\Phi_S = \frac{1}{2} + \frac{3}{22}\epsilon$ . The value of  $\Phi$  enables us to establish the size of the tricritical domain as well as to obtain  $\langle R^2 \rangle$  near the theta point for  $22w \ln N/L \gg 1$  as

$$\langle R^2 \rangle = Nl \exp(2.245 w) \{ 1 - 0.014 [\ln(N/L)]^{-1} + 0.66(2N/\pi)^{1/2} \exp(1.12 w) \times [22w \ln(N/L)]^{4/11} \delta g + \dots \}. \tag{8}$$

Results for temperatures below the theta point where the chain undergoes collapse, the coil-globule transition, will be presented elsewhere.

The inadequacy of fixed  $s$  renormalisation for polymers emerges readily when calculating any physical quantities because the finite portions left after regularisation contain terms in  $\ln(2\pi/sL)$  which are removed by the choice of  $s$  for which  $2\pi/sL \equiv 1$ .

However, if  $s$  is a Laplace variable, any choice of single  $L$  incorrectly leaves logarithmic terms after transformation.

The new set of theta point exponents are simply understood as follows. Renormalisation prescriptions must be introduced based on physical considerations of observables. The fixed  $s$  four-vertex part is not a measurable for polymers, while the second virial coefficient is the quantity generally chosen to establish the theta point empirically. This different renormalisation prescription naturally produces different exponents for fixed  $N$ . Averaging over arbitrary distributions in  $N$  leaves the same exponents, of course. It is clear, however, that these exponents are relevant only for sufficiently long polymer chains.

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## References

- Amit D 1978 *Field Theory, The Renormalization Group and Critical Phenomena* (London: McGraw-Hill)
- Baumgärtner A 1982 *J. Physique* **43** 1407-11
- Brezin E, LeGuillou J C and Zinn-Justin C 1976 in *Phase Transitions and Critical Phenomena* vol 6 ed C Domb and M Green (London: Academic)
- Daoud M, Pincus P, Stockmayer W H and Witten T 1983 *Macromolecules* in press
- de Gennes P G 1979 *Scaling Concepts in Polymer Physics* (Ithaca: Cornell University Press)
- Duplantier B 1983 Private communication
- Edwards S F 1966 *Proc. Phys. Soc.* **88** 266-80
- Fisher M E 1968 *J. Phys. Soc. Japan* **26** (Suppl.) 44-6
- Freed K F and Kosmas M K 1978 *Phys. Rev. B* **20** 215-22
- Freed K F and Kholodenko A L 1983 *J. Stat. Phys.* **30** 437-47
- Imry Y, Deutscher G, Bergman D J and Alexander S 1973 *Phys. Rev. A* **7** 744-6
- Isaacson J and Lubensky T C 1983 *preprint*
- Kholodenko A L and Freed K F 1983 *J. Chem. Phys.* **78** 7390-411
- 1984 *J. Chem. Phys.* in press
- Kremer K, Baumgärtner A and Binder K 1981 *J. Phys. A: Math. Gen.* **15** 2879-97
- Marqusee J A and Deutch J M 1981 *J. Chem. Phys.* **75** 5179-85
- Oono Y 1976a *J. Phys. Soc. Japan* **40** 917
- 1976b *J. Phys. Soc. Japan* **41** 2095-7
- Stephen M J 1975 *Phys. Lett.* **53A** 363-4