A renormalisation group approach to the entropy of a single polymer

David J Elderfield

Department of Theoretical Physics, The University, Manchester M13 9PL, UK

Abstract. Employing the $n \to 0$ field theoretic analogue we derive renormalisation group equations directly for the polymer system which may be solved to exhibit the scaling behaviour of the entropy $S(L)$ of a single polymer of L links. An elegant parametric representation of the crossover from random flight to self-avoiding behaviour as the chain length L or expansion factor $\alpha = \langle R^2 \rangle / \langle R^2 \rangle_\theta$ increases is described, for which explicit representations are constructed to $O(\varepsilon^2)$ in the ε expansion. In the asymptotic domain $\alpha \gg 1$ or $L \gg 1$ the expected scaling behaviour is observed.

1. Introduction

Following the pioneering work of Edwards (1966) it is widely believed that the entropy $S(L)$ of a polymer chain of L links may generally be parametrised·by the form

$$S - AL - B = (\gamma - 1) \ln L$$

where $\gamma = \gamma(d)$ is a universal function of the spatial dimension d and A, B independent of L summarise the short-range (non-universal) correlations. For self-avoiding or free-flight models this structure is adequately confirmed by direct enumeration of the polymer configurations on a lattice (see McKenzie 1976 for a review). More generally for a polymer obeying excluded-volume statistics (Edwards 1966) we would expect to observe a crossover from free-flight ($\gamma = 1$) to self-avoiding ($\gamma \simeq 6/d + 2$) behaviour as L increases and important long-range correlations develop, however, at present only the asymptotic behaviour is discussed in the literature (des Cloizeaux 1976). In this paper we develop a parametric description of the universal crossover scaling function $m(\bar{L})$ which controls the behaviour of the subtracted entropy $\bar{S}$

$$\bar{S} \equiv S - AL - B = m(\bar{L}).$$

Here A, B and $L/\bar{L}$ independent of L control the non-universal aspects of S. Employing the $n \to 0$ analogue field theory to derive renormalisation group equations directly for the polymer system we show that $\bar{S}$ may be described in the compact parametric form

$$\bar{S} = S - AL - B = + \int_0^p \frac{\mathrm{d}x}{\beta(x)} \left(\frac{1}{\nu(x)} - 2 + \eta(x) \right) + k(p) \qquad (k(0) = 0)$$

where the parameter p may be expressed in terms of the renormalised length $\bar{L}$

(proportional to L) by means of the relation

$$\exp - \int^p \frac{dx}{\beta(x)\nu(x)} = \bar{L},$$

or, more usefully, directly in terms of the expansion factor $\alpha = \langle R^2 \rangle / \langle R^2 \rangle_\theta$ which is directly measurable

$$\cdot \alpha = \langle R^2 \rangle / \langle R^2 \rangle_\theta = f(p) \exp + \int_0^p \frac{dx}{\beta(x)} \left(\frac{1}{\nu(x)} - 2 \right).$$

Here $k(p)$, $f(p)$ may be constructed perturbatively in p in terms of the subtracted 'entropy' $\bar{S}$ and expansion factor α at the renormalisation group matching point $\tilde{L} = 1$, $\bar{u} = p$ $(\tilde{L} \neq \bar{L})$, whilst the functions $\beta(x)$, $\nu(x)$, $\eta(x)$ are known at least to $O(x^4)$ in the literature (see Brézin *et al* 1976)

$$k(p) \equiv \bar{S}(\bar{u}, \tilde{L})|_{\bar{u}=p, \tilde{L}=1}$$

$$\alpha(p) \equiv \alpha(\bar{u}, \tilde{L})|_{\bar{u}=p, \tilde{L}=1}.$$

The non-universal functions A, B are independent of the chain length and therefore of little intrinsic interest.

In the asymptotic region $\bar{L} \gg 1$ or $\alpha \gg 1$, we obtain the expected scaling structure with *full control* of the universal content of the constant term

$$\bar{S}(\bar{L}) = S - AL - B = \gamma - 1(\ln \bar{L} - v(\varepsilon))[1 + O((\bar{L})^{-\omega})]$$

or more usefully

$$\bar{S}(\alpha) = S - AL - B = \gamma - 1[\ln(\alpha^{1/(2\nu-1)}) - w(\varepsilon)](1 + O(\bar{L})^{-\omega})$$

To *second* order in ε we find that the universal amplitudes ($\bar{L}$ or α fixed) are of the form

$$v(\varepsilon) = \frac{2}{\varepsilon} \left[1 + \left(\frac{1-\chi}{2} \right) \varepsilon + O(\varepsilon^2) \right]$$

$$\omega(\varepsilon) = \frac{2}{\varepsilon} (1 - \tfrac{43}{32}\varepsilon + O(\varepsilon^2)).$$

More generally, by direct computation to $O(\varepsilon^2)$ for a dimensionally regularised theory we obtain the explicit results

$$\bar{S} \equiv S - AL - B = \frac{(1-\gamma)}{\omega} \ln(1 - p/u^*) - \frac{p}{3\varepsilon} \left(1 + \frac{\varepsilon}{2} \right) \left[1 + \frac{p}{8} (13 - 16\chi) \right] + O(\varepsilon^3)$$

where the parameter p may be determined in terms of $\bar{L}$ or α from the relations

$$\alpha = (1 - p/u^*)^{(1-2\nu)/\omega} \left[1 - \frac{p}{6} \left(\frac{59}{16} - \chi \right) \right]$$

$$(1 - p/u^*)^{-\varepsilon/2\omega} p = (1 - \bar{u}/u^*) \bar{u} \tilde{L}^{\varepsilon/2} \equiv \bar{L}^{\varepsilon/2}.$$

Here χ is the Euler number: $\chi = 0.5771 \ldots$.

After a brief introduction to the excluded volume model and its field-theoretic analogue in the first section, we then proceed to derive and solve a series of exact renormalisation group equations which describe the scaling properties of the entropy in the second and final sections.

2. Entropy, excluded volume models and the field-theoretical analogue

The excluded volume model is based on a simple phenomenological short-range repulsion between the monomers so that the energy $E(\mathscr{C})$ of a polymer configuration $\mathscr{C}$ may be written for a continuous chain in the form

$$E(\mathscr{C}) \equiv \frac{g}{4!} \int_0^N \mathrm{d}s \int_0^N \mathrm{d}s' \, \delta(r(s) - r(s')) \tag{2.1}$$

where the vector $r(s)$ $0 < s < N$ parametrises the chain of $L = N\Lambda^2$ 'monomers'. Here Λ is representative of the inverse monomer spacing. In the context of the canonical ensemble approach we may therefore express the entropy S in the form

$$S \equiv -\underset{\mathscr{C}}{\mathrm{Tr}}\, p \ln p = E(g) + \ln(N(g)) \tag{2.2}$$

where the ensemble probability $p(\mathscr{C})$ is given by the equation

$$p(\mathscr{C}) = \frac{\exp - E(\mathscr{C})}{\mathrm{Tr} \exp - E(\mathscr{C})} \tag{2.3}$$

and the functions $E(g)$, $C_N(g)$ are defined as follows:

$$C_N(g) = \underset{\mathscr{C}}{\mathrm{Tr}} \exp - E(\mathscr{C}) \tag{2.4}$$

$$C_N(g) E(g) = \underset{\mathscr{C}}{\mathrm{Tr}}\, E(\mathscr{C}) \exp - E(\mathscr{C}) = -g \frac{\partial}{\partial g} (C_N(g)). \tag{2.5}$$

Specialising to the continuous gaussian chain model of Edwards (1966) we may trivially rewrite (2.4), (2.5) in terms of an effective Hamiltonian $H(\mathscr{C})$

$$H(\mathscr{C}) = \int_0^N \mathrm{d}s \left(\frac{\partial r(s)}{\partial s}\right)^2 + \frac{g}{4!} \int_0^N \mathrm{d}s \int_0^N \mathrm{d}s' \, \delta(r(s) - r(s')) \tag{2.6}$$

by means of the relation

$$\underset{\mathscr{C}}{\mathrm{Tr}}\, f(\mathscr{C}) = \int [\mathrm{d}r] \exp\left[-\int_0^N \left(\frac{\partial r}{\partial s}\right)^2 \mathrm{d}s\right] f(\mathscr{C})$$

for all functions $f(\mathscr{C})$. Here $\int [\mathrm{d}r]$ denotes a functional integration. For the restricted ensemble $r(N) - r(0) = \boldsymbol{R}$ one finds that

$$C_N(\boldsymbol{R}, g) \equiv \underset{\substack{\mathscr{C} \\ r(N)-r(0)=\boldsymbol{R}}}{\mathrm{Tr}} \exp - \beta E(\mathscr{C}) = \int [\mathrm{d}r] \delta(r(N) - r(0) - \boldsymbol{R}) \exp - H(\mathscr{C}) \tag{2.7}$$

from which the entropy S may be derived via the equations (2.4), (2.5) and the obvious relation

$$C_N(g) = \int \mathrm{d}R^d \, C_N(\boldsymbol{R}, g). \tag{2.8}$$

We should remark that the entropy S relative to the free ($g = 0$) rather than the absolute entropy, which is infinite, will be computed.

The particular importance of (2.7) lies in the following isomorphism between $C_N(\mathbf{R})$ and a two-point field-theoretic Green function $G^2(R, t)$ (see Elderfield 1978)

$$G^2(\mathbf{R}, t) = \int_0^N dN \exp[-(a_c\Lambda^2 + t)N]C_N(\mathbf{R}, g) \qquad (2.9)$$

where the Green function is defined by the relation

$$G^2(\mathbf{R}, t) = \lim_{n \to 0} \int [d\phi]\phi_1(\mathbf{R})\phi_1(0) \exp -H(\phi) \qquad (2.10)$$

for the $O(n)$ symmetric field-theoretic Hamiltonian $H(\phi)$

$$H(\phi) = \int dx^d \sum_{\alpha=1}^n (\nabla\phi^\alpha(x))^2 + (t + a_c\Lambda^2)(\phi^\alpha(x))^2 + \frac{u\Lambda^\varepsilon}{4!}\left[\sum_{\alpha=1}^n (\phi^\alpha(x))^2\right]^2. \qquad (2.11)$$

Here $\phi^\alpha(x)$ is an n-component field for which the fluctuations are cut off at a momentum scale Λ reflecting the finite monomer size. The ϕ^4 coupling arises directly from the excluded volume interaction $g = u\Lambda^\varepsilon > 0$. Equation (2.9) relates the polymer limit $L = N\Lambda^2 \gg 1$ to the approach of the ferromagnetic transition in the analogue field theory, for choosing $a_c(u)$ such that $t = 0$ locates the transition, it is well known that the susceptibility χ is of the form

$$\chi \equiv \int dR^\alpha \, G^2(R, t, u) = \frac{1}{t}(t\phi(u)/\Lambda^2)^{1-\gamma}(1 + O(t/\Lambda^2)^{+\omega}) \qquad (2.12)$$

which implies (des Cloizeaux 1976) that the entropy S (2.2) scales as follows

$$S = \left(a_c - \frac{\partial a_c}{\partial \ln u}\right)L + (\gamma - 1)\left[\ln L + \left(u^2 \frac{\partial(\ln \phi/u)}{\partial u}\right) + \left(\frac{\ln \Gamma(\gamma)}{\gamma - 1}\right)\right](1 + O(L^{-\omega})). \qquad (2.13)$$

Here $\gamma, \omega > 0$ are critical exponents associated with the $n \to 0$ Wilson–Fisher fixed point of the renormalisation group, whilst $a_c(u)$, $\phi(u)$ are non-universal functions of the coupling u which depend strongly on the small length scale details of the underlying chain; hindered rotation etc.

More generally outside of the asymptotic domain $L \gg 1$ we would expect S to depend strongly on the dimensionless parameter $z \equiv uL^{\varepsilon/2}$. Indeed if $z \ll 1$, perturbation theory is valid and we find directly that the entropy S exhibits random flight ($\gamma = 1$) behaviour.

$$S = \left(a_c - \frac{\partial a_c}{\partial \ln u}\right)L + O(z). \qquad (2.14)$$

We seek here to describe this crossover as L increases by employing the field-theoretic analogy to generate a set of renormalisation group equations which describe the scaling properties of S as a function of L, u. Following the development of S from random flight to self-avoiding behaviour we shall find that the entropy may be written in the form

$$S - AL - B = m(\bar{L}) \qquad (2.15)$$

where $m(\bar{L})$ is universal up to a simple rescaling of the renormalised length $\bar{L}(m(0) = 0)$. The non-universal structure of S appears only in the functions $A, B, \bar{L}/L$ which are determined by the short-range correlations in the model and are independent of L. It is important to observe that the non-universal parameter $\bar{L}$ (proportional to L) will be a

common feature of all polymer functions. In particular the expansion factor $\alpha = \langle R^2 \rangle / \langle R^2 \rangle_\theta$ may be expressed as a universal function $\alpha(\bar{L})$ of $\bar{L}$ (Elderfield 1980). In order to facilitate the comparison of $S(\bar{L})$ with numerical studies it would be useful to eliminate $\bar{L}$ in favour of α which is directly measurable so we shall simultaneously construct representations for $S(\bar{L})$ and $\alpha(\bar{L})$.

Our approach to the crossover functions $m(\bar{L})$, $\alpha(\bar{L})$ leads naturally to a parametric representation in terms of a parameter p for which we shall construct explicit expressions correct to $O(\varepsilon^2)$ in the ε expansion. We obtain the results

$$S - AL - B = \left(\frac{1-\gamma}{\omega}\right) \ln(1 - p/u^*) - \frac{p}{3\varepsilon}\left(1 + \frac{\varepsilon}{2}\right)\left(1 + \frac{p}{2}(13 - 16\chi)\right) + O(\varepsilon^3) \tag{2.16}$$

where the parameter p may be determined in terms of $\bar{L}$ or α from the relations

$$\alpha = (1 - p/u^*)^{(1-2\upsilon)/\omega}\left[1 - \frac{p}{6}\left(\frac{59}{16} - \chi\right)\right] \tag{2.17}$$

$$(1 - p/u^*)^{-\varepsilon/2\omega}p = (1 - \bar{u}/u^*)^{-\varepsilon/2\omega}\bar{u}(\tilde{L})^{\varepsilon/2} \equiv \bar{L}^{\varepsilon/2}. \tag{2.18}$$

Here χ is the Euler number: $\chi = 0.5771 \ldots$. The functions $A, B, L/\bar{L}$ are independent of L and strongly model dependent (non-universal) so we shall not construct explicit representations for them. In the asymptotic regime $\bar{L} \gg 1$ ($\alpha \gg 1$) we may identify as expected the critical exponents γ, ν exactly (to all orders in ε) as those apertaining to the $n \to 0$ Wilson–Fisher fixed point discussed by many authors. An observation of independent interest is that the configuration energy E has the asymptotic form

$$E = \frac{2}{\varepsilon}(1 - \gamma)(1 + O(\bar{L}^{-\omega})) \tag{2.19}$$

a result which does not follow trivially from the known scaling form (2.12).

3. The renormalisation group in $d = 4 - \varepsilon$ dimensions

Employing the techniques of Brézin *et al* (1976 BLZ) based on renormalised perturbation theory, we shall now investigate the scaling properties of the entropy S (2.2) and expansion factor $\alpha = \langle R^2 \rangle / \langle R^2 \rangle_\theta$ via those of the irreducible field-theoretic function $\Gamma(q)$ which is related to the polymer functions $C_N(u)$ (2.7), (2.8), E (2.5) and the mean-square polymer size $\langle R^2 \rangle$ through the function $Z(q) = L_t^{-1}(1/\Gamma(q))$ as follows (cf (2.9))

$$C_N(q, u) \equiv \int dR^d \exp(iq \cdot R)C_N(R, u) = \exp a_c L L_t^{-1}\left(\frac{1}{\Gamma(q)}\right)$$

$$\equiv Z(q, N, u) \exp a_c L \tag{3.1}$$

$$E = -u\frac{\partial}{\partial u}\ln C_N(q, u)\bigg|_{q=0} = -u\frac{\partial}{\partial u}\ln Z(q, N, u)\bigg|_{q=0} - \left(u\frac{\partial a_c}{\partial u}\right)L \tag{3.2}$$

$$\langle R^2 \rangle = -2d\frac{\partial}{\partial q^2}\ln C_N(q, u)\bigg|_{q=0} = -2d\frac{\partial}{\partial q^2}\ln Z(q, N, u)\bigg|_{q=0}. \tag{3.3}$$

Here L_t^{-1} represents the operation of Laplace inversion with respect to t (2.9) and $L = N\Lambda^2$ characterises the number of links in the chain where Λ is representative of the

inverse monomer spacing. Following BLZ we shall construct a renormalised theory depending on a new length scale $\mu \ll \Lambda$ for which we may display the scaling properties of $C_N(q)$ and whence E, $\langle R^2 \rangle$, S in terms of a series of renormalisation group equations which are exact in the limit $\mu \ll \Lambda$. Analysing the structure of these equations we shall extract the critical exponents and display the form of crossover scaling functions in terms of a parametric representation.

To derive the renormalisation group equations for a ϕ^4 field theory in $d \leq 4$ dimensions we construct a parallel theory described in terms of a set of renormalised vertex functions $\bar{\Gamma}^N$ (N legs) and new couplings $\bar{u}$, $\bar{t}$ which are related to the bare or unrenormalised functions Γ^N of variables u, t as follows

$$Z_t \bar{t} = Z_\phi t$$
$$Z_u \bar{u} = Z_\phi^2 u (\Lambda/\mu)^\varepsilon$$
$$\bar{\Gamma}(q, \bar{u}, \bar{t}, \mu) = Z_\phi^{N/2} \Gamma(q, u, t, \Lambda). \tag{3.4}$$

If we now choose the function Z_ϕ, Z_u, Z_t such that the vertex functions $\bar{\Gamma}$ are finite in the limit $\Lambda \to \infty$ at fixed $\bar{u}$, $\bar{t}$ the resulting theory scales exactly as a function of the renormalised variables $\bar{u}$, $\bar{t}$, u. This procedure effectively factors out the non-universal features of the theory which depend on the short-range correlations by means of a rescaling Z_ϕ and the introduction of dressed (or renormalised variables) $\bar{u}$, $\bar{t}$ in places of the bare variables u, t. To fix the renormalisation functions Z_ϕ, Z_u, Z_t we shall employ the technique of renormalising around the critical point (a_c chosen such that $\Gamma^2(q, t) = 0$ at q^2, $t = 0$). Introducing the vertex functions $\Gamma^{NP}(p_1 \ldots p_N, q_1 \ldots q_P)$ containing P insertions of the operator $\phi^2(q)$ and the renormalised version.

$$\bar{\Gamma}^{NP} = (Z_t/Z_\phi)^P Z_\phi^{N/2} \Gamma^{NP} \qquad (N > 0) \tag{3.5}$$

we may determine Z_ϕ, Z_u, Z_t, a_c perturbatively in $\bar{u}$ by demanding that the following constraints be obeyed:

$$\bar{\Gamma}^2(q, \bar{t})|_{\bar{t}=q^2=0} = 0 \qquad \text{(fixes } a_c)$$

$$\frac{\partial \bar{\Gamma}^2}{\partial q^2}(q, \bar{t})|_{\bar{t}=0, q^2=\mu^2} = 1 \qquad \text{(fixes } Z_\phi)$$

$$\Gamma^4(q_1, \ldots, q_4, \bar{t})|_{\bar{t}=0 \, Sp(\mu)} = \bar{u}\mu^\varepsilon \qquad \text{(fixes } Z_u) \tag{3.6}$$

$$\Gamma^{21}(q_1, q_2, p, \bar{t})|_{\bar{t}=0} = 1 \qquad \text{(fixes } Z_t).$$

Here $Sp(\mu)$ stands for the point $qi \cdot qj = \frac{1}{3}(4Sij - 1)$. For this choice the functions $\bar{\Gamma}^{NP}$ are finite ($\Lambda \to \infty$, $\bar{u}$, $\bar{t}$ fixed) at the critical point $\bar{t} = 0$ for all $P, N > 0$, whence the massive ($\bar{t} \neq 0$) functions $\bar{\Gamma}^N(\bar{t})$ are also renormalised for they may be developed in a Taylor series as follows

$$\bar{\Gamma}^N(p_1 \ldots p_N, \bar{t}, \bar{u}, \mu)$$

$$= \lim_{t(q) \to t\delta(q)} \sum_{k=0}^{\infty} \prod_{i=1}^{k} \int \frac{dq_i \bar{t}(q_i)}{k!} \bar{\Gamma}^{Nk}(q_1 \ldots q_k, p_1 \ldots p_N)$$

$$= Z_\phi^{N/2} \Gamma^N(p_1 \ldots p_N, t, u, \Lambda) \qquad \text{cf (3.5) and (3.4).}$$

Naturally before going to the limit of uniform t one has to perform partial summations on the massive propagator.

The fundamental renormalisation group equation may now be derived directly from the above by observing (BLZ) that the bare functions $\Gamma^N(q)$ are certainly independent of the arbitrary length scale μ so by implication

$$\left[\mu \frac{\partial}{\partial \mu} + \beta(\bar{u}) \frac{\partial}{\partial \bar{u}} - \left(\frac{1}{\nu(\bar{u})} - 2\right)\bar{t}\frac{\partial}{\partial \bar{t}} - \eta(\bar{u})\right]\bar{\Gamma}(q, \bar{u}, \bar{t}, \mu) = 0 \qquad (3.7)$$

where $\bar{\Gamma} = \bar{\Gamma}^2$ and the functions $\beta(\bar{u})$, $\nu(\bar{u})$, $\eta(\bar{u})$ are defined as follows

$$\beta(\bar{u}) \equiv \mu \frac{\partial}{\partial \mu}\bigg|_{y,t,\Lambda} \bar{u} = -\varepsilon\bar{u} + \tfrac{4}{3}(1 + \tfrac{1}{2}\varepsilon)\bar{u}^2 - \tfrac{7}{6}\bar{u}^3 + O(\bar{u}^4)$$

$$\left(\frac{1}{\nu(\bar{u})} - 2\right) \equiv \mu \frac{\partial}{\partial \mu}\bigg|_{u,t,\Lambda} \ln \bar{t} = -\frac{\bar{u}}{3}\left(1 + \frac{\varepsilon}{2}\right) + \tfrac{5}{36}\bar{u}^2 + O(\bar{u}^3) \qquad (3.8)$$

$$\eta(\bar{u}) \equiv \mu \frac{\partial}{\partial \mu}\bigg|_{u,t,\Lambda} \ln Z_\phi = \tfrac{1}{36}\bar{u}^2 + O(\bar{u}^3).$$

The expressions for $\beta(\bar{u})$, $\nu(\bar{u})$, $\eta(\bar{u})$ enumerated above were computed for a dimensionally regularised ϕ^4 theory and are correct to $O(\varepsilon^2)$ in the ε expansion ($\bar{u} = O(\varepsilon)$, $d = 4 - \varepsilon$). As usual a factor of $S_d^{-1} = 2^{d-1}\pi^{d/2}\Gamma(d/2)$ has been absorbed into the coupling $\bar{u}$. The importance of (3.7) lies in the simple structure of $\beta(\bar{u})$, $\nu(\bar{u})$, $\eta(\bar{u})$ for by construction they are independent of $\bar{t}$ and furthermore independent of μ. Naturally, outside the dimensional regularisation scheme employed above there will be corrections of $O(\mu/\Lambda)$ to (3.7), however in the critical domain q^2, $t \ll \Lambda^2$ we may always choose $\mu \ll \Lambda$. Strictly the functions $\beta(\bar{u})$, $\nu(\bar{u})$, $\eta(\bar{u})$ are universal only at the fixed point u^* defined as usual by $\beta(u^*) = 0$, however, this remanent dependence on the details of the regularisation and renormalisation procedure may always be absorbed by a further rescaling of the primary variables $\bar{u}$, $\bar{t}$ so that (3.7) is indeed an adequate description of the universal scaling structure expected.

In order to determine the scaling structure of C_N, E, $\langle R^2 \rangle$ from (3.7), we first rewrite (3.1), (3.2), (3.3) in terms of the fully renormalised function $\bar{Z} = L_{\bar{t}}^{-1}(1/\bar{\Gamma}(q)) = Z_t Z$ of the renormalised length $\bar{N} \equiv N Z_t/Z_\phi$ conjugate to $\bar{t}$.

$$C_{\bar{N}}(q, \bar{u}) = \exp(a_c L) Z_t(\bar{u}) \bar{Z}(q, \bar{u}, \bar{N}) \qquad (3.9)$$

$$\langle R^2 \rangle (\bar{N}, \bar{u}) = -2d \frac{\partial}{\partial q^2} \ln \bar{Z}(q, \bar{u}, \bar{N})\bigg|_{q=0}. \qquad (3.10)$$

By contrast the expression for E is rather complicated. Parametrising E in terms of the fully renormalised functions $\bar{X}$, $\bar{Y}$

$$X = \frac{\partial \ln Z}{\partial \ln \bar{u}}(q, \bar{N}, \bar{u})\bigg|_{q=0}$$

$$Y = \frac{\partial \ln Z}{\partial \ln \bar{N}}(q, \bar{N}, \bar{u})\bigg|_{q=0} \qquad (3.11)$$

and non-universal amplitudes A, B, C

$$A(\bar{u}, \mu/\Lambda) = -\frac{\partial \ln \bar{u}}{\partial \ln u}\bigg|_{\Lambda}$$

$$B(\bar{u}, \mu/\Lambda) = -\frac{\partial \ln \bar{N}}{\partial \ln u}\bigg|_{\Lambda,N} \qquad (3.12)$$

$$C(\bar{u}, \mu/\Lambda) = -\frac{\partial \ln Z_t}{\partial \ln u}\bigg|_{\Lambda}$$

leads to the following representation for the subtracted 'energy' $\bar{E}$

$$\bar{E} = E + \left(u\frac{\partial}{\partial u} - a_c\right)L = A\bar{X} + B\bar{Y} + C. \qquad (3.13)$$

Outside the dimensional regularisation scheme employed here (cf (3.7) *et seq.*) there will in general be corrections $O(\mu/\Lambda)$ to (3.13) however, in the critical domain q^2, $t \ll \Lambda^2$ these non-universal terms can always be suppressed by choosing $\mu \ll \Lambda$ (Λ finite). The non-universal functions A, B, C are intimately related to the renormalisation group functions $\beta(\bar{u})$, $\nu(\bar{u})$, $\eta(\bar{u})$ (3.8) as follows

$$A = \beta(\bar{u})/\bar{u}\varepsilon \qquad B = \left(\frac{1}{\nu(\bar{u})} - 2\right)\bigg/\varepsilon \qquad C = \left(\frac{1}{\nu(\bar{u})} - 2 + \eta(\bar{u})\right)\bigg/\varepsilon \qquad (3.14)$$

for in a dimensional regularisation scheme the functions Z_ϕ, Z_u, Z_t depend solely on the dimensionless variable $u(\Lambda/\mu)^\varepsilon$. Of course, for other regularisations these relations may be modified by small terms $O(\mu/\Lambda)$ which can again be ignored.

We are thus led to focus our attention on the fully renormalised functions $\bar{X}$, $\bar{Y}$ (3.11) and $\bar{Z} = L_t^{-1}(1/\bar{\Gamma}(q))$ which may be expected to satisfy renormalisation group equations similar to (3.7). To derive these equations the first step is to commute the operation of Laplace inversion through (3.7) to give the expression

$$\left[\mu\frac{\partial}{\partial\mu} + \beta(\bar{u})\frac{\partial}{\partial u} + \left(\frac{1}{\nu(\bar{u})} - 2\right)\bar{N}\frac{\partial}{\partial\bar{N}}\right]\ln\bar{Z} = -\left[\frac{1}{\nu(\bar{u})} - 2 + \eta(\bar{u})\right]. \qquad (3.15)$$

Operating on this equation with $\bar{u}\,\partial/\partial\bar{u}$, $\bar{N}\,\partial/\partial\bar{N}$ and $\partial/\partial q^2$ cf (3.9), (3.10), (3.11) we are then led to the complementary renormalisation group equations for $\bar{X}$, $\bar{Y}$ and $\langle R^2\rangle/\bar{N}$ collected below:

$$\left[\mu\frac{\partial}{\partial\mu} + \beta(\bar{u})\frac{\partial}{\partial\bar{u}} + \left(\frac{1}{\nu(\bar{u})} - 2\right)\bar{N}\frac{\partial}{\partial\bar{N}}\right]\bar{X}$$

$$= -\left(\bar{u}\frac{\partial}{\partial\bar{u}}(\beta(\bar{u})/\bar{u})\right)\bar{X} - \left(\bar{u}\frac{\partial}{\partial\bar{u}}\left(\frac{1}{\nu(\bar{u})} - 2\right)\right)\cdot\bar{Y} - \bar{u}\frac{\partial}{\partial\bar{u}}\left(\frac{1}{\nu(\bar{u})} - 2 + \eta(\bar{u})\right)$$

$$(3.16)$$

$$\left[\mu\frac{\partial}{\partial\mu} + \beta(\bar{u})\frac{\partial}{\partial\bar{u}} + \left(\frac{1}{\nu(\bar{u})} - 2\right)\bar{N}\frac{\partial}{\partial\bar{N}}\right]\bar{Y} = 0 \qquad (3.17)$$

$$\left[\mu\frac{\partial}{\partial\mu} + \beta(\bar{u})\frac{\partial}{\partial\bar{u}} + \left(\frac{1}{\nu(\bar{u})} - 2\right)\bar{N}\frac{\partial}{\partial\bar{N}}\right]\langle R^2\rangle/\bar{N} = -\left(\frac{1}{\nu(\bar{u})} - 2\right)\langle R^2\rangle/\bar{N}. \qquad (3.18)$$

Formally the equations (3.15)–(3.18) may be solved in order to display the scaling properties of $\bar{X}, \bar{Y}, \bar{Z}$ and $\langle R^2 \rangle$ by means of the method of characteristics. Defining functions $\bar{u}(\lambda), \bar{N}(\lambda), \mu(\lambda)$ as follows

$$\mu(\lambda) = \lambda\mu \qquad\qquad \mu(1) = \mu \qquad\qquad (3.19)$$

$$\frac{d \ln \bar{N}(\lambda)}{d \ln \lambda} = \left(\frac{1}{\nu(\bar{u}(\lambda))} - 2\right) \qquad \bar{N}(1) = \bar{N} \qquad (3.20)$$

$$\frac{d\bar{u}(\lambda)}{d \ln \lambda} = \beta(\bar{u}(\lambda)) \qquad\qquad \bar{u}(1) = \bar{u} \qquad (3.21)$$

allows us to rewrite the renormalisation group equations in the following integrable forms

$$\frac{d \ln \bar{Z}}{d \ln \lambda} = -\left(\frac{1}{\nu(\bar{u}(\lambda))} - 2 + \eta(\bar{u}(\lambda))\right) \qquad (3.22)$$

$$\frac{d \ln \bar{X}}{d \ln \lambda} = -\left[\left(\bar{u}\frac{\partial}{\partial \bar{u}}(\beta/\bar{u})\right)\bar{X} + \left(\bar{u}\frac{\partial}{\partial \bar{u}}\left(\frac{1}{\nu(\bar{u})} - 2\right)\right)\bar{Y} + \bar{u}\frac{\partial}{\partial \bar{u}}\left(\frac{1}{\nu(\bar{u})} - 2 + \eta(\bar{u})\right)\right] \qquad (3.23)$$

$$\frac{d \ln \bar{Y}}{d \ln \lambda} = 0 \qquad (3.24)$$

$$\frac{d\langle R^2 \rangle/\bar{N}}{d \ln \lambda} = -\left(\frac{1}{\nu(\bar{u}(\lambda))} - 2\right)\langle R^2 \rangle/\bar{N}(\lambda). \qquad (3.25)$$

Integrating equations (3.22)–(3.25) directly we obtain the solutions

$$\ln\left[\frac{\bar{Z}(q, \bar{N}, \bar{u}, \mu)}{\bar{Z}(q, \bar{N}(\lambda), \bar{u}(\lambda), \lambda\mu)}\right] = \int_{\bar{u}}^{\bar{u}(\lambda)} \frac{dx}{\beta(x)}\left(\frac{1}{\nu(x)} - 2 + \eta(x)\right) \qquad (3.26)$$

$$\beta(\bar{u})\bar{X}(\bar{N}, \bar{u}, \mu)/\bar{u}$$

$$= \beta(\bar{u}(\lambda))\bar{X}(\bar{N}(\lambda), \bar{u}(\lambda), \lambda\mu)/\bar{u}(\lambda) + \bar{Y}(\bar{N}, \bar{u}, \mu)\left(\frac{1}{\nu(\bar{u}(\lambda))} - \frac{1}{\nu(\bar{u})}\right)$$

$$+ \left(\frac{1}{\nu(\bar{u}(\lambda))} - 2 + \eta(\bar{u}(\lambda))\right) - \left(\frac{1}{\nu(\bar{u})} - 2 + \eta(\bar{u})\right) \qquad (3.27)$$

$$\bar{Y}(N, \bar{u}, \mu) = Y(\bar{N}(\lambda), \bar{u}(\lambda), \lambda\mu) \qquad (3.28)$$

$$\frac{\langle R^2 \rangle}{\bar{N}}(\bar{N}, \bar{u}, \mu) = \frac{\langle R^2 \rangle}{\bar{N}(\lambda)}(\bar{N}(\lambda), \bar{u}(\lambda), \lambda\mu) \exp + \int_{\bar{u}}^{\bar{u}(\lambda)} \frac{dx}{\beta(x)}\left(\frac{1}{\nu(x)} - 2\right). \qquad (3.29)$$

If we now introduce these solutions into the fundamental equations (3.9), (3.13), (3.14) we find the expressions for C_N, E which complement the result (3.29) for $\langle R^2 \rangle$.

$$\ln C_{\bar{N}}(q, \bar{u}, \mu) = \left[\int_{\bar{u}}^{\bar{u}(x)} \frac{dx}{\beta(x)}\left(\frac{1}{\nu(x)} - 2 + \eta(x)\right) + \ln \bar{Z}(\bar{N}(\lambda), \bar{u}(\lambda), \lambda\mu)\right]$$

$$+ [a_c L + \ln Z_t(\bar{u})]. \qquad (3.30)$$

$$E(\bar{N}, \bar{u}, \mu) = [\bar{E}(\bar{N}(\lambda), \bar{u}(\lambda), \lambda\mu)] - \left[\left(u\frac{\partial}{\partial u} a_c\right)L\right]. \qquad (3.31)$$

The expressions for $\ln C_N, \langle R^2 \rangle$ presented above are exact within the context of an ε

expansion ($\bar{u} = O(\varepsilon)$) in contrast to the result for E which will be modified by uninteresting non-universal corrections $O(\mu/\Lambda)$ (Λ finite) if we do not employ a dimensional regularisation (see (3.13) *et seq.*).

To exhibit the scaling structure of $\ln C_{\bar{N}}, E, \langle R^2 \rangle$ we may now employ the freedom in the length scale λ. To fix λ we make the choice $\tilde{L}(\lambda) \equiv \bar{N}(\lambda)(\lambda\mu)^2 = 1$ for the renormalised polymer length $\tilde{L}$ so that the functions $\bar{Z}(\lambda)$, $\bar{E}(\lambda)$, $\langle R^2 \rangle/\bar{N}(\lambda)$ describe the physics of short polymers ($\tilde{L} \simeq 1$) in the renormalised language and therefore may realistically be computed perturbatively in the interaction $\bar{u}(\lambda)$. Observing now that the functions $\langle R^2 \rangle/\bar{N}, \bar{Z}, \bar{E}$ are dimensionless we find that we may rewrite (3.29), (3.30), (3.31) in terms of $p \equiv \bar{u}(\lambda)$ as follows

$$\langle R^2 \rangle/2\bar{N}d = f(p) \exp \int_{\bar{u}}^{p} \frac{dx}{\beta(x)}\left(\frac{1}{\nu(x)} - 2\right)$$

$$\ln C_N - [a_c L + \ln Z_i(\bar{u})] = g(p) + \int_{\bar{u}}^{p} \frac{dx}{\beta(x)}\left(\frac{1}{\nu(x)} - 2 + \eta(x)\right) \tag{3.32}$$

$$E + \frac{\partial a_c}{\partial \ln u} = h(p)$$

where the functions $f(p)$, $h(p)$, $g(p)$ may be determined perturbatively in p from the structure of the theory at the matching point, i.e.

$$f(p) \equiv \frac{\langle R^2 \rangle}{2\bar{N}d}(\bar{u}, \tilde{L})\bigg|_{\bar{u}=p, \tilde{L}=1} = -\frac{\partial \ln \bar{Z}(q)}{\partial q^2}\bigg|_{q=0, \bar{u}=p, \tilde{L}=1}$$

$$g(p) \equiv \ln \bar{Z}(q, \bar{u}, \tilde{L})\big|_{q=0, \bar{u}=p, \tilde{L}=1} \tag{3.33}$$

$$h(p) \equiv \bar{E}(\bar{u}, \tilde{L})\big|_{\bar{u}=p, \tilde{L}=1} = -\frac{1}{\varepsilon}\mu \frac{\partial}{\partial \mu} \ln \bar{Z}(q)\bigg|_{q=0, \bar{u}=p, \tilde{L}=1}.$$

Strictly the functions f, g, h will depend also on the dimensionless parameter μ/Λ (Λ finite), however, the renormalisation programme employed here ensures that such terms are of $O(\mu/\Lambda)$ and therefore may safely be suppressed in the critical domain q^2, $N^{-1} < \mu^2 \ll \Lambda^2$ ($\bar{Z}, \langle R^2 \rangle/\bar{N}, \bar{E}$ finite $\Lambda \to \infty$ at fixed $\bar{N}, \bar{u}, \mu$).

We learn from (3.32), (3.33) that the parameter $p = \bar{u}(\lambda)$ is of fundamental importance for it alone controls the scaling behaviour of the polymer functions ($a_c, \bar{u}$ by construction independent of L). Integrating the trajectory equations (3.19)–(3.21) for $\tilde{L}(\lambda) = 1$ allows us to determine $p = p(\tilde{L})$ in the form

$$\exp - \int^{p} \frac{dx}{\beta(x)\nu(x)} = \exp - \int^{\bar{u}} \frac{dx}{\beta(x)\nu(x)} \tilde{L} \equiv \bar{L} \qquad (\tilde{L} = \tilde{L}(0)) \tag{3.34}$$

where $\bar{L}$, proportional to the renormalised length $\tilde{L}$, is designed to absorb the non-universal effects of the crossover. The scaling form of the $\bar{L}$ (or L) $\gg 1$ limit arises directly from this equation for if β vanishes with positive derivative at some point u^* then asymptotically $p = \bar{u}(\lambda) \to u^*$. Perturbatively we may locate a non-trivial fixed point u^* ($\beta'(u^*) > 0$) from the explicit representation for $\beta(\bar{u})$ (3.8) (the Wilson–Fisher fixed point) so we may realistically solve (3.34) for the asymptotic form of $p(\bar{L})$ by linearising about this point. Employing the linear form $\beta(\bar{u}) = \omega(\bar{u} - u^*)/\nu$ where $\nu = \nu(u^*)$ and $\omega \simeq \nu\beta(u^*)$ are respectively the correlation length and crossover

exponents (BLZ) we find the relation

$$(1 - p/u^*)^{-1/\omega} = \bar{L}(1 + O((\bar{L})^{-\omega})). \tag{3.35}$$

In contrast, for $\bar{L} \ll 1$ $p \to 0$ and we recover the perturbative result valid near the Flory temperature θ; $u \sim (1 - \theta/T)$. Solving (3.34) we obtain the expression

$$p = \bar{L}^{\varepsilon/2}(1 + O(\bar{L}^{\varepsilon/2})) \tag{3.36}$$

where for $T \sim \theta$ $p = uL^{\varepsilon/2}[1 + O(1 - \theta/T)]$ (finite) and may be identified with the standard crossover variable $z = uL^{\varepsilon/2}$ (cf (2.14)). To follow the development of the polymer functions as $\bar{L}$ increases from zero (random flight) to asymptotic (self-avoiding) values we may therefore usefully identify the point $p = 0$ with the Flory temperature by phenomenologically choosing $\bar{L} \sim L(1 - \theta/T)^{2/\varepsilon}$ for all u rather than the conventional choice $u \sim (1 - \theta/T)$ associated with perturbation theory in the excluded volume parameter. We shall therefore rewrite (3.32), (3.34) in the normalised forms

$$\alpha \equiv \langle R^2 \rangle / aN = f(p) \exp + \int_0^p \frac{dx}{\beta(x)}\left(\frac{1}{\nu(x)} - 2\right) \tag{3.37}$$

$$[\ln C_N - (a_c L + b)]_{p=0}^p = g(p) + \int_0^p \frac{dx}{\beta(x)}\left(\frac{1}{\nu(x)} - 2 + \eta(x)\right) \tag{3.38}$$

$$\left[E + \frac{\partial a_c}{\partial \ln u}\right]_{p=0}^p = h(p) \tag{3.39}$$

where $p = \bar{u}(\lambda)$ may be eliminated in terms of the crossover parameter $\bar{L}$ by means of (3.34) and the non-universal functions a_c, $b \equiv \ln Z_t(\bar{u}) + \int^u dx(1/\nu(x) - 2)/\beta(x)$ and $a \equiv \langle R^2 \rangle$ $(p = 0)/2Nd$ i.e. $\langle R^2 \rangle_\theta/2Nd$ are the subtractive and multiplicative renormalisations required to isolate the universal scaling forms.

In particular for the asymptotic domain $\bar{L} \gg 1$ we may employ the above linearisation to obtain the expressions

$$\alpha \equiv \langle R^2 \rangle / \langle R^2 \rangle_\theta = p(\varepsilon)(\bar{L})^{2\nu - 1}(1 + O((\bar{L})^{-\omega})) \tag{3.40}$$

$$[\ln C_N - (a_c L + b)]_{p=0}^p = q(\varepsilon) + (\gamma - 1)\ln \bar{L}(1 + O((\bar{L})^{-\omega})) \tag{3.41}$$

$$\left[E + \frac{\partial a_c}{\partial \ln u}\right]_{p=0}^p = r(\varepsilon)(1 + O((\bar{L})^{-\omega}) \tag{3.42}$$

where the amplitudes $p(\varepsilon)$, $q(\varepsilon)$, $r(\varepsilon)$ are universal up to a common rescaling of $\bar{L}$.

$$p(\varepsilon) = f(u^*) \exp\left[-\int^\alpha \frac{dx}{\beta(x)}\left(\frac{1}{\nu(x)} - 2\right)\right]_{\alpha=0}$$

$$q(\varepsilon) = g(u^*) - \left[\int^\alpha \frac{dx}{\beta(x)}\left(\frac{1}{\nu(x)} - 2 + \eta(x)\right)\right]_{\alpha=0} \tag{3.43}$$

$$r(\varepsilon) = h(u^*) = \frac{2}{\varepsilon}(1 - \gamma) \qquad \text{(exact, see below)}.$$

Here γ is the usual critical exponent associated with the susceptibility of the analogue field theory as expected ($\gamma = \nu(2 - \eta)$). The amplitude $r(\varepsilon)$ governing the asymptotic limit of the energy E (3.42) may in fact be derived directly in terms of the critical exponent γ by employing the renormalisation equations. Observing from (3.13), (3.14)

and (3.15) that $\bar{E}$, $\bar{Y}$ satisfy the following identities (up to corrections $O(\mu/\Lambda)$) at the matching point $\tilde{L} = \bar{N}\mu^2 = 1$ for the fixed point coupling $\bar{u} = u^*$ $(\beta(u^*) = 0)$

$$\bar{E}(u^*, 1) = \left(\frac{1}{\nu(u^*)} - 2\right) \bar{Y}(u^*, 1) + \left(\frac{1}{\nu(u^*)} - 2 + \eta(u^*)\right)$$

$$\bar{Y}(u^*, 1)/\nu(u^*) = -\left(\frac{1}{\nu(u^*)} - 2 + \eta(u^*)\right),$$

(3.44)

we find on eliminating $\bar{Y}(u^*, 1)$ that $r(\varepsilon) \equiv \bar{E}(u^*, 1) = 2(1 - \gamma)/\varepsilon$ (cf (3.33)).

The entropy $S(\bar{L})$ of a polymer chain may now be determined directly from (2.2), (3.38), (3.39) in the parametric form

$$\bar{S} = S - AL - B \equiv m(p) = \int_0^p \frac{dx}{\beta(x)} \left(\frac{1}{\nu(x)} - 2 + \eta(x)\right) + k(p) \qquad (k(0) = 0) \qquad (3.45)$$

where the parameter p may be expressed in terms of $\bar{L}$ (proportional to the length of the chain) by means of the relation

$$\exp - \int_0^p \frac{dx}{\beta(x)\nu(x)} = \bar{L},$$

or more usefully directly in terms of the expansion factor $\alpha = \langle R^2 \rangle / \langle R^2 \rangle_\theta$ (3.37), (3.40) which is directly measurable.

$$\alpha = \langle R^2 \rangle / \langle R^2 \rangle_\theta = f(p) \exp \int_0^p \frac{dx}{\beta(x)} \left(\frac{1}{\nu(x)} - 2\right) \qquad \text{cf (3.37).}$$

Here $k(p)$, $f(p)$ may be constructed perturbatively in p in terms of the subtracted 'entropy' $\bar{S}$ and expansion factor α at the matching point $\tilde{L} = 1$, $\bar{u} = p$

$$k(p) \equiv \bar{S}(\bar{u}, \tilde{L})|_{\bar{u} = p, \tilde{L} = 1} = g(p) + h(p) \qquad \text{cf (3.38), (3.39)}$$

$$f(p) \equiv \alpha(\bar{u}, \tilde{L})|_{\bar{u} = p, \tilde{L} = 1} \qquad \text{cf (3.37).}$$

The non-universal functions $A = (a_c - \partial a_c/\partial \ln u)$, $B = b$ (cf (3.38) *et seq.*) are independent of the chain length L and therefore of little interest.

In the asymptotic domain $\bar{L} \gg 1$ or $\alpha \gg 1$ we obtain the expected structure cf (2.13) with full control of the universal content of the constant term ($\bar{L}$ or α fixed)

$$\bar{S}(\bar{L}) \equiv S - AL - B = (\gamma - 1)(\ln \bar{L} - v(\varepsilon))[1 + O((\bar{L})^{-\omega})]$$

or

$$\bar{S}(\alpha) \equiv S - AL - B = (\gamma - 1)[\ln(\alpha^{1/(2\nu-1)}) - w(\varepsilon)](1 + O((\bar{L})^{-\omega})).$$

Here the amplitudes $v(\varepsilon)$, $w(\varepsilon)$ are universal up to the usual freedom of a rescaling of the crossover variable ($\bar{L}$ or α)

$$v(\varepsilon) = \frac{2}{\varepsilon} - \frac{q(\varepsilon)}{\gamma - 1} = \frac{2}{\varepsilon}\left(1 + \left(\frac{1 - \chi}{2}\right)\varepsilon + O(\varepsilon^2)\right) \qquad \text{(cf (3.43) and Appendix)}$$

$$w(\varepsilon) = v(\varepsilon) + \frac{\ln p(\varepsilon)}{2\nu - 1} = \frac{2}{\varepsilon}(1 - \tfrac{43}{32}\varepsilon + O(\varepsilon^2)).$$

Carrying through the programme outlined above we obtain to $O(\varepsilon^2)$ the following expressions by direct computation for a dimensionally regularised theory (see the

Appendix for details)

$$\bar{S} \equiv S - AL - B = \left(\frac{1-\gamma}{\omega}\right) \ln(1 - p/u^*) - \frac{p}{3\varepsilon}\left(1 - \frac{\varepsilon}{2}\right)\left[1 + \frac{p}{8}(13 - 16\chi)\right]O(\varepsilon^3)$$

where the parameter p may be determined in terms of $\bar{L}$ or α from the relations

$$\alpha = (1 - p/u^*)^{(1-2\nu)/\omega}[1 - \tfrac{1}{6}p(\tfrac{59}{16} - \chi)]$$

$$(1 - p/u)^{-\varepsilon/2\omega}p = (1 - \bar{u}/u^*)^{-\varepsilon/2\omega}\bar{u}\tilde{L}^{\varepsilon/2} \equiv \bar{L}^{\varepsilon/2}.$$

Here χ is the Euler number: $\chi = 0.5771\ldots$.

4. Discussion

Using the $n \to 0$ analogue field theory we have shown by means of a series of direct renormalisation group equations that the entropy $S(L)$ of a single polymer of length L should be discussed in terms of a universal subtracted 'entropy' $\bar{S}$ which as expected exhibits a crossover from free-flight to self-avoiding behaviour as the renormalised length $\bar{L}$ (proportional to L) or expansion factor $\alpha = \langle R^2 \rangle / \langle R^2 \rangle_\theta$ increases

$$\bar{S} \equiv S - AL - B = m(\bar{L} \text{ or } \alpha).$$

Here A, B, $\bar{L}/L$ are strongly model dependent (non-universal) and independent of L and therefore of little interest. By solving the renormalisation group equations we have developed a compact parametric description of the universal crossover scaling function $m(p)$ of the form

$$m(p) = \int_0^p \frac{dx}{\beta(x)}\left(\frac{1}{\nu(x)} - 2 + \eta(x)\right) + k(p) \qquad (k(0) = 0)$$

where the parameter p may be expressed in terms of $\bar{L}$ (proportional to L) by means of the relation

$$\exp - \int^p \frac{dx}{\beta(x)\nu(x)} = \bar{L},$$

or more usefully directly in terms of the expansion factor $\alpha = \langle R^2 \rangle / \langle R^2 \rangle_\theta$ which is directly measurable

$$\alpha = f(p) \exp + \int_0^p \frac{dx}{\beta(x)}\left(\frac{1}{\nu(x)} - 2\right).$$

Here $k(p)$, $f(p)$ may be constructed perturbatively in p in terms of the subtracted entropy $\bar{S}$ and expansion factor α at the matching point $\tilde{L} = 1$, $\bar{u} = p$

$$k(p) = \bar{S}(\bar{u}, \tilde{L})|_{\bar{u}=p, \tilde{L}=1}$$

$$f(p) = \alpha(\bar{u}, \tilde{L})|_{\bar{u}=p, \tilde{L}=1}.$$

where $\tilde{L}$ ($\propto \bar{L}$) and $\bar{u}$ are renormalised parameters defined in the text ($\tilde{L}$ proportional to L). For a dimensionally regularised scheme the functions $\beta(x)$, $\nu(x)$, $\eta(x)$ are known perturbatively to at least $O(x^4)$ in the literature (see, for example, BLZ).

Carrying through the programme outlined above to $O(\varepsilon^2)$ in the expansion (see the Appendix) we find the following explicit representation for a dimensionally regularised system

$$\bar{S} = S - AL - B = \frac{(1-\gamma)}{\omega} \ln(1-p/u^*) - \frac{p}{3\varepsilon}\left(1+\frac{\varepsilon}{2}\right)\left(1+\frac{p}{8}(13-16\chi)\right) + O(\varepsilon^3).$$

The parameter p may be determined in terms of $\bar{L}$ or α from the relations

$$\alpha = (1-p/u^*)^{(2\nu-1)/\omega}[1-\tfrac{1}{6}p(\tfrac{59}{16}-\chi)]$$

$$(1-p/u^*)^{-\varepsilon/2\omega}p = (1-\bar{u}/u^*)^{-\varepsilon/2\omega}\bar{L}^{\varepsilon/2} \equiv \bar{L}^{\varepsilon/2}.$$

Here γ, ν, ω are the usual critical exponents associated with the $n \to 0$ Wilson–Fisher fixed point u^*

$$\nu = \nu(u^*)$$

$$\gamma = \nu(2-\eta) \qquad (\eta = \eta(u^*))$$

$$\omega = \nu\beta'(u^*)$$

whilst χ is the Euler number; $\chi = 0.5771\dots$. Naively our expressions are fully universal for they depend solely on the dimensionless crossover variable $\bar{L}$ or α, however, direct computation (Elderfield 1980) shows that the perturbative term $k(p)$ depends on the regularisation scheme whence the observation of full universality (up to a rescaling of α or $\bar{L}$) is not entirely beyond question. Naturally the critical exponents are, by contrast, fully universal (BLZ).

In the asymptotic domain $\bar{L} \gg 1$ or $\alpha \gg 1$ we obtain the expected scaling structure (2.13) with full control of the universal content of the constant term ($\bar{L}$ or α fixed)

$$\bar{S}(\bar{L}) = S - AL - B = (\gamma-1)(\ln\bar{L}-v(\varepsilon))(1+O((\bar{L})^{-\omega}))$$

or

$$\bar{S}(\alpha) = S - AL - B = (\gamma-1)(\ln(\alpha^{1/(2\nu-1)})-w(\varepsilon))(1+O((\bar{L})^{-\omega})).$$

The amplitudes $v(\varepsilon)$, $w(\varepsilon)$ are universal up to the usual freedom of a rescaling of the crossover variable $\bar{L}$ or α. To *second* order in ε we find the results

$$v(\varepsilon) = \frac{2}{\varepsilon}\left(1+\left(\frac{1-\chi}{2}\right)\varepsilon + O(\varepsilon^2)\right) \qquad w(\varepsilon) = \frac{2}{\varepsilon}(1-\tfrac{43}{32}\varepsilon + O(\varepsilon^2)).$$

A direct comparison of our expressions for S with numerical simulations is hampered by the dominant and non-universal linear term so we may usefully construct instead the universal combination

$$S - \frac{\partial S}{\partial \ln L} = \int_0^p \frac{dx}{\beta(x)}\left(\frac{1}{\nu(x)}-2+\eta(x)\right)$$

$$+ \left[k(p)+\beta(p)\nu(p)k(p)+\nu(p)\left(\frac{1}{\nu(p)}-2+\eta(p)\right)\right]$$

by observing from (3.45) that $p(\bar{L})$ ($\bar{L}$ proportional to L) satisfies the relation

$$\frac{dp}{d\ln\bar{L}} = -\beta(p)\nu(p).$$

Conventionally polymer physics is analysed in terms of a crossover variable $Z \sim L^{\varepsilon/2}$

which may be identified in terms of the crossover variable $\bar{L}$ discovered here by the choice

$$Z = \bar{L}^{\varepsilon/2} \sim L^{\varepsilon/2}.$$

The description of the entropy S as a function of $\bar{L}$ is therefore, despite the impractibility of a direct measurement of $\bar{L}$, of fundamental interest for it is through $\bar{L}$ that we may introduce a direct measure of the deviation from Flory temperature (random flight) conditions by the phenomenological approach

$$Z = \bar{L}^{\varepsilon/2} \sim (1 - \theta/T)L^{\varepsilon/2}$$

employed in the literature. On a practical level, however, the analysis of computer simulations directly in terms of the expansion factor α which is directly measurable would seem to be more useful.

Acknowledgments

Appendix 1.

For the interested reader we assemble here some notes on the computation for the scaling form of $\bar{S}$, α to $O(\varepsilon^2)$ quoted in the text. The functions Z_ϕ, Z_t, Z_u (and $\beta(\bar{u})$, $\eta(\bar{u})$, $\nu(\bar{u})$ cf (3.4) and (3.8)) are available in the literature to at least $O(\bar{u}^4)$ for the dimensionally regularised ϕ^4 system employed here (BLZ 1976) so in order to construct the scaling form of $\bar{S}$, α we need only compute the trajectory integrals $\int^P \ldots \mathrm{d}x/\beta(x)$ (and construct perturbative representations valid at the renormalisation group matching point ((3.45) *et seq.*)).

A1.1 The trajectory integrals

To perform the integrals to $O(\varepsilon^2)$, the essential step is to observe that the β function may be developed in the form (3.8)

$$\frac{1}{\beta(\bar{u})} = -\frac{1}{\varepsilon}\left(\frac{1}{\bar{u}} + \frac{\varepsilon(\nu/\omega)}{(u^* - \bar{u})}\right)(1 + O(\varepsilon\bar{u}))$$

where $\omega = \nu\beta'(u^*)$ for the $O(\varepsilon\bar{u})$ corrections may be properly ignored at this order since they contain contributions from the functions $\beta(\bar{u})$ at $O(\bar{u}^4)$ ($\bar{u} = O(\varepsilon)$). With this philosophy we find, after some tedious algebra, the results

$$\int^p \frac{\mathrm{d}x}{\beta(x)\nu(x)} = \frac{1}{\omega}\ln(1 - p/u^*) - \frac{2}{\varepsilon}\ln p \tag{A1}$$

$$\int^p \frac{\mathrm{d}x}{\beta(x)}\left(\frac{1}{\nu(x)} - 2\right) = \left(\frac{1-2\nu}{\omega}\right)\ln(1 - p/u^*) - \tfrac{11}{96}p \tag{A2}$$

$$\int^p \frac{\mathrm{d}x}{\beta(x)}\eta(x) = \frac{\eta}{\omega}\ln(1 - p/u^*) + \frac{p}{48}, \tag{A3}$$

whence in particular we obtain the parametric equation (3.34) in the integrated form

$$(1 - p/u^*)^{-\varepsilon/2\omega} p = \bar{u}(1 - \bar{u}/u^*)^{-\varepsilon/2\omega} \tilde{L}^{\varepsilon/2} \equiv \bar{L}^{\varepsilon/2}. \tag{A4}$$

Here ν, η, ω are the usual critical exponents associated with the $n \to 0$ Wilson–Fisher fixed point u^* (correct to $O(\varepsilon^2)$).

A1.2 $f(p)$, $k(p)$

To construct $f(p)$, $k(p)$ to $O(\varepsilon^2)$ we only require (rather paradoxically) the perturbative expansions to order $\bar{u}$ (or one loop). Of primary interest are the functions $\bar{Z}(q)$, $\partial \bar{Z}(q)/\partial q^2$ taken at zero momentum (cf (3.33)) which are given to first order by the expansions

$$\bar{Z}(q)|_{q=0} = L_{\bar{t}}^{-1}\left(\frac{1}{\bar{\Gamma}(q)}\right)\Big|_{q=0} = \left(1 - \frac{\bar{u}}{3\varepsilon}\left(\frac{A(\varepsilon)(\bar{N}\mu^2)^{\varepsilon/2}}{\Gamma(1+\varepsilon/2)} + 1 + \frac{\varepsilon}{2}\right) + O(\bar{u}^2)\right)$$

and

$$\frac{\partial \bar{Z}}{\partial q^2}\Big|_{q=0} = L_{\bar{t}}^{-1}\left(\left(\frac{1}{\bar{\Gamma}(q)}\right)^2\right)\Big|_{q=0} + O(\bar{u}^2) = \bar{N}\left[1 - \frac{2\bar{u}}{3\varepsilon}\left(\frac{A(\varepsilon)(N\mu^2)^{\varepsilon/2}}{\Gamma(2+\varepsilon/2)} + 1 + \frac{\varepsilon}{2}\right) + O(\bar{u}^2)\right]$$

for $Z_\phi = 1 + O(\bar{u}^2)$, $Z_{\bar{u}} = 1 + O(\bar{u})$, $Z_{\bar{t}} = 1 + (\bar{u}/3\varepsilon)(1 + \tfrac{1}{2}\varepsilon) + O(\bar{u}^2)$ (BLZ) and the underlying bare vertex function $\Gamma(q)$ is given by the expression

$$\Gamma(q) = q^2 + t + \frac{u}{3\varepsilon}(t/\Lambda^2)^{-\varepsilon/2} A(\varepsilon) + O(u^2).$$

Here $A(\varepsilon)/\varepsilon = \int dq^d (q^2+1)^{-1}$ (S_d absorbed into u). Employing (3.33) leads directly to the result for $f(p)$ required and the intermediate results $h(p)$, $g(p)$

$$f(p) \equiv (\partial/\partial q^2)\ln Z(q)\Big|_{\substack{q=0 \\ \bar{u}=p, \tilde{L}=1}} = (1 + \tfrac{1}{6}p(\chi - 3)) + O(p^2)$$

$$g(p) \equiv \ln Z(q)\Big|_{\substack{q=0 \\ \bar{u}=0, \tilde{L}=1}} = \tfrac{1}{6}p(\chi - 1) + O(p^2)$$

$$h(p) \equiv -\frac{1}{\varepsilon}\mu\frac{\partial}{\partial\mu}\ln Z(q)\Big|_{\substack{q=0 \\ \bar{u}=p, \tilde{L}=1}} = -(p/3\varepsilon)(1 + \tfrac{1}{2}\varepsilon\chi) + O(p^2)$$

$$(\chi = 0.5771 \ldots \text{the Euler number}). \tag{A5}$$

A slight complication occurs for $h(p)$ for we see that $h(p) \sim p/\varepsilon$ whence we require the two loop or $O(\bar{u}^2)$ term in this case. Fortunately however we know that asymptotically $p \to u^*$ and $h(p) \to 2(1-\gamma)/\varepsilon$ (3.43) so we may determine the $O(p^2)$ correction in terms of γ, u^*.

$$h(p) = -\frac{p}{3\varepsilon}\left(1 + \frac{\varepsilon}{2}\chi\right)[1 + (13 - 16\chi)/8]p + O(p^2)).$$

Observing finally that the function $k(p) \equiv \bar{S}(p)$ is directly related to $g(p)$, $h(p)$ ((3.45) et seq.) we obtain the result

$$k(p) = -\frac{p}{3\varepsilon}\left(1 + \frac{\varepsilon}{2}\right)\left(1 + \frac{p}{8}(13 - 16\chi) + O(p^2)\right). \tag{A6}$$

Collecting the results (A1)–(A6) inclusive, a simple substitution into (3.45) now yields the $O(\varepsilon^2)$ scaling forms quoted. We should emphasise that the $O(\varepsilon^2)$ corrections to $k(p)$; $f(p)$ may certainly be ignored for they are of the same magnitude as those arising from the $O(\varepsilon^3)$ corrections to the trajectory integrations.

References

Brézin E, le Guillou J C and Zinn-Justin J 1976 *Phase Transitions and Critical Phenomana* vol VI, ed. C Domb and M S Green (New York: Academic)
des Cloizeaux J 1976 *J. Physique* **37** 431
Edwards S F 1966 *Proc. Phys. Soc.* **88** 265
Elderfield D J 1978 *J. Phys. A: Math. Gen.* **11** 2483
—— 1980 *J. Phys. C: Solid State Phys.* **13** 5583
McKenzie D S 1976 *Phys. Rep.* **27** 125–247