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Scaling properties of the entropy of polymer solutions

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Abstract. Direct renormalisation group equations are derived and solved for the entropy $S(c_p, L, \{P(x)\}, o_v)$ of a polymer solution with specified polydispersity $c_p(x) \equiv c_p(1/L)P(x/L)$. A two-parameter description of the universal scaling function \bar{S} is developed which characterises the scaling behaviour of the entropy for all temperatures $T \geq \theta$, 'the Flory temperature', and all concentrations c_p . Explicit representations are constructed parametrically for all values of the 'overlap' $o_v \sim uL^2c_p$ to $O(\varepsilon^2)$ in the ε expansion. Dilute solution expressions are reproduced, the limit $o_v \gg 1$ of semi-dilute physics is discussed and a simple phenomenological model is proposed.

1. Introduction and outline

Following the work of des Cloizeaux (1980) and Schäfer and Witten (1980, to be referred to as sw) on the scaling properties of polydisperse polymer solutions, we develop a parametric representation for the solution entropy $S(c_p, L, o_v, \{P(x)\})$ valid for arbitrary polydispersity $c_p(x)$ throughout the physical domain. Here we have defined the reduced distribution $P(x)$,

$$c_p(x) = c_p(1/L)P(x/L), \quad (1.1)$$

such that the overall polymer concentration is c_p , the average link number per polymer is L and $o_v \equiv uL^2c_p$ characterises the 'overlap' between the individual polymers. As usual the parameter $u > 0$ is a measure of the short-range repulsive force between individual monomers. By means of a series of direct renormalisation group equations we show that the entropy $S(c_p, L, o_v, \{P(x)\})$ may usefully be discussed in terms of a universal scaling function \bar{S} ,

$$\bar{S}c_p = S - c_p(AL + B) + \int dx [c_p(x) \ln c_p(x) - c_p(x)], \quad (1.2)$$

which, depending only weakly on the nature of the reduced distribution, may otherwise be parametrised *completely* in terms of a renormalised link number \tilde{L} and overlap \tilde{o}_v . Extending the approach of Elderfield (1981, hereafter referred to as I) we develop a compact parametric representation for \bar{S} valid for all values of $\tilde{o}_v \geq 0$, \tilde{L} which is of the general form

$$\begin{aligned} \bar{S} = & \left[\int^{pu^*} \frac{dx}{\beta(x)\nu(x)} (1 - \gamma(x)) - \frac{1}{\tilde{o}_v} \exp\left(\int^{pu^*} \frac{dx}{\beta(x)\nu(x)} (2 - \nu(x)d)\right) \right] \\ & - pu^* F\left(\left[\tilde{o}_v \exp\left(\int^{pu^*} \frac{dx}{\beta(x)\nu(x)} (2 - \nu(x)d)\right)\right], p\right) \end{aligned} \quad (1.3)$$

where the parameter $p \in [0, 1]$ may be eliminated in terms of the renormalised polymer length $\tilde{L} \sim L$ and renormalised overlap $\tilde{o}_v \sim o_v$ through the relation

$$\exp\left(-\int^{pu^*} \frac{dx}{\beta(x)\nu(x)}\right) = \tilde{L} \left[1 + \tilde{o}_v \exp\left(\int^{pu^*} \frac{dx}{\beta(x)\nu(x)}(2 - \nu(x)d)\right)\right]^{-1} \tag{1.4}$$

and where the function $F(x, p)$ is of the form

$$pF(x, p) = \frac{1}{2}p \left(1 - \frac{pu^*}{3}\right) (1+x)^{\epsilon/2} \int \frac{dk^d}{S_d} \left(\frac{1}{x} \ln[1 + xf(k)] - \frac{f(k)}{k^2 + xf(k)}\right) + (4xp/3\epsilon)(1 + \frac{1}{2}\epsilon) + (2 \text{ loops}). \tag{1.5}$$

Here $f(k) \equiv \frac{2}{3}[1 - (1/k^2)(1 - \tilde{P}(k^2))]$ where $\tilde{P}(k^2) \equiv \int dx \exp(-k^2x)$. $P(x)$ is the Laplace transform of the reduced distribution and the functions $\beta(x)$, $\gamma(x)$, $\nu(x)$ are known to at least $O(x^4)$ in the literature (see Brézin *et al* 1976). As usual the scale of p is determined by the Wilson-Fisher fixed point u^* of the renormalisation group equations. We should also remark that the parameters $A, B, \tilde{o}_v/o_v, \tilde{L}/L$ independent of c_p, L summarise the effect of short-range correlations in the solution, so they are strongly model-dependent or non-universal and therefore of little intrinsic interest.

Of course the primary limitation of the above representation is the evaluation of F , for even at the one-loop level, which corresponds rather paradoxically to an $O(\epsilon^2)$ correction, we will need to evaluate the integrals numerically. In general it is therefore a non-trivial task to gauge the degree to which the precise nature of the reduced distribution $P(x)$ modifies the behaviour of \bar{S} . We shall therefore seek a phenomenological representation exhibiting the correct analytic structure of \bar{S} in the domains of dilute $o_v \ll 1$ and semi-dilute $o_v \gg 1$ physics of particular interest and which for general values of the ‘overlap’ o_v should at least be numerically representative. In defence of (1.3) *et seq.*, we should of course emphasise again that the one-loop approximation gives a representation for \bar{S} valid up to corrections of $O(\epsilon^3)$ in the ϵ expansion, whilst the truncated expression $F = 0$ is sufficient to control the behaviour up to terms of $O(\epsilon^2)$.

For most practical purposes we shall be interested in the dilute $o_v \ll 1$ and semi-dilute $o_v \gg 1$ limits of the above representation. Here many simplifications occur and we find for dilute solutions the expressions derived in I:

$$\bar{S} = \int^{pu^*} \frac{dx}{\beta(x)\nu(x)} [1 - \gamma(x)] + g(p), \tag{1.6}$$

where $g(p) = -pu^*F(0, p)$ and where p may be eliminated in terms of the scaling variable $\tilde{z} \equiv \tilde{L}^{\epsilon/2}$ through the relation

$$\exp\left(-\int^{pu^*} \frac{dx}{\beta(x)\nu(x)}\right) = \tilde{L} = \tilde{z}^{2/\epsilon}. \tag{1.7}$$

Here $g(p)$ may be developed as a power series in $pu^* = O(\epsilon)$. Similarly, in the semi-dilute region $\tilde{o}_v \gg 1$, we obtain the parametric representation

$$\bar{S} = \int^{pu^*} \frac{dx}{\beta(x)\nu(x)} [1 - \gamma(x)] - \frac{1}{6}\tilde{o}_v \exp\left(\int^{pu^*} \frac{dx}{\beta(x)\nu(x)}(2 - \nu(x)d)\right) (1 + f(p)) \tag{1.8}$$

where $\frac{1}{6}f(p) = pu^* \lim_{x \rightarrow \infty} F(x, p)/x$ and where now p is to be eliminated in terms of the

scaling variable $\bar{x} = (\tilde{\delta}_v/\tilde{L})^{-\varepsilon/2}$ appropriate to the limit $o_v \gg 1$ through the relation

$$\exp\left(\int^{\rho u^*} \frac{dx}{\beta(x)\nu(x)}(1 - \nu(x)d)\right) = \frac{\tilde{L}}{\tilde{\delta}_v} = \bar{x}^{2/\varepsilon}. \quad (1.9)$$

Deep in the asymptotic critical regimes $\bar{z} \gg 1$ ($o_v \ll 1$) or $\bar{x} \gg 1$ ($o_v \gg 1$), by linearising (1.6), (1.7), (1.8) and (1.9) about the point $p = 1$, we obtain the expressions

$$\bar{S} \stackrel{o_v \ll 1}{=} (\gamma - 1) \ln [\bar{z}^{2/\varepsilon}][1 + O(\bar{z}^{-2\omega/\varepsilon})], \quad (1.10)$$

$$\bar{S} \stackrel{o_v \gg 1}{=} [(\gamma - 1) \ln \bar{x}^{(2/\varepsilon)(\nu d - 1)} - \frac{1}{6}\tilde{\delta}_v \bar{x}^{(2/\varepsilon)[(d\nu - 2)/(d\nu - 1)]}(1 + O(\bar{x}^{-(2/\varepsilon)[\omega/(\nu d - 1)]})] \quad (1.11)$$

where we have by rescaling \bar{z} , \bar{x} chosen $f(1) = g(1) = 0$ and where γ , ν , ω are the usual critical exponents associated with the Wilson-Fisher fixed point in d spatial dimensions. The dilute solution results obtained above were discussed in detail in I and are in full agreement with the expectations of Edwards (1966) and des Cloizeaux (1976); however, in contrast the semi-dilute expressions are derived here for the first time. For semi-dilute physics, we observe from (1.11) that in the asymptotic critical domain the logarithmic correction dominates the usual corrections to scaling $\sim \bar{x}^{-(2\omega/\varepsilon)/(\nu d - 1)}$, $1 < \nu d < 2$. We have discussed the asymptotic form of $S(c_p, o_v, L)$ outside the dilute limit $o_v \ll 1$; however, their approach is limited to the development of systematic corrections to the dilute problem for which the scaling corrections are controlled by \bar{z} (rather than \bar{x}) and therefore these authors fail to construct the dominant logarithmic correction properly for the semi-dilute limit $o_v \gg 1$.

By construction the function $F(x, p)$ modifies only the amplitude of the 'singularity' already present in the truncated expression ($F = 0$) for the two limits $o_v \ll 1$, $o_v \gg 1$ of particular interest. Corrections of this type may to $O(\varepsilon^2)$ be eliminated by a simple rescaling of the primary variables \tilde{L} , $\tilde{\delta}_v$, whence we shall propose the following phenomenological representation:

$$\bar{S} = \left(\frac{1 - \gamma}{\omega}\right) \ln(1 - p) - \frac{1}{6}\tilde{\delta}_v (1 - p)^{(2 - \nu d)/\omega} \\ (1 - p)^{-\varepsilon/2\omega} p = \tilde{L}^{\varepsilon/2} [1 + \tilde{\delta}_v (1 - p)^{(2 - \nu d)/\omega}]^{-\varepsilon/2}.$$

Valid to $O(\varepsilon)$ for all $\tilde{\delta}_v$, \tilde{L} and specifically to $O(\varepsilon^2)$ by construction in the limits of dilute $o_v \ll 1$ and semi-dilute $o_v \gg 1$ physics, the representation exhibits the correct analytic structure in the limits (see Daoud and Jannink 1976) of particular interest, and therefore may realistically be extrapolated to give a description of the physics in $d = 3$ dimensions. Effectively the weak remanent dependence of \bar{S} on the polydispersity is absorbed by a rescaling of \tilde{L} , $\tilde{\delta}_v$, so in contrast to (1.3) the parametrisation $(\tilde{L}, \tilde{\delta}_v)$ is complete.

In outline, following a brief introduction to the excluded volume problem and the field theoretical analogue in § 2, § 3 describes the development of a series of direct renormalisation group equations, which are then employed in § 4 to determine to scaling structure of the entropy S via that of a universal scaling function $\bar{S}(\tilde{\delta}_v, \tilde{L})$ of two parameters. We discuss the completeness and nature of the parametrisation by reference to the various limiting regimes of Daoud and Jannink (1976), and propose a phenomenological model which exhibits full universality and exhibits the correct analytic structure in various limits.

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 $E(\mathcal{C})$ of a configuration \mathcal{C} of M polymers each labelled by an index m ($m = 1, 2, \dots, M$) may be written for a system of continuous chains in the form

$$E(\mathcal{C}) = \frac{u\Lambda^\epsilon}{4!} \sum_{m=1}^M \sum_{k=1}^M \int_0^{N_m} ds_m \int_0^{N_k} ds_k \delta[\mathbf{r}(s_m) - \mathbf{r}(s_k)]. \quad (2.1)$$

Here the polymer m consists of $L_m = N_m \Lambda^2$ 'links' where Λ is representative of the inverse monomer spacing and each point on the chain is located by a vector $\mathbf{r}_m(s_m)$ $0 < s_m < N_m$, $m = 1, 2, \dots, M$. Phenomenologically, the dimensionless coupling u is taken to be of the form $u \sim (1 - \theta/T)$ where θ is the Flory temperature.

Following the work of des Cloizeaux (1980), Elderfield (1980) and sw, we develop a grand canonical approach to the polydisperse polymer solution by defining a grand partition functional Z_p as follows:

$$Z_p = 1 + \sum_{M=1}^{\infty} \frac{1}{M!} \prod_{i=1}^M \int_0^{\infty} dN_i \exp \mu(N_i) \sum_{\substack{\mathcal{C} \\ \text{Fixed } N_i \\ i=1, 2, \dots, m}} \exp[-E(\mathcal{C}, \{N_i\}, M)] \quad (2.2)$$

where the polydispersity is defined as a continuous function of the parameter N rather than the link number $L = N \Lambda^2$ by the relation

$$c_p(N) = (1/V) \partial \ln Z_p / \partial \mu(N). \quad (2.3)$$

For this ensemble an entropy S (per unit volume) is defined by the relation

$$S = -\frac{1}{V} \sum_{\mathcal{C}} \frac{1}{M!} \prod_i \int dN_i p(\{N_i\}, M) \ln(p(\{N_i\}, M)) \quad (2.4)$$

where the ensemble probability $p(\{N_i\}, M)$ is defined by

$$p(\{N_i\}, M) = \exp\left(\sum_{i=1}^M \mu(N_i)\right) \exp[-E(\mathcal{C}, \{N_i\}, M)]. \quad (2.5)$$

As usual we may rewrite (2.4) and (2.5) in the familiar form

$$S = E + \ln Z_p - \int dx \mu(x) c_p(x) \quad (2.6)$$

where E is the average configuration energy per unit volume

$$E \equiv -\frac{1}{V} u \frac{\partial}{\partial u} \ln Z_p \Big|_{\mu}. \quad (2.7)$$

In the free chain limit ($u = 0$) the functional may be enumerated exactly to give the ideal gas expression

$$S = -\int dx \{c_p(x) \ln [c_p(x)/P^1(x)] - c_p(x)\} \quad (2.8)$$

where $P^1(x)$ is the number of internal degrees of freedom of a polymer chain of $L = x \Lambda^2$ links. We shall choose the normalisation $P^1(x) = 1$ at $u = 0$ so that we compute the

entropy $S + \langle c_p \ln c_p - c_p \rangle$ relative to a gas of free chains, rather than the absolute entropy which is infinite for continuous chains.

Specialising to the continuous gaussian chain model of Edwards (1966), which although rather crude is amply justified at least in $d = 4 - \varepsilon$ dimensions (ε small) by the universality of the long chain $L = N\Lambda^2 \gg 1$ limit, we may now rewrite (2.2) and (2.4) in terms of an effective Hamiltonian \mathcal{H} ,

$$\mathcal{H}(\mathcal{C}, \{N_i\}, M) = \frac{1}{2} \sum_{m=1}^M \int ds_m \left(\frac{\partial \mathbf{r}_m(s_m)}{\partial s_m} \right)^2 + \frac{u}{4!} \Lambda^\varepsilon \sum_{m=1}^M \sum_{k=1}^M \int_0^{N_m} ds_m \int_0^{N_k} ds_k \delta[\mathbf{r}_m(s_m) - \mathbf{r}_k(s_k)], \quad (2.9)$$

by means of the relation

$$\sum_{\mathcal{C}} f(\mathcal{C}) = \int [d\mathbf{r}] \exp \left[- \sum_{m=1}^M \int_0^{N_m} ds_m \left(\frac{\partial \mathbf{r}_m(s_m)}{\partial s_m} \right)^2 \right] \quad (2.10)$$

valid for all functions $f(\mathcal{C})$, which defines the Edwards model. Here $\int [d\mathbf{r}]$ denotes a functional integration. Rewriting (2.2), we find on taking the logarithm the expression

$$\frac{1}{V} \ln Z_p = \sum_{M=1}^{\infty} \frac{1}{M!} \prod_{i=1}^M \int dN_i e^{\mu(N_i)} P^M(\{N_i\}, u) \quad (2.11)$$

where $P^M(\{N_i\})$ is the associated connected partition function for M polymers defined as usual by the equations

$$P^M(\{N_i\}) = \frac{\partial^M \ln Z_p}{\partial h(N_1) \dots \partial h(N_m)}, \quad h(N) = \ln \mu(N). \quad (2.12)$$

($h(N)$ is not associated with vertex irreducibility in the sense of des Cloizeaux (1980).)

For our purposes, the particular value of (2.11) lies in the existence of a simple isomorphism between the functions $P^M(\{N_i\})$ and the connected Green functions (taken at zero momentum) of the following field theory:

$$H(\{\phi\}) = \frac{1}{2} \sum_{\alpha=1}^M \sum_{i=1}^n (\nabla \phi_{i\alpha})^2 + a_c \Lambda^2 (\phi_{i\alpha})^2 + \frac{1}{2} \sum_{\alpha=1}^M \sum_{i=1}^n t_\alpha (\phi_{i\alpha})^2 + \frac{u \Lambda^\varepsilon}{4!} \left(\sum_{\alpha=1}^M \sum_{i=1}^n (\phi_{i\alpha}(x))^2 \right)^2 + \sum_{\alpha=1}^M \sum_{i=1}^n h_{i\alpha} \phi_{i\alpha}. \quad (2.13)$$

Here $\phi_{i\alpha}$ is an $n \times m$ component field for which the fluctuations are cut off at a momentum scale Λ , reflecting the finite monomer size, and the ϕ^4 coupling arises directly from the excluded volume interaction. Extending the work of Emery (1975), one may easily show that

$$G^{2M}(t_1, \dots, t_M) = \prod_{i=1}^M \int_0^\infty dN_i \exp[-N_i(a_c \Lambda^2 + t_i) P^M(\{N_i\})] \quad (2.14)$$

where $G^{2M}(t_1, \dots, t_M)$ is the connected Green function defined in terms of the field theoretical free energy $\ln Z_F$ taken in the limit $n \rightarrow 0$:

$$G^{2M}(t_1, \dots, t_m) = \frac{1}{V} \lim_{n \rightarrow 0} \lim_{|h| \rightarrow 0} \frac{\partial^{2M} \ln Z_F(h)}{\partial^2 h_{11} \partial^2 h_{12} \dots \partial^2 h_{1M}}. \quad (2.15)$$

To illustrate the power of the analogy (2.14), it is useful to examine the structure of the entropy for a dilute (or single polymer) problem which may be defined directly in terms of $P^1(N)$ by the relation

$$S^1 \equiv \sum_{\mathcal{G}} p \ln p = \left(1 - u \frac{\partial}{\partial u}\right) \ln P^1(N, u) \quad (2.16)$$

(see I). Equation (2.14) 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 $t=0$ ($M=1$) locates the transition, it is well known that the susceptibility χ is of the form

$$\chi \equiv G^2(t, u) = \frac{1}{t} \left(\frac{t\phi(u)}{\Lambda^2}\right)^{1-\gamma} \left\{1 + O\left[\left(\frac{t}{\Lambda^2}\right)^\omega\right]\right\} \quad (2.17)$$

which implies that the entropy S^1 (2.16) scales as follows:

$$S^1 = \left(a_c - \frac{\partial a_c}{\partial \ln u}\right)L + \left\{(\gamma - 1) \left[\ln L + \left(\frac{u\partial(\phi/u)}{\partial \ln u} + \frac{\ln \Gamma(\gamma)}{\gamma - 1}\right)\right]\right\} (1 + O(L^{-\omega})). \quad (2.18)$$

Here $\gamma, \omega > 0$ are critical exponents associated with the $n \rightarrow 0$ 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 the asymptotic domain $L \gg 1$ we would expect S^1 to depend strongly on the dimensionless combination $\bar{z} \sim uL^{\varepsilon/2}$. Indeed, if $\bar{z} \ll 1$, perturbation theory is valid and we find directly that the entropy exhibits random flight ($\gamma = 1$) behaviour

$$S^1 = (a_c - \partial a_c / \partial \ln u)L + O(z). \quad (2.19)$$

In I we showed by means of a series of direct renormalisation group equations developed from the field theory that we can describe the scaling properties of S as a function of L, u in terms of a universal scaling function $m(\tilde{L})$ of a parameter \tilde{L} (proportional to L) which is a common feature of all polymer functions:

$$S^1 - AL - B = m(\tilde{L}) \quad (m(0) = 0). \quad (2.20)$$

For example, the parameter \tilde{L} may be eliminated directly in terms of the expansion factor $\alpha \equiv \langle R^2 \rangle / \langle R^2 \rangle_\theta = \alpha(\tilde{L})$ which is also a universal function of \tilde{L} . The function $m(\tilde{L})$ was constructed in terms of an elegant parametric representation, which to order ε^2 in the ε expansion takes the form

$$m(\tilde{L} \text{ or } \alpha) = \left(\frac{1-\gamma}{\omega}\right) \ln(1-p) - \frac{4p}{9} \left(1 + \frac{21\varepsilon}{32}\right) \left(1 + \frac{\varepsilon p}{6}(13 - 16\chi)\right) \quad (2.21)$$

where p may be eliminated in terms of \tilde{L} or α from the relations

$$\bar{\alpha} = (1-p)^{(1-2\nu)/\omega} \left[1 - \frac{\varepsilon p}{9} \left(\frac{59}{16} - \chi\right)\right], \quad (1-p)^{-\varepsilon/2\omega} p = \tilde{L}^{\varepsilon/2}. \quad (2.22)$$

Here χ is the Euler number: $\chi = 0.5771 \dots$. The non-universal structure of S^1 appears only in the functions $A, B, \tilde{L}/L$ which, determined by the short-range correlations and independent of L , are of little intrinsic interest. The analogy thus allows us to describe in precise detail the nature of the crossover from free flight (2.19) to swelled chain (2.18)

behaviour as important long-range correlations develop, and identify in a simple way the degree to which the polymer system exhibits universal characteristics.

We shall here extend these methods to show that more generally the scaling properties of the entropy $S(c_p, o_v, L)$ of a polydisperse solution may be described in terms of a universal scaling function $\bar{S}(\tilde{L}, \tilde{o}_v)$,

$$c_p \bar{S} \equiv S - (AL + B)c_p + \left(\int dx c_p(x) \ln c_p(x) - c_p(x) \right), \quad (2.23)$$

of the scaling variables $\tilde{z} = \tilde{L}^{\varepsilon/2}$, $\tilde{x} = (\tilde{o}_v/\tilde{L})^{-\varepsilon/2}$. Constructing \bar{S} , we find to $O(\varepsilon^2)$ the expression

$$\bar{S} = \frac{(1-\gamma)}{\omega} \ln(1-p) - \frac{1}{\delta} \tilde{o}_v (1-p)^{(2-\nu d)/\omega} + pu^* F(\tilde{o}_v (1-p)^{(2-\nu d)/\omega}, p) \quad (2.24)$$

where the parameter $p \in [0, 1]$ may be eliminated in terms of \tilde{L} and \tilde{o}_v through the relation

$$(1-p)^{-\varepsilon/2\omega} p = \tilde{L}^{\varepsilon/2} [1 + \tilde{o}_v (1-p)^{(2-\nu d)/\omega}]^{-\varepsilon/2} \quad (2.25)$$

and the function $F(x, p)$ (an $O(\varepsilon^2)$ effect) depends on the nature of the reduced distribution $P(x)$ (1.1). The primary limitation of (2.24) is the function $F(x, p)$ which must generally be constructed numerically; however, in the limits of dilute $o_v \ll 1$ and semi-dilute $o_v \gg 1$ physics which are of principal interest, we may set $F = 0$ by choosing the scales suitably, i.e.

$$pu^* F(0, p) = pu^* \lim_{x \rightarrow \infty} \frac{F(x, p)}{x} = O(\varepsilon^3). \quad (2.26)$$

Strictly \bar{S} is therefore only fully universal as a function of \tilde{L} , \tilde{o}_v in the limits $o_v \ll 1$, $o_v \gg 1$ where $F(x, p)$ and the associated polydispersity effects can be suppressed.

Guided by the feature (2.26) of the full representation (2.24), which is readily extendable at least formally to any desired accuracy, we shall argue that the truncated expression

$$\bar{S} = [(1-\gamma)/\omega] \ln(1-p) - \frac{1}{\delta} \tilde{o}_v (1-p)^{(2-\nu d)/\omega} \quad (2.27)$$

provides a useful phenomenological description of the physics throughout the parameter space spanned by \tilde{L} , $\tilde{o}_v \geq 0$. In contrast to (2.24), the two-parameter description is complete for (2.27) so that, having fixed the scales \tilde{L} , \tilde{o}_v , no further freedom exists. To $O(\varepsilon)$ the two representations (2.24) and (2.27) are fully equivalent, whilst by construction in the domains of dilute and semi-dilute physics, we may extend this equivalence to $O(\varepsilon^2)$; cf (2.26).

For practical purposes we shall in general be interested in a phenomenological representation of the entropy $S(c_p, L, T)$ as a function of c_p , L and the temperature T rather than the variables \tilde{o}_v and \tilde{L} employed above. We therefore extend the usual phenomenological choice $u \sim 1 - \theta/T$, where θ is the Flory temperature associated with the structure of the perturbative domain $u \ll 1$, by defining

$$\tilde{L}^{\varepsilon/2} = a(1 - \theta/T)L^{\varepsilon/2} \quad \tilde{o}_v = ab(1 - \theta/T)L^2 c_p,$$

where a , b independent of c_p , L , T are to be obtained from experiment ((4.19) *et seq.*). It is important to observe that through (2.25) the trajectories $p(c_p, L, \tau = 1 - \theta/T)$ exhibit scaling behaviour as a function of a single crossover variable $\tilde{z} = \tilde{L}^{\varepsilon/2}$ or $\tilde{x} = (\tilde{o}_v/\tilde{L})^{-\varepsilon/2}$

only in the dilute or semi-dilute limits. Indeed, in general, as the temperature increases from θ at fixed L, c_p it is theoretically possible to probe in sequence all four ($T > \theta$) regions of a Daoud and Jannink (1976) type plot, as illustrated in figure 1.

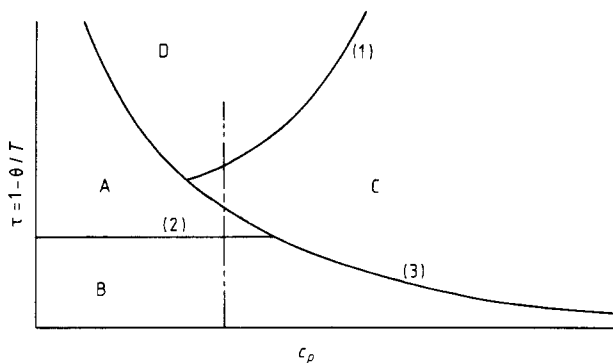


Figure 1. Regions of a Daoud–Jannink type plot. A: Dilute critical; $\bar{x} \gg 1, o_v \ll 1$. B: Dilute θ (tricritical); $\bar{x}, o_v \ll 1$. C: Semi-dilute θ (tricritical); $\bar{x} \ll 1, o_v \gg 1$. D: Semi-dilute critical; $\bar{x} \gg 1, o_v \gg 1$. The curves are: (1) $\tau(\tau L c_p)^{-\epsilon/2} = \text{constant}$; (2) $\tau L^{\epsilon/2} = \text{constant}$; (3) $o_v \sim \tau L^2 c_p = \text{constant} \sim 1$.

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

To investigate the scaling properties of the entropy $S(c_p, o_v, L)$ (2.4) for arbitrary polydispersity we employ the techniques of Brézin *et al* (1976; BLZ) to develop renormalisation group equations via the properties of the connected polymer functions $P^M(N_1, \dots, N_m)$ (2.11) and their field theoretical analogues $G^{2M}(t_1, \dots, t_M)$ (2.15) (cf (2.14)). Following BLZ, we shall factor out the non-universal features of the entropy by constructing a renormalised theory depending on a new length scale $\bar{\Lambda} \ll \Lambda$ and new parameters \bar{u}, \bar{N}_α . By direct analogy (see I) with the field theoretical development, we define renormalised polymer functions $\bar{P}^M(\{\bar{N}\}, \bar{u}, \bar{\Lambda})$ by the relations

$$\begin{aligned} \bar{P}^M(\{\bar{N}\}, \bar{u}, \bar{\Lambda}) &= z_t^{-M} P^M(\{N\}, u, \Lambda) \exp\left(-a_c \sum_{\alpha=1}^M L_\alpha\right), \\ z_u \bar{u} &= u (\Lambda / \bar{\Lambda})^\epsilon z_\phi^2, \\ z_\phi \bar{N}_\alpha &= z_t N_\alpha, \quad \alpha = 1, 2, \dots, M, \end{aligned} \tag{3.1}$$

where L_α is the link number of the α polymer $L_\alpha = N_\alpha \Lambda^2$, $\alpha = 1, 2, \dots, M$, and the functions $a_c(u, \Lambda)$, $z_\phi(u)$, $z_u(u)$, $z_t(u)$ are chosen to ensure that the renormalised functions \bar{P}^M are finite in the limit $\Lambda \rightarrow \infty$ at fixed \bar{u}, \bar{N}_α , $\alpha = 1, 2, \dots, M$. Perturbatively in u , $a_c(u, \Lambda)$ renders \bar{P} finite in $d < 4$ dimensions and then z_ϕ, z_u, z_t (independent of $\{N_\alpha\}$ by construction) remove the remaining logarithmic divergences as $d \rightarrow 4$. In the field theoretic representation these equations correspond directly to the renormalisation scheme of BLZ, i.e.

$$\begin{aligned} G^{2M}(\{\bar{t}\}, \bar{u}, \bar{\Lambda}) &= z_\phi^{-M} G^{2M}(\{t\}, u, \Lambda), \\ z_u \bar{u} &= u (\Lambda / \bar{\Lambda})^\epsilon z_\phi^2, \\ z_t \bar{t}_\alpha &= z_\phi t_\alpha, \quad \alpha = 1, 2, \dots, M, \end{aligned} \tag{3.2}$$

so we refer the reader to BLZ (or I) for a detailed discussion of the construction of z_u, z_v, z_ϕ . Naturally we could implement (3.1) from first principles without reference to the field theory; however, the functions z_u, z_ϕ, z_i are known (up to an irrelevant finite renormalisation) to at least $O(\bar{u}^4)$ in the literature, so this exercise is pointless.

In terms of these renormalised functions $\bar{P}^M(\{x\})$ we may now rewrite the free energy functional of fugacities $h(x)^\dagger$,

$$\frac{1}{V} \ln Z_p = \sum_{M=1}^{\infty} \prod_{i=1}^M \int dx_i h(x_i) P^M(\{x_i\}, u, \Lambda), \quad (3.3)$$

in the form

$$\frac{1}{V} \ln Z_p = \sum_{M=1}^{\infty} \prod_{i=1}^M \int dx_i \bar{h}(x_i) \bar{P}^M(\{x_i\}, \bar{u}, \bar{\Lambda}). \quad (3.4)$$

Here the renormalised/bare fugacities are related as follows:

$$\bar{h}(xz_i/z_\phi) = z_\phi h(x) \exp[a_c(x\Lambda^2)]. \quad (3.5)$$

The fundamental renormalisation group equations may now be derived directly from the above by observing (BLZ) that the bare functions $P^M(\{N\}, u, \Lambda)$ are certainly independent of the arbitrary length scale $\bar{\Lambda}$, so by implication

$$\left[\bar{\Lambda} \frac{\partial}{\partial \bar{\Lambda}} + \beta(\bar{u}) \frac{\partial}{\partial \bar{u}} + \left(\frac{1}{\nu(\bar{u})} - 2 \right) \sum_{\alpha=1}^M \bar{N}_\alpha \frac{\partial}{\partial \bar{N}_\alpha} + M \left(\frac{\gamma(\bar{u}) - 1}{\nu(\bar{u})} \right) \right] \bar{P}^M = 0 \quad (3.6)$$

where the functions $\beta(\bar{u})$, $\gamma(\bar{u})$, $\nu(\bar{u})$ are defined as follows:

$$\begin{aligned} \beta(\bar{u}) &\equiv \bar{\Lambda} \left. \frac{\partial}{\partial \bar{\Lambda}} \right|_{u, \{N\}, \Lambda, a_c} \bar{u} = -\varepsilon \bar{u} + \frac{4}{3} (1 + \frac{1}{2}\varepsilon) \bar{u}^2 - \frac{7}{6} \bar{u}^3 + O(\bar{u}^4) \\ \left(\frac{1}{\nu(\bar{u})} - 2 \right) &\equiv \bar{\Lambda} \left. \frac{\partial}{\partial \bar{\Lambda}} \right|_{u, \{N\}_{(\alpha \neq \beta)}, \Lambda, a_c} \ln \bar{N}_\alpha \\ &= -\frac{1}{3} \bar{u} (1 + \varepsilon/2) + \frac{5}{36} \bar{u}^2 + O(\bar{u}^3) \quad (\text{independent of } \alpha) \\ \left(\frac{\gamma(\bar{u}) - 1}{\nu(\bar{u})} \right) &\equiv \bar{\Lambda} \left. \frac{\partial}{\partial \bar{\Lambda}} \right|_{u, \{N\}, \Lambda, a_c} \ln z_i = \frac{1}{3} \bar{u} (1 + \varepsilon/2) - \frac{1}{6} \bar{u}^2 + O(\bar{u}^3). \end{aligned} \quad (3.7)$$

The expressions for $\beta(\bar{u})$, $\nu(\bar{u})$, $\gamma(\bar{u})$ enumerated above were computed for a dimensionally regularised ϕ^4 theory and are correct to order ε^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 (3.6) lies in the simple structure of $\beta(\bar{u})$, $\gamma(\bar{u})$, $\nu(\bar{u})$, for by construction they are independent of $\{\bar{N}\}$ and furthermore independent of $\bar{\Lambda}$. Naturally, outside the dimensional regularisation scheme employed here, there will be corrections of order $\bar{\Lambda}/\Lambda$ to (3.7); however, in the polymer domain $N\Lambda^2 \gg 1$ we may always choose $\bar{\Lambda} \ll \Lambda$. Strictly, the functions $\beta(\bar{u})$, $\gamma(\bar{u})$, $\nu(\bar{u})$ are only universal at the fixed point u^* defined as usual by $\beta(u^*) = 0$; however, this remanent dependence on short-range details may always be absorbed by a further rescaling of the primary variables \bar{u} , $\{\bar{N}_\alpha\}$ so that (3.6) is indeed an adequate description of the universal scaling structure expected.

\dagger Here $y \equiv x\Lambda^2$ rather than x is related to the number of links per chain.

To derive the renormalisation group equation for $\ln Z_p$ from (3.4) and (3.6), we need the following identity (integration by parts),

$$\sum_{M=1}^{\infty} \prod_{i=1}^M \int dx_i \bar{h}(x_i) \left[\sum_{k=1}^M \left(x_k \frac{\partial}{\partial x_k} \right) \bar{P}^M(x_1 \dots x_M) \right] = - \int dx \left[\left(1 + x \frac{\partial}{\partial x} \right) \ln \bar{h}(x) \right] \frac{\partial \ln Z_p}{\partial \ln \bar{h}(x)}, \quad (3.8)$$

valid for polydispersities $c_p(x)$ vanishing sufficiently fast in the limits $x \rightarrow 0$ or ∞ . Using (3.8), (3.4) and (3.6), we now find after some manipulation the renormalisation group equation for $\ln Z_p$,

$$\left[\bar{\Lambda} \frac{\partial}{\partial \bar{\Lambda}} + \beta(\bar{u}) \frac{\partial}{\partial \bar{u}} + \left(\frac{1}{\nu(\bar{u})} - 2 \right) \int_0^{\infty} dx \left(x \frac{\partial}{\partial x} \ln \bar{h}(x) \right) \frac{\partial}{\partial \ln \bar{h}(x)} \right] \frac{1}{V} \ln Z_p + \eta(\bar{u}) c_p = 0 \quad (3.9)$$

where $\eta(\bar{u})$ is given in terms of $\nu(\bar{u})$, $\gamma(\bar{u})$ by the relation

$$\gamma(\bar{u}) = \nu(\bar{u})(2 - \eta(\bar{u})) \quad (3.10)$$

and by definition $c_p = \int dx \bar{c}_p(x) \equiv (1/V) \int dx \partial \ln Z_p / \partial \ln \bar{h}(x)$ (cf (2.3)). Of course only the total concentration $c_p = \int dx c_p(x)$ is invariant under our renormalisation prescription (3.5). For example, the renormalised/bare polymer concentrations are related as follows,

$$\bar{c}_p(x) \equiv \partial \ln Z_p / \partial \ln \bar{h}(x) = (z_\phi/z_t) c_p(x z_\phi/z_t), \quad (3.11)$$

leading to the invariance $c_p = \int dx c_p(x) = \int dx \bar{c}_p(x)$ of the total concentration.

For our purposes it is however useful to have a renormalisation group equation in which the polymer concentration $\bar{c}_p(x)$ is an explicit scaling variable so we define the Legendre transform $\ln \bar{\Xi}_p$ of $\ln Z_p$ with respect to $\bar{c}_p(x)$, i.e.

$$\frac{1}{V} \ln \bar{\Xi}_p = \frac{1}{V} \ln Z_p - \int dx \bar{c}_p(x) \bar{\mu}(x)$$

where

$$(1/V) \frac{\partial \ln \bar{\Xi}_p}{\partial \bar{c}_p(x)} = -\bar{\mu}(x) \quad (3.12)$$

or equivalently

$$(1/V) \frac{\partial \ln Z_p}{\partial \bar{\mu}(x)} = \bar{c}_p(x).$$

Here $\bar{\mu}(x)$ is the renormalised chemical potential $\bar{\mu}(x) = \ln \bar{h}(x)$. Observing that the properties of Legendre transformations (3.12) ensure that $\bar{\Lambda} \partial \ln Z_p / \partial \bar{\Lambda} = \bar{\Lambda} \partial \ln \bar{\Xi}_p / \partial \bar{\Lambda}$ etc, we may therefore trivially rewrite (3.9) after integration by parts in the final form

$$\left\{ \bar{\Lambda} \frac{\partial}{\partial \bar{\Lambda}} + \beta(\bar{u}) \frac{\partial}{\partial \bar{u}} - \left(\frac{1}{\nu(\bar{u})} - 2 \right) \int dx \left[\left(1 + x \frac{\partial}{\partial x} \right) \bar{c}_p(x) \right] \frac{\partial}{\partial \bar{c}_p(x)} \right\} \frac{1}{V} \ln \bar{\Xi}_p + \eta(\bar{u}) c_p = 0. \quad (3.13)$$

Again we assume that the polydispersity $\bar{c}_p(x)$ vanishes sufficiently fast in the limits $x \rightarrow 0$ or ∞ .

Returning now to the primary definition (2.4) and (2.6), the reader will see that we now have a direct renormalisation group equation for the difference $S - E$, so to complete our task we need only develop a similar equation for the configurational

energy E . By contrast to our above considerations the examination of E is rather complicated. We first parametrise E in terms of fully renormalised functions $X \equiv (1/V)\partial \ln Z_p/\partial \ln u$, $\bar{c}_p(x)$ and non-universal amplitudes $A(u)$, $B(x, u)$ as follows:

$$E = -u \frac{\alpha}{\partial u} \ln Z_p \Big|_{\{h(x)\}} = Ax - \int dx B(x)\bar{c}_p(x) \tag{3.14}$$

where

$$A \equiv -\partial \ln \bar{u} / \partial \ln u,$$

$$B \equiv \frac{\partial \ln \bar{h}(x)}{\partial \ln u} \Big|_{\{h(x)\}} \left(\frac{z_\phi}{z_t} (x\Lambda^2) \frac{\partial a_c}{\partial \ln u} + \frac{\partial \ln z_\phi}{\partial \ln u} \right) + \frac{\partial \ln \bar{h}(x)}{\partial \ln x} \frac{\partial \ln (z_\phi/z_t)}{\partial \ln u}$$

(cf (3.5)). Outside the dimensional regularisation scheme employed here (cf (3.6) *et seq.*) there will in general be corrections of $O(\bar{\Lambda}/\Lambda)$ to (3.14). However, in the critical domain $L \gg 1$ etc these non-universal terms may be suppressed by choosing $\bar{\Lambda} \ll \Lambda$ (Λ finite). The non-universal components A , $\partial \ln z_\phi / \partial \ln u$, $\partial \ln (z_\phi/z_t) / \partial \ln u$ are intimately related to the renormalisation group functions $\beta(\bar{u})$, $\gamma(\bar{u})$, $\nu(\bar{u})$ (or $\eta(\bar{u})$, cf (3.10)) as follows:

$$A = \beta(\bar{u})/\bar{u}\epsilon,$$

$$\frac{\partial \ln z_\phi}{\partial \ln u} = -\eta(\bar{u})/\epsilon, \quad \frac{\partial \ln (z_t/z_\phi)}{\partial \ln u} = \left(\frac{1}{\nu(\bar{u})} - 2 \right) / \epsilon, \tag{3.15}$$

for in a dimensional regularisation scheme the functions z_ϕ , z_t , z_u depend solely on the dimensionless variable $u(\Lambda/\bar{\Lambda})^\epsilon$. Again, for other regularisations these relations may be modified by small terms of $O(\bar{\Lambda}/\Lambda)$ which can again be ignored. Following I, we find it useful to rewrite (3.14) in terms of a subtracted energy \bar{E} ,

$$\bar{E} = E + c_p L \frac{\partial a_c}{\partial \ln u} = \frac{\beta(\bar{u})}{\bar{u}\epsilon} X - \frac{1}{\epsilon} \left(\frac{1}{\nu(\bar{u})} - 2 \right) Y + \frac{\eta(\bar{u})}{\epsilon} c_p \tag{3.16}$$

where X and $Y \equiv (1/V) \int dx [(1+x\partial/\partial x)\bar{c}_p(x)] \partial \ln \bar{\Xi}_p / \partial \bar{c}_p(x)$ can be expected to satisfy exact renormalisation group equations similar to (3.13). Here L is the average number of links per polymer, defined by the relation $L = N\Lambda^2$ where $Nc_p = \int dx xc_p(x)$. Without loss of generality we may set $\Lambda = 1$, so in § 4, in order to simplify the discussion, we shall not distinguish between $L = N\Lambda^2$ and N .

Operating now on (3.13) with $\bar{u}\partial/\partial\bar{u}$ and $\int dx [(1+x\partial/\partial x)c_p(x)]\partial/\partial c_p(x)$, we find the required renormalisation group equations for X , Y in the form

$$\left\{ \bar{\Lambda} \frac{\partial}{\partial \bar{\Lambda}} + \beta(\bar{u}) \frac{\partial}{\partial \bar{u}} - \left(\frac{1}{\nu(\bar{u})} - 2 \right) \int dx \left[\left(1 + x \frac{\partial}{\partial x} \right) \bar{c}_p(x) \right] \frac{\partial}{\partial \bar{c}_p(x)} \right\} X$$

$$= - \left[\bar{u} \frac{\partial}{\partial \bar{u}} \left(\frac{\beta}{\bar{u}} \right) \right] X + \left[\bar{u} \frac{\partial}{\partial \bar{u}} \left(\frac{1}{\nu(\bar{u})} - 2 \right) \right] Y - \left(\bar{u} \frac{\partial \eta(\bar{u})}{\partial \bar{u}} \right) c_p,$$

$$\left\{ \bar{\Lambda} \frac{\partial}{\partial \bar{\Lambda}} + \beta(\bar{u}) \frac{\partial}{\partial \bar{u}} - \left(\frac{1}{\nu(\bar{u})} - 2 \right) \int dx \left[\left(1 + x \frac{\partial}{\partial x} \right) \bar{c}_p(x) \right] \frac{\partial}{\partial \bar{c}_p(x)} \right\} Y = 0. \tag{3.17}$$

To display the scaling structure of the entropy $S(c_p, L, o_v)$ we must now solve the above renormalisation group equation ((3.13), (3.16), (3.17)). As usual we shall employ the method of characteristics. Defining functions $\bar{u}(\lambda)$, $\bar{c}_p(x, \lambda)$, $\bar{\Lambda}(\lambda)$ of a scale

parameter λ as follows,

$$\begin{aligned} \bar{\Lambda}(\lambda) &= \lambda \bar{\Lambda}, \\ d\bar{u}(\lambda)/d \ln \lambda &= \beta[\bar{u}(\lambda)], \quad \bar{\Lambda}(1) = \bar{\Lambda}, \quad \bar{u}(1) = \bar{u}, \end{aligned} \tag{3.18}$$

$$\frac{d\bar{c}_p(x, \lambda)}{d \ln \lambda} = -\left(\frac{1}{\nu(\bar{u})} - 2\right) \left(1 + x \frac{\partial}{\partial x}\right) \bar{c}_p(x, \lambda), \quad \bar{c}_p(x, 1) = \bar{c}_p(x), \tag{3.19}$$

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

$$\begin{aligned} \frac{1}{V} d \ln \bar{\Xi}_p / d \ln \lambda + \eta(\bar{u}) \bar{c}_p(\lambda) &= 0, \\ dY(\lambda)/d \ln \lambda &= 0, \\ (d/d \ln \lambda) \left[\frac{\beta}{u} X - \left(\frac{1}{\nu} - 2\right) Y + \eta c_p \right] &= 0. \end{aligned} \tag{3.20}$$

The trajectory equation for $\bar{c}_p(x, \lambda)$ is however unnecessarily complicated, for if we introduce the reduced distribution $\bar{P}(x)$

$$\bar{c}_p = c_p(1/\bar{N})\bar{P}(x/\bar{N}) \tag{3.21}$$

we may rewrite (3.19) in terms of a function $\bar{c}_p(x, \bar{N}(\lambda))$ where $\bar{N}(\lambda)$ satisfies the differential equation

$$d \ln \bar{N}(\lambda) / d \ln \lambda = (1/\nu(\bar{u}) - 2), \quad \bar{N}(1) = \bar{N}. \tag{3.22}$$

For arbitrary $\bar{c}_p(x)$ we shall define \bar{N} such that $\bar{N} = \int dx x \bar{P}(x)$, i.e. $\bar{L} = \bar{N} \bar{\Lambda}^2$ (proportional to L , cf (1.3)) plays the role of the average link number per polymer in the renormalised system.

In this form the equations (3.20) may be formally integrated as functions of $\bar{u}(\lambda)$, $\bar{N}(\lambda)$, $\bar{\Lambda}(\lambda)$ to give the solutions

$$\frac{1}{V} \ln \left[\frac{\bar{\Xi}_p(c_p, \bar{u}, \bar{N}, \bar{\Lambda})}{\bar{\Xi}_p(c_p, \bar{u}(\lambda), \bar{N}(\lambda), \lambda \bar{\Lambda})} \right] = c_p \int_{\bar{u}}^{\bar{u}(\lambda)} dx \frac{\eta(x)}{\beta(x)} \tag{3.23}$$

and

$$\begin{aligned} \frac{\beta(\bar{u})}{\bar{u}} X(c_p, \bar{u}, \bar{N}, \bar{\Lambda}) &= \frac{\beta(\bar{u}(\lambda))}{\bar{u}(\lambda)} X(c_p, \bar{u}(\lambda), \bar{N}(\lambda), \lambda \bar{\Lambda}) + Y(c_p, \bar{u}, \bar{N}, \bar{\Lambda}) \left(\frac{1}{\nu(\bar{u})} - \frac{1}{\nu(\bar{u}(\lambda))} \right) \\ &+ c_p(\eta(\bar{u}(\lambda)) - \eta(\bar{u})), \end{aligned} \tag{3.24}$$

$$Y(c_p, \bar{u}, \bar{N}, \bar{\Lambda}) = Y(c_p, \bar{u}(\lambda), \bar{N}(\lambda), \lambda \bar{\Lambda}). \tag{3.25}$$

More usefully, we may reformulate (3.24) and (3.25) into the following scaling relationship for the subtracted energy (3.16):

$$\bar{E}(c_p, \bar{u}, \bar{N}, \bar{\Lambda}) = \bar{E}(c_p, \bar{u}(\lambda), \bar{N}(\lambda), \lambda \bar{\Lambda}). \tag{3.26}$$

The reader will observe that the total concentration c_p of polymers is *invariant* under the above renormalisation group transformation, a feature which simplifies considerably a discussion of the renormalisation group trajectories in the physical parameter space. Also we should emphasise again that whilst (3.23), (3.24) and (3.25) are exact in

the context of an ε expansion, the expression (3.26) will in contrast be modified by uninteresting non-universal corrections $O(\bar{\Lambda}/\Lambda)$ (Λ finite) if we do not employ a dimensional regularisation (cf (3.14) *et seq.*).

To construct now the scaling relation for the entropy, we first observe that the equations (2.6), (3.5), (3.12) and (3.16) imply

$$S = c_p [(a_c - \partial a_c / \partial \ln u)L - \ln z_\phi] + \bar{E} + (1/V) \ln \bar{\Xi}_p \quad (3.27)$$

where \bar{E} , $\ln \bar{\Xi}_p$ satisfy simple scaling relations in contrast to the bracketed term which is non-universal. For our purposes we are particularly interested in the structure of the subtracted entropy

$$c_p \bar{S} = S - c_p \left[\left(a_c - \frac{\partial a_c}{\partial \ln u} \right) L + \ln z_\phi \right] + \left(\int dx \bar{c}_p(x) \ln \bar{c}_p(x) - \bar{c}_p(x) \right) \quad (3.28)$$

which both transforms simply under the renormalisation group and furthermore can be expected to depend only weakly on the polydispersity (cf (2.7), $u = 0$). Using (3.23), (3.26) and the additional relations

$$\begin{aligned} \frac{d}{d \ln \lambda} \left(\int dx \bar{c}_p(x) \ln \bar{N} \bar{c}_p(x) \right) &= 0, & \text{i.e. } \langle \bar{c}_p \ln \bar{N} \bar{c}_p \rangle \text{ invariant,} \\ \frac{\bar{N}(\lambda)}{\bar{N}} &= \exp \left[\int_{\bar{u}}^{\bar{u}(\lambda)} \frac{dx}{\beta(x)} \left(\frac{1}{\nu(x)} - 2 \right) \right], & \text{cf (3.21),} \end{aligned} \quad (3.29)$$

we find that \bar{S} scales as follows under the renormalisation group:

$$\bar{S}(c_p, \bar{N}, \bar{u}, \bar{\Lambda}) = \bar{S}(c_p, \bar{N}(\lambda), \bar{u}(\lambda), \lambda \bar{\Lambda}) + \int_{\bar{u}}^{\bar{u}(\lambda)} \frac{dx}{\beta(x)\nu(x)} (1 - \gamma(x)). \quad (3.30)$$

This final relation is fundamental to the following discussion, for by a careful choice of the free parameter λ we show that the entropy S exhibits the properties of scaling and universality through the scaling function \bar{S} . As expected, we find that the universal structure of \bar{S} is not drastically modified by the polydispersity.

4. The universal crossover scaling function \bar{S}

To exhibit the scaling structure of \bar{S} we shall use the freedom in the scale parameter λ ,

$$\bar{S}(c_p, \bar{N}, \bar{u}, \bar{\Lambda}) = \bar{S}(c_p, \bar{N}(\lambda), \bar{u}(\lambda), \lambda \bar{\Lambda}) + \int_{\bar{u}}^{\bar{u}(\lambda)} \frac{dx(1 - \gamma(x))}{\beta(x)\nu(x)}. \quad (4.1)$$

As usual we seek a value for λ such that $\bar{S}(\lambda)$ may realistically be evaluated perturbatively with the usual loop expansion. In contrast to I, the situation is rather complicated, for the scaling structure is described in terms of two competing scales L , o_v/L . The scaling structure of \bar{S} is dominated by L in the dilute regime ($o_v \ll 1$); then, as the 'overlap' $o_v \sim uL^2 c_p$ grows, the scale o_v/L becomes more important until finally in the semi-dilute regime ($o_v \gg 1$) the physics is controlled solely by the scale o_v/L (proportional to the average monomer concentration $c_m \sim Nc_p$).

For a suitable choice of λ we shall construct $\bar{S}(\lambda)$ in terms of the vertex irreducible expansion of des Cloizeaux (1980) (sw). Following this author, we find that the thermodynamic functions of primary interest may be described in terms of a vertex

irreducible functional $V(\{g(x)\})$ which to one-loop accuracy takes the form ($\Lambda = 1$ without loss of generality, i.e. $L = N$)

$$V(\{g(x)\}) = \int dx g(x) + \frac{1}{2} \int dk^d \left\{ \frac{2u}{3k^2} \int dx g(x)x - \ln \left[1 + \frac{2u}{3} \int dx \frac{g(x)}{k^2} \left(x - \frac{1}{k^2} (1 - e^{-k^2x}) \right) \right] \right\} + 2 \text{ loops} \tag{4.2}$$

where $g(x)$ is related to bare fugacity $h(x)$ (3.3) by the *exact* relation

$$h(x) \equiv \exp \mu(x) = g(x) \exp(-a_c x + \frac{1}{6} u L c_p x). \tag{4.3}$$

Of fundamental importance are the connection formulae from which $c_p(x)$, $\ln Z_p$ may be derived as functionals of $g(x)$; they are

$$(1/V) \ln Z_p = V(\{g(x)\}) + \frac{1}{6} u (N c_p)^2, \tag{4.4}$$

$$c_p(x) = g(x) \partial V / \partial g(x) \equiv c_p (1/N) P(x/N). \tag{4.5}$$

Here c_p , u , N are bare parameters associated with the unrenormalised theory described by a reduced polydispersity $P(x)$ which must be eliminated in terms of the renormalised parameters \bar{c}_p , \bar{u} , N , (3.1), (3.11), and polydispersity $\bar{P}(x)$, (3.10), before (4.1) is implemented.

Manipulating (4.2), (4.3) and (4.4), we find after some rescaling that $\ln Z_p$, and $\langle \mu \rangle$ may be expressed conveniently in terms of two dimensionless parameters $z = uL^{\epsilon/2}$ and $o_v = uL^2 c_p$ ($\Lambda = 1$ without loss of generality, i.e. $L \equiv N$) as follows:

$$\frac{1}{V} \ln Z_p = c_p \left\{ 1 + \frac{1}{6} o_v + \frac{1}{2} z \int dk^d \left[\frac{f(k)}{k^2 + o_v f(k)} - \frac{1}{o_v} \ln \left(1 + \frac{o_v f(k)}{k^2} \right) \right] \right\},$$

$$\langle \mu \rangle \equiv \int dx c_p(x) \mu(x) = \langle c_p \ln c_p \rangle + c_p \left(\frac{1}{6} o_v - a_c L \right) - c_p \frac{z}{2} \left[\int dk^d \left(\frac{2}{3k^2} - \frac{f(k)}{k^2 + o_v f(k)} \right) \right] \tag{4.6}$$

where $f(k) = \frac{2}{3}(1 - (1/k^2)(1 - \tilde{P}(k^2)))$ and $L = N$ ($\Lambda = 1$). Here $\tilde{P}(x)$ is the Laplace transform of the reduced distribution $P(x)$, (4.5):

$$\tilde{P}(x) = \int_0^\infty dy e^{-yx} P(x). \tag{4.7}$$

Similarly we find that the average interaction energy E (cf (2.7), (4.6) and (4.7)) is of the general form

$$E \equiv - \frac{1}{V} \frac{\partial \ln Z_p}{\partial \ln u} \Big|_{\{h(x)\}} = - \frac{1}{V} \frac{\partial \ln \Xi_p}{\partial \ln u} \Big|_{c_p(x)}$$

$$= - \frac{1}{2} c_p \left[\frac{o_v}{3} + z \int dk^d \left(\frac{2}{3k^2} - \frac{f(k)}{(k^2 + o_v f(k))} \right) \right] - c_p L \frac{\partial a_c}{\partial \ln u}. \tag{4.8}$$

Here $(1/V) \ln \Xi_p = (1/V) \ln Z_p - \int dx \mu(x) c_p(x)$ is the Legendre transformation of $\ln Z_p$ with respect to the unrenormalised concentration $c_p(x)$ ($\ln \Xi_p \neq \ln \bar{\Xi}_p$, cf (3.12)). Returning now to the primary definition (2.6) for the entropy, we obtain from (3.11),

(3.28), (4.6) and (4.8) the following expression for \bar{S} in terms of the bare parameters z, o_v :

$$\bar{S} = -\left[\frac{1}{6}o_v + \frac{1}{2}z \int dk^d \frac{1}{o_v} \ln\left(1 + o_v \frac{f(k)}{k^2}\right) - \frac{f(k)}{k^2 + o_v f(k)}\right] + 2 \text{ loops.} \quad (4.9)$$

If we now define renormalised parameters \bar{o}_v, \bar{z} (cf (3.1), (3.11), (3.20))

$$\begin{aligned} S_d \bar{o}_v &= \bar{u} \bar{\Lambda}^\epsilon \bar{N}^2 c_p = o_v [1 - (4\bar{u}/3\epsilon)(1 + \frac{1}{2}\epsilon) + O(\bar{u}^2)], \\ S_d \bar{z} &= \bar{u} (\bar{N} \bar{\Lambda}^2)^{\epsilon/2} = z [1 + \frac{1}{3}\bar{u} + O(\bar{u}^2)], \end{aligned} \quad (4.10)$$

related as shown to the bare parameters o_v, z through the functions z_ϕ, z_u, z_t tabulated by BLZ to $O(\epsilon^4)$, we find that we may rewrite (4.9) in the form

$$\begin{aligned} \bar{S}(c_p, \bar{N}, \bar{u}, \bar{\Lambda}) &= -\left\{\frac{1}{6}\bar{o}_v \left[1 + \frac{4\bar{u}}{3\epsilon} \left(1 + \frac{\epsilon}{2}\right)\right] \right. \\ &\quad \left. + \frac{\bar{z}}{2} \left(1 - \frac{\bar{u}}{3}\right) \left[\int \frac{dk^d}{S_d} \frac{1}{\bar{o}_v} \ln\left(1 + \frac{o_v f(k)}{k^2}\right) - \frac{f(k)}{(k^2 + \bar{o}_v f(k))}\right]\right\} \end{aligned} \quad (4.11)$$

to which the scaling relation (4.1) applies. Although all terms of $O(\epsilon^2)$ have been dropped, the expression (4.11) controls the behaviour of \bar{S} through (4.1) to $O(\epsilon^2)$ in the ϵ expansion; for these terms are of the same magnitude as the $O(\epsilon^3)$ corrections to the trajectory equation ((3.18), (3.21)) solutions we employ (see I).

To fix the value of λ , (4.1), we shall demand that the loop corrections do not significantly modify the behaviour of the mean field theory expression evaluated at the scale λ . In order to choose a suitable λ , we observe that in dilute $o_v \ll 1$ and semi-dilute $o_v \gg 1$ regimes which are of particular interest, the behaviour of the one-loop correction

$$\bar{S}^1 \equiv z \int \frac{dk^d}{S_d} \frac{1}{o_v} \left[\ln\left(\frac{1 + \bar{o}_v f(k)}{k^2}\right) - \frac{\bar{o}_v f(k)}{k^2 + \bar{o}_v f(k)} \right] \quad (4.12)$$

may be characterised very simply. For the dilute limit $o_v \ll 1$ we may expand systematically in \bar{o}_v to give the virial expression

$$\bar{S}^1 \sim \bar{z}[1 + O(\bar{o}_v)], \quad \bar{o}_v \ll 1,$$

which as the overlap o_v increases is smoothly modified until asymptotically semi-dilute behaviour is observed†,

$$\bar{S}^1 \sim \bar{z}(\bar{o}_v)^{(d-2)/2}, \quad \bar{o}_v \gg 1.$$

If therefore we fix λ by demanding that the parameters $\bar{z}(\lambda) = \bar{z}(\bar{u}(\lambda), \bar{N}(\lambda), \lambda \bar{\Lambda})$ and $\bar{o}_v(\lambda)$ satisfy the matching condition

$$\bar{u}(\lambda) = \bar{z}(\lambda)[1 + \bar{o}_v(\lambda)]^{-\epsilon/2}, \quad (4.13)$$

we find that $\bar{S}^1(\lambda)$ only modifies the ‘amplitude’ of the terms present at the mean field level of approximation (no loops), and furthermore vanishes under θ temperature conditions $\bar{u} = 0$ (all o_v, L).

To appreciate the full significance of the matching constraint (4.13), we must evaluate the behaviour of $\bar{S}(c_p, \bar{u}, \bar{N}, \bar{\Lambda})$ through (4.1) and the trajectory equations (3.18) and (3.21). Integrating the trajectory equations subject to (4.13), we find

† For $o_v \gg 1$ large momenta dominate the integration, and most generally $f(k) \rightarrow \frac{2}{3}$ as $k \rightarrow \infty$.

through (4.1) that $\bar{S}(c_p, \bar{u}, \bar{N}, \lambda)$ may be written in the parametric form

$$\bar{S}(c_p, \bar{u}, \bar{L}, \bar{\Lambda}) = \left[\int^{\bar{u}} \frac{dx}{\beta(x)\nu(x)} (1 - \gamma(x)) - \frac{1}{\bar{\delta}_v} \exp\left(\int^{\bar{u}} \frac{dx}{\beta(x)\nu(x)} (2 - \nu(x)d)\right) \right] - p u^* F\left(\bar{\delta}_v \exp\left(\int^{\bar{u}} \frac{dx}{\beta(x)\nu(x)} (2 - \nu(x)d)\right), P\right) \tag{4.14}$$

where $p \equiv \bar{u}(\lambda)/u^* \in [0, 1]$ may be eliminated through the constraint equation

$$\exp\left(-\int^{\bar{u}} \frac{dx}{\beta(x)\nu(x)}\right) = \tilde{L} \left[1 + \bar{\delta}_v \exp\left(\int^{\bar{u}} \frac{dx}{\beta(x)\nu(x)} (2 - \nu(x)d)\right) \right]^{-1}. \tag{4.15}$$

Here the rescaled parameters $\bar{\delta}_v \sim \delta_v$, $\tilde{L} \sim \bar{L} \equiv (\bar{N}\bar{\Lambda}^2)$ are designed to absorb the non-universal effects of the crossover from θ temperature to critical conditions as the parameter p runs from zero to one. Explicitly, we have defined

$$\tilde{L} = \bar{L} \exp\left(-\int^{\bar{u}} \frac{dx}{\beta(x)\nu(x)}\right), \quad \bar{\delta}_v = \delta_v \exp\left(-\int^{\bar{u}} \frac{dx}{\beta(x)\nu(x)} (2 - \nu(x)d)\right), \tag{4.16}$$

and absorbed a further non-universal factor into \bar{S} , i.e.

$$\bar{S} \rightarrow \bar{S} - \int^{\bar{u}} \frac{dx}{\beta(x)\nu(x)} (1 - \gamma(x)).$$

The universal function $pF(x, p)$ which we have isolated in (4.14) summarises the effect of the loop corrections at the scale λ and is of the form

$$pF(x, p) = \frac{1}{2}p \left(1 - \frac{pu^*}{3}\right) (1+x)^{\epsilon/2} \int \frac{dk^d}{S_d} \left[\frac{1}{x} \ln\left(1 + \frac{xf(k)}{k^2} - \frac{f(k)}{k^2 + xf(k)}\right) \right] + (4/3\epsilon)xp(1 + \frac{1}{2}\epsilon) + 2 \text{ loops}, \tag{4.17}$$

where x is related to $\bar{\delta}_v$ through the trajectory relation

$$x = \bar{\delta}_v \exp\left(\int^{\bar{u}} \frac{dx}{\beta(x)\nu(x)} (2 - \nu(x)d)\right). \tag{4.18}$$

As usual, the scale of p is fixed by the non-trivial fixed point of the renormalisation group equations ($\beta(u^*) = 0$, $\beta'(u^*) > 0$; the Wilson-Fisher fixed point $u^* = \frac{3}{4}\epsilon(1 + \frac{5}{32}\epsilon + O(\epsilon^2))$).

At first sight the representation (4.14), (4.15), (4.17) is rather unwieldy; however, two special features we have incorporated lead to particularly simple expressions in the physical domains of dominant interest, i.e. dilute $o_v \ll 1$, semi-dilute $o_v \gg 1$ and θ temperature or free chain (all o_v) limits. We first observe that we may identify the point $p = 0$ with θ temperature conditions, for in this limit

$$\bar{S}(c_p, \bar{L}, \bar{\delta}_v, \bar{\Lambda}) = -\frac{1}{\bar{\delta}_v} + O(p) \tag{4.19}$$

where the small term of order p corresponds through (4.15) to the usual perturbative corrections to the θ temperature ($u < 1$) state. Explicitly integrating (4.15) for $p \ll 1$ (cf (3.7)), we obtain the expression

$$p = \tilde{L}^{\epsilon/2} (1 + \bar{\delta}_v)^{-\epsilon/2}$$

which reduces in the dilute region to $p \sim \tilde{L}^{\epsilon/2}$ and in the semi-dilute domain to

$p \sim (\tilde{L}/\tilde{\delta}_v)^{\varepsilon/2}$. Now conventionally the θ temperature regime is parametrised in terms of $z = uL^{\varepsilon/2}$ (dilute solutions $o_v \ll 1$) or $x = u(uLc_p)^{-\varepsilon/2}$ (semi-dilute domain $o_v \gg 1$) where phenomenologically the choice $u \sim 1 - \theta/T$ is made. Here θ is the Flory temperature. For our purposes, however, we find on examining the defining equations for \tilde{L} , $\tilde{\delta}_v$ that for $u \ll 1$

$$\begin{aligned} \tilde{L} &= u^{2/\varepsilon}L(1 + O(1 - \theta/T)) \\ \tilde{\delta}_v &= uL^2c_p(1 + O(1 - \theta/T)) \end{aligned} \quad (\Lambda = 1, N \equiv L)$$

whence within our representation $\bar{S}(\tilde{\delta}_v, \tilde{L})$ we naturally extend this phenomenology to the entire physical domain by defining

$$\tilde{L} \equiv g^{2/\varepsilon}L, \quad \tilde{\delta}_v \equiv gfL^2c_p, \tag{4.20}$$

where the functions $g(T), f(T)$ satisfy the constraints $g \sim 1 - \theta/T$ and $f \sim \text{constant}$ for $\theta \sim T$. Of course, to fit \bar{S} to experimental data we would take the simplest parametrisation

$$g = a(1 - \theta/T), \quad f = b,$$

where a, b are constants (independent of c_p, L, T), although strictly this choice lies outside the initial parametrisation in terms of u defined by the model (cf (4.16)). In contrast, for the limit $p \rightarrow 1$, we observe asymptotic scaling behaviour through either the scaling variable $\bar{z} \equiv \tilde{L}^{\varepsilon/2}$ or $\bar{x} \equiv (\tilde{\delta}_v/\tilde{L})^{-\varepsilon/2}$ depending on the magnitude of the overlap o_v . Linearising (4.15) about $p = 1$, we find as expected that p is driven to its fixed point through the relation

$$(1 - p)^{-1/\omega} = \tilde{L}/(1 + \tilde{\delta}_v(1 - p)^{(2 - \nu d)/\omega}) \tag{4.21}$$

which reduces to the familiar expressions $(1 - p) \sim \tilde{L}^{-\omega}, o_v \ll 1$, or $(1 - p) \sim (\tilde{\delta}_v/\tilde{L})^{\omega/(\nu d - 1)}, o_v \gg 1$, in the limits of dilute and semi-dilute physics. The form of \bar{S} is also more complicated, for $F(x, p)$ takes a simple form only in the limits $x \sim o_v \ll 1$ or $x \sim o_v \gg 1$. For dilute solutions we find (see (4.12) *et seq.*) by linearisation that \bar{S} is of the form

$$\bar{S} = \{[(1 - \gamma)/\omega] \ln(1 - p) + g(p)\}(1 + O(\tilde{\delta}_v)) \tag{4.22}$$

where $g(p) = -u^*pF(0, p)$ may be developed as a power series in p ($g(0) = 0$) and p may be determined through (4.21), i.e. $(1 - p) = \tilde{L}^{-\omega}[1 + O(\tilde{L}^{-\omega}, \tilde{\delta}_v)]$. On the other hand, in the semi-dilute regime $o_v \gg 1$ we find (see (4.12) *et seq.*) that \bar{S} reduces to the form

$$\bar{S} = \{[(1 - \gamma)/\omega] \ln(1 - p) - \frac{1}{\delta} \tilde{\delta}_v(1 - p)^{(2 - \nu d)/\omega} (1 + f(p))\}(1 + O(1/o_v)) \tag{4.23}$$

where $\frac{1}{\delta}f(p) = \lim_{x \rightarrow \infty} (pu^*/x)F(x, p)$ may again be developed as a power series in p ($f(0) = 0$). Here p is to be eliminated through the relation $(1 - p) = (\tilde{\delta}_v/\tilde{L})^{\omega/(1 - \nu d)}$ (4.21). As $p \rightarrow 1$ we therefore obtain the scaling behaviour

$$\bar{S} = [(\gamma - 1) \ln \bar{z}^{2/\varepsilon} + g(1)](1 + O(o_v, \bar{z}^{-2\omega/\varepsilon})), \tag{4.24}$$

$$\bar{S} = [(\gamma - 1) \ln \bar{x}^{(2/\varepsilon)[1/(\nu d - 1)]}$$

$$- \frac{1}{\delta} \tilde{\delta}_v \bar{x}^{(2/\varepsilon)[(\nu d - 2)/(\nu d - 1)]} (1 + f(1)) \left(1 + O\left(\frac{1}{\tilde{\delta}_v}, \bar{x}^{-(2\omega/\varepsilon)/(\nu d - 1)}\right) \right), \tag{4.25}$$

in terms of the crossover scaling variables $\bar{z} \equiv \tilde{L}^{\varepsilon/2}$ or $\bar{x} \equiv (\tilde{\delta}_v/\tilde{L})^{-\varepsilon/2}$ depending on the magnitude of the overlap o_v . In I the result (4.24) was discussed in some detail, so we

shall restrict our attention to the new result (4.25). sw have also discussed the asymptotic structure of S throughout the physical domain; however, their approach fails to generate the dominant logarithmic correction ($1 < \nu d < 2$) which must be distinguished from the usual exponentiated correction to scaling $\sim \bar{x}^{-(2/\epsilon)/(\nu d - 1)}$. Effectively the work of these authors is restricted to the evaluation of systematic corrections to the dilute problem for which the corrections to scaling are always controlled by $\bar{z} \equiv \tilde{L}^{\epsilon/2}$. The parameters $\tilde{L}, \tilde{\delta}_v$ will be a common feature of most thermodynamic functions (see I), so the reduced entropy \bar{S} will exhibit full universality; a considerable improvement on the work of sw.

Overall we see that the matching condition (4.13) and the absorption of the non-universal elements (4.16) lead to simple expressions in the domains of particular interest, despite the unwieldy form of (4.14) for general values of the overlap parameter o_v . To simplify the representation further we may employ the freedom in the matching condition by demanding that instead

$$1 = a\tilde{L}/[1 + abo_v(\lambda)] \tag{4.26}$$

where a, b independent of L, c_p can be freely chosen. Of course, order by order in ϵ , the representation ((4.14) *et seq.*) is invariant under this rescaling; however, there is a certain ambiguity in the continuation to $d = 3$ which we can exploit. For example, in the dilute regime $o_v \ll 1$ we find (see I) that to $O(\epsilon^2)$ the reduced entropy \bar{S} is of the form

$$\bar{S} = [(1 - \gamma)/\omega] \ln(1 - p) + g(p) + A(\ln a)p + O(\epsilon^3) \tag{4.27}$$

where p may be obtained from the relation

$$(1 - p)^{-\epsilon/2\omega} p = \bar{z} a^{\epsilon/2} \tag{4.28}$$

and $A(\epsilon)$ is independent of \bar{u}, c_p, \tilde{L} . From I we know that $g(p)$ is of the form

$$g(p) = -(pu^*/3\epsilon)(1 + \frac{1}{2}\epsilon)(1 + \frac{1}{8}pu^*(13 - 16\chi)) \tag{4.29}$$

where χ is the Euler number: $\chi = 0.5771 \dots$. Now we are perfectly free to choose ‘ a ’ such that it cancels the effect of $g(p)$ to give the representation

$$S = [(1 - \gamma)/\omega] \ln(1 - p) + O(\epsilon^3) \tag{4.30}$$

where p is now determined from the relation valid to

$$(1 - p)^{-\epsilon/2\omega} p = \bar{z} \exp[-u^*/6A(\epsilon)] \sim \bar{z}. \tag{4.31}$$

In I this choice was not made, for we wish to fix the scale consistently in both \bar{S} and the expansion factor $\alpha = \langle R^2 \rangle / \langle R^2 \rangle_\theta$. By the same mechanism we can also choose b such that $f(p) = 0$ to $O(\epsilon^3)$ in the semi-dilute limit $o_v \gg 1$, for the loop correction again only modifies the amplitude of the leading term (4.25).

Phenomenologically we are therefore led to consider the truncated representation

$$\bar{S} = [(1 - \gamma)/\omega] \ln(1 - p) - \frac{1}{6}\tilde{\delta}_v(1 - p)^{(2-\nu d)/\omega} \tag{4.32}$$

which describes the entire domain $\tilde{L}, \tilde{\delta}_v \geq 0$ correctly to $O(\epsilon)$ (see comments following (4.11)), whilst in the regions of dilute $o_v \ll 1$ or semi-dilute $o_v \gg 1$ physics of primary interest the error is only $O(\epsilon^3)$. In contrast to the exact representation (4.14), the two-parameter description is complete for (4.32), for we have effectively absorbed the remanent dependence on the polydispersity exhibited by $F(x, p)$ into a simple rescaling

of the variables $\tilde{\delta}$, \tilde{L} .[†] Readers familiar with the field theoretical approach to polymer physics will observe that we could in principle identify Goldstone type terms in $F(x, p)$ which are not controlled by the ε expansion (see sw); however, for \bar{S} the effects are weak and cannot be separated from the inherent ambiguities associated with the continuation of our results to $d = 3$.

5. Discussion

Using a series of direct renormalisation group equations, we have shown that the entropy $S(c_p, L, o_v, \{P(x)\})$ of a polymer solution with specified polydispersity $c_p(x) = c_p(1/L)P(x/L)$ may usefully be discussed in terms of a universal scaling function $\bar{S}(\tilde{\delta}_v, \tilde{L})$,

$$c_p \bar{S} = S - (AL + B)c_p + \left(\int dx c_p(x) \ln[c_p(x)] - c_p(x) \right), \quad (5.1)$$

which depending only weakly on the polydispersity may otherwise be parametrised completely in terms of a renormalised average link number \tilde{L} per polymer and overlap $\tilde{\delta}_v$. Here $A, B, \tilde{\delta}_v/o_v, \tilde{L}/L$ are strongly model-dependent (non-universal) and independent of c_p, L and therefore of little interest. Extending the approach of I we have developed a compact parametric description of \bar{S} valid for all $\tilde{L}, \tilde{\delta}_v \geq 0$ which describes the scaling properties of the entropy. In its most general form we may represent \bar{S} by the parametric equation

$$\begin{aligned} \bar{S} = & \left[\int^{pu^*} \frac{dx}{\beta(x)\nu(x)} (1 - \gamma(x)) - \frac{1}{\tilde{\delta}_v} \exp\left(\int^{pu^*} \frac{dx}{\beta(x)\nu(x)} (2 - \nu(x)d) \right) \right] \\ & - pu^* F\left(\tilde{\delta}_v \exp\left(\int^{pu^*} \frac{dx}{\beta(x)\nu(x)} (2 - \nu(x)d) \right), P \right) \end{aligned} \quad (5.2)$$

where $p \in [0, 1]$ is to be eliminated in terms of the renormalised polymer length $\tilde{L} \sim L$ and renormalised overlap $\tilde{\delta}_v \sim o_v = uL^2 c_p$ through the relation

$$\exp\left(- \int^{pu^*} \frac{dx}{\beta(x)} \right) = \tilde{L} \left[1 + \tilde{\delta}_v \exp\left(\int^{pu^*} \frac{dx}{\beta(x)\nu(x)} (2 - \nu(x)d) \right) \right]^{-1} \quad (5.3)$$

and the function $F(x, p)$ is a smooth function of x, p (see (4.17)) which can be constructed perturbatively in pu^* for the limits of dilute $o_v \ll 1$ or semi-dilute $o_v \gg 1$ physics which are of primary interest. Unfortunately the function $F(x, p)$, which in the context of a ε expansion is an $O(\varepsilon^2)$ effect, must in general be computed numerically. The functions $\beta(x), \nu(x), \gamma(x)$ are intimately related to the critical exponents as usual (BLZ):

$$\gamma = \gamma(u^*), \quad \nu = \nu(u^*), \quad \omega = \nu\beta'(u^*), \quad (5.4)$$

where u^* is the Wilson–Fisher fixed point of the renormalisation group equations; $u^* = \frac{3}{4}\varepsilon(1 + \frac{5}{32}\varepsilon + O(\varepsilon^2))$.

For practical purposes we require a parametrisation for S as a function of c_p, L and the reduced temperature $\tau = 1 - \theta/T$ where θ is the Flory temperature rather than the

[†] Strictly $F(x, p)$ will be modified by terms from the trajectory integrals evaluated to $O(\varepsilon^2)$ in the ε expansion; however, such modifications are unimportant to the general argument.

variables \tilde{L}, \tilde{o}_v employed above. We have therefore extended the usual phenomenological choice $u \sim 1 - \theta/T$ associated with the structure of the perturbative $u \ll 1$ domain by defining

$$\tilde{L}^{\varepsilon/2} = a(1 - \theta/T)L^{\varepsilon/2}, \quad \tilde{o}_v = ab(1 - \theta/T)L^2c_p, \tag{5.5}$$

where a, b independent of c_p, L, τ are to be obtained from experiment (see (4.19) *et seq.*).

Carrying through the programme outlined above to $O(\varepsilon^2)$ in the ε expansion, we obtain the following representation for a dimensionally regularised system:

$$\bar{S} = [(1 - \gamma)/\omega] \ln(1 - p) - \frac{1}{6}\tilde{o}_v(1 - p)^{(2-\nu d)/\omega} - pu^*F(o_v(1 - p)^{(2-\nu d)/\omega}, p). \tag{5.6}$$

The parameter p is to be eliminated in terms of \tilde{L}, \tilde{o}_v or c_p, L, τ (5.5) through the relation

$$(1 - p)^{-\varepsilon/2\omega}p = \tilde{L}^{\varepsilon/2}[1 + o_v(1 - p)^{(2-\nu d)/\omega}]^{-\varepsilon/2}. \tag{5.7}$$

Here γ, ν, ω are the critical exponents defined by (5.4) and the function F is given for arbitrary specified polydispersity by equation (4.17) where we can ignore the two-loop corrections, for through the trajectory equations (see I, and remarks following (4.11)) these terms are effectively of $O(\varepsilon^3)$ in the ε expansion. Through (5.1), (5.6), (5.7) we have a complete description of the scaling properties of the entropy S throughout the parameter space, $\tilde{L}, o_v \geq 0$ or $c_p, L, \tau \geq 0$ to order ε^2 in the ε expansion, although in general the function $F(x, p)$ must be evaluated numerically. Apparently only the exponential polydispersity $P(x) = e^{-x}$ is susceptible to analytic techniques, and we obtain for this case the expression

$$F(x, p) = (1/4\varepsilon)(1 - \frac{1}{3}pu^*)(1 + x)^{\varepsilon/2}\{(1/x)[1 - (1 + \frac{2}{3}x)^{2-\varepsilon/2}] \times (1 + \varepsilon/4) + \frac{4}{3}(1 + \frac{2}{3}x)^{1-\varepsilon/2}\} + (4/3\varepsilon)x(1 + \varepsilon/2). \tag{5.8}$$

By construction, however, in the domains of dilute $o_v \ll 1$ and semi-dilute $o_v \gg 1$ physics

$$\lim_{x \rightarrow 0} pu^*F(x, p) = g(p), \quad \lim_{x \rightarrow \infty} \frac{pu^*}{x}F(x, p) = \frac{1}{6}f(p), \tag{5.9}$$

where the functions $g(p), f(p)$ may be constructed perturbative in pu^* ($f(0), g(0) = 0$), whence for the limits of particular practical interest F only modifies the amplitude of the leading term. For dilute solutions we recover for $o_v \ll 1$ the results of I which describe the crossover from random flight to self-avoiding behaviour as the parameter $\bar{z} \sim uL^{\varepsilon/2}$ increases. In contrast, for $o_v \gg 1$ we obtain the new result

$$\bar{S} = [(1 - \gamma)/\omega] \ln(1 - p) - \frac{1}{6}\tilde{o}_v(1 - p)^{(2-\nu d)/\omega}(1 + f(p)), \tag{5.10}$$

$$(1 - p)^{\varepsilon/2\omega(1-\nu d)}p = (\tilde{L}/\tilde{o}_v)^{\varepsilon/2} \equiv \bar{x}^{\varepsilon/2},$$

which in the asymptotic critical regime $\bar{x} \gg 1$ reduces to the form (after rescaling)

$$\bar{S} = [(\gamma - 1)\ln \bar{x}^{(2/\varepsilon)(1/\nu d - 1)} - \frac{1}{6}\tilde{o}_v\bar{x}^{(2/\varepsilon)[(d\nu - 2)/(d\nu - 1)]}(1 + O(\bar{x}^{-2\omega/\varepsilon(\nu d - 1)})]. \tag{5.11}$$

We may usefully compare (5.11) with the asymptotic analysis of sw which is valid outside the dilute polymer regime $o_v \ll 1$. The approach of these authors is somewhat misleading, for in developing systematic corrections to the dilute expression, the corrections to scaling are controlled by \bar{z} rather than \bar{x} as required for semi-dilute physics, $o_v \gg 1$, so that in particular the dominant logarithmic correction $1 < \nu d < 2$ is not properly identified.

Of course the primary limitation of the above representation is that F will generally need to be computed numerically for each polydispersity $P(x)$; however, to $O(\varepsilon^2)$ at least the effect of F may be minimised by using the inherent ambiguity in any continuation to $d = 3$ dimensions. Choosing the scales \tilde{L} , \tilde{o}_v suitably, we may for arbitrary polydispersity effectively absorb F completely in the limits of dilute or semi-dilute physics, i.e.

$$pu^*F(0, p) \equiv f(p) \equiv O(\varepsilon^3), \quad pu^* \lim_{x \rightarrow \infty} \frac{F(x, p)}{x} \equiv g(p) \equiv O(\varepsilon^3). \quad (5.12)$$

Finally we therefore propose the truncated representation ($F = 0$)

$$\begin{aligned} \bar{S} &= [(1 - \gamma)/\omega] \ln(1 - p) - \frac{1}{6} \tilde{o}_v (1 - p)^{(2-\nu d)/\omega}, \\ (1 - p)^{-\varepsilon/2} p &= \tilde{L}^{\varepsilon/2} [1 + \tilde{o}_v (1 - p)^{(2-\nu d)/\omega}]^{-\varepsilon/2}, \end{aligned} \quad (5.13)$$

which exhibits full universality as a function of \tilde{L} , \tilde{o}_v as a phenomenological description of the entire parameter space \tilde{L} , $\tilde{o}_v \geq 0$ or c_p , L , $\tau \geq 0$. Valid to $O(\varepsilon)$ for all \tilde{L} , \tilde{o}_v and specifically to $O(\varepsilon^2)$ by construction in the limits $o_v \ll 1$ or $o_v \gg 1$, the expression (5.13) exhibits the 'correct' analytic structure in the various limits of particular interest, and therefore may realistically be extrapolated to give a description of the physics in $d = 3$ dimensions. In contrast to the exact (to $O(\varepsilon^2)$) representation (5.6), (5.7), the two-parameter \tilde{L} , \tilde{o}_v description is complete, for we have effectively absorbed the remanent dependence on the polydispersity exhibited by \bar{S} through F by a simple rescaling of these variables. Physically the expression (5.13) is very appealing, for we observe that as the 'overlap' o_v increases the structure will change qualitatively from dilute to semi-dilute physics when

$$L/(1 + g\langle R^2 \rangle^{d/2} c_p) \sim 1, \quad (5.14)$$

which locates the point at which extra (rather than intra) polymer contacts begin to dominate. Here we have taken the dilute critical form for the trajectory $p(c_p, L, o_v)$ and defined $g \equiv A_2(\langle R^2 \rangle)^{-d/2}$ (independent of L for $o_v \ll 1$) where A_2 is the second virial coefficient (or excluded volume) and $\langle R^2 \rangle \sim L^{2\nu}$ is the mean square size of a polymer.

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