A Semiempirical Crossover Analysis of Phase Separation in Polymer Solutions

Binny J. Cherayil

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560012, India

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ABSTRACT: The thermodynamic temperature variable appropriate for the description of the scaling behavior of chain dimensions R and density correlations ξ in polymer solutions in the critical through mean field limits is identified by setting up and solving the renormalization group (RG) equation for the system. The solution to the RG equation is obtained by expressing the set of renormalization constants that relate the bare parameters of the Hamiltonian to their renormalized counterparts as approximate resummed expansions in the coupling constants of the system. These expansions, which include unknown coefficients, are so defined that certain calculated asymptotic limits of R and ξ are reproduced. In satisfying these matching conditions, the unknown coefficients are determined self-consistently; they in turn fix the form of the relevant crossover variable. The predicted measure of distance to the critical temperature is found in this way to coincide with de Gennes's original proposal. This semiempirical approach to the calculation of asymptotic and crossover behavior in polymer solutions provides a more rigorous alternative to simple scaling prescriptions but eschews the elaborate mathematical machinery of field-theoretic methods.

1. Introduction

When an initially homogeneous polymer solution approaches the temperature T_c and composition ψ_c at which it separates into two distinct phases, the thermodynamics of the system becomes nonanalytic in the molecular weight of the chains M and the distance to the critical point $t \equiv |T - T_c|/T_c$.[1] Specifically, properties like the osmotic compressibility and the surface tension become powers of M and t. The exponents in these power laws are characteristically nonclassical, in the sense that they cannot be obtained from calculations at a mean field level of approximation and are not simply related to the engineering dimensions of the parameters that describe the state of the system. In this respect, the polymer solution behaves in much the same way as a simple liquid at its critical point, aside from the molecular weight dependence. Indeed, each is characterized by the same power laws in t for a given property P.

The anomalous thermodynamics of simple fluids (and other related systems) is known to originate in the large fluctuations of one or more thermodynamic variables (such as the density) and is now generally understood as being determined by the character of the equations that govern the evolution of the Hamiltonian of the system under the action of the twin operations of coarse-graining and rescaling that form the elements of the renormalization group (RG).[2] These evolution or RG trajectory equations either flow into a fixed point of the RG transformation, in which case the system is at a critical point, or flow toward but ultimately away from it, in which case the system is close to but not at the critical point. Furthermore, the eigenvalues of the matrix of coefficients of the linearized trajectory equations are related to the exponents that describe the singularities in the free energy of the system.

Among other things, RG calculations identify those combinations of thermodynamic variables (temperature, composition, chemical potential, etc.) in terms of which something analogous to a law of corresponding states can be derived for a given class of substances (simple fluids, binary mixtures, polymer solutions, etc.). When used to plot thermodynamic data from within a class, such “scaling variables” typically generate single universal curves.[3] From an experimental point of view, data reduction of this kind holds a special appeal, both for its ability to present complex information succinctly and for its utility as a marker of common underlying physical phenomena. The interpretation of experimental trends is often facilitated by knowing which combination of physical quantities is relevant, and which is not.

In this context, the proper scaling variables for polymer solutions in the critical and Θ point limits have proved to be somewhat elusive,[4] although several possibilities have been suggested. For instance, de Gennes has argued[5] that the natural measure of distance to the critical point is not the reduced temperature t but a temperature τ, defined by

$$\tau = \frac{t}{T_\Theta - T_c} \tag{1}$$

where T_Θ is the Θ temperature (defined operationally as the temperature at which the osmotic second virial coefficient of the solution vanishes). Since $T_\Theta - T_c \sim N^{-1/2}$ in Flory theory, N being a chain length, de Gennes has identified τ with the composite variable $tN^{1/2}$ (or equivalently with the variable $tM^{1/2}$, where M is a molecular weight). As discussed in ref 6, if the classical (mean field) behavior of a property P of the polymer solution is known, the variable τ can be used to predict the chain length exponents in the relation

$$P \sim N^{\zeta_a} t^a \tag{2}$$

that occurs near T_c. Although quite successful, the scheme is purely phenomenological and has so far not been rigorously justified. Efforts to do so have led to other candidate temperature scaling variables, including $tN^{0.31}$, $tN^{0.62}$, and $tN^{0.38}$ (refs 1, 6, and 7, respectively). Of these, the first has been obtained by a thermodynamic scaling analysis of the kind originally used in

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Widom's study of the near-critical region in simple fluid and magnetic systems,[8] while the second and third have been obtained by combining renormalization group calculations with certain known experimental results; they also rest on the finding, inferred from experiment, that the size of a chain R near T_c is given by

$$R \sim N^{0.46} \tag{3}$$

Any of these temperature fields when plotted against a scaled concentration field $\eta \equiv |\phi - \phi_c|/\phi_c$ (with $\phi_c \sim N^{-1/2}$ if τ is used, and $\phi_c \sim N^{-(0.38\pm0.03)}$ if the others are used) does about equally well in reducing the available experimental data to a single universal curve,[7] making it difficult to distinguish between them in any fundamental way. At the same time they are all derived from models that suffer from weaknesses of one kind or another. The present paper therefore attempts to offer a more general perspective on the question of scaling variables in the critical domain, with the specific intention of identifying the proper temperature variable. It also aims at laying the foundations for a thoroughgoing treatment of chain behavior in the crossover region between the critical and mean field limits.

These objectives will be met if the RG equation for a polymer−solvent system can be set up and solved for one or more solution properties P. The following section describes how this might be accomplished by identifying the set of "bare" parameters that characterize the Hamiltonian H_0 of the system at microscopic distances. No attempt is made to derive the form of this Hamiltonian from first principles; its existence is taken as given. The bare parameters are then related to a set of renormalized counterparts by requiring the invariance of the bare parameters to changes in a macroscopic phenomenological length scale L. This requirement leads to the renormalization group equation, which is derived in section 3 and subsequently solved approximately. Certain matching conditions are then invoked in section 4 to determine, finally, the sought for scaling variable.

2. Model Parameters

Near a critical point, it is often adequate to describe the thermodynamics of simple fluids by a Hamiltonian H_f of the following form:[2]

$$H_f = \int d\mathbf{r}\left[\frac{1}{2}(\nabla\phi(\mathbf{r}))^2 + t_o\phi(\mathbf{r})^2 + g_o\phi(\mathbf{r})^4\right] \tag{4}$$

where t_o is the reduced temperature and g_o is a measure of the strength of the interaction between local density fluctuations $\phi(\mathbf{r})$. The set of parameters t_o and g_o can be regarded as defining a particular point in the space of parameters that represent all possible realizations of fluid Hamiltonians, including those that are located at or in the vicinity of the critical point. Parameters from one region of this space are mapped into those of another through the renormalization group equation, whose solution determines the trajectory of the mapping and the scaling fields on which it depends.

As mentioned earlier, the temperature exponents for phase separation in polymer solutions are the same as those of simple fluids, so the set of parameters appropriate to the description of polymer and solvent together should include, on the one hand, a set of fluid parameters (t_o and g_o), and on the other, a set of parameters characteristic of polymers. The following additional parameters are therefore required to describe the Hamiltonian H_o of the polymer solution: a chain length N_o and an interaction energy V_o that measures the strength of the excluded volume effect. Below the Θ point (and above T_c) both attractive and repulsive components of the intermolecular potential are known to be important in determining chain properties. These components of the potential are usually described by two- and three-body interactions, respectively.[9] In the present context, the strength of these interactions may be characterized by the parameters ν_2^o and ν_3^o. The set of bare parameters t_o, g_o, ν_2^o, ν_3^o, and N_o are therefore expected to be sufficient to locate H_o in the parameter space whose basins of attraction characterize the critical properties of the polymer solution.

These parameters are all dimensioned quantities, and their dimensions can be expressed in terms of the length scale L that is characteristic of macroscopic distances. These dimensions are determined by the form of H_o, which (in units of the thermal energy k_BT) is itself dimensionless. Since H_o is not known (nor sought), we *assume* that the dimensions are given by

$$[N_o] = L,\quad [\nu_2^o] = L^{-\epsilon/2},\quad [\nu_3^o] = L^{1-\epsilon},\quad [t_o] = L^{-1},\quad [g_o] = L^{-\epsilon/2},\quad [\mathbf{r}] = L^{1/2} \tag{5}$$

where $\epsilon = 4 - d$ and d is the number of spatial dimensions. The dimensions of vectorial distances are included in this set for completeness. No rigorous justification of this assumption can be offered, other than to state that it is motivated by the known dimensions of these parameters when they are used to describe polymer and solvent separately within the context of field theory.[9,10]

3. Renormalization Group Equation

The passage from bare to renormalized parameters can be formally expressed as[10]

$$u_2^o = Z_2u_2 \tag{6a}$$

$$u_3^o = Z_3u_3 \tag{6b}$$

$$w_o = Z_ww \tag{6c}$$

$$t_o = Z_tt \tag{6d}$$

$$N_o = Z_N^{-1}N \tag{6e}$$

where u_2^o, u_3^o, and w_o are dimensionless analogues of ν_2^o, ν_3^o, and g_o defined by

$$u_2^o = \nu_2^oL^{\epsilon/2} \tag{7a}$$

$$u_3^o = \nu_3^oL^{-1+\epsilon} \tag{7b}$$

$$w_o = g_oL^{\epsilon/2} \tag{7c}$$

The coefficients Z_2, Z_3, Z_w, Z_t, and Z_N are renormalization constants, about which more will be said shortly.

In Wilson's original formulation of the method,[2] renormalization involves the stepwise elimination of short wavelength fluctuations of the order parameter from the Hamiltonian in such a way as to ensure the invariance of the form of the Hamiltonian to each step of the transformation. This is achieved by suitable redefinition of the parameters that enter into the

Hamiltonian. Alternatively, the method may be implemented within the framework of perturbation theory, using ϵ as a small expansion parameter. Here, renormalization involves redefining the parameters of the theory so as to eliminate, systematically, the singularities in ϵ that appear in the perturbation expansion as $d \to d_c$, where d_c is the value of d at which the strength of the interaction has the engineering dimensions L^o. The process is referred to as the minimal subtraction of poles. The relation between the original (bare) and redefined parameters is just that given by eq 6, with the renormalization constants defined, in general, as singular expansions in u_2, u_3, and w.

Within this alternative approach, eq 6 must be seen as being purely formal. Two- and three-body interactions have their own characteristic scale of energy, and hence their own distinct critical dimensions. No systematic application of the process of minimal subtraction of poles can eliminate the singularities associated with two different critical dimensions. Accordingly, there is no *practical* perturbative technique by which to determine renormalization constants when two- and three-body interactions are present in the problem (although there have been some interesting attempts.[11]) Nevertheless, such a scheme is possible *in principle*, so we shall regard eq 6 as meaningful and later introduce simplifications that will allow it to be used in calculations.

With these preliminaries, consider a property P_o of the polymer solution that is calculated in terms of bare parameters. (P_o will refer specifically either to the end-to-end distance of the chain R_o or the correlation length of the density fluctuations ξ_o.) Since P_o diverges when $\epsilon \to 0$, the physically relevant quantity is a function P that is free of such singularities and that depends only on the renormalized parameters and the length scale L. The relation between P_o and P is given by

$$P_o(u_2^o,u_3^o,N_o,t_o,\epsilon) = P(u_2,u_3,w,N,t,L) \tag{8}$$

(If P were a free energy, there would have been an additional term in eq 8 that eliminated from the specific heat a singular contribution that could not otherwise have been eliminated by multiplicative renormalization.[10])

Since P_o is independent of L, the following identity holds for constant values of the bare parameters:

$$L\frac{\partial P_o}{\partial L}\bigg|_B = 0 \tag{9}$$

where the subscript B denotes constancy of ν_2^o, ν_3^o, g_o, t_o, and N_o. If it is now assumed that Z_2, Z_3, and Z_N are functions only of u_2 and u_3 (since the singularities associated with chain properties are not expected to be altered by proximity to T_c) and that Z_w and Z_t are functions of u_2, u_3, and w, then by applying the chain rule of differentiation to eq 9, keeping in mind the definitions (6a)–(6e), one arrives at the renormalization group equation for the system:

$$\Big[L\frac{\partial}{\partial L} + \beta_2(u_2,u_3)\frac{\partial}{\partial u_2} + \beta_3(u_2,u_3)\frac{\partial}{\partial u_3} + \beta_w(u_2,u_3,w)\frac{\partial}{\partial w} + N\gamma_N(u_2,u_3)\frac{\partial}{\partial N} - t\gamma_t(u_2,u_3,w)\frac{\partial}{\partial t}\Big]P = 0 \tag{10}$$

where

$$\beta_2(u_2,u_3) = L\frac{\partial u_2}{\partial L} \tag{11a}$$

$$\beta_3(u_2,u_3) = L\frac{\partial u_3}{\partial L} \tag{11b}$$

$$\beta_w(u_2,u_3,w) = L\frac{\partial w}{\partial L} \tag{11c}$$

$$\gamma_N(u_2,u_3) = L\frac{\partial \ln Z_N}{\partial L} \tag{11d}$$

$$\gamma_t(u_2,u_3,w) = L\frac{\partial \ln Z_t}{\partial L} \tag{11e}$$

Equation 10 is now simplified by setting β_3 to 0, an approximation that is a variant of the decoupling method introduced by Douglas and Freed in their renormalization group analysis of diblock copolymers and polymer mixtures.[12] The approximation means that u_3 assumes its fixed point or scale invariant value and physically amounts to the requirement (crudely speaking) that repulsive ternary interactions be "fully developed". Such a condition is not expected to alter chain statistics substantially. But it also means that the pair interaction is now to be understood as an effective interaction, i.e., $u_2 = u_2(u_3^*)$, where u_3^* is the value of u_3 at which $L\ \partial u_3/\partial L = 0$. We shall denote this effective pair interaction as u, and the corresponding β function as β_u. We shall continue to use the same symbols for the other functions in eq 10, but they are understood to apply to the above decoupling limit.

In this limit, the solution to the RG equation can be obtained by the method of characteristics,[10] and it is given by

$$P(u,w,N,t,L) = P(u(l),w(l),N(l),t(l),L(l)) \tag{12}$$

where the scaling variables *u(l)*, *w(l)*, etc., on the right hand side of eq 12 are solutions of the following ordinary differential equations:

$$l\frac{dL(l)}{dl} = L(l) \qquad L(1) = L \tag{13a}$$

$$l\frac{du(l)}{dl} = \beta_u(u(l)) \qquad u(1) = u \tag{13b}$$

$$l\frac{dw(l)}{dl} = \beta_w(u(l),w(l)) \qquad w(1) = w \tag{13c}$$

$$l\frac{dN(l)}{dl} = N(l)\gamma_N(u(l)) \qquad N(1) = N \tag{13d}$$

$$l\frac{dt(l)}{dl} = -t(l)\gamma_t(u(l),w(l)) \qquad t(1) = t \tag{13e}$$

Although the renormalization constants needed to evaluate the functions β_u, β_w, etc., are not presently known, their general structure is, and this is sufficient to reach some broad conclusions.

The solution of eq 13a is immediate:

$$L(l) = Ll \tag{14}$$

As before, the zeroes of the functions β_u and β_w determine the fixed points u^* and w^* of the system. Quite generally, therefore, these functions can be written as

$$\beta_u(u) = \frac{\epsilon}{2}u\left(1 - \frac{u}{u^*} + O(u^2)\right) \tag{15}$$

$$\beta_w(u,w) = \frac{\epsilon}{2}\, w\left(1 - (1 + a)\,\frac{w}{w^*} + a\,\frac{u}{u^*} + O(u^2,w^2,uw)\right) \tag{16}$$

where a is an undetermined constant, which is 0 when the system contains no polymers. This form of the β functions ensures that $u = u^*$ and $w = w^*$ are indeed the solutions of $\beta_u(u^*) = \beta_w(u^*,w^*) = 0$. Equation 13b can now be solved:

$$u(l) = \frac{u\,l^{\epsilon/2}}{1 - \bar{u} + \bar{u}l^{\epsilon/2}} \tag{17}$$

where $\bar{u} = u/u^*$. To solve eq 13c, one first of all introduces an integrating factor, $h(l,a)$, defined as[12]

$$h(l,a) = \exp\left[-\frac{a\epsilon}{2u^*}\int_1^l \mathrm{d}x\,\frac{u(x)}{x}\right] = (1 - \bar{u} + \bar{u}l^{\epsilon/2})^{-a} \tag{18}$$

The change of variables

$$w(l) = \frac{1}{h(l,a)\,y(l)} \tag{19}$$

leads to an equation in y:

$$l\,\frac{\mathrm{d}y(l)}{\mathrm{d}l} + \frac{\epsilon}{2}\,y(l) = \frac{\epsilon}{2}\,\frac{(1 + a)\epsilon}{w^*h(l,a)} \tag{20}$$

along with the boundary condition $y(1) = 1/w$. Equation 20 can now be solved by inspection, so that finally

$$w(l) = \frac{w\,l^{\epsilon/2}}{h(l,a)\left[1 + \frac{\epsilon}{2}(1 + a)\bar{w}g(l,a)\right]} \tag{21}$$

where $\bar{w} = w/w^*$ and

$$g(l,a) \equiv \int_1^l \mathrm{d}x\,\frac{x^{\epsilon/2-1}}{h(x,a)} = \frac{2}{\epsilon\bar{u}(1 + a)}[(1 - \bar{u} + \bar{u}l^{\epsilon/2})^{1+a} - 1] \tag{22}$$

The functions γ_N and γ_t control the exponents ν_F and ν that near the critical point characterize the scaling of the end-to-end distance R and the correlation length ξ, respectively. In the absence of expressions for the renormalization constants $\{Z\}$ that would have determined these functions as expansions in u and w to a given order, one can instead use the following approximations, which are designed to reproduce the asymptotic critical limits of R and ξ

$$\gamma_N(u) = \alpha\bar{u} + O(u^2) \tag{23}$$

$$\gamma_t(u,w) = \chi\bar{w} + b\bar{u} + O(u^2,w^2,uw) \tag{24}$$

where $\alpha = (1 - 1/2\nu_F)$, $\chi = (1 - 1/2\nu)$, and b is a second unknown constant (which is likewise 0 in the absence of polymers; i.e., it is 0 for simple fluids). The constant ν_F is the exponent in the putative scaling relation $R \sim N^{\nu_F}$ that is expected to occur in the limit $t \to 0$, N finite; it is also unknown. The constant ν is the exponent that describes the divergence of the correlation length near the critical point. The approximations of eqs 23 and 24 are in the same spirit as those used by Chen et al.[13] in their study of the mean field to Ising crossover in simple fluids and allow $N(l)$ and $t(l)$ to be determined exactly. For instance, $N(l)$ is easily shown to be given by

$$N(l) = N(1 - \bar{u} + \bar{u}l^{\epsilon/2})^{2\alpha/\epsilon} \tag{25}$$

The calculation of $t(l)$ is less straightforward and requires some discussion; $t(l)$ is given explicitly by the integral

$$t(l) = t\,\exp\left[-\int_1^l \frac{\mathrm{d}x}{x}\,\gamma_t(u(x),w(x))\right] \tag{26}$$

which, using eqs 17 and 21, involves the evaluation of the following integrals:

$$I_1 = \frac{b}{u^*}\int_1^l \frac{\mathrm{d}x}{x}\,u(x) = \ln(1 - \bar{u} + \bar{u}l^{\epsilon/2})^{2b/\epsilon} \tag{27}$$

and

$$I_2 = \frac{\chi}{w^*}\int_1^l \frac{\mathrm{d}x}{x}\,w(x) \tag{28}$$

The change of variables

$$z = g(x,a) = \int_1^x \mathrm{d}y\,\frac{y^{\epsilon/2-1}}{h(y,a)} \tag{29}$$

allows I_2 to be obtained exactly:

$$I_2 = \ln\left[1 + \frac{\epsilon}{2}(1 + a)\bar{w}g(l,a)\right]^{2\chi/(1+a)\epsilon} \tag{30}$$

with $g(l,a)$ given by eq 22. Thus $t(l)$ becomes

$$t(l) = t\left[1 + \frac{\epsilon}{2}(1 + a)\bar{w}g(l,a)\right]^{-2\chi/(1+a)\epsilon}[1 - \bar{u} + \bar{u}l^{\epsilon/2}]^{-2b/\epsilon} \tag{31}$$

4. Asymptotic Limits

In this section we show how the asymptotic analysis of the general crossover solutions obtained above fixes the unknown coefficients b and ν_F in eq 24 and thereby determines the appropriate temperature scaling variable for the crossover between the critical and mean field limits.

The limit $l \to \infty$ corresponds to the approach to the fixed point of the renormalization group equation, as is evident from eqs 17 and 21 and the expression for $h(l\to\infty,a)$. Specifically,

$$u(l\to\infty) \to u^* \tag{32}$$

and

$$w(l\to\infty) \to w^* \tag{33}$$

Thus $\bar{u} \to 1$ and $\bar{w} \to 1$. Similarly, the corresponding expressions for $N(l)$ and $t(l)$ become

$$N(l\to\infty) \to N(\bar{u})^{2\alpha/\epsilon}l^{\alpha} \tag{34}$$

and

$$t(l\to\infty) \to t(\bar{w})^{-2\chi/(1+a)\epsilon}\,(\bar{u})^{-2\chi a/(1+a)\epsilon-2b/\epsilon}l^{-b-\chi} \tag{35}$$

With these limits in hand, the scaling relations for R and ξ can now be deduced. To begin with, consider ξ, which can be written quite generally as

$$\xi(l) = f(u(l),w(l),t(l),N(l),L(l)) \tag{36}$$

Here f is some unknown function of the indicated crossover variables. In the fixed point limit, using results derived earlier, eq 36 becomes

$$\xi = f(u^*,w^*,tl^{-b-\chi},Nl^{\alpha},Ll) \tag{37}$$

Scaling this relation by some length s, we obtain

$$\xi = s^{1/2}f\left(u^*,w^*,stl^{-b-\chi},\frac{N}{s}l^{\alpha},\frac{L}{s}l\right) \tag{38}$$

On choosing $s = t^{-1}l^{\chi+b}$, eq 38 reduces to

$$\xi = t^{-1/2}l^{(\chi+b)/2}f(u^*,w^*,1,tNl^{\alpha-b-\chi},tLl^{1-b-\chi}) \tag{39}$$

The further choice $l = (Lt)^{-1/(1-b-\chi)}$ leads to

$$\xi = t^{-1/2}(Lt)^{-(b+\chi)/2(1-b-\chi)}f\left(u^*,w^*,1,1,\frac{N}{L}(Lt)^{1/2\nu_F(1-b-\chi)}\right) \tag{40}$$

The implications of this relation for a simple fluid are easily determined. In this case, $b = 0$ and there is no u or N dependence in the original scaling function f of eq 36. Hence,

$$\xi \sim t^{-1/2-\chi/2(1-\chi)} \sim t^{-\nu} \tag{41}$$

as expected from the chosen form of γ_t. The exponent ν is known from experiments and RG calculations to have the value 0.63.

For solutions of polymers, the correlation length has been determined experimentally to scale as[1]

$$\xi \sim t^{-\nu}N^{\zeta_\nu} \tag{42}$$

The exponent ν is 0.63 as before, while ζ_ν has been estimated as 0.197[14] (although the value 0.28 has also been reported[15]). To recover this form from the general expression for ξ, we postulate that the function f of eq 40 varies as the power ζ_ν of its last argument in the limit $t \to 0$, N finite. This then reproduces the correct N dependence of ξ, but in order that it also reproduce the correct temperature dependence, we must have

$$\frac{1}{2} + \frac{1}{2}\left(\frac{b+\chi}{1-b-\chi}\right) - \frac{\zeta_\nu}{2\nu_F(1-b-\chi)} = \nu \tag{43}$$

which provides one equation in the two unknowns b and ν_F.

A second equation can be obtained by carrying out a similar asymptotic analysis of R. As before, we start with the crossover expression for this quantity

$$R = F(u(l),w(l),t(l),N(l),L(l)) \tag{44}$$

where F is another unknown function (different from f). The limit $l \to \infty$ applied to eq 44 yields

$$R = F(u^*,w^*,tl^{-b-\chi},Nl^{\alpha},Ll) \tag{45}$$

Dimensional analysis of this equation in terms of the length scale s leads to

$$R = s^{1/2}F\left(u^*,w^*,stl^{-b-\chi},\frac{N}{s}l^{\alpha},\frac{L}{s}l\right) \tag{46}$$

The choice $s = Nl^{\alpha}$ and subsequently $l = (N/L)^{1/(1-\alpha)}$ now produces

$$R = N^{1/2}\left(\frac{N}{L}\right)^{\alpha/2(1-\alpha)}F(u^*,w^*,tN(N/L)^{(\alpha-b-\chi)/(1-\alpha)}) \tag{47}$$

Near the critical point, with $t \to 0$ and N finite, the function $F(x)$ is assumed to vary as $F = 1 + O(x)$, so that R is given by

$$R \sim N^{\nu_F} \tag{48}$$

As in the case of the correlation length, this is the expected result, since γ_N was chosen so that R reproduced its postulated scaling form near T_c.

Asymptotically close to the Θ temperature T_Θ, with $N \to \infty$, $t \to 0$, experiments and theory suggest that[16]

$$R \sim \tau_\Theta^{-1/3}N^{1/3} \tag{49}$$

where $\tau_\Theta \equiv 1 - T/T_\Theta$, which equals t to within additive corrections of order $N^{-1/2}$. To recover the Θ point limit from eq 47, the function F must behave as $F(x) \sim x^{-1/3}$; if this is assumed, then in order for the resulting N dependence of R to match the N dependence of eq 49, the following relation must hold

$$\nu_F - \frac{2}{3}\nu_F(1-b-\chi) = \frac{1}{3} \tag{50}$$

which provides a second equation in b and ν_F, These unknowns are now readily determined to be

$$\nu_F = \frac{\nu-\zeta_\nu}{3\nu-1} \tag{51}$$

$$b = \frac{\zeta_\nu}{2\nu\nu_F} \tag{52}$$

5. Discussion

Substituting the experimental values $\nu = 0.63$ and $\zeta_\nu = 0.197$ into eqs 51 and 52, one finds that $b = 0.32$ and $\nu_F = 0.49$. Close to T_c, therefore, the average radial dimensions of the chains in solution are predicted to be essentially equal to their unperturbed dimensions. This suggests that the scaling relation of (3), deduced from experiment, may well reflect only the incomplete approach to the true asymptotic critical domain.

Sanchez[1] argues from an analysis of the available experimental data that the exponent ζ_ν should actually be 0.19, which is numerically very close to de Gennes's original proposal of 0.185.[5] Interestingly, if this latter value is used in eq 51 (with $\nu = 0.63$ as before), ν_F is found to be *exactly* 1/2 and $b = 0.29$. These values, if substituted into eq 47, establish that the scaling variable that appears in the universal scaling function F is $tN^{1/2}$; $tN^{1/2}$ should therefore be the appropriate variable for the description of the crossover from the critical to mean field limits. This contrasts with Sanchez's suggestion that the appropriate scaling variable is $tN^{\zeta_\nu/\nu} = tN^{0.31}$.

As alluded to earlier, there have been reports[15] that $\zeta_\nu = 0.28$. This would imply from our equations that ν_F

$= 0.41$, a result seen in neither experiment nor theory. We tend to believe that the estimate $\zeta_\nu = 0.28$ is in error.

The foregoing results are only meant to be suggestive; of perhaps greater import is the methodology of the semiempirical renormalization group approach itself, which offers a relatively simple and convenient route to the study of various universal aspects of critical phenomena in polymer solutions. It avoids the elaborate mathematical machinery of field-theoretic perturbation calculations yet goes beyond simple scaling prescriptions. Moreover, it makes no appeal to such extraneous considerations as the dependence of $T_\Theta - T_c$ on N, which is central to de Gennes's treatment of crossover.

The method seems to be well-suited to the calculation of the generalized scaling expression for the free energy of the polymer solution in the regime of large order parameter fluctuations. If a matching procedure is introduced to extend this expression to the regime of small-order parameter fluctuations, the complete thermodynamics of the solution in the mean field through critical limits can, potentially, be determined. This would prove useful in efforts to derive equations of state for polymeric systems. Similar phenomenological methods are expected to be applicable to the study of critical dynamics in solutions of polymers. Here alternatives to the field theoretic and naive scaling approaches would be especially valuable.

References and Notes

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