Chain-length distribution in a model of equilibrium polymerization

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Using renormalization-group techniques, I derive a general scaling form of the chain-length distribution for the equilibrium-polymerization model of des Cloizeaux [J. Phys. (Paris) **36**, 281 (1975)]. The result allows more freedom than was assumed in some previous work. This disproves arguments suggesting that in semidilute polymer solutions there exists a phase related to some anomaly of the zero-component field theory. The scaling function of the chain-length distribution is calculated to first order in ϵ. It varies with the overlap of the chains and, in general, differs somewhat from a Schultz distribution. No anomaly related to the semidilute limit is found. Some rather nontrivial aspects of the result are well understood in terms of de Gennes "blob" concept.

I. MOTIVATION

As is well known, the large-scale behavior of sufficiently dilute solutions of long flexible molecules can be explained[1] by use of renormalization-group techniques as applied to simplified models. These models ignore all chemical microstructure except for chain connectedness and excluded volume, i.e., they include a local repulsive pseudopotential among chain segments. Typical solutions are polydisperse, which means that they contain a smooth distribution of chain lengths n. We may describe such a system by a grand-canonical ensemble of model chains, characterized by a chemical potential $\mu(n)$ conjugate to the concentration $c_p(n)$ of chains of length n. The special form

$$\mu(n)=\mu_0+n\mu_1 \tag{1}$$

defines an ensemble which is in chemical equilibrium with respect to a fictitious polymerization reaction of breaking and recombining chains. This "equilibrium-polymerization model" of des Cloizeaux,[2] shows some distinguishing simplification: Its perturbation expansion order by order is identical to that of the standard Landau-Ginzburg-Wilson (LDW) spin model,[3] in the formal limit of vanishing spin dimensionality. Many results of interest therefore can be obtained by simply translating from the "magnetic" spin formulation to polymer language.

Some years ago it has been claimed[4] that the equilibrium ensemble shows some instability occurring for a system of strongly interpenetrating chains. To elucidate the issue it is appropriate to recall some basic results[2,5] relating the polymer system to LGW theory.

The magnetic field h_0 of the LGW model is related to the fugacity of polymer chains:

$$h_0^2 \sim e^{\mu_0+\mu_1} . \tag{2}$$

The critical temperature T_c corresponds to the chemical potential per segment μ_{1c} of an infinitely long chain, and the temperature T and the segment chemical potential μ_1 are related by

$$T-T_c \sim \mu_{1c}-\mu_1 . \tag{3}$$

The total concentration of chains

$$c_p=\sum_n c_p(n) \tag{4}$$

obeys

$$c_p \sim h_0 M_0 , \tag{5}$$

where M_0 is the magnetization per spin of the LGW model. Finally the segment concentration

$$c_l=\sum_n n c_p(n) \tag{6}$$

to the lowest-order (tree) approximation is found as

$$c_l \sim M_0^2 , \tag{7}$$

resulting in an expression for the (number-averaged) chain length

$$N=\frac{c_l}{c_p} \sim \frac{M_0}{h_0} . \tag{8}$$

In all these relations I ignored prefactors, which are not important in the sequel.

It follows from Eq. (8) that the limit of infinitely long chains corresponds to the magnetization curve. (See Fig. 1.) We may distinguish two limiting cases. Starting at $T>T_c$ and approaching T_c along a path infinitesimally close to the axis $h_0=0$, we deal with an extremely dilute system $c_l \sim 0 \sim c_p$ of isolated chains. On the other hand, approaching the magnetization curve along a path $M_0=\text{const}>0$, we are concerned with a system of finite segment concentration $c_l>0$. For N large enough, the chains then must interpenetrate strongly, the degree of interpenetration being measured by the "overlap"

$$s \sim c_p R_G^d . \tag{9}$$

Here R_G is the radius of gyration of an isolated chain and d denotes the spatial dimension of the system. With the

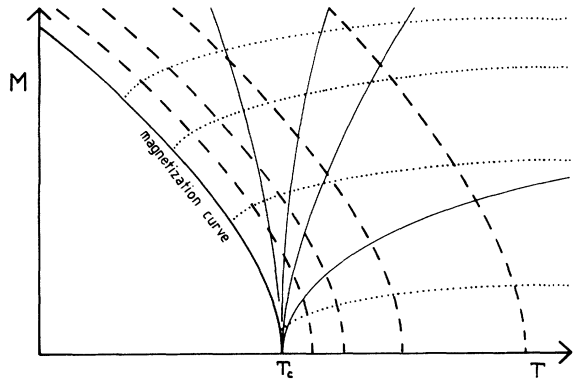

FIG. 1. Phase diagram illustrating the mapping from magnetic to polymer variables. Dashed or dotted lines are lines of constant chain length, or segment concentration, respectively. Thin lines correspond to constant overlap. Chain length and overlap increase from right to left, both being infinite on the magnetization curve. Segment concentration increases from bottom to top.

well known relation $R_G \sim N^{\nu}$ ($\nu \approx 0.6$ for $d=3$), which holds under good solvent conditions, we find

$$s \sim c_p N^{\nu d} = c_l N^{\nu d - 1} \to \infty \ , \tag{10}$$

as $N \to \infty$, with c_l fixed: For large N, the overlap gets large also for small segment concentration. This is the so-called "semidilute" regime, which corresponds to the neighborhood of the magnetization curve close to T_c. I want to stress that in all these considerations I assume that the thermodynamic limit is taken first, the limit $h_0 \to 0$ being taken afterwards. Thus I do not consider finite-size problems. The number of chains in the system is infinite, each chain occupying a vanishing fraction of the total volume.

So far I have presented the conventional picture of the equilibrium-polymerization ensemble. This picture has been challenged[4] by a claim that some singularity is found for a *finite* value of the overlap, corresponding to *nonvanishing* h_0. It was suggested that this singularity signals the transition from an overlapping phase as described above to another, so-called "dense" phase, found in a parameter region corresponding to some neighborhood of the magnetization curve. The distinguishing feature of this latter phase is presumably the existence of an infinitely long chain *which fills a finite fraction of the volume*. This claim, if true, would be of some interest from a practical point of view, since the model has been used to explain features of equilibrium polymerization and of macromolecules still able to undergo polymerization reactions. (See Ref. 6 and references given therein.) It is even more interesting from a principle point of view, postulating a most subtle instability of field theory in the limit of vanishing spin dimensionality. Since such formal limits are used in a variety of problems like physics of disordered media or defect lines in liquid crystals, this claim clearly deserves some detailed analysis.

Now, for dimensions $d > 2$ the arguments originally given for the existence of a dense phase have been disproven.[7,8] Neither the free energy nor the scattering functions show any anomaly. All quantities vary smoothly in all the parameter regions ranging from the limit of isolated chains to the semidilute limit of infinite overlap or, equivalently, from $T > T_c, h_0 = M_0 = 0$ to $T < T_c, h_0 = 0, M_0 \neq 0$.

It should be noted that special effects occur for $d=2$. This could have been foreseen, since for $d=2$ a non-self-avoiding random walk fills the volume. Indeed, it is found[9] that also for self-avoiding chains there is a transition to a situation where a single chain fills a finite part of the volume. This dense phase, however, occurs for $h_0 = 0$ on the magnetization curve. Even for $d=2$ this phenomenon therefore is not related to the instability postulated in Ref. 4, which occurs for $h_0 > 0$.

Recently the controversy has been raised to the next higher level by the claim[10] that the transition to a dense phase can be seen in the chain-length distribution. A scaling ansatz for $c_p(n)$ has been used to argue that an infinitely long chain indeed is created spontaneously above a certain degree of interpenetration. Recent Monte Carlo simulations,[11] however, show no sign of that instability. Using the scaling ansatz of Ref. 10, the authors interpret this as indicating a special value of some exponent occurring in the scaling ansatz. Furthermore, Wheeler and Petschek[12] recently derived a rigorous bound on the chain-length distribution, which, for finite chain fugacity, i.e., finite h_0, excludes the possibility of an infinitely long chain.

There still remains , however, the question whether the scaling ansatz used in Refs. 10 and 11 is correct to begin with. The relevant part of that ansatz is best formulated in terms of the reduced-chain-length distribution $p(y)$, which is defined via the equation

$$c_p(n) = \frac{c_p}{N} p\left[\frac{n}{N}\right], \quad y = \frac{n}{N} \ . \tag{11}$$

According to Ref. 10 [compare Eq. (7)], the ansatz

$$p(y) = \text{const} \times y^{\gamma - 1} \exp(-\text{const} \times y) \tag{12}$$

holds independently of the overlap. Here $\gamma > 1$ is some standard critical exponent. The form (12) is known to be rigorously correct in the limit of isolated chains. On the other hand, it is also known that for the equilibrium ensemble $p(y)$ depends on the overlap. If in the limit of large overlap $p(y)$ would reduce to a simple exponential

$$p(y) \sim e^{-y}, \quad \text{as } s \to \infty \ , \tag{13}$$

then the argument of Ref. 10 would break down. Indeed, this is the behavior expected according to more conventional ideas. Its physical basis[13] is "screening." An isolated self-repelling chain swells in order to diminish its interaction energy, the swelling reducing the average segment density within the coil. Now consider a semidilute solution and imagine the chains divided into subchains of length $n_B \ll n$, each subchain being swollen due to the excluded-volume interaction. The average density due to the segments forming a subchain scales as $n_B / n_B^{\nu d}$. A

critical value n_B^* of n_B is reached if this density is of the order of the total segment density in the solution:

$$n_B^{*1-\nu d} \sim c_l \ . \tag{14}$$

A decomposition into swollen subchains of size $n_B > n_B^*$ is not favorable, since we lose entropy without gaining energy by decreasing the locally measured total segment density. Beyond subchain size n_B^* the excluded volume interaction thus is ineffective or "screened." In semidilute solution conventional theory therefore envisages the chain as a sequence of swollen subchains, so called "blobs", the interaction among blobs being negligible. For an equilibrium ensemble of noninteracting chains the reduced-chain-length distribution follows Eq. (13), however.

These considerations lead to the following prediction for the shape of $p(y)$ in the semidilute regime. (See Fig. 2.) Chains small compared to the size n_B^* of a blob are fully swollen, which leads to a distribution consistent with Eq. (12):

$$p(y) \sim y^{\gamma-1} \quad \text{for } y \ll \frac{n_B^*}{N} = y^* \ll 1 \ . \tag{15}$$

Indeed, these chains are so small that they slip through the holes[14] of the transient network made up from the chains of average size, without being seriously perturbed by the interchain interaction. They thus essentially behave as isolated chains. For $y \sim y^*$ the behavior (15) crosses over to the simple exponential (13), which is fully developed for $y \sim 1 \gg y^*$. For extremely long chains in the ensemble we expect to see a third regime[13] not yet addressed above: For finite N the screening of the blob interaction is not complete, but there survives a small repulsion of strength $\sim 1/N$. For extremely long chains this repulsion again swells the coils, leading to a behavior of the form (12), with some rescaled variable y. For $d=3$ the crossover to this new behavior is expected to occur around $n \sim N^2 \gg N$. It should, however, be stressed that for long chains in the semidilute regime the bulk of the distribution $p(y)$ follows Eq. (13).

This argument is heuristic and certainly not capable of identifying a possible singularity. I therefore here use the renormalization group to derive the general scaling form of $c_p(n)$ or $p(y)$, equivalently, explicitly showing that the ansatz (12) is quite restricted and cannot be justified on general grounds. I then use renormalized perturbation theory and ϵ expansion to work out an approximate form of $p(y)$. Even though the ϵ expansion is known to be only asymptotic, its higher order behavior is well controlled,[15] and low order results typically compare very well to experiment.[16] Furthermore, a minimal requirement for any scaling ansatz is its consistency with the ϵ expansion. It is found that the ansatz (12) for general overlap is inconsistent with the ϵ expansion, and indeed in the limit $s \to \infty$ the result reduces to Eq. (13). The ϵ expansion thus supports the conventional picture. Furthermore, for s large, but not infinite, the ϵ expansion also is consistent with the discussion of the extreme tails as $y \to 0$ or as $y \to \infty$, as given above.

The scenario of Ref. 10 goes beyond the spin-polymer analogy, in that $p(y)$ cannot be calculated from the LGW model in its standard form. However, using the general formalism of Ref. 17, we easily can calculate $p(y)$ in the loop expansion. I here present a detailed discussion of the results. The calculation makes extensive use of results given in Refs. 8 and 17, which are not rederived here. Equations taken from these references will be referred to as Eqs. (I. . .) (Ref. 8) or Eqs. (II. . .),[17] respectively.

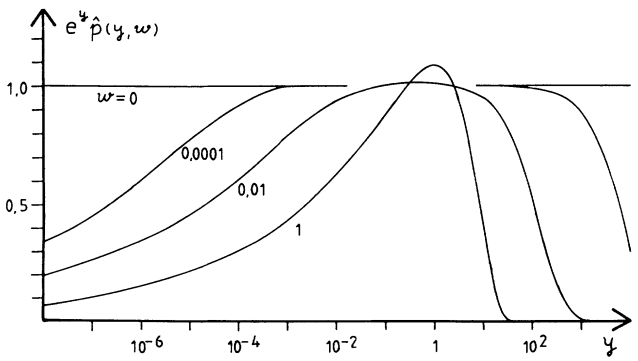

FIG. 2. Semilogarithmic plot of $e^y \hat{p}(y,w)$ for $w=0$, 10^{-4}, 10^{-2}, 1.

II. SCALING THEORY OF THE CHAIN-LENGTH DISTRIBUTION

Equations (II 3.13) and (II 3.15) establish the general expression

$$c_p(n) = \kappa^d S_\kappa \oint \frac{dt_1}{2\pi i} e^{n_R t_1} \frac{M(t_1)}{h(t_1)} \oint \frac{dt'}{4\pi i} e^{-n_R t'} h^2(t') \ , \tag{16}$$

where the following notation is used.

κ: momentum scale of the renormalized theory.

S_κ: renormalization factor of the chain length,

$$n_R = S_\kappa n \ . \tag{17}$$

[For the relation of S_κ to the renormalization factors of the LGW model, see Eq. (II 3.3).]

$h(t)$: renormalized Laplace transform with respect to n of $\exp[\mu(n)]$:

$$M(t) = \frac{2\pi i}{\kappa^d \Omega} \frac{\delta}{\delta h(t)} \ln Z \ ,$$

where Z is the grand partition function and Ω denotes the volume of the system.

For the equilibrium ensemble (1) $h^2(t')$ takes the form

$$h^2(t') = \frac{h^2}{t - t'} \ , \tag{18}$$

where h or t are the renormalized magnetic field or the renormalized reduced temperature of the equivalent LGW model, respectively, both made dimensionless by extracting appropriate powers of κ. They are related to

$\mu(n)$ by

$$h^2=Z\kappa^{-d-2}2(4\pi)^{-d/2}l^{-d-2}e^{\mu_0+\mu_1} \tag{19}$$

[compare Eq. (I 2.16)], or

$$t=(\mu_{1c}-\mu_1)S_\kappa^{-1} . \tag{20}$$

Here l is the microscopic length scale of the unrenormalized model (giving essentially the size of the segments), Z denotes the field renormalization factor, and μ_{1c} is the chemical potential per segment of an infinitely long chain.

With the form (18) the second contour integral in Eq. (16) is easily evaluated. [I have to apologize for an error in Fig. 1(a) of Ref. 17: The arrows giving the direction of integration should be inverted.] The result can be written in the form

$$c_p(n)=\kappa^d S_\kappa \frac{h^2}{2} e^{-n_R t} \oint \frac{dt_1}{2\pi i} e^{n_R t_1} \tilde{G}(t_1,t,h^2,g) , \tag{21}$$

where $\tilde{G}(\cdots)=M(t_1)/h(t_1)$, and g denotes the renormalized coupling constant. For the equilibrium model under consideration $\tilde{G}(\cdots)$ is given by the set of all diagrams contributing to the renormalized dimensionless transverse spin correlation function in external field h and at momentum zero, with the only modification that the open transverse line has its own "temperature" variable t_1, different from the temperature t of all other lines. Of course closed propagator loops are eliminated by taking the limit of zero spin dimensionality.

To write down the general nonlinear scaling law we introduce the scaling parameter

$$\lambda=\kappa l \tag{22}$$

and we recall that all renormalization factors and renormalized variables are functions of λ, the functional dependence being given by the renormalization-group equations. We thus find the nonlinear scaling law

$$l^d c_p(n)=\lambda^d S_\kappa(\lambda)\frac{h^2(\lambda)}{2}\mathcal{C}(n_R(\lambda),t(\lambda),h^2(\lambda),g(\lambda)) , \tag{23}$$

where the definition of the scaling function $\mathcal{C}(\cdots)$ is obvious from a comparison to Eq. (21).

The "excluded volume limit" $l^d c_l \to 0$, $N\to\infty$, $s=l^d c_l N^{\nu d}$ arbitrary, is governed by the fixed point $g(\lambda)\equiv g^*$ of the renormalization group. At g^*, the λ dependence of all quantities is known rigorously:

$$\begin{aligned} &S_\kappa(\lambda)\sim\lambda^{1/\nu} , \\ &n_R(\lambda)=\lambda^{1/\nu}\hat{n} , \\ &t(\lambda)=\lambda^{-1/\nu}\hat{t} , \\ &h^2(\lambda)=\lambda^{-d-2+\eta}\hat{h}^2 . \end{aligned} \tag{24}$$

Here ν or η are standard critical exponents, and the quantities $\hat{n}$, etc., are proportional to their unrenormalized counterparts, with nonuniversal but constant proportionality factors. Using these equations and fixing λ by

$$n_R(\lambda)=1 \tag{25}$$

we find the scaling law

$$l^d c_p(n)=\text{const}\times\frac{\hat{h}^2}{2}\hat{n}^{\gamma-1}\mathcal{C}^*(\hat{n}\hat{t},\hat{h}^2\hat{n}^{\nu d+\gamma}) , \tag{26}$$

where $\gamma=\nu(2-\eta)$. Equation (26) can be written in the equivalent form

$$l^d c_p(n)=\text{const}\times\frac{\hat{h}^2}{2}\hat{n}^{\gamma-1}\mathcal{C}^{**}(\hat{n}\hat{h}^{2/(\nu d+\gamma)},\hat{t}\hat{h}^{-2/(\nu d+\gamma)}) . \tag{27}$$

I should stress that Eq. (23) is a rigorous result of the renormalization group, holding for all λ, up to corrections of order $\sim\lambda^2$. To extract the scaling form (26) or (27) we therefore can use the simple condition $n_R(\lambda)=1$, even though this choice is not appropriate for the actual calculation of the scaling functions $\mathcal{C}^*$ or $\mathcal{C}^{**}$ in all the parameter regions of interest. In the next section I will replace condition (25) by the more complicated choice (30), which incorporates the screening. It is easily checked that these conditions are completely equivalent as far as the scaling form is concerned.

Starting from Eq. (27), it is not hard to derive the scaling form of the reduced-chain-length distribution. The calculation being straightforward but lengthy, I relegate it to the Appendix. I find the simple result

$$p(y)=\bar{p}(y,\hat{s}) , \tag{28}$$

where

$$\hat{s}=\text{const}\times s=\hat{s}(\hat{t}\hat{h}^{-2/(\nu d+\gamma)}) . \tag{29}$$

This shows that $p(y)$ in general does depend on the overlap. I want to stress that $\bar{p}(y,\hat{s})$ is a universal function, independent of the technical details of the renormalization scheme. Only the scale of $\hat{s}$ is not universal.

Let us now consider the scaling ansatz of Ref. 10 in the light of the results presented here. Equation (27) has the same structure as Eq. (5) of Ref. 10, except that in this work a simple exponential form is postulated for the $\hat{n}$ dependence of $\mathcal{C}^{**}$. In terms of $p(y)$ this leads to the form (12), independent of $\hat{s}$. It should be clear that this ansatz is consistent with our result, but the general scaling form established here is much richer than the postulate of Ref. 10. General arguments restricting the form of the scaling functions $\mathcal{C}^{**}$ or $\bar{p}$ are lacking, except for the rigorous bound established in Ref. 12 and the qualitative arguments based on the blob picture. I therefore proceed to calculate $\bar{p}$ in the loop expansion.

III. ANALYSIS OF THE REDUCED-CHAIN-LENGTH DISTRIBUTION

I use the formalism of Ref. 8, fixing the scaling parameter λ by relation (I 4.15):

$$1=\frac{1}{N_R}+2gc_{lR} \ . \tag{30}$$

Here N_R is the renormalized average chain length

$$N_R=S_\kappa N \ , \tag{31}$$

and c_{lR} is the renormalized segment concentration

$$c_{lR}=\kappa^{-d}S_\kappa c_l \ . \tag{32}$$

The rationale behind the choice (30) is to take the length scale $\kappa^{-1}=l/\lambda$ [cf. Eq. (22)] of the renormalized theory to be of the order of the density correlation length ξ_d in the solution. Indeed, the right-hand side of Eq. (30) equals $\xi_d^2\kappa^2/d$ to lowest order approximation. In terms of the blob picture ξ_d can be identified with the size of the blob, so that each renormalized segment effectively represents one blob, and N_R gives the number of blobs in an average chain. The number of segments per blob is N/N_R, and n_R gives the number of blobs in the special chain considered, this interpretation following from Eqs. (17) and (31):

$$n_R=n/(N/N_R) \ . \tag{33}$$

Since the crossover from $g=0$ to $g=g^*$ is of no interest for the problem at hand, I restrict the analysis to the excluded-volume fixed point g^*. Introducing the notation $w=1/N_R$ we can use Eq. (30) to express c_{lR} and

$$c_{pR}=\frac{c_{lR}}{n_R}=\kappa^{-d}c_p \tag{34}$$

in terms of the scaling variable w, which is related to the overlap s by Eq. (I 4.17):

$$(1-w)w^{1-\nu d}=\text{const}\,\hat{s} \ . \tag{35}$$

This relation easily is derived from Eqs. (24) and (34). The dilute limit $\hat{s}\to 0$ is attained for $w\to 1$, whereas the semidilute limit $\hat{s}\to\infty$ is reached for $w\to 0$. The reduced-chain-length distribution naturally is found as function of the scaling variables $y=n_R/N_R=n/N$ and w, a presentation which by virtue of Eq. (35) is equivalent to the form (28),

$$\bar{p}(y,\hat{s})=\hat{p}(y,w(\hat{s})) \ . \tag{36}$$

It is a standard calculation to determine $\hat{p}(y,w)$ to first order in $\epsilon=4-d$. I sketch the essential steps in the Appendix. I find

$$\hat{p}(y,w)=\exp\left\{-y\left[1-\frac{\epsilon}{8}\frac{w\ln w}{1-w}\right]+\frac{\epsilon}{8}\left[(w-2)\frac{w\ln w}{1-w}+w\gamma_{\text{Eu}}+w\ln y-(1-w)e^{y/w}E_1\left[\frac{y}{w}\right]\right]+O(\epsilon^2)\right\} , \tag{37}$$

where γ_{Eu} denotes Euler's number, and $E_1(x)$ is the exponential integral

$$E_1(x)=\int_x^\infty ds\frac{e^{-s}}{s} \ . \tag{38}$$

Before analyzing this result in various limits I check the normalization. By construction $\hat{p}(y,w)$ must obey the relation

$$\int_0^\infty dy\,\hat{p}(y,w)=1=\int_0^\infty dy\,y\,\hat{p}(y,w) \ . \tag{39}$$

This most economically is checked by calculating the Laplace transform

$$\begin{aligned}\tilde{p}(x,w)&=\int_0^\infty dy\,e^{-xy}\hat{p}(y,w)\\&=\frac{1}{1+x}\left[1-\frac{\epsilon}{8}w\left[\ln(1+x)+\frac{2-w}{1-w}\ln w-\frac{\ln w}{(1+x)(1-w)}\right]\right]+\frac{\epsilon}{8}w(1-w)\frac{\ln[w(1+x)]}{1-w(1+x)}+O(\epsilon^2) \ .\end{aligned} \tag{40}$$

Expanding with respect to x, I find

$$\tilde{p}(x,w)=1-x+\frac{\tilde{p}\,''}{2}x^2+\frac{\tilde{p}\,'''}{6}x^3+O(x^4) \ , \tag{41}$$

where

$$\tilde{p}\,''=2+\frac{\epsilon}{4}\frac{w}{1-w}\left[1+\frac{\ln w}{1-w}\right]+O(\epsilon^2) \ , \tag{42a}$$

$$\tilde{p}\,'''=-6-\frac{3}{8}\epsilon\frac{w}{(1-w)^2}\left[3-5w+(4-6w)\frac{\ln w}{1-w}\right]+O(\epsilon^2) \ . \tag{42b}$$

The first two terms in Eq. (41) demonstrate the correct normalization. Equation (42a) to order ϵ coincides with Eq. (I 5.26), derived from the density autocorrelations, a result which holds by virtue of an exact sum rule.

The results for $\bar{p}''$ and $\bar{p}'''$ allow for another check of interest. Often it is assumed that polydispersity takes the form of a "Schultz distribution"

$$p_\sigma(y)=\frac{\sigma}{\Gamma(\sigma)}(\sigma y)^{\sigma-1}e^{-\sigma y}\ , \tag{43}$$

where Γ denotes the Γ function. It is easily checked that these distributions obey the relation

$$\bar{p}_\sigma'''=-\bar{p}_\sigma''(2\bar{p}_\sigma''-1)\ . \tag{44}$$

The results (42) obey this relation only in the dilute ($w\to 1$) or semidilute ($w\to 0$) limits. In general the equilibrium distribution $\hat{p}(y,w)$ is not in the class (43).

I now consider the limiting behavior in w of $\hat{p}(y,w)$, taking $y>0$ fixed. In the dilute limit $w\to 1$ Eq. (37) yields

$$\hat{p}(y,1)=\exp\left[-y\left[1+\frac{\epsilon}{8}\right]+\frac{\epsilon}{8}(1+\gamma_{\rm Eu}+\ln y)+O(\epsilon^2)\right]\ . \tag{45}$$

By virtue of the well known expansion $\gamma=1+\epsilon/8+O(\epsilon^2)$ this is consistent with the rigorous result

$$\hat{p}(y,1)=p_\gamma(y)=\frac{\gamma^\gamma}{\Gamma(\gamma)}y^{\gamma-1}e^{-\gamma y}\ , \tag{46}$$

which derives from the fact that $\tilde{G}(\cdots)$ [see Eq. (21)] in the isolated chain limit takes the form

$$\tilde{G}(t_1,t,0,g^*)=\text{const}\,t_1^{-\gamma}\ .$$

In the semidilute limit $w\to 0$ we use the asymptotic behavior

$$E_1(x)\sim\frac{e^{-x}}{x}\quad\text{as } x\to\infty \tag{47}$$

to find the simple result

$$\hat{p}(y,0)=e^{-y}=p_1(y)\ . \tag{48}$$

We now are in the position to again discuss the scaling ansatz of Ref. 10, which assumes that $\hat{p}(y,w)$ for all overlap is given by Eq. (46). Being inconsistent with the ϵ expansion this form cannot be correct. Rather in the limit of large overlap $\hat{p}(y,w)$ reduces to the form predicted by the heuristic blob model. Since all the argument of Ref. 10 is based on the assumption $\hat{p}(y,w)\equiv p_\gamma(y)$, the prediction of a dense phase is unfounded. I note in passing that the result (37) is consistent with the bound established in Ref. 12.

Above we found that $\hat{p}(y,w)$ cannot be represented by a Schultz distribution (43) with some effective exponent $\sigma(w)$. Rather the behavior is more complicated, and indeed our result is consistent with the power law $\hat{p}(y,w)\sim y^{\gamma-1}$ $y\to 0$, independent of $w>0$. Inserting into Eq. (37) the asymptotic behavior

$$E_1\left[\frac{y}{w}\right]=E_1(n_R)\sim-\ln n_R-\gamma_{\rm Eu}+O(n_R) \tag{49}$$

we find

$$\hat{p}(y,w)=\exp\left[\frac{\epsilon}{8}\left[\ln n_R+\gamma_{\rm Eu}-\frac{w\ln w}{1-w}\right]+O(n_R,\epsilon^2)\right]\ , \tag{50}$$

which can be interpreted as approximating

$$\hat{p}(y,w)=a(w)n_R^{\gamma-1}[1+O(n_R)]\ . \tag{51}$$

To understand this result we recall Eq. (33): $n_R\ll 1$ implies that we consider a chain much smaller than a blob. As pointed out in the Introduction such chains feel no interaction with the other chains. Their relative distribution therefore should follow the law (46). Note that this result is completely analogous to the momentum dependence of the spin correlation function of the LGW model. For finite temperatures $t>0$ this function for small momenta q, corresponding to large length scales, is a regular function of q^2. However, for large momenta, corresponding to small spatial distances, it develops the anomalous power-law behavior characteristic of the critical point. Similiarly here $p(y)$ is a regular function for chains of average size, but exhibits the nontrivial singular behavior for very small chains.

We can exhibit this behavior more directly. Indeed, starting from Eqs. (21) and (A16) and using condition (25): $n_R(\lambda)=1$, we find

$$l^d c_p(n)=\text{const}\times\hat{n}^{\gamma-1}\frac{\hat{h}^2}{2}\exp\left\{-y\left[1+\frac{\epsilon}{8}\frac{y}{2g^*c_{lR}}\ln\left[1+\frac{2g^*c_{lR}}{y}\right]\right]+\frac{\epsilon}{8}\frac{1}{y+2g^*c_{lR}}\{y(\gamma_{\rm Eu}-1)-2g^*c_{lR}[1+\ln(y+2g^*c_{lR})]+\exp(y+2g^*c_{lR})E_1(y+2g^*c_{lR})\}+O(\epsilon^2)\right\}\ . \tag{52}$$

With the present choice of λ, c_{lR} takes the form

$$c_{lR}=\text{const}\times\hat{s}y^{\nu d-1}\ , \tag{53}$$

vanishing for $y\to 0$, $\hat{s}=\text{const}$. In that limit we therefore can expand the exponential integral to find the simple result

$$l^d c_p(n)=\text{const}\times\hat{n}^{\gamma-1}\frac{\hat{h}^2}{2}\ , \tag{54}$$

in keeping with Eqs. (15) or (51). This result is valid for $y\ll 1, c_{lR}\ll 1$, or $n/N\ll 1, c_l n^{\nu d-1}\ll 1$, equivalently. The latter condition can be written as

$$\left[\frac{N}{n}l^d c_p\right]n^{\nu d}\ll 1\ , \tag{55}$$

which is easily interpreted. $c_p N/n$ gives the number density of subchains resulting from dividing the chains into elementary pieces of length n. Equation (55) states that this fictitious system of subchains must have negligible overlap, a criterion equivalent to the discussion given in the context of Eq. (15).

We note that the choice (25), $n_R(\lambda)=1$ is not adequate for a discussion of the region $y\sim 1$ in a strongly overlapping system $c_{lR}\sim s\to\infty$. In that limit we again encounter logarithmically divergent terms in Eq. (52). We can avoid this problem by combining Eqs. (25) and (30) in the form

$$1=\frac{1}{n_R}+2g^* c_{lR}\ . \tag{56}$$

With this choice of λ we find a smooth crossover from the power law (54) to the simple exponential behavior (48). Combined with Eq. (52) this gives the optimal representation of $c_p(n)$ or $\bar{p}(y,\hat{s})$, based on a one-loop calculation. Since, however, Eq. (56) has to be evaluated numerically and since accurate data on $p(y)$ are missing, I do not pursue this matter further.

To complete the discussion I treat the limit of extremely long chains. In the limit $y\to\infty$ Eqs. (37) and (47) yield

$$\hat{p}(y,w)=\exp\left[-y\left[1-\frac{\epsilon}{8}\frac{w\ln w}{1-w}\right]+\frac{\epsilon}{8}\left[w\ln y+w\gamma_{\text{Eu}}-(2-w)\frac{w\ln w}{1-w}\right]+O\left[\epsilon^2,\frac{1}{y}\right]\right]\ . \tag{57}$$

The term $w\ln y$ again signals the occurrence of some nontrivial power law, which can be understood as follows.[13] For $w>0$ the screening is not perfect, the residual interaction among blobs being of the order of $g^* w$. For extremely long chains this interaction again builds up excluded-volume correlations and thus leads to a distribution of the form $p(y,w)\sim y^{\gamma-1}\exp[-b(w)y]$. Within the present calculation we cannot correctly recover that exponent. This needs another renormalization, tailored specifically for the anomalously large chains. We, however, can determine the region where this behavior is expected. The relevant chain lengths n_R obviously obey

$$\frac{\epsilon}{8}w\ln n_R\sim\frac{1}{4}\frac{n_R^{\epsilon/2}-1}{N_R}\gtrsim 1\ ,$$

implying $n_R\gtrsim N_R^{2/\epsilon}$. This is easily understood from the fact that naive perturbation theory proceeds in powers of $g_{\text{eff}}n^{\epsilon/2}$, where in the semidilute region $g_{\text{eff}}\sim g/N$. We thus expect the expansion to break down for $n^{\epsilon/2}/N\gg 1$.

To illustrate my results, I in Fig. 2 for selected values of w have plotted $e^y\hat{p}(y,w)$, as given by Eq. (37), setting $\epsilon=1$. In the semidilute limit $w=0$ this function reduces to the straight line $e^y\hat{p}(y,0)\equiv 1$. For $0<w\ll 1$ the tails of the function drop down to zero, but the central part over several decades of y closely follows the $w=0$ result. If we approach the dilute limit $w=1$, the tails merge and the plateau vanishes. [Note that for $w=1$, I used the exact result (46).] On the side of short chains the plateau starts around $y\sim w$. In keeping with our discussion this corresponds to $n_R\sim 1$, i.e., to chains consisting of a single blob. For large chains the plateau ends around $y\sim 0.1/w$, corresponding to $n_R\sim 0.1N_R^2$. Clearly in the large overlap region the bulk of the chain-length distribution follows the simple exponential law.

IV. CONCLUSIONS

To summarize, I here have derived a general scaling form of the chain-length distribution for equilibrium polymerization based on the model of des Cloiseaux. This form is much more general than assumed in some previous work. A first order calculation shows that the distribution is not in the class of Schultz distributions and clearly rules out the ansatz of Ref. 10 which also was used in the interpretation of the Monte Carlo data of Ref. 11. The result, however, obeys a rigorous bound recently derived.[12] In the semidilute limit the result reduces to an exponential distribution, modified by power-law prefactors in the extreme wings. This is well understood in terms of the blob concept.

I have restricted the explicit discussion to the excluded-volume limit $g\equiv g^*$. Outside the limit we have to take care of the λ dependence of the running coupling constant $g(\lambda)$. This mainly will effect the tail of the distribution for short chains. With the choice $n_R(\lambda)=1$, $g(\lambda(n))$ will decrease with decreasing n, which yields an effective exponent $\gamma_{\text{eff}}(n)-1$ decreasing with decreasing chain length.

All the work presented here presupposes the normal thermodynamic limit. For finite systems we clearly expect pronounced finite size effects for chains which can span the linear size L of the container. In particular for $t<0, hL^d\lesssim 1$ the character of the chain-length distribution might change completely. These effects possibly can be calculated by the methods of Ref. 18. This, however, is a much harder problem.

APPENDIX

Scaling form of $p(y)$

I start from Eq. (27) written as

$$l^d c_p(n)=a\hat{n}^{\gamma-1}\hat{h}^2\mathcal{C}^{**}(u,v)\ , \tag{A1}$$

where I introduced the notation

$$u=\hat{n}\,\hat{h}^{2/(vd+\gamma)},\quad v=\hat{t}\,\hat{h}^{-2/(vd+\gamma)}\ , \tag{A2}$$

and a is some nonuniversal constant. Summing over n, I find

$$\begin{aligned} l^d c_p &= \frac{a}{b}\hat{h}^2\int d\hat{n}\,\hat{n}^{\gamma-1}\mathcal{C}^{**}(u,v) \\ &= \frac{a}{b}\hat{h}^{2vd/(vd+\gamma)}\int du\,u^{\gamma-1}\mathcal{C}^{**}(u,v)\ , \end{aligned} \tag{A3}$$

where b is a nonuniversal constant relating $\hat{n}$ to n:

$$\hat{n}=bn\ . \tag{A4}$$

Similarly I find

$$\begin{aligned} l^d c_l &= \frac{a}{b^2}\hat{h}^2\int d\hat{n}\,\hat{n}^{\gamma}\mathcal{C}^{**}(u,v) \\ &= \frac{a}{b^2}\hat{h}^{(2vd-2)/(vd+\gamma)}\int du\,u^{\gamma}\mathcal{C}^{**}(u,v)\ . \end{aligned} \tag{A5}$$

Equations (A3) and (A5) yield the expression for N,

$$\begin{aligned} \hat{N} &= \hat{h}^{-2/(vd+\gamma)}\frac{\int du\,u^{\gamma}\mathcal{C}^{**}(u,v)}{\int du\,u^{\gamma-1}\mathcal{C}^{**}(u,v)} \\ &= \hat{h}^{-2/(vd+\gamma)}\bar{u}(v)\ . \end{aligned} \tag{A6}$$

From Eqs. (A3) and (A6) we can construct an expression for the overlap

$$\hat{s}=\frac{b}{a}l^d c_p\hat{N}^{vd}=\frac{\left[\int du\,u^{\gamma}\mathcal{C}^{**}(u,v)\right]^{vd}}{\left[\int du\,u^{\gamma-1}\mathcal{C}^{**}(u,v)\right]^{vd-1}}\ , \tag{A7}$$

which formally can be solved for

$$v=v(\hat{s})\ . \tag{A8}$$

The variable u can be rewritten as

$$u=\frac{\hat{n}}{\hat{N}}\hat{N}\,\hat{h}^{2/(vd+\gamma)}=y\bar{u}(v(\hat{s}))\ . \tag{A9}$$

Substituting these results into the expression for $p(y)$ we find

$$\begin{aligned} p(y) &= \bar{p}(y,\hat{s}) \\ &= y^{\gamma-1}\mathcal{C}^{**}(y\bar{u}(\hat{s}),v(\hat{s})) \\ &\quad\times\frac{\left[\int du\,u^{\gamma}\mathcal{C}^{**}(u,v(\hat{s}))\right]^{\gamma}}{\left[\int du\,u^{\gamma-1}\mathcal{C}^{**}(u,v(\hat{s}))\right]^{\gamma+1}}\ . \end{aligned} \tag{A10}$$

First-order calculation of $\hat{p}(y,w)$

To one-loop order $\mathcal{C}(\cdots)$ [Eq. (23)] is found as

$$\mathcal{C}(n_R,t,h^2,g^*)=e^{-n_R t}\oint\frac{dt_1}{2\pi i}\frac{e^{n_R t_1}}{t_1+g^* c_{lR}}\left[1+\frac{D}{t_1+gc_{lR}}\right]\ , \tag{A11}$$

where D is the contribution of the second diagram in Fig. 10 of Ref. 8, with the only modification that the solid line represents a propagator of mass t_1+gc_{lR}.

Taking all counterterms into account and shifting $t_1+gc_{lR}\to t_1$, I find

$$\begin{aligned} \mathcal{C}(n_R,t,h^2,g)=e^{-n_R(t+gc_{lR})}\Bigg\{ & 1+g\oint\frac{dt_1}{2\pi i}\frac{e^{n_R t_1}}{t_1}\left[\int\frac{d^dk}{(2\pi)^d}\frac{1}{k^2(k^2+t_1)}-\mathcal{S}_d I_1\right] \\ & +g\cdot 2gc_{lR}\oint\frac{dt_1}{2\pi i}\frac{e^{n_R t_1}}{t_1^2}\left[\int\frac{d^dk}{(2\pi)^d}\frac{1}{\left[\frac{1}{N_R}+2gc_{lR}+k^2\right](k^2+t_1)}-\mathcal{S}_d I_1\right]\Bigg\}\ , \end{aligned} \tag{A12}$$

where

$$\mathcal{S}_d=2(4\pi)^{-d/2}\Gamma^{-1}(d/2)\ ,$$

$$I_1=\frac{1}{\epsilon}+\frac{1}{2}+O(\epsilon)\ .$$

Evaluating the integrals I find

$$\mathcal{C}(n_R,t,h^2,g)=e^{-n_R(t+gc_{lR})}\left[1+\frac{\mathcal{S}_d}{2}\frac{g}{\frac{1}{N_R}+2gc_{lR}}\right.$$
$$\times\left[\frac{1}{N_R}(\ln n_R+\gamma_{\mathrm{Eu}}-1)-2gc_{lR}\left\{1+\ln\left[\frac{1}{N_R}+2gc_{lR}\right]\right.\right.$$
$$\left.\left.+\exp\left[n_R\left[\frac{1}{N_R}+2gc_{lR}\right]\right]E_1\left[n_R\left[\frac{1}{N_R}+2gc_{lR}\right]\right]\right\}\right]$$
$$\left.-g\mathcal{S}_d gc_{lR}n_R\left[1+\ln\left[\frac{1}{N_R}+2gc_{lR}\right]\right]\right]. \tag{A13}$$

I eliminate $t+gc_{lR}$ with the help of the equation

$$t+gc_{lR}=\frac{1}{N_R}\left[1+\frac{\mathcal{S}_d}{2}g\left\{1-\left[\frac{1}{N_R}+2gc_{lR}\right]\left[\ln\left[\frac{1}{N_R}+2gc_{lR}\right]+1\right]\right.\right.$$
$$\left.\left.+\frac{1}{2gc_{lR}}\left[\frac{\ln N_R}{N_R}+\left[\frac{1}{N_R}+2gc_{lR}\right]\ln\left[\frac{1}{N_R}+2gc_{lR}\right]\right]\right\}\right]. \tag{A14}$$

With the choice (30) this equation reduces to Eq. (I 5.5). At the fixed point

$$g^*=\mathcal{S}_d^{-1}\frac{\epsilon}{4}[1+O(\epsilon)] \tag{A15}$$

the final result for the scaling function $\mathcal{C}$ can be written in the form

$$\mathcal{C}(n_R,t,h^2,g^*)=\exp\left[-\frac{n_R}{N_R}\left[1+\frac{\epsilon}{8}\frac{\ln(1+2g^*c_{lR}N_R)}{2g^*c_{lR}N_R}\right]\right.$$
$$+\frac{\epsilon}{8}\frac{1}{\frac{1}{N_R}+2g^*c_{lR}}\left\{\frac{1}{N_R}(\ln n_R+\gamma_{\mathrm{Eu}}-1)\right.$$
$$-2g^*c_{lR}\left[1+\ln\left[\frac{1}{N_R}+2g^*c_{lR}\right]\right.$$
$$\left.\left.\left.+\exp\left[\frac{n_R}{N_R}(1+2g^*c_{lR}N_R\right]\right.\right.\right.$$
$$\left.\left.\left.\left.\times E_1\left[\frac{n_R}{N_R}(1+2g^*c_{lR}N_R)\right]\right]\right\}+O(\epsilon^2)\right]. \tag{A16}$$

To derive the result (37) for $\hat{p}(y,w)$ I use condition (30): $1=1/N_R+2g^*c_{lR}$ together with

$$w=\frac{1}{N_R},$$

$$2g^*c_{pR}=w(1-w),$$

$$g^*h^2=w^2(1-w)\left[1+\frac{\epsilon}{8}-\frac{\epsilon}{8}\frac{w\ln w}{1-w}\right],$$

the latter relation resulting from Eqs. (I 4.19), (I 5.4), and (I 5.8).

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