

A SCALING PICTURE OF A SINGLE-CHAIN POLYMER IN THE DENSE PHASE

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A scaling picture implying hyperscaling, is presented for a single-chain polymer (or self-avoiding walk) above the critical bond fugacity for the formation of an infinite chain in terms of closely packed "correlation blobs". Some experimentally testable predictions are noted.

The behavior of an isolated polymer chain in solution is often modeled by a self-avoiding random walk, which is in turn related to an n -component spin model in the limit $n \rightarrow 0$ [1]. If each link (or monomer) of a self-avoiding walk is assigned a fugacity z , the walk undergoes a transition from a finite (average) chain length or dilute phase, to an infinite chain length or dense phase as z increases through its critical threshold z_c (see e.g. ref. [1]). This transition is usually studied as z approaches z_c from below, the nature of the chain above z_c being seldom discussed. There are, however, two approaches, both somewhat formal, that can be used to study the chain in the dense phase. One is that of des Cloizeaux [2] (see also ref. [3]) in which a many-chain system is first mapped onto an n -component spin model in a magnetic field, H , in the limit $n \rightarrow 0$. In this case, the transition is sharp only when $H \rightarrow 0$, corresponding to a system with few chains^{†1}. The other is to consider the self-avoiding walk generating function as the analog of the partition function (rather than the susceptibility as in the spin model mapping [1]), and analyze the resulting free energy in terms of a single scaling field [4].

^{†1} We do not address the possibility of some difficulty in regarding the limit of zero polymer density as corresponding to an isolated chain.

Both of these approaches lead to critical exponents for $z > z_c$ without giving much insight as to the nature of the chain configuration itself. However, as pointed out in ref. [3], this problem may be quite close to that encountered in the study of the equilibrium polymerization of materials such as liquid sulfur. (For experimental results, see e.g. ref. [5].) Thus, the structure of the dense chain is of more than abstract interest.

In this note, we show that a simple scaling description, based on a physical picture of a polymer above z_c , is consistent with the results obtained previously by more formal methods [3,4]. In addition, we make predictions that should be testable on materials such as liquid sulfur. Our basic postulate is as follows: For $z > z_c$, a single-chain polymer can be described as a series of successive "correlation blobs", of linear dimension ξ , the density-density correlation length, which fill the space, thus squeezing each other into a close-packed configuration. Within each blob, the chain is swollen in the same way as a finite self-avoiding walk, being only weakly affected by squeezing (cf. fig. 1). This idea of close-packed blobs is similar to various blob concepts de Gennes [6] and co-workers have introduced. However, de Gennes' blob for a polymer chain squeezed into a confined geometry (such as a tube) has a *fixed* size imposed by the geometry, and the blob in the semi-dilute regime, which

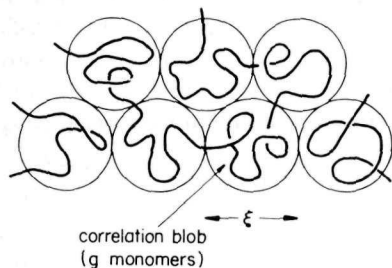


Fig. 1. Schematic picture of blobs for a polymer chain at $z > z_c$.

results from squeezing by *other* chains, was not used to describe the polymerization transition. In contrast, our blob has a size dependent on z and is used in an essential manner to describe polymerization.

Some of the consequences of the present blob picture follow directly by considering the properties of the chain as a function of the blob size. Thus, consider a chain in a large volume V . Since the blobs are assumed to be close-packed, the number of blobs, m , and their linear dimension, ξ , are related to V by

$$V \sim m\xi^d. \quad (1)$$

On the other hand, the number of blobs and the number of monomers per blob, g , are related through

$$N = mg, \quad (2)$$

where N is the total number of monomers in V . If we now consider the monomer density Φ (regarded as an order parameter in ref. [4]), we find

$$\Phi \equiv \langle N \rangle / V \sim \langle g \rangle \xi^{-d}, \quad (3)$$

where $\langle \rangle$ denotes the number average in the grand canonical ensemble at fugacity z . In addition, we expect from the spin model mapping [1,2]

$$\xi \sim (\Delta z)^{-\nu}, \quad (4)$$

where $\Delta z \equiv z - z_c$. If we now use the second part of our hypothesis, in the form

$$\xi \sim \langle g \rangle^\nu, \quad (5)$$

we immediately obtain

$$\Phi \sim (\Delta z)^{\nu-1}. \quad (6)$$

This result was also derived in ref. [4] using finite-size scaling principles [7]. In ref. [3], a corresponding relation

$$\Phi \sim (\Delta z)^{1-\alpha} \quad (7)$$

was obtained where α is the specific heat exponent of the corresponding n -vector model as $n \rightarrow 0$. Thus, the result (6) is consistent with (7) provided that the hyperscaling relation $2 - \alpha = d\nu$, holds for the (n -vector model) exponents α and ν . For a pseudo-one-dimensional system of a strip of arbitrary width (with periodic boundary condition across the strip containing a polymer that cannot go backward along the strip) Φ can be calculated exactly. In this case, (6) holds with $\nu = 1$, the value appropriate for $d = 1$.

We note that it is possible to derive (5) if we start from (6) as given (say, by other theoretical arguments or by experiments), implicitly assuming the first part of our hypothesis. Thus, (4) and (6) together yield

$$\Phi \sim (\Delta z)^{-1} \xi^{-d}, \quad (8)$$

combining (3) and (8), we obtain

$$\langle g \rangle \sim (\Delta z)^{-1}, \quad (9)$$

which, by using (4), gives (5). Since we have assumed that monomers within a correlation blob belong to a single chain segment, (5) implies that this segment obeys similar statistics as the full self-avoiding walk below z_c .

Let us now consider some directly observable quantities. First, Φ as, say, a function of temperature is observable by rapidly quenching the solution and dissolving away non-polymeric monomers [5]. In addition, light or neutron scattering experiments should provide measurements of ξ in the standard manner, and also of the fluctuation χ in the monomer density N/V from the low angle scattered intensity ($q \rightarrow 0$). Thus, (6) can be rewritten by using (4) as

$$\Phi \sim \xi^{(1/\nu)-d}. \quad (10)$$

Also, we have a new prediction,

$$\chi = \frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle} = \frac{d\Phi/dz}{\Phi} \sim \xi^{1/\nu}, \quad (11)$$

by use of (4) and (6). These relations have not so far been tested experimentally although specific heat measurements of liquid sulfur may correspond to measuring χ [3].

In summary, we have presented a simple picture of close-packed blobs that leads directly to scaling predictions for a polymer chain in its dense phase above z_c . The explicit, detailed nature of these "correlation

blobs" is not yet known (much like the other "blobs" discussed by de Gennes [6] and co-workers). However, some type of multiple nearest-neighbor contacts between chain segments may, perhaps, appropriately define the blob. This possibility is currently under investigation; in particular, we seek to satisfy, for a system of linear dimension L ,

$$\langle g \rangle_{L, z=z_c} \sim L^{1/\nu}, \quad (12)$$

which follows from (9) by finite-size scaling [7].

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