

## Bounds on the polymer length distribution in equilibrium polymerization

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We obtain upper bounds on the polymer-length distribution in a class of models for equilibrium polymerization. This rules out a recent claim for the existence of a “collapsed” phase in which a nonzero fraction of the monomers are in infinite polymer(s). We discuss the behavior of finite systems, in which a collapse of sorts *does* occur, and indicate how this collapse disappears in the thermodynamic limit.

### I. INTRODUCTION

The statistical mechanics of isolated polymer chains,<sup>1</sup> polydisperse chain polymer solutions<sup>2-6</sup> and equilibrium polymerization of chains<sup>7-9</sup> have all been usefully modeled by the  $n \rightarrow 0$  limit of the  $n$ -vector model of magnetism. Recently it has been claimed<sup>10,11</sup> that interacting chain polymers in equilibrium should have a “collapsed” phase in which there is a nonzero density of monomers in polymers which are infinitely long in the large volume (thermodynamic) limit. This claim, if correct, would have significant consequences for the theory of polydisperse polymer solutions and equilibrium polymerization. The claim has been challenged recently by Schäfer,<sup>12</sup> who calculates the polymer distribution using renormalization-group techniques and finds no evidence for this condensation and positive evidence for the conventional view of semidilute polymer solutions.

In this paper we obtain upper bounds for the length distribution of polymers in a very general class of models, including the model in question, that rule out the possibility of such a collapsed phase. Our results and those of Schäfer are complementary: Our bound is very weak, but the argument is rigorous, straightforward, and very general, demonstrating with finality that the proposed condensation cannot occur in any physically realizable spatial dimensionality. Schäfer’s work gives much more precise predictions, but involves considerably more complex calculations that rely on acceptance of the renormalization-group machinery and the accuracy of perturbation theory, and it is carried out only in translationally invariant systems with spatial dimensionality greater than two.

In the model under consideration,<sup>10</sup> each site of a regular lattice of  $N_0$  sites with coordination number  $q$  in  $d$  dimensions may be *empty* or occupied by a *monomer*. A *polymer bond* can form between monomers on nearest-neighbor (connected) sites. Allowed states consist of patterns of bonds such that there are only chain polymers.

That is, no more than two bonds meet at any given lattice site and there are no ring polymers — it is impossible in allowed states to move from any site on the lattice back to that site along polymer bonds without moving along the same bond twice. In addition, in this model, only chains having at least one bond (two monomers) are allowed. That is, no *isolated* monomers are allowed. The partition function for this model is given by

$$\hat{Z}(\eta, \kappa) = \sum_{l,p} \kappa^l \eta^{2p} U_{p,l}, \quad (1)$$

where  $\eta$  is the statistical weight associated with a chain end,  $\kappa$  is the statistical weight for a bond, and  $U_{p,l}$  is the number of distinct configurations of  $p$  different chains containing a total of  $l$  bonds on a lattice containing  $N_0$  sites. This model is related by simple mathematical mappings to both the  $n \rightarrow 0$  limit of the  $n$ -vector model and the model of equilibrium polymerization studied by Wheeler and co-workers<sup>7-9</sup> in which “polymers” consisting of a single active monomer are also allowed.

The specific claim made in Ref. 10 is that there is a nonzero positive value of  $\eta$ , say  $\eta^*$ , below which, in the thermodynamic limit, and for  $\kappa$  greater than some finite  $\kappa_c$ , a nonzero fraction of the monomers are in polymers of infinite length. Specifically, it is asserted that the density of bonds in finite polymers is strictly less than the total density of bonds in polymers when  $\eta < \eta^*$  and  $\kappa > \kappa_c$ . This claim seems counterintuitive in view of the fact that, in equilibrium, any interior bond in a long polymer can break with a nonzero (albeit, perhaps small) probability,  $p = \eta^2/\kappa$ , independent of the length of the polymer or the size of the system. If the length of (number of bonds in) the polymer,  $N$ , is so great that  $pN \gg 1$ , there will be a high probability that at least one bond will be broken. If one of the remaining segments is still much longer than  $1/p$ , the same argument can be employed again. It thus seems unlikely that a monomer will be found in a polymer of length much greater than  $1/p$ .

This intuitive argument is not correct as it stands be-

cause of a complication mentioned presently. It can be made rigorous, and we do so in the next section. We remark here that if the model is modified so that each polymer is "isolated," in the sense that there are no allowed configurations in which a monomer is adjacent to more than two other monomers (whether or not it is bonded to them), then simple transfer matrix methods readily establish a bound on the length distribution that decays exponentially with polymer length, directly confirming the above intuitive argument.

A complication arises if parts of other polymers, or remote parts of the same polymer, may lie adjacent to the polymer under consideration, because then the same state with smaller polymers can arise in more than one way by cutting longer polymers. One must then be careful not to overweight such states with short polymers in bounding the probability of a state with long polymers.

This complication is surmounted in the next section by a recursive procedure that bounds the *conditional* probability that a sequence of  $n$  bonds extending from a given bond has (at least one) additional bond at its end. The result is a bound on the probability  $P(N)$  that a polymer bond is in a polymer of length  $N$  or greater:

$$P(N) \leq N p_m^{N-1}, \quad (2)$$

where

$$p_m = \frac{(q-1)\kappa}{(q-1)\kappa + \min(1, \eta^2)}, \quad (3)$$

and where  $\min(x, y)$  is the smaller of  $x$  and  $y$ . Note that  $p_m$  does not depend on the system size  $N_0$  and that  $p_m < 1$  for all  $\eta > 0$ .

We prove these results in Sec. II, below, for the model described by the partition function (1). In Sec. III we generalize the proof to a much broader class of models.

A collapse, of sorts, *does* occur in *finite* systems to a state of essentially a single polymer on the lattice, but this is accompanied by anomalously *low* (rather than high) molecular weight, and the effect vanishes in the thermodynamic limit. This, and consequences of the bounds are discussed in Sec. IV.

## II. BOUND ON THE LENGTH DISTRIBUTION

Consider a particular bond on the lattice and a specific track of  $n_1$  bonds extending from its "right-hand" end and a specific track of  $n_2$  bonds extending from its "left-hand" end. [Right-hand and left-hand ends of every bond are unambiguously, if arbitrarily, defined by sequentially numbering the lattice sites in some specific arbitrary order and defining the right-hand end of any bond to be that with the larger of these numbers.] Let  $S_t$  be the set of all states with the above-specified  $n_1 + n_2 + 1$  bonds definitely present and *no* additional bond extending from the end of the right-hand track of  $n_1$  bonds, and let  $S_c$  be the set of all states with the specified bonds present and *at least one* additional bond extending from the end of the right-hand track of  $n_1$  bonds. Let  $W_t$  and  $W_c$  be the statistical weights of these sets of *terminated* and *continued* states, respectively.

Each state in  $S_c$  can be viewed as the *progeny* of a unique *parent* state in  $S_t$ , which is obtained from its progeny by removing the additional bond extending from the end of the right-hand chain of  $n_1$  bonds. The ratio of the statistical weight of any particular progeny state in  $S_c$  to its parent state in  $S_t$  is *at most*

$$\frac{\kappa}{\min(1, \eta^2)}. \quad (4)$$

[It is equal to  $\kappa/\eta^2$  if the bond extending the chain of  $n_1$  bonds is in turn connected to another bond, and equal to  $\kappa$  if the additional bond terminates the chain at  $n_1 + 1$  bonds.]

A state in  $S_t$  can be parent to more than one state in  $S_c$ . This occurs if more than one of the nearest-neighbor sites of the terminal site of the right-hand chain of  $n_1$  bonds is either empty or a polymer end. It is clear, however, that a state in  $S_t$  is parent to no more than  $q - 1$  states in  $S_c$ , corresponding to the (at most)  $q - 1$  sites *other* than the one already in the chain of length  $n_1$  to which this terminal site could be bonded in a state in  $S_c$ . As a consequence, the ratio  $W_c/W_t$  may be bounded by

$$W_c/W_t \leq \frac{(q-1)\kappa}{\min(1, \eta^2)}. \quad (5)$$

Therefore, the probability that the bond originally in question has a chain of (at least)  $n_1 + 1$  bonds to its right (including the specified  $n_1$ ) and at least the specified  $n_2$  to its left *given that* it has (at least) the specified  $n_1$  to its right and the specified  $n_2$  to its left is bounded above by

$$\frac{W_c}{W_c + W_t} \leq p_m \equiv \frac{(q-1)\kappa}{(q-1)\kappa + \min(1, \eta^2)}. \quad (6)$$

Each distinct track of  $n_1 + n_2 + 1$  bonds through the selected bond gives the same bound. Consequently, we may bound the conditional probability,  $P(n_1 + 1, n_2 | n_1, n_2)$ , that there are at least  $n_1 + 1$  and  $n_2$  bonds extending from the bond of interest *given that* there are at least  $n_1$  and  $n_2$  bonds extending from it by

$$P(n_1 + 1, n_2 | n_1, n_2) \leq p_m. \quad (7)$$

By exactly the same reasoning, we conclude that the conditional probability  $P(n_1, n_2 + 1 | n_1, n_2)$  is also bounded above by  $p_m$ .

The probability that a given bond has strings of (at least)  $n_1$  and  $n_2$  bonds to its right and left, respectively, satisfies the recurrence relations

$$P(n_1, n_2) = P(n_1 - 1, n_2)P(n_1, n_2 | n_1 - 1, n_2) \quad (8)$$

and

$$P(n_1, n_2) = P(n_1, n_2 - 1)P(n_1, n_2 | n_1, n_2 - 1), \quad (9)$$

provided that all of the arguments are non-negative integers. Combining these recurrence relations with the inequalities for the conditional probabilities, we obtain the inequalities:

$$P(n_1, n_2) \leq P(n_1 - 1, n_2)p_m \quad (10)$$

and

$$P(n_1, n_2) \leq P(n_1, n_2 - 1)p_m. \quad (11)$$

Applying these inequalities recursively, we conclude that

$$P(n_1, n_2) \leq P(0, 0)p_m^{(n_1+n_2)}. \quad (12)$$

Observing that  $P(0, 0) \leq 1$  and that, to ensure a polymer of length  $N$  through the chosen bond,  $n_1$  may be any integer from 0 to  $N - 1$ , we conclude that the probability that a given polymer bond is in a polymer of length at least  $N$  is bounded by Eq. (2). [Adding probabilities for the states with different  $n_1$  counts states more than once, of course, since these are probabilities for having *at least*  $n_1$  and  $n_2$  bonds attached to the bond of interest, but since we are obtaining an upper bound on the probability, this only strengthens the inequality (2).]

### III. BOUNDS FOR MORE GENERAL MODELS

The method employed in Sec. II is very general. Note, first, that the argument applies unchanged to a lattice on which different sites,  $i$ , may have different coordination numbers,  $q_i$ , so long as there is a uniform upper bound

$$q_i \leq q \quad (13)$$

on the coordination number for any site. This immediately extends the bound to include models of equilibrium polymerization on *decorated lattices*<sup>13</sup> and *fractals*.<sup>14</sup>

The argument can be extended even further, to models in which each site is able to be connected by a polymer bond to any of an infinite number of other sites. Consider a rather arbitrary collection of  $N_0$  sites, each of which may contain a monomer or be empty. For each site,  $i$ , there is a statistical weight,  $\eta_i$ , associated with a polymer end at that site, and for each pair of sites,  $i, j$ , there is a statistical weight,  $\kappa_{i,j}$ , associated with a polymer bond between monomers on these sites. The rules for allowed states are the same as for the model in Sec. I. The partition function for this model may be written as

$$\hat{Z}(\eta, \kappa) = \sum_{\text{states}} \prod_{\langle i, j \rangle} \kappa_{i,j} \prod_l \eta_l, \quad (14)$$

where the sum is over all allowed states, and the products are over all bonds,  $\langle i, j \rangle$ , and polymer ends,  $l$ , in the state. For a regular lattice with uniform  $\eta_i$ , equal to  $\eta$ , and with  $\kappa_{i,j}$  equal to  $\kappa$  between nearest neighbors and zero otherwise, this reduces to the partition function in Eq. (1). Provided that there is a positive uniform *lower* bound on the  $\eta_i$ ,

$$\eta_i \geq \eta > 0, \quad (15)$$

and a uniform *upper* bound on a weighted *sum* of the statistical weights of possible bonds to any site,

$$\sum_j \kappa_{i,j} \frac{\eta_i \eta_j}{\eta^2} \leq K, \quad (16)$$

independent of the site,  $i$ , and of the number of sites,

$N_0$ , then the argument in Sec. II goes through essentially unchanged, with  $K$  replacing  $(q-1)\kappa$ . Using the notation developed in Sec. II, the ratio of the statistical weight of any particular progeny state in  $S_c$  to its parent state in  $S_i$  is *at most*

$$\frac{\kappa_{i,j}}{\min(\eta_i/\eta_j, \eta_j/\eta_i)} \leq \frac{\kappa_{i,j}\eta_i\eta_j}{\eta^2 \min(1, \eta^2)}, \quad (17)$$

where the terminal site of the specified chain of  $n_1$  bonds is assumed to lie at the site  $i$  and the additional bond is between the  $i$  and  $j$  sites. This equation replaces Eq. (4) in Sec. II. Summing over all sites,  $j$ , to which the terminal site,  $i$ , might be connected, one finds as a bound on the ratio of the statistical weight of all possible progeny to that of the parent, in place of Eq. (5),

$$W_c/W_i \leq \sum_j \frac{\kappa_{i,j}\eta_i\eta_j}{\eta^2 \min(1, \eta^2)} \leq \frac{K}{\min(1, \eta^2)}. \quad (18)$$

The argument then proceeds exactly as in Sec. II to give the bound in Eqs. (2) and (3), but with  $(q-1)\kappa$  replaced by  $K$  as given in Eq. (16).

This generalization establishes the bound for a very general class of models of equilibrium polymerization, including polymerization on disordered lattices and amorphous collections of sites as well as on rather general sets for which the notion of spatial dimensionality may be rather vague. The physical motivation for the bound (16) is that a monomer on a given site should not be readily able to bond with monomers on sites that are very "far away" from it in a spatial sense. Since each site is capable of supporting a monomer, it should have associated with it a "volume" that is nonzero and bounded below. As a consequence, only a limited number of sites will be able to fit within a given distance of any site, and hence the effective coordination number will be finite.

### IV. DISCUSSION

The bound (2) is sufficient to guarantee that, even in the thermodynamic limit, *fraction one* of the monomers are in polymers of finite length for all nonzero values of  $\eta$ . To see this, note that for any finite system size,  $N_0$ , there is an upper bound on the maximum possible length,  $N$ , of a polymer:  $N \leq N_0$ . As a consequence, our bound establishes that the fraction of bonds in polymers of length *less than*  $N$  is *at least*  $f = 1 - P(N)$  for any finite  $N_0$ , no matter how large. Since  $1 - P(N)$  tends rapidly to unity as  $N$  becomes large, *independently* of  $N_0$ , it can be concluded that a fraction arbitrarily close to unity of the bonds (and therefore also of the monomers) are in finite polymers even as  $N_0 \rightarrow \infty$ .

The conclusion in Ref. 10 that a nonzero fraction of the monomers are in infinite polymer(s) for nonzero  $\eta$  was deduced from the assumption of a particular *scaling form* for the distribution of polymer lengths. It follows from the bound (2) that the proposed scaling form is incorrect. The form proposed there is more restrictive than is required by scaling. A more recent analysis of the scaling form for the polymer length distribution using renormalization-group techniques<sup>12</sup> finds results in

accord with our bound.

The bound we have obtained is very weak. We make use only of the large number of ways to cut a very long polymer, not of the (also very large) number of ways to move the two separate pieces relative to each other on the lattice. In translationally invariant systems with spatial dimensionality,  $d$ , greater than two, it is expected, based on both mean-field treatments such as Tobolsky-Eisenberg theory<sup>15</sup> and on renormalization-group arguments on the corresponding  $n \rightarrow 0$  magnet,<sup>3,6</sup> and it is demonstrated in Ref. 12 using direct renormalization-group methods on polymers, that the polymer distribution for  $\kappa > \kappa_c$  is in fact bounded by an exponential of the form

$$P(N) \leq N \exp(-\lambda N \sqrt{K_1}). \quad (19)$$

Here  $\lambda$  is a constant that depends on the value of  $\kappa$ , vanishes as  $\kappa \rightarrow \kappa_c$ , and is expected to vary proportionally to  $(1 - \kappa/\kappa_c)^{1-\alpha-\beta}$  in this limit, and  $\alpha$  and  $\beta$  are the usual critical exponents governing the heat capacity singularity and the shape of the coexistence curve of the  $n \rightarrow 0$  vector model. [Here, and below,  $\kappa_c$  refers specifically to the *critical* value of  $\kappa$ , which may be defined as the smallest value of  $\kappa$  for which, if a polymer end is known to be at the origin in an infinite system, then in the limit  $\eta \rightarrow 0$  followed by the limit  $\kappa \rightarrow \kappa_c$  from below, this polymer chain is infinitely long.]

Although (2) rules out the collapse to infinite polymers in an infinite system at nonzero  $\eta$ , there are two senses in which a collapse of sorts *does* occur as  $\eta$  becomes small. First, in the thermodynamic limit, both mean-field theories, such as Flory theory of polymer solutions<sup>16</sup> applied to equilibrium polymerization<sup>17,18</sup> and (equivalently) Tobolsky-Eisenberg theory of equilibrium polymerization,<sup>15</sup> as well as renormalization-group analysis for  $d > 2$  of the  $n \rightarrow 0$  vector model<sup>3,6</sup> and polymers directly,<sup>19</sup> predict that the polymer concentration vanishes proportionally to  $\eta$  as  $\eta \rightarrow 0$ :

$$\phi_p \equiv \frac{n_p}{N_0} \sim \frac{1}{2} \eta m_o(\kappa), \quad (20)$$

where  $n_p$  is the number of polymers on the lattice, so that the limit

$$m_o(\kappa) \equiv \lim_{\eta \rightarrow 0} \lim_{N_0 \rightarrow \infty} \frac{2n_p}{\eta N_0} \quad (21)$$

exists and is a nonzero, finite function of  $\kappa$  for  $\kappa > \kappa_c$ . Here  $m_o(\kappa)$  is the spontaneous magnetization per site of the corresponding  $n \rightarrow 0$  vector model (in the thermodynamic limit), and vanishes proportionally to  $(1 - \kappa/\kappa_c)^\beta$  as  $\kappa \rightarrow \kappa_c$ . In contrast, the bond density is predicted to be weakly varying with  $\eta$ , approaching a constant as  $\eta \rightarrow 0$ :

$$\phi_l \equiv \frac{n_b}{N_0} \sim \phi_l^o(\kappa), \quad (22)$$

where  $n_b$  is the number of polymer bonds on the lattice, and where  $\phi_l^o(\kappa)$  is essentially (minus) the zero-field internal energy of the corresponding  $n$ -vector model. As a consequence of these predictions, the mean number of

bonds per polymer,  $P \equiv \phi_l/\phi_p$ , diverges proportionally to  $\eta^{-1}$  as  $\eta \rightarrow 0$ . This is, in a certain sense, a ‘‘collapse’’ to infinite polymer(s), but one which occurs only in the limit that  $\eta$  actually reaches 0. The bound (2) rules out the presence of infinite polymers for nonzero  $\eta$ .

There is a second, more interesting sense in which a ‘‘collapse’’ occurs in *finite* systems with spatial dimensionality greater than two, and it is illuminating to examine the  $N_0$  dependence of the value of  $\eta$  for which this occurs. Flory theory can also be applied to equilibrium polymerization on finite lattices,<sup>20,21</sup> where it makes specific predictions about the way the system crosses over from behavior dominated by finite size at very small  $\eta$  (where eventually, as  $\eta \rightarrow 0$ , the lattice must be empty) to essentially thermodynamic limiting behavior at larger  $\eta$  when  $\kappa > \kappa_c$ . These predictions are corroborated by Monté Carlo simulations<sup>20</sup> of the model described by Eq. (1) in three dimensions for  $\kappa > \kappa_c$ . These results will be presented in detail elsewhere. Here we simply report briefly the results relevant to the present discussion.

Suppose that  $\kappa$  is fixed with  $\kappa > \kappa_c$ , and  $N_0$  is sufficiently large. We require that the critical correlations are short ranged compared to the linear dimensions of the lattice. [This requires that the shortest spatial dimension be large compared to  $\xi_0(1 - \kappa/\kappa_c)^{-\nu}$  where  $\nu$  is the critical exponent for the correlation length, and  $\xi_0$  is a constant.] In addition, we require that  $N_0$  be sufficiently large that  $N_0 m_o(\kappa)$  is large compared to unity, where  $m_o(\kappa)$  is given by (21). [Sufficiently near the critical point, this latter requirement is guaranteed by the former, but for larger  $\kappa$  it can be an independent requirement.]

For  $\eta$  small, but sufficiently large that  $\eta N_0 m_o \gg 1$ , the quantities  $\phi_l$ ,  $\phi_p$  and  $P$  have essentially the same behavior as they do in the thermodynamic limit. With decreasing  $\eta$ , however, as the number of polymers,  $n_p \approx \frac{1}{2} \eta N_0 m_o$ , becomes comparable to unity, a smooth, continuous collapse occurs with decreasing  $\eta$  to a state with a single polymer on the lattice. That is,  $n_p$  no longer decreases as  $\frac{1}{2} \eta N_0 m_o$ , but rather ‘‘sticks’’ at  $n_p = 1$ . The bond density still remains essentially constant during this collapse. As a consequence, the mean concentration of polymers actually rises *above* its expected value at the same  $\eta$  and  $\kappa$  on a larger lattice, and the mean size of the polymers,  $P$ , falls *below* its expected value,  $\phi_l/(\eta m_o)$ , for larger lattices, with  $\eta P$  varying as  $\phi_l/\eta N_0$  rather than remaining constant at  $\phi_l/m_o$ , as would be expected in the thermodynamic limit.

At much smaller values of  $\eta$ , the single polymer also goes away, leaving an empty lattice. This occurs at an exponentially small value of  $\eta$  given (within powers of  $N_0$ ) by

$$\eta \sim \exp[-\frac{1}{2} N_0 \beta p(0, \kappa) v_o], \quad (23)$$

where  $p(0, \kappa)$  is the thermodynamic limit of the osmotic pressure in the limit as  $\eta \rightarrow 0$ , and  $v_o$  is the volume per lattice site. This value of  $\eta$  decreases exponentially with lattice size, and so is well separated from the ‘‘collapse’’ value of  $\eta$  for large  $N_0$ . The quantity  $\eta P$  is unaffected by this process, and continues to be given by  $\phi_l/\eta N_0$  all the way to  $\eta = 0$ .

Thus, in a finite system, while there *is* a nonzero value

of  $\eta$  below which the system “collapses” to a state in which virtually all of the monomers are in a single polymer, we see that this collapse does *not* lead to anomalously long polymers, but is actually accompanied by a *lower* than expected molecular weight. Moreover, this collapse occurs at a value of  $\eta$ , say  $\eta^*(N_0)$ , that itself tends to zero proportionally to  $N_0^{-1}$  as  $N_0 \rightarrow \infty$ . It therefore disappears entirely in the thermodynamic limit. As a consequence, for  $d > 2$ , there seems to be no evidence for the proposed<sup>10</sup> collapse transition, and there appears to be positive evidence that polymer lengths obey well the predictions of Flory theory and renormalization-group analysis of polymers and the  $n \rightarrow 0$  vector model.

It has been recognized for some time<sup>22,23</sup> that spatial dimensionality  $d = 2$  is special for polymers. The behavior of polymer models for small  $\eta$ , and in particular in the thermodynamic limit followed by the limit  $\eta \rightarrow 0$  for  $\kappa > \kappa_c$ , is expected to differ in some qualitative ways in two dimensions<sup>24–26</sup> (and also in one dimension<sup>27</sup>) from that for  $d > 2$ . Our bounds in Secs. II and III apply without modification in one and two dimensions. Thus,

whatever differences may exist in the limit  $\eta \rightarrow 0$  between systems with  $d > 2$  and those in  $d = 2$  or  $d = 1$ , there can be no infinite polymer, in either  $d = 2$  or  $d = 1$ , for any *nonzero* value of  $\eta$ , in contrast to the claims in Ref. 10 concerning  $d = 2$ . In this respect, our results are somewhat stronger than those of Schäfer,<sup>12</sup> who considers only  $d > 2$ .

We note, in closing, that the bounds obtained in Secs. II and III apply equally well to the corresponding models in which *ring* polymers as well as chains are allowed. Nothing in the derivations depended on the absence of rings and a demonstration of the nonexistence of infinite rings as well as infinite chains in such systems is an immediate extension. This generalizes still further the applicability of these bounds.

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