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Trees at an Interface

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A lattice tree at an interface between two solvents of different quality is examined as a model of a branched polymer at an interface. Existence of the free energy is shown, and the existence of critical lines in its phase diagram is proven. In particular, there is a line of first order transitions separating a positive phase from a negative phase (the tree being predominantly on either side of the interface in these phases), and a curve of localization–delocalization transitions which separate the delocalized positive and negative phases from a phase where the tree is localized at the interface. This model is generalized to a branched copolymer which is examined in a certain averaged quenched ensemble. Existence of a thermodynamic limit is shown for this model, and it is also shown that the model is self-averaging. Lastly, a model of branched polymers interacting with one another through a membrane is considered. The existence of a limiting free energy is shown, and it is demonstrated that if the interaction is strong enough, then the two branched polymers will adsorb on one another.

KEY WORDS: Trees; phase transition; adsorbing; localization–delocalization; branched copolymer; self-averaging.

1. INTRODUCTION

Models of self-avoiding walks and lattice trees which interact with an interface (the polymer adsorption problem) continues to receive considerable attention. The problem was introduced more than two decades ago,(1, 2) and has received considerable attention since. Further study of various aspects of the polymer adsorption problem was carried out by De'Bell and Lookman,(3) Vanderzande,(4) Vrbová and Whittingtons,(5, 6, 7) Janse van Rensburg,(8, 9) and Eisenriegler.(10) The problem was also considered for models of copolymers(11) and branched copolymers,(12) where the issue of self-averaging in these models was considered.

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Let t_n be the number of lattice trees with n vertices, counted modulo translation, in d dimensions. The coordinates of a vertex V will be denoted $(X(V), Y(V),..., Z(V))$, with $Z(V)$ the dth coordinate. The hyperplane $Z=0$ will also be an interface which divides the d dimensional space into two half-spaces, a positive half-space with vertices with positive Z-coordinate (*positive vertices*), and a negative half-space with vertices with negative Z-coordinates (*negative vertices*). Vertices in the tree which are contained in the hyperplane $Z=0$ are called *visits*. The *growth constant* of lattice trees is defined by

$$\tau_d = \lim_{n\to\infty} [t_n]^{1/n} \qquad \text{in } d \text{ dimensions} \tag{1.1}$$

and this limit is known to exist.[13] Moreover, $t_n \leqslant \tau_d^n$ for all $n > 0$.

A tree counted by t_n is said to be *attached* if it has a vertex V such that $Z(V) \in \{-1, 0, 1\}$.[2] The number of attached trees with n vertices and v visits to the plane $Z=0$ will be denoted by $t_n^>(v)$. An attached tree is a *positive tree* if it does not have any negative vertices. The number of positive trees with v visits will be denoted by $t_n^+(v)$. A negative tree is likewise an attached tree with no positive vertices. By reflection, the number of negative trees with n vertices and v visits is equal to the number of positive trees with n vertices and v visits: $t_n^-(v) = t_n^+(v)$, and notice that $t_n^+(0) = t_n$ as well. The partition functions of models of attached and positive trees which interacts with the $Z=0$ plane are[9, 12]

$$t_n^>(z) = \sum_{v=0}^{n} t_n^>(v)\, z^v, \qquad t_n^+(z) = \sum_{v=0}^{n} t_n^+(v)\, z^v \tag{1.2}$$

where z is an activity conjugate to the number of visits.[3] The existence of limiting free energies in these models are known,[9] and are defined by

$$\mathscr{F}^>(z) = \lim_{n\to\infty} \frac{1}{n} \log t_n^>(z), \qquad \mathscr{F}^+(z) = \lim_{n\to\infty} \frac{1}{n} \log t_n^+(z) \tag{1.3}$$

[2] Attached trees are usually defined by rooting a vertex of the tree in the surface. Constructive techniques are more complicated if the tree has a root (it destroys translational degrees of freedom) since the rooted vertex enjoys special status, and must be treated separately. This alternative definition for an attached tree avoids the creation of a root, and simplifies the constructions leading for example to the existence of a limiting free energy.

[3] Observe that I use the argument of the function to distinguish between the number of trees, and its generating function. In particular, the symbol "v" will always indicate the number of visits, and its generating variable ("conjugate" to v) will be z. That is, if $t_n(v)$ is the number of trees with n vertices and v visits, then $t_n(z)$ is its generating function, defined by $t_n(z) = \sum_v t_n(v)\, z^v$. This convention is analogous to the generating function notation $g(x) = \sum_n g_n x^n$, where $g(x)$ and g_n are distinguished by their arguments.

Microcanonical *density functions* of visits are also known to exist in these models;[9] they are defined via the Legendre transforms of the limiting free energies above:

$$\begin{aligned}
\log \mathscr{P}^{>}(\varepsilon) &= \inf_{z>0} \{\mathscr{F}^{>}(z) - \varepsilon \log z\} = \lim_{n\to\infty} \frac{1}{n} \log t_n^{>}(\lfloor \varepsilon n \rfloor) \\
\log \mathscr{P}^{+}(\varepsilon) &= \inf_{z>0} \{\mathscr{F}^{+}(z) - \varepsilon \log z\} = \lim_{n\to\infty} \frac{1}{n} \log t_n^{+}(\lfloor \varepsilon n \rfloor)
\end{aligned} \tag{1.4}$$

Naturally,[14]

$$\begin{aligned}
\mathscr{F}^{>}(z) &= \sup_{0<\varepsilon<1} \{\log \mathscr{P}^{>}(\varepsilon) + \varepsilon \log z\} \\
\mathscr{F}^{+}(z) &= \sup_{0<\varepsilon<1} \{\log \mathscr{P}^{+}(\varepsilon) + \varepsilon \log z\}
\end{aligned} \tag{1.5}$$

The limiting free energies in Eq. (1.3) are non-analytic functions of z. In particular, there are critical values of z, namely $z_c^{>}$ and z_c^{+}, such that

$$\begin{aligned}
\mathscr{F}^{>}(z) &\begin{cases} = \log \tau_d & \text{if} \quad z \leqslant z_c^{>} \\ > \log \tau_d & \text{if} \quad z > z_c^{>} \end{cases} \\
\mathscr{F}^{+}(z) &\begin{cases} = \log \tau_d & \text{if} \quad z \leqslant z_c^{+} \\ > \log \tau_d & \text{if} \quad z > z_c^{+} \end{cases}
\end{aligned} \tag{1.6}$$

It is known that $1 \leqslant z_c^{>} < z_c^{+} \leqslant \tau_d/\tau_{d-1}$, where τ_{d-1} is the growth constant of trees in $(d-1)$ dimensions. In addition, the following relation involving z_c^{+} and $z_c^{>}$ are known:[9]

$$\frac{z_c^{+}}{z_c^{>}} \geqslant \sqrt{1+\tau_d^{-1}}, \qquad z_c^{+} \geqslant 1 + \tau_d^{-1} \tag{1.7}$$

and it is also a conjecture that $z_c^{>} = 1$. The critical values of z can be defined in terms of the density functions by[14]

$$\log z_c^{+} = -\left[\frac{d^{+}}{d\varepsilon} \log \mathscr{P}^{+}(\varepsilon)\right]_{\varepsilon=0^{+}} \tag{1.8}$$

and similarly for $z_c^>$. Many of these results were derived in terms of a model of adsorbing and collapsing lattice trees (similar results are known for models of adsorbing and collapsing walks and polygons[5–7, 9] and the density function for adsorbing and collapsing polygons has also been examined[8]).

In this paper a model of branched polymers at an interface is examined. In particular, let $t_n^>(v_+, v_-)$ be the number of attached trees with v_+ positive vertices and v_- negative vertices (and consequently $n-(v_+ + v_-)$ *visits* in the interface $Z=0$). The partition function of this model is defined by

$$t_n^>(z_+, z_-) = \sum_{v_+, v_- = 0}^{n+1} t_n^>(v_+, v_-)\, z_+^{v_+} z_-^{v_-} \tag{1.9}$$

and it is apparent that this model is related to the model of adsorbing attached trees with partition function $t_n^>(z)$. In Section 2, I consider the limiting free energy of this model, and shows that it is a non-analytic function. A likely phase diagram which includes a line of first order transitions which meets a curve of localization–delocalization transitions in a triple point is proposed and discussed in Section 2.2. In Section 3 a branched copolymer version of this model is discussed. Existence of the free energy, the general structure of the phase diagram, and self-averaging in an averaged lexicographic quenched ensemble are all examined.

A model of two branched polymers interacting with one another through a membrane can be defined by two lattice trees rooted in the origin and each confined to a half-space. The interaction between the trees is defined by an activity of shared visits (contacts) in the $Z=0$ plane. I show that if the interaction is strong enough, then the trees will adsorb in the membrane, with a density of contacts, regardless of the quality of the solvent on either side of the membrane. Since both trees are random structures, this is also a model of a branched polymer interacting with a random environment.[15] More precisely, consider the visits of one tree to the membrane to alter the properties of the membrane. Then one may think of the membrane as consisting of two types of vertices, randomly (but not independently) distributed. The second tree interacts with these vertices in the membrane, and may be thought of as adsorbing onto a membrane with a random chemical structure. I solve for this model in an annealed ensemble here, where both trees are taken to infinity to define the critical limit. A potentially more interesting case would involve a quenched model, or a model where the trees are taken to infinity independently. It should be apparent to the reader that different outcomes will be encountered in these cases, but I shall leave them for a subsequent paper.

2. TREES AT AN INTERFACE

2.1. The Limiting Free Energy

The existence of a thermodynamic limit in a model of trees defined by the partition function $t_n^>(z_+, z_-)$ in Eq. (1.9) follows from the basic construction of concatenation.[13, 16, 17] Consider Fig. 1. Two attached trees are present, one with n vertices, and the second with m vertices. These two trees must be joined into a single tree, and this is most easily achieved by using *a most popular height argument*.[2, 14] The *top vertex* in an attached tree is its lexicographic most vertex, and the *bottom vertex* is its lexicographic least vertex. Let $t_n^>(v_+, v_- \mid [h_t h_b])$ be the number of attached trees with a top vertex t such that $Z(t) = h_t$ and a bottom vertex b such that $Z(b) = h_b$. The partition function of these trees is defined by

$$t_n^>(z_+, z_- \mid [h_t h_b]) = \sum_{v_+, v_-} t_n^>(v_+, v_- \mid [h_t h_b])\, z_+^{v_+} z_-^{v_-} \tag{2.1}$$

and there are "most popular" values h_t^* and h_b^* (which are dependent on n) for h_b and h_t such that

$$t_n^>(z_+, z_- \mid [h_t^* h_b^*]) \geqslant t_n^>(z_+, z_- \mid [h_t h_b]) \tag{2.2}$$

for all values $[h_t h_b]$. With these definitions, the existence of a thermodynamic limit can be demonstrated.

Theorem 2.1. The limiting free energy for attached trees at an interface exists and is defined by

$$\mathscr{F}(z_+, z_-) = \lim_{n \to \infty} \frac{1}{n} \log t_n^>(z_+, z_-)$$

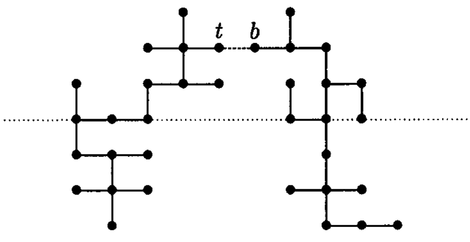

Fig. 1. Concatenation of two attached trees. The top vertex t and bottom vertex b has the same Z-coordinate, and by adding the dashed edge between them a new tree is found.

Proof. Consider first a model of attached trees with top and bottom vertices at the same height from the $Z=0$ plane (or with the same Z-component: $Z(t)=Z(b)=h$). Translate two such trees *parallel to the interface* until the top vertex of the first is one step from the bottom vertex of the second, and join them into a single tree by adding an edge between these vertices (see Fig. 1). If the first tree has n vertices, $v_+ - w_+$ positive vertices and $v_- - w_-$ negative vertices; and the second has m vertices, w_+ positive vertices and w_- negative vertices, then the outcome is a tree with $n+m$ vertices, v_+ positive vertices in the positive half-space and v_- negative vertices. Thus

$$\sum_{w_+=0}^{v_+} \sum_{w_-=0}^{v_-} t_n^>(v_+ - w_+, v_- - w_- \mid [hh])\, t_m^>(w_+, w_- \mid [hh]) \\ \leqslant t_{n+m}^>(v_+, v_- \mid [hh])$$

Multiply this by $z_+^{v_+} z_-^{v_-}$ and sum over v_+ and v_-. This gives

$$t_n^>(z_+, z_- \mid [hh])\, t_m^>(z_+, z_- \mid [hh]) \leqslant t_{n+m}^>(z_+, z_- \mid [hh])$$

Hence, $t_n^>(z_+, z_- \mid [hh])$ is a supermultiplicative function for every value of z_+ and z_- in $[0, \infty)$. By a general theorem on supermultiplicative functions[18] the following limit exits:

$$\lim_{n\to\infty} \frac{1}{n} \log t_n^>(z_+, z_- \mid [hh]) = \mathscr{F}(z_+, z_-) \tag{2.3}$$

and it is finite since $t_n^>(z_+, z_- \mid [hh]) \leqslant t_n^>[\max\{1, z_+, z_-\}]^{n+1}$. Next, consider the fact that $[hh]$ can take at most most $2n+1$ different values in an attached tree with n vertices. Let $[h^*h^*]$ be the most popular of these values, and notice that the limit in Eq. (2.3) is also defined for these choices of h.

There are most popular values for h_t and h_b in $t_n^>(z_+, z_- \mid [h_t h_b])$ in Eq. (2.2), denoted by $[h_t^* h_b^*]$, such that

$$t_n^>(z_+, z_-) = \sum_{[h_t h_b]} t_n^>(z_+, z_- \mid [h_t h_b]) \leqslant (2n+1)^2\, t_n^>(z_+, z_- \mid [h_t^* h_b^*])$$

Next, notice that a tree counted by $t_n^>(z_+, z_- \mid [h_t^* h_b^*])$ can be concatenated with a tree counted by to $t_n^>(z_+, z_- \mid [h_b^* h_t^*])$, by using the construction above. This shows that

$$[t_n^>(z_+, z_- \mid [h_t^* h_b^*])]^2 \leqslant t_{2n}^>(z_+, z_- \mid [h_t^* h_t^*])$$

where the fact that $t_n^>(z_+, z_- \mid [h_t^* h_b^*]) = t_n^>(z_+, z_- \mid [h_b^* h_t^*])$ was used. These inequalities give the following string of inequalities:

$$\begin{aligned} t_n^>(z_+, z_- \mid [h^* h^*]) \leqslant t_n^>(z_+, z_-) &= \sum_{[h_t h_b]} t_n^>(z_+, z_- \mid [h_t h_b]) \\ &\leqslant (2n+1)^2\, t_n^>(z_+, z_- \mid [h_t^* h_b^*]) \\ &\leqslant (2n+1)^2 \sqrt{t_{2n}^>(z_+, z_- \mid [h_t^* h_t^*])} \\ &\leqslant (2n+1)^2 \sqrt{t_{2n}^>(z_+, z_- \mid [h^* h^*])} \end{aligned}$$

Take logarithms of the above, divide by n and let $n \to \infty$. By the squeeze theorem for limits, and by Eq. (2.3) above,

$$\lim_{n \to \infty} \frac{1}{n} \log t_n^>(z_+, z_-) = \mathscr{F}(z_+, z_-)$$

This completes the proof. ∎

The limiting free energy $\mathscr{F}(z_+, z_-)$ is in fact related to the limiting free energy of attached trees adsorbing in the $Z = 0$ plane, given by $\mathscr{F}^>(z)$ in Eq. (1.3). In particular, if $z_+ = z_- = z$, then

$$\sum_{v_+, v_-} t_n^>(v_+, v_-)\, z^{v_+ + v_-} = \sum_{v_1=0}^{n+1} \sum_{v_2=0}^{v_1} t_n^>(v_1 - v_2, v_2)\, z^{v_1} = \sum_{v=0}^{n+1} t_n^>(v)\, z^{n-v} \tag{2.4}$$

where it was noted that trees counted by to $t_n^>(v_1 - v_2, v_2)$ all have exactly $n - v_1 = v$ visits. Comparison with Eq. (1.3) shows that

$$\mathscr{F}(z, z) = \mathscr{F}^>(1/z) + \log z \tag{2.5}$$

Thus, some information about $\mathscr{F}(z_+, z_-)$ along the diagonal in the (z_+, z_-)-plane can be obtained by considering the known properties of $\mathscr{F}^>(z)$. It follows immediately that $\mathscr{F}(z_+, z_-)$ is a non-analytic function. In fact, there is a non-analyticity in $\mathscr{F}(z, z)$ for z somewhere in the interval $[\tau_{d-1}/\tau_d, 1]$, and the conjecture that $z_c^> = 1$ implies that $\mathscr{F}(z, z)$ is conjectured to be non-analytic at $z = 1$.

2.2. The Phase Diagram of Trees at an Interface

There are non-analyticities in $\mathscr{F}(z_+, z_-)$ at points other than the conjectured non-analyticity at the origin. In particular, non-analyticities corresponding to phase boundaries between a localized and a delocalized phase should be present. The connection to adsorbing attached trees pointed out above indicates that there is an adsorbed phase in this model (which will be refered to as the "localized" phase).

To demonstrate the existence of phase boundaries, consider the following argument: Translate an attached tree counted by $t_n^>(v_+, v_-)$ in the Z-direction, until all its vertices are positive. Since each such translation gives a unique outcome,

$$t_n^>(v_+, v_-) \leqslant t_n^>(n, 0) \tag{2.6}$$

Consider now the case that $z_+ \geqslant 1$ and $z_- < 1$. Then

$$\sum_{v_+, v_-} t_n^>(v_+, v_-)\, z_+^{v_+} z_-^{v_-} \geqslant t_n^>(n, 0)\, z_+^n \tag{2.7}$$

if only one term in the sum on the left hand side is kept. On the other hand,

$$\sum_{v_+, v_-} t_n^>(v_+, v_-)\, z_+^{v_+} z_-^{v_-} \leqslant t_n^>(n, 0) \sum_{v_+, v_-} z_+^{v_+} z_-^{v_-} \leqslant t_n^>(n, 0)\, \frac{(n+1)\, z_+^n}{1 - z_-} \tag{2.8}$$

since $z_- < 1$, and since v_+ takes on one of at most $(n+1)$ values. By Eqs. (1.1), (2.6) and (2.7) it follows that (after taking logarithms, dividing by n, and letting $n \to \infty$)

$$\mathscr{F}(z_+, z_-) = \log \tau_d + \log z_+, \qquad \text{for} \quad z_+ \geqslant 1 \quad \text{and} \quad z_- < 1 \tag{2.9}$$

Similarly,

$$\mathscr{F}(z_+, z_-) = \log \tau_d + \log z_-, \qquad \text{for} \quad z_+ < 1 \quad \text{and} \quad z_+ \geqslant 1 \tag{2.10}$$

In other words, $\mathscr{F}(z_+, z_-)$ is a linear function in the second and fourth quadrants in the $(\log z_+, \log , z_-)$-plane. This linearity must be broken in the first and third quadrant, and so $\mathscr{F}(z_+, z_-)$ must be nonanalytic in both those quadrants.

Theorem 2.2. The limiting free energy $\mathscr{F}(z_+, z_-)$ is a non-analytic function. In particular, it has a non-analyticity at origin of the $(\log z_+, \log z_-)$-plane, and its gradient is discontinuous along the line $z_+ = z_-$, $z_+ \geqslant 1$. Moreover, for every $z_+ < 1$ there are non-analyticities in $\mathscr{F}(z_+, z_-)$ at a critical value of z_- in $[z_+, 1]$, and for every $z_- < 1$ at a critical value of z_+ in $[z_-, 1]$.

Proof. Suppose that $z_+ > 1$ and $z_- > 1$. Without loss of generality, let $z_+ \geqslant z_-$. If only the term with $v_+ = n$ is kept in $\sum_{v_+, v_-} t_n^>(v_+, v_-)\, z_+^{v_+} v_-^{v_-}$, then

$$\sum_{v_+, v_-} t_n^>(v_+, v_-)\, z_+^{v_+} z_-^{v_-} \geqslant t_n^>(n, 0)\, z_+^n$$

Thus, by taking logarithms, dividing by n and letting $n \to \infty$, $\mathscr{F}(z_+, z_-) \geqslant \log \tau_d + \log z_+$. On the other hand, by using Eq. (2.6), and noting that $t_n^>(v_+, v_-) = t_n^>(v_-, v_+)$,

$$\begin{aligned}
\sum_{v_+, v_-} t_n^>(v_+, v_-)\, z_+^{v_+} z_-^{v_-} &\leqslant \sum_{v_+, v_-} t_n^>(v_+, v_-)\, z_+^{v_+ + v_-} \\
&\leqslant 2 \sum_{v_+ \geqslant v_-} t_n^>(v_+, v_-)\, z_+^{v_+ + v_-} \\
&\leqslant 2 \sum_{v_+ \geqslant v_-} t_n^>(n, 0)\, z_+^{v_+ + v_-} \\
&\leqslant n(n+1)\, t_n^+(0)\, z_+^{n+1}
\end{aligned}$$

since $t_n^>(n, 0) = t_n^+(0)$. Again, take logarithms, divide by n, and let $n \to \infty$, this gives $\mathscr{F}(z_+, z_-) \leqslant \log \tau_d + \log z_+$. Thus, taken together with Eqs. (2.9) and (2.10),

$$\mathscr{F}(z_+, z_-) = \log \tau_d + \log z_+, \qquad \text{if} \quad z_+ \geqslant z_- \quad \text{and} \quad z_+ \geqslant 1$$

Similarly,

$$\mathscr{F}(z_+, z_-) = \log \tau_d + \log z_-, \qquad \text{if} \quad z_- \geqslant z_+ \quad \text{and} \quad z_- \geqslant 1$$

Thus, the gradient of $\mathscr{F}(z_+, z_-)$ is discontinuous along the line $z_+ = z_-$ in the (z_+, z_-)-plane, where $z_+ \geqslant 1$.

Lastly, consider the case that both $z_+ \leqslant 1$ and $z_- \leqslant 1$. By again only keeping one term in $\sum_{v_+, v_-} t_n^>(v_+, v_-)\, z_+^{v_+} z_-^{v_-}$, it follows that

$$\sum_{v_+, v_-} t_n^>(v_+, v_-)\, z_+^{v_+} z_-^{v_-} \geqslant t_n^>(0, 0)$$

Thus,

$$\mathscr{F}(z_+, z_-) \geqslant \log \tau_{d-1} \tag{2.11}$$

In other words, for every fixed value of z_-, $\mathscr{F}(z_+, z_-) > \log \tau_d + \log z_+$, if z_+ is small enough, and it follows by comparison to Eq. (2.9), that there

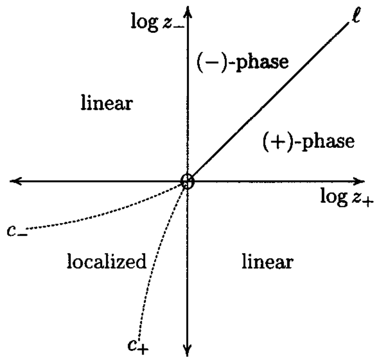

Fig. 2. The expected phase diagram of trees at an interface. The limiting free energy is a linear function of $\log z_-$ in the $(-)$-phase, and a linear function of $\log z_+$ in the $(+)$-phase. The gradient of the limiting free energy is discontinuous along the line $z_+ = z_-$ for $z_+ \geqslant 1$, which defines a line of first order transitions separating the $(-)$-phase and $(+)$-phase. A critical curve outlining the localized phase defines a localization–delocalization transition in this model; presumably this is a line of continuous transitions. The critical curves c_+ and c_- are expected to meet the origin, but this is not proven in the text.

is a non-analyticity in the third quadrant in $\mathscr{F}(z_+, z_-)$ for every $z_- < 1$ at a critical value of z_+ (the locus of these critical points is denoted by c_+ in Fig. 2). By symmetry, $\mathscr{F}(z_+, z_-)$ also has a non-analyticity for every $z_+ < 1$ at a critical value of z_- (the locus of these points is denoted c_- in Fig. 2). Notice that since $\log \tau_d + \log z_+$ gets arbitrarily small as $z_+ \to 0^+$ (and similarly for $\log \tau_d + \log z_-$), the phase boundaries c_+ and c_- must be distinct for small enough z_+ or z_-. ∎

The phase diagram of this model is well described by the results in Theorem 2.2 in the first, second and fourth quadrants of the (z_+, z_-)-plane. The only interesting points are those along the line $z_+ = z_-$ for $z_+ \geqslant 1$, where the gradient of $\mathscr{F}(z_+, z_-)$ is discontinuous, and so a *first* order transition occurs in the model along this line. The phases corresponding to the delocalized regime will be called the $(+)$-phase and $(-)$-phase. The thermodynamic properties of these phases are the same (with z_+ and z_- interchanged), but they coexist along the line of first order transitions. The situation is somewhat more complicated in the third quadrant. If both z_+ and z_- are small enough, then the tree should adsorb in the interface. This transition will localize the tree in the interface, and it is called a *localization–delocalization* transition. In analogy with the adsorption transition, it seems likely that this is a continuous transition. The existence of an adsorption transition in a model of attached trees *implies* the existence of the localized phase, and from the argument in the preceding section, it appears that the localized phase will be indistinghuishable from the adsorbed phase of the attached tree. The localization–delocalization occurs along two critical curves (c_+ and c_- in Fig. 2), and these curves meet in the line $z_+ = z_-$ in the point $(z_c^>, z_c^>)$. Thus, the conjecture that $z_c^> = 1$ seems to indicate that c_+ and c_- meet in the origin in Fig. 2.

That c_+ and c_- are distinct in most of the third quadrant is seen as follows. Consider first the lower bound on $\mathscr{F}(z_+, z_-)$ derived above (Eq. (2.3) in the proof of Theorem 2.2), namely $\mathscr{F}(z_+, z_-) \geqslant \log \tau_{d-1}$. In particular, if $\mathscr{F}(z_+, z_-) = \log \tau_d + \log z_-$ in the $(-)$-phase, then a comparison with the bound $\mathscr{F}(z_+, z_-) \geqslant \log \tau_{d-1}$ indicates that c_- should be confined to the strip $[0, 1] \times [\tau_{d-1}/\tau_d, 1]$. Similarly, the phase boundary c_+ is confined to $[\tau_{d-1}/\tau_d, 1] \times [0, 1]$. It is in fact possible to improve somewhat on these estimates by assuming that c_+ and c_- are continuous at $z_+ = 0$ and $z_- = 0$ respectively and then showing that at least one point on each of c_+ and c_- are in the interior of the third quadrant in Fig. 2.

Theorem 2.3. The free energy of attached trees at an interface, $\mathscr{F}(z_+, z_-)$, is non-analytic in the points $(0, [z_c^+]^{-1})$ and $([z_c^+]^{-1}, 0)$.

Proof. Notice that

$$t_n^>(0, z_-) = \sum_{v_-=0}^{n+1} t_n^>(0, v_-)\, z_-^{v_-} = z_-^n \sum_{v_-=0}^{n+1} t_n^+(n - v_-)[z_-^{-1}]^{n-v_-}$$

Take logarithms, divide by n and let $n \to \infty$. This shows that

$$\mathscr{F}(0, z_-) = \log z_- + \mathscr{F}^+(z_-^{-1})$$

By Eq. (1.6), $\mathscr{F}^+(z)$ is non-analytic at $z = z_c^+$, and so $\mathscr{F}(0, z_-)$ is non-analytic at $z_- = [z_c^+]^{-1}$. A similar argument at the point $(z_+, 0)$ completes the proof. ▌

Theorem 2.3 shows that if the phase boundaries c_+ and c_- are continuous at $z_+ = 0$ and $z_- = 0$ respectively, then at least part of each are in the interior of the third quadrant in Fig. 2. In these cases the curve c_+ in Fig. 2 could be asymptotic to $z_+ = [z_c^+]^{-1}$, and c_- could be asymptotic to $z_- = [z_c^+]^{-1}$.

3. BRANCHED COPOLYMERS INTERACTING AT AN INTERFACE

A model of branched copolymers can be constructed by coloring the vertices in a lattice tree. There are two aspects in this coloring. The first is a sequence of colors, say $\chi = (\chi_1, \chi_2,...)$, and the second is a rule for assigning the colors to the vertices in the tree. Some colorings of the tree can be done using a different approach. For example, since any tree is a bipartite graph, an alternating coloring of the tree can be defined by using the bipartition of the vertex set. Block colorings of a tree can be defined by using the connectivity properties of the tree. For example, a 2-colored tree is said to be a model of a 2-block copolymer if there is an edge which can be deleted to cut the tree into two monochromatic subtrees. More generally, an N-colored tree is a model of a N-block copolymer if $N-1$ edges, each with two end-vertices of different color, can be deleted to leave N monochromatic subtrees. These models of block copolymers are regular if all blocks have the same size. Notice that a 2-colored tree can also be a regular N-block copolymer if there are $N-1$ edges joining vertices of different colors which can be deleted to leave monochromatic blocks all of the same size (and each of either color). The number of blocks of a given color will vary from tree to tree, and depends on the connectivity properties of the tree. Thermodynamic limits can be taken in such a block copolymer model by either taking the number of blocks to infinity, or by taking the size of the blocks to infinity. Some models of adsorbing alternating and block branched copolymers have also been discussed,[(12)] and I shall not consider those here again.

A random coloring of a tree can be constructed by assigning colors in a random sequence χ to the vertices in the tree. To make this more precise, let $\chi_i \in Y$ be one of N colors (labeled by 1, 2,..., N) sampled from the probability space Y. Define the product space $X = Y \times Y \times Y \times \cdots$ (it is also a probability space); and an element $\chi \in X$ is a random sequence of colors, each color identically distributed and independent. X has a probability measure $\mu(X) = 1$. A particularly simple assignment of colors in χ to vertices in a tree T is to use a lexicographic rule:[(12)] χ_1 is assigned to the lexicographic least vertex, χ_2 to the next, and so on. Observe that χ is an infinite sequence, and the tree is finite with (say) $n+1$ vertices; the coloring is done by assigning the first $n+1$ colors in χ, and then discarding the remaining part of the sequence. If each tree in an ensemble of trees is colored by χ in this way, then a model of a *lexicographic quenched branched copolymer* is obtained. Several results are known for this in the averaged lexicographic quenched ensemble, and in an annealed ensemble. In particular, existence of the limiting free energy, the existence of a critical adsorption activity, and self-averaging, are all known for the adsorbing averaged lexicographic quenched branched copolymer.[(12)] This model is of course unphysical, and it is notable that the coloring of a tree is dependent on its embedding. Thus, this is not a true quenched model, and it is difficult to imagine a physical situation where it would be of relevance. One may imagine other models for coloring the vertices in the tree, but those models seem quite hard. So far, this remains the only quenched branched copolymer which have been treated with some measure of success, and it is an open problem to find other models of quenched branched copolymers and to treat them successfully.

Annealed models of branched copolymers at an interface is no more interesting than the homopolymer models studied in Section 2 (and this is also known for models of adsorbing polygons[14] and trees[12]). In particular, let the activity of a positive vertex be z_+ with probability p, and y_+ with probability $q = 1 - p$; and of a negative vertex be z_- with probability p, y_- with probability q. That is, a vertex is colored either such that it interacts with activities z_+ and z_- (with probability p), or with activities y_+ and y_- (with probability q). Then the partition function in this model is

$$\begin{aligned}
&t_n^A(z_+, z_-; y_+, y_-)\\
&\quad = \sum_{v_+, v_- = 0}^{n} t_n^>(v_+, v_-) \sum_{w_+ = 0}^{v_+} \binom{v_+}{w_+} (pz_+)^{w_+} (qy_+)^{v_+ - w_+}\\
&\qquad \times \sum_{w_- = 0}^{v_-} \binom{v_-}{w_-} (pz_-)^{w_-} (qy_-)^{v_- - w_-}\\
&\quad = \sum_{v_+, v_- = 0}^{n} t_n^>(v_+, v_-)(pz_+ + qy_+)^{v_+} (pz_- + qy_-)^{v_-}\\
&\quad = t_n^>(pz_+ + qy_+, pz_- + qy_-) \qquad (3.1)
\end{aligned}$$

Thus, the annealed free energy is given by

$$\mathscr{F}^A(z_+, z_-; y_+, y_-) = \mathscr{F}(pz_+ + qy_+, pz_- + qy_-) \qquad (3.2)$$

with $\mathscr{F}(z_+, z_-)$ defined in Theorem 2.1. The phase diagram is similar to Fig. 2, with the necessary reinterpretations of the axes, and this model is no more interesting than the model in Section 2. Moreover, there are localized–delocalized transitions in this model, and a line of first order transitions seperating a $(+)$-phase from a $(-)$-phase. This sums up the situation for an annealed model with two types of monomers, but the situation is no more difficult if there are more than two types of monomers. All that will change is the replacement of the binomial factors in Eq. (3.1) with multinomial factors (and more activities), and the outcome will be generally similar.

3.1. An Averaged Lexicographic Quenched Branched Copolymer at an Interface

Let $\chi \in X$ be a random sequence of colors in the set $\mathscr{C} = \{1, 2,..., N\}$. Each color will be assigned an activity: z_i^+ will be the activity of a positive vertex of color i, and similarly, z_i^- will be the activity of a negative vertex of color i. I shall denote these activities by

$$\{z_\chi^+\} = \{z_1^+, z_2^+,..., z_N^+\} \tag{3.3}$$

and

$$\{z_\chi^-\} = \{z_1^-, z_2^-,..., z_N^-\} \tag{3.4}$$

In addition, define

$$\{z_\chi\} = \{z_\chi^+; z_\chi^-\} \tag{3.5}$$

The activity of a vertex V of color $\chi(V)$ in a tree colored lexicographically by χ is given by

$$z(V) = z_{\chi(V)}^+ \theta(Z(V)-1) + z_{\chi(V)}^- \theta(-Z(V)-1) + \delta(Z(V), 0) \tag{3.6}$$

where $\theta(t) = 1$ if $t \geqslant 0$ and zero otherwise. In other words, $z(V) = z_{\chi(V)}^+$ if V is positive, $z(V) = z_{\chi(V)}^-$ if V is negative, and $z(V) = 1$ if V is a visit.

Let $\tau_n(\chi)$ be the set of trees with n edges and colored lexicographically by χ. It is understood that only the first $n+1$ colors in χ is assigned to vertices of trees in $\tau_n(\chi)$; the remaining colors are truncated from χ. Let the number of trees in $\tau_n(\chi)$ (counted up to translation) be $t_n(\chi)$. The weight of a tree T counted by $t_n(\chi)$ is determined by the colors of its vertices and the activities. In this case I do not distinghuish between positive and negative vertices (since the trees are not attached), so weigh all vertices by the activities $\{z_\chi^*\} = \{z_1^*, z_2^*,..., z_N^*\}$, analogous to the above. Then the weight of a tree T is

$$w(T) = \prod_{V \in T} z_\chi^*(V) \tag{3.7}$$

The partition function of this model is therefore

$$t_n(\{z_\chi^*\} \mid \chi) = \sum_{T \in \tau_n(\chi)} w(T) \tag{3.8}$$

Trees counted by $t_n(\{z_\chi^*\} \mid \chi_1)$ and by $t_m(\{z_\chi^*\} \mid \chi_2)$ can be concatenated by translating a tree from the first so that its top vertex is one step to the left of the bottom vertex of the second tree. Since the vertices are colored in a lexicographic increasing sequence,

$$t_n(\{z_\chi^*\} \mid \chi_1)\, t_m(\{z_\chi^*\} \mid \chi_2) \leqslant t_{n+m+1}(\{z_\chi^*\} \mid \chi_1\chi_2) \tag{3.9}$$

where $\chi_1\chi_2$ are interpreted as the first $n+1$ colors from χ_1, followed by $m+1$ colors from χ_2. Take the logarithm of this, and the average lexicograhic quench is defined by

$$\langle \log t_n(\{z_\chi^*\} \mid \chi\rangle_\chi = \int_X d\chi \log t_n(\{z_\chi^*\} \mid \chi) \tag{3.10}$$

This shows that if the average is taken over $\chi_1\chi_2$ in Eq. (3.9), then

$$\langle \log t_n(\{z_\chi^*\} \mid \chi)\rangle_\chi + \langle \log t_m(\{z_\chi^*\} \mid \chi)\rangle_\chi \leqslant \langle \log t_{n+m+1}(\{z_\chi^*\} \mid \chi)\rangle_\chi \tag{3.11}$$

This superadditive inequality implies that there exists a limiting free energy in this model,[18] defined by

$$\mathscr{F}^*(\{z_\chi^*\}) = \lim_{n\to\infty} \frac{1}{n} \langle \log t_n(\{z_\chi^*\} \mid \chi)\rangle_\chi \tag{3.12}$$

and it is finite since $t_n(\{z_\chi^*\} \mid \chi) \leqslant t_n[\max\{z_\chi^*\}]^n$. Observe that positive trees may be used here instead. Since any tree can be translated to become a positive tree, and exactly two positive trees can be translated to the same tree, it is the case that

$$t_n(\{z_\chi^*\} \mid \chi) \leqslant t_n^+(\{z_\chi^*\} \mid \chi) \leqslant 2t_n(\{z_\chi^*\} \mid \chi) \tag{3.13}$$

with the consequence that

$$\mathscr{F}^*(\{z_\chi^*\}) = \lim_{n\to\infty} \frac{1}{n} \langle \log t_n^+(\{z_\chi^*\} \mid \chi)\rangle_\chi \tag{3.14}$$

However, the real intent is to examine a model of attached colored trees at an interface, with different activities on either side of the interface defined by Eq. (3.5). If $\tau_n^>(\chi)$ is the set of attached trees colored lexicographically by χ, then the partition function in this model is

$$t_n^>(\{z_\chi\} \mid \chi) = \sum_{T\in\tau_n^>(\chi)} \prod_{V\in T} z(V) \tag{3.15}$$

with $z(V)$ given by Eq. (3.5). Define the weight of each tree by

$$w(T) = \prod_{V \in T} z(V) \tag{3.16}$$

so that $t_n^{>}(\{z_\chi\} \mid \chi) = \sum_{T \in \tau_n^{>}(\chi)} w(T)$. To see that there is a limiting free energy in this model of attached trees, consider $t_n^{>}(\{z_\chi\} \mid \chi \mid [h_t h_b])$; the partition function of trees with heights of top and bottom vertices h_t and h_b.

Examine first the partition function $t_n^{>}(\{z_\chi\} \mid \chi \mid [hh])$, where both the heights of the top and bottom vertices are the same. In particular, let S be a tree counted by $t_n^{>}(\{z_\chi\} \mid \chi_1 \mid [hh])$, and let T be a tree counted by $t_m^{>}(\{z_\chi\} \mid \chi_2 \mid [hh])$. Since the top and bottom vertices of S and T have the same heights, T can be translated parallel to the $Z=0$ plane such that its bottom vertex has X-coordinate one step bigger than the X-coordinate of the top vertex of S (see Fig. 1), and with all other coordinates of these vertices the same. S and T can now be concatenated into a new tree $S \oplus T$ by adding a single edge between the top vertex of S and the bottom vertex of T. Since all the vertices in T are lexicographic larger than the vertices in S, and the colors in χ_1 and χ_2 are assigned lexicographically to S and T, the coloring of $S \oplus T$ is given by the concatenated sequence $\chi_1 \chi_2$ (where it is kept in mind that $\chi_1 \chi_2$ is composed of the first $(n+1)$ colors from χ_1, followed then by the first $(m+1)$ colors from χ_2). Moreover, the weight of $S \oplus T$ is $w(S)\, w(T)$, since the Z-components of all vertices are unchanged. Therefore,

$$t_n^{>}(\{z_\chi\} \mid \chi_1 \mid [hh])\, t_m^{>}(\{z_\chi\} \mid \chi_2 \mid [hh]) = \sum_S \sum_T w(S)\, w(T) = \sum_S \sum_T w(S \oplus T) \tag{3.17}$$

where the sum over S is over all trees counted by $t_n^{>}(\{z_\chi\} \mid \chi_1 \mid [hh])$, and the sum over T is over all trees counted by $t_m^{>}(\{z_\chi\} \mid \chi_2 \mid [hh])$. But there are also many trees counted by $t_{n+m+1}^{>}(\{z_\chi\} \mid \chi_1 \chi_2 \mid [hh])$ which are not generated by the concatenation, therefore

$$t_n^{>}(\{z_\chi\} \mid \chi_1 \mid [hh])\, t_m^{>}(\{z_\chi\} \mid \chi_2 \mid [hh]) \leqslant t_{n+m+1}^{>}(\{z_\chi\} \mid \chi_1 \chi_2 \mid [hh]) \tag{3.18}$$

The consequence of Eq. (3.18) is the following theorem.

Theorem 3.1. The limiting free energy

$$\mathscr{F}^q(\{z_\chi\}) = \lim_{n \to \infty} \frac{1}{n} \langle \log t_n^{>}(\{z_\chi\} \mid \chi) \rangle_\chi$$

of an attached tree model of a copolymer at an interface in the averaged lexicographic quenched model exists and is a convex function in the logarithms of each of its activities.

Proof. By Eq. (3.18),

$$\log t_n^>(\{z_\chi\}) \mid \chi_1 \mid [hh]) + \log t_n^>(\{z_\chi\} \mid \chi_2 \mid [hh]) \leqslant \log t_{n+m+1}^>(\{z_\chi\} \mid \chi_1\chi_2 \mid [hh])$$

Take the average of the quenches $\chi_1\chi_2$ in the inequality above, this immediately shows that

$$\langle \log t_n^>(\{z_\chi\}) \mid \chi \mid [hh])\rangle_\chi + \langle \log t_m^>(\{z_\chi\} \mid \chi \mid [hh])\rangle_\chi \leqslant \langle \log t_{n+m+1}^>(\{z_\chi\} \mid \chi \mid [hh])\rangle_\chi$$

Notice furthermore that

$$t_n^>(\{z_\chi\} \mid \chi \mid [hh]) \leqslant t_n^>[\max_\chi \{z_\chi\}]^n$$

and it follows that

$$\lim_{n\to\infty} \frac{1}{n} \langle \log t_n^>(\{z_\chi\} \mid \chi \mid [hh])\rangle_\chi = \mathscr{F}^q(\{z_\chi\})$$

exists and is finite.[18] That it is convex in the logarithm of its activities follows from a standard application of the Cauchy–Schwartz inequality. The same most popular arguments for $[hh]$ and $[h_b h_t]$ are now used as in Theorem 2.1 to see that

$$\lim_{n\to\infty} \frac{1}{n} \langle \log t_n^>(\{z_\chi\} \mid \chi)\rangle_\chi = \mathscr{F}^q(\{z_\chi\})$$

This completes the proof. ∎

More can be said about $\mathscr{F}^q(\{z_\chi\})$. In particular, suppose that for each color in $\mathscr{C}$, $z_\chi^+ \geqslant 1$ and $z_\chi^+ \geqslant z_\chi^-$. Consider any tree T counted by $t_n^>(\{z_\chi\} \mid \chi)$. T can be translated normal to the interface until all its vertices are positive vertices, and this construction changes at most $n+1$ trees into one tree with positive vertices. Since $z_\chi^+ \geqslant z_\chi^-$, this shows that

$$t_n^>(\{z_\chi\} \mid \chi) \leqslant (n+1)\, t_n^+(\{z_\chi^+\} \mid \chi) \tag{3.19}$$

On the other hand, every tree counted by $t_n^+(\{z^+\chi\} \mid \chi)$ also contributes to $t_n^>(\{z_\chi\} \mid \chi)$, which means that

$$t_n^>(\{z_\chi\} \mid \chi) \geqslant t_n^+(\{z_\chi^+\} \mid \chi) \tag{3.20}$$

Therefore, if the logarithms of Eqs. (3.19) and (3.20) are taken, and if those inequalities are averaged with respect to χ, divided by n, and $n \to \infty$, then it follows that $\mathscr{F}^q(\{z_\chi\})$ is only a function of the activities $\{z_\chi^+\}$ (and is independent of $\{z_\chi^-\}$). In other words, under the conditions that $z_\chi^+ \geqslant z_\chi^-$, and $z_\chi^+ \geqslant 1$ for each χ, it is energetically favourable to the tree to have all of its vertices in one phase. In addition, since there is no entropic disadvantage to translating the tree, it will delocalize into the prefered phase.

Alternatively, if any activity in $\{z_\chi^-\}$ is large enough, then $\mathscr{F}^q(\{z_\chi\})$ will be dependent on it. In particular, if $w_i(\chi)$ is the number of vertices of color i in the first $n+1$ colors in the sequence χ, then since there is at least one tree with all vertices negative, and if the logarithm is taken of the above, and the average

$$t_n^>(\{z_\chi\}) \mid \chi) \geqslant \prod_{i \in \mathscr{C}} [z_i^-]^{w_i(\chi)} \tag{3.21}$$

and if the logarithm is taken of the above, and the average over all χ is done, then

$$\langle \log t_n^>(\{z_\chi\} \mid \chi) \rangle_\chi \geqslant \frac{n}{N} \left(\sum_{i \in \mathscr{C}} \log z_i^- \right) \tag{3.22}$$

Dividing by n, and taking $n \to \infty$ gives

$$\mathscr{F}^q(\{z_\chi\} \geqslant \frac{1}{N} \left(\sum_{i \in \chi} \log z_i^- \right) \tag{3.23}$$

and so if one of the z_χ^- is increased enough, then $\mathscr{F}^q(\{z_\chi\})$ will be dependent on it.

Theorem 3.2. Suppose that $z_i^+ \geqslant z_i^-$ $z_i^+ \geqslant 1$ for each $i \in \chi$, then $\mathscr{F}^q(\{z_\chi\})$ is a function only of $\{z_\chi^+\}$. On the other hand, if z_i^- is now increased (where i is fixed), then $\mathscr{F}^q(\{z_\chi\})$ will become a function of z_i^-, for large enough values of z_i^-. This is also true if the roles of $\{z_\chi^+\}$ and $\{z_\chi^-\}$ are interchanged.

Thus, the ($2N$-dimensional) phase space of this model has some critical surfaces. In particular, it appears that in the subspaces $z_i^+ \geqslant z_i^-$ and $z_i^- \geqslant z_i^+$ the free energy is dominated by positive and negative trees respectively, with no intersections with the interface. These phases are the positive and negative phases identified for the model in Section 2. Increasing any one of the activities z_i^- will take the positive phase through a transition, which presumably results in a phase with vertices of color i predominantly negative, and the remaining vertices predominantly positive. This is a localized phase, and there is a phase boundary into it for each i.

There also is a localization–delocalization transition in this model; in particular, in the subspaces defined by $z_i^+ = z_+$ and $z_i^- = z_-$ for all $i \in \chi$ the model in Section 2 is recovered, and the phase diagram in Fig. 2 is therefore a section through the phase diagram in the model here.

3.2. Self-Averaging in the Lexicographic Quenched Branched Copolymer at an Interface

In this section the issue of self-averaging in the above model is considered. The proof that this model is self-averaging is similar to the proof that the adsorbing lexicographic quenched branched polymer model is self-averaging,[12] and it has two steps. In the first instance, using concatenation, I show that for almost all sequences of colors χ_0 sampled from X, it is the case that $\liminf_{n\to\infty}[\log t_n^>(\{z_\chi\} \mid \chi_0)]/n \geqslant \mathscr{F}^q(\{z_\chi\})$. Next, it is shown that the averaged quenched free energy is also an upper bound on the lim sup for almost all sequences $\chi_0 \in X$. Together, these two results show that the model is indeed self-averaging.

Theorem 3.3. Let $\chi_0 \in X$ be a random sequence of independent identically distributed colors. Then

$$\liminf_{n\to\infty} \frac{1}{n} \log t_n^>(\{z_\chi\} \mid \chi_0) \geqslant \mathscr{F}^q(\{z_\chi\})$$

with probability one.

Proof. Define $n = mM + r$, and cut the sequence χ_0 into subsequences $\{\chi_i\}_{i=1}^{\infty}$ each of length M, and let χ_r be the first r colors in the $(m+1)$th subsequence. Define the following:

$$\{v_\chi\} \equiv \{v_1^+, v_2^+,..., v_N^+; v_1^-, v_2^-,..., v_N^-\}$$

where v_i^+ is the number of positive vertices of color i, etc. Then

$$t_n^>(\{z_\chi\} \mid \chi) = \sum_{\{v_\chi\}} t_n^>(\{v_\chi\} \mid \chi)\{z_\chi\}^{\{v_\chi\}}$$

where $\{z_\chi\}^{\{v_\chi\}}$ is interpreted as $[z_1^+]^{v_1^+} [z_2^+]^{v_2^+} \cdots [z_N^-]^{v_N^-}$.

Concatenate trees counted by $t^{>}_{M-1}(\{w_{\chi_i}\} \mid \chi_i \mid [hh])$ for $i=1, 2,..., m$, and one tree counted by $t^{>}_{n}(\{w_{\chi_r}\} \mid \chi_r \mid [hh])$ to find a tree counted by $t^{>}_{n}(\{v_{\chi_0}\} \mid \chi_0 \mid [hh])$, using the construction described before Eq. (3.17). This shows that

$$\left[\prod_{i=1}^{m} t^{>}_{M-1}(\{w_{\chi_i}\} \mid \chi_i \mid [hh])\right] t^{>}_{r}(\{w_{\chi_r}\} \mid \chi_r \mid [hh])\, \delta\left(\{v_{\chi_0}\} - \sum_i \{w_{\chi_i}\}\right)$$
$$\leqslant t^{>}_{n}(\{v_{\chi_0}\} \mid \chi_0 \mid [hh])$$

Multiply this by $\{z_\chi\}^{\{v_{\chi_0}\}}$, and sum over all the $\{v_{\chi_0}\}$; this shows that

$$\left[\prod_{i=1}^{m} t^{>}_{M-1}(\{z_{\chi_i}\} \mid \chi_i \mid [hh])\right] t^{>}_{r}(\{z_{\chi_r}\} \mid \chi_r \mid [hh]) \leqslant t^{>}_{n}(\{z_{\chi_0}\} \mid \chi_0 \mid [hh])$$

Fix M, and choose the most popular value of $[hh]=[h^*h^*]$ in $t^{>}_{M-1}(\{z_{\chi_i}\} \mid \chi_i \mid [hh])$. Take the logarithm of the above, divide by n, and now take the lim inf of the right hand side. Then $n \to \infty$ and this shows that

$$\liminf_{m\to\infty} \frac{1}{m} \sum_{i=1}^{m} \frac{1}{M} \log t^{>}_{M-1}(\{z_{\chi_i}\} \mid \chi_i \mid [h^*h^*])$$
$$\leqslant \liminf_{n\to\infty} \frac{1}{n} \log t^{>}_{n}(\{z_{\chi_0}\} \mid \chi_0 \mid [h^*h^*])$$

By the weak law of large numbers,[20] it follows for almost all random sequences χ_0 that the left hand side above is the averaged lexicographic quenched free energy

$$\left\langle \frac{1}{M} \log t^{>}_{M-1}(\{z_\chi\} \mid \chi \mid [h^*h^*])\right\rangle_\chi \leqslant \liminf_{n\to\infty} \frac{1}{n} \log t^{>}_{n}(\{z_{\chi_0}\} \mid \chi_0 \mid [h^*h^*])$$
$$\leqslant \liminf_{n\to\infty} \frac{1}{n} \log t^{>}_{n}(\{z_{\chi_0}\} \mid \chi_0)$$

The same arguments as in Theorem 2.1 can now be applied to the left hand side of the last inequality to remove $[h^*h^*]$. Taking $M \to \infty$ then gives

$$\mathscr{F}^{q}(\{z_\chi\}) \leqslant \liminf_{n\to\infty} \frac{1}{n} \log t^{>}_{n}(\{z_{\chi_0}\} \mid \chi_0)$$

which completes the proof. ∎

Since X is a probability space with uniform measure $\mu(X)=1$, the averaged lexicographic quenched free energy is defined by

$$\mathscr{F}^q(\{z_\chi\}) = \lim_{n\to\infty} \frac{1}{n} \int_X d_\chi \log t_n^>(\{z_\chi\} \mid \chi) \tag{3.24}$$

In addition, Theorem 3.3 shows that

$$\mathscr{F}^q(\{z_\chi\}) \leqslant \liminf_{n\to\infty} \frac{1}{n} \log t_n^>(\{z_\chi\} \mid \chi_0) \tag{3.25}$$

for almost all $\chi_0 \in X$. In fact, this last inequality is an equality.

Theorem 3.4. For almost all $\chi_0 \in X$,

$$\mathscr{F}^q(\{z_\chi\}) = \liminf_{n\to\infty} \frac{1}{n} \log t_n^>(\{z_\chi\} \mid \chi_0)$$

Proof. First apply Fatou's lemma to Eq. (3.24):

$$\begin{aligned}\mathscr{F}^q(\{z_\chi\}) &= \lim_{n\to\infty} \frac{1}{n} \int_X d\chi \log t_n^>(\{z_\chi\} \mid \chi) \\ &\geqslant \int_X d\chi \liminf_{n\to\infty} \frac{1}{n} \log t_n^>(\{z_\chi\} \mid \chi)\end{aligned} \tag{3.26}$$

Next, decompose X into disjoint sets $X = X_- \cup X_0 \cup X_+$ by defining

$$\liminf_{n\to\infty} \frac{1}{n} \log t_n^>(\{z_\chi\} \mid \chi_0) = \mathscr{F}^q(\{z_\chi\}), \qquad \text{if} \quad \chi_0 \in X_0$$

$$\liminf_{n\to\infty} \frac{1}{n} \log t_n^>(\{z_\chi\} \mid \chi_0) < \mathscr{F}^q(\{z_\chi\}), \qquad \text{if} \quad \chi_0 \in X_-$$

$$\liminf_{n\to\infty} \frac{1}{n} \log t_n^>(\{z_\chi\} \mid \chi_0) > \mathscr{F}^q(\{z_\chi\}), \qquad \text{if} \quad \chi_0 \in X_+$$

By Eq. (3.25) above, $\mu(X_-)=0$. On the other hand, suppose that $\mu(X_+)=a>0$, so that $\mu(X_0)=1-a$. Then

$$\int_X d\chi \liminf_{n\to\infty} \frac{1}{n} \log t_n^>(\{z_\chi\} \mid \chi) > a\mathscr{F}^q(\{z_\chi\}) + (1-a)\, \mathscr{F}^q(\{z_\chi\}) = \mathscr{F}^q(\{z_\chi\})$$

This is in contradiction with Eq. (3.26) above, so that $\mu(X_+)=0$. Thus,

$$\liminf_{n\to\infty} \frac{1}{n} \log t_n^{>}(\{z_\chi\} \mid \chi_0) = \mathscr{F}^q(\{z_\chi\})$$

for almost all $\chi_0 \in X$. ∎

The only remaining issue is to show that the lim inf in Theorem 3.4 can be replaced by a limit.

Theorem 3.5. For almost all $\chi_0 \in X$,

$$\mathscr{F}^q(\{z_\chi\}) = \lim_{n\to\infty} \frac{1}{n} \log t_n^{>}(\{z_\chi\} \mid \chi_0)$$

Proof. Suppose that

$$\liminf_{n\to\infty} \frac{1}{n} \log t_n^{>}(\{z_\chi\} \mid \chi) > \mathscr{F}^q(\{z_\chi\})$$

for any $\chi \in U$, where $\mu(U)>0$. The proof proceeds by showing that this gives a contradiction. There exists a $\varepsilon_\chi > 0$ such that for any $\chi \in U$, there is a convergent sequence

$$\frac{1}{n_i} \log t_{n_i}^{>}(\{z_\chi\} \mid \chi) > \mathscr{F}^q(\{z_\chi\}) + \varepsilon_\chi/2$$

for an infinite set of integers $\{n_i\}$. For each $\chi \in U$, define

$$T_n(\chi) = \frac{1}{n_{i+1}} \log t_{n_{i+1}}^{>}(\{z_\chi\} \mid \chi) > \mathscr{F}^q(\{z_\chi\}), \qquad \text{if} \quad n_i < n \leqslant n_{i+1}$$

Then $\lim_{n\to\infty} T_n(\chi)$ exists for each $\chi \in U$. For all values of n, and $\chi \in U$,

$$T_n(\chi) > \mathscr{F}^q(\{z_\chi\}) + \varepsilon_\chi/2.$$

Put $T_n(\chi) = \mathscr{F}^q(\{z_\chi\})$ if $\chi \notin U$, then $T_n(\chi)$ is measurable on X, and by the Lebesque Dominated Convergence Theorem,

$$\int_U d\chi \lim_{n\to\infty} T_n(\chi) = \lim_{n\to\infty} \int_U d\chi\, T_n(\chi) = \lim_{i\to\infty} \int_U d\chi \frac{1}{n_i} \log t_{n_i}^{>}(\{z_\chi\} \mid \chi)$$

Thus, integrating now over all of X,

$$\lim_{n\to\infty}\int_X d\chi \frac{1}{n}\log t_n^>(\{z_\chi\}\mid\chi)=(1-\mu(U))\,\mathscr{F}^q(\{z_\chi\})+\mu(U)(\mathscr{F}^q(\{z_\chi\})$$
$$+\int_U d\chi[\varepsilon_\chi/2])>\mathscr{F}^q(\{z_\chi\})$$

in contradiction with Eq. (3.24). ∎

4. A MODEL OF INTERACTING BRANCHED BLOCK COPOLYMERS AT AN INTERFACE

Let A be a red tree with n edges, and B be a blue tree with n edges, both rooted at the vertex v in the $Z=0$ plane. Suppose furthermore that A is a *positive tree*, and B is a *negative tree*. Thus, a model of a branched diblock copolymer at an interface with each block confined to either side of the interface is obtained. A *contact* between the red and blue blocks is a vertex in the $Z=0$ plane which are in both blocks (that is, it is a visit shared between the blue and red subtrees). Let $t^\delta_{n,n}(v_+, v_-, c)$ be the number of such trees, with n edges each in the red and blue subtrees, with v_+ positive red vertices, and v_- negative blue vertices, and with c contacts (shared visits) in the $Z=0$ plane (the common root of the two blocks are not counted as a contact or shared visit). One such tree is illustrated in Fig. 3.

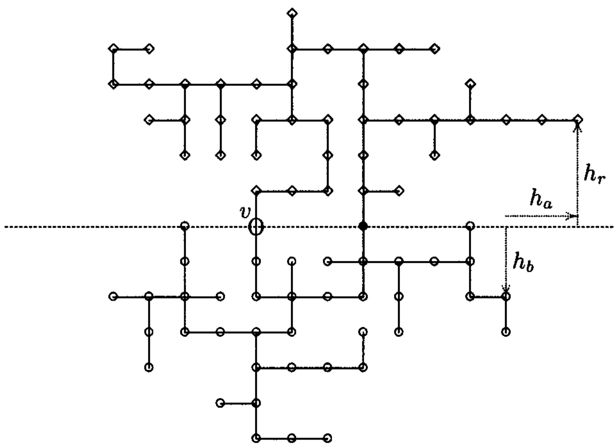

Fig. 3. An attached tree model of a 2-block copolymer which interacts at the interface. The tree is rooted at O, and monomers in the blocks are indicated by ◇ and ○. There is one shared visit ●. The height of the top vertex in the block with vertices denoted by ◇ is h_r, while it is h_b for the top vertex of the block with vertices ○. The difference between the projected images of the top vertices in the $Z=0$ plane is h_a.

The partition function of this model is

$$t^{\delta}_{n,n}(z_+, z_-, z) = \sum_{v_+, v_- = 0}^{n} \sum_{c=0}^{n} t^{\delta}_{n,n}(v_+, v_-, c)\, z_+^{v_+} z_-^{v_-} z^c \tag{4.1}$$

The activity z is conjugate to the number of contacts. The existence of a thermodynamic limit in this model is shown by using a "double concatenation" and most popular height arguments.

Let h_r be the height of the top vertex of the positive block above the $Z=0$ plane, and h_b be the height of the top vertex of the negative block below the $Z=0$ plane. Let h_a be the difference between the projected images of the top vertices of the red and blue blocks in the $Z=0$ plane (h_a is a $(d-1)$-dimensional vector). Define $t^{\delta}_{n,n}(v_+, v_-, c \mid [h_r h_b h_a])$ as the number of trees counted by $t^{\delta}_{n,n}(v_+, v_-, c)$, and with heights and difference $[h_r h_b h_a]$ between top vertices. A similar set of definitions for the bottom vertices of the two blocks define the trees counted by $t^{\delta}_{n,n}(v_+, v_-, c \mid [(h_r h_b h_a])$, and with bottom vertices of heights and difference $[b_r b_b b_a]$ between bottom vertices; the number of such trees is $t^{\delta}_{n,n}(v_+, v_-, c \mid [h_r h_b h_a][b_r b_b b_a])$. Define the partition function

$$\begin{aligned} &t^{\delta}_{n,n}(z_+, z_-, z \mid [h_r h_b h_a][b_r b_b b_a]) \\ &\quad = \sum_{v_+, v_- = 0}^{n} \sum_{c=0}^{n} t^{\delta}_{n,n}(v_+, v_-, c \mid [h_r h_b h_a][b_r b_b b_a])\, z_+^{v_+} z_-^{v_-} z^c \end{aligned} \tag{4.2}$$

Theorem 4.1. The limit

$$\mathscr{F}(z_+, z_-, z \mid [h_1 h_2 h]) = \lim_{n \to \infty} \frac{1}{n} \log t^{\delta}_{n,n}(z_+, z_-, z \mid [h_1 h_2 h][h_1 h_2 h])$$

exists for all finite $z_+ > 0$, $z_- > 0$ and $z > 0$. Moreover, it is convex in each argument.

Proof. Consider a tree A counted by $t^{\delta}_{n,n}(v_+ - v_0, v_- - v_1, c - c_0 \mid [h_1 h_2 h][h_1 h_2 h])$ and a tree B counted by $t^{\delta}_{m,m}(v_0, v_1, c_0 \mid [h_1 h_2 h][h_1 h_2 h])$. Translate B parallel to the $Z=0$ plane until the bottom vertices of both its blocks are one step removed in the X-direction from the corresponding top vertices of the blocks of A. Since the heights and difference of both these trees are $[h_1 h_2 h]$, this is possible. Join the two trees into one tree by adding two edges; one between the top and bottom vertices of the red blocks, and the second between the top and bottom vertices of the blue block; and change the root of the second tree into a contact. This construction gives a tree counted by $t^{\delta}_{n+m+1,n+m+1}(v_+, v_-, c \mid [h_1 h_2 h][h_1 h_2 h])$, and since the deleted root can be chosen in at most $n+m+1$ ways, the outcome is the following inequality:

$$\sum_{v_0=0}^{v_+} \sum_{v_1=0}^{v_-} \sum_{c_0=0}^{c} t^{\delta}_{n,n}(v_+ - v_0, v_- - v_1, c - c_0 \mid [h_1 h_2 h][h_1 h_2 h]) \\ \times t^{\delta}_{m,m}(v_0, v_1, c_0 \mid [h_1 h_2 h][h_1 h_2 h]) \\ \leqslant (n+m+1)\, t^{\delta}_{n+m+1,n+m+1}(v_+, v_-, c+1 \mid [h_1 h_2 h][h_1 h_2 h])$$

Multiply this inequality by $z_+^{v_+} z_-^{v_-} z^c$, and sum over v_+, v_- and over c to obtain

$$t^{\delta}_{n,n}(z_+, z_-, z \mid [h_1 h_2 h][h_1 h_2 h])\, t^{\delta}_{m,m}(z_+, z_-, z \mid [h_1 h_2 h][h_1 h_2 h]) \\ \leqslant z^{-1}(n+m+1)\, t^{\delta}_{n+m+1,n+m+1}(z_+, z_-, z \mid [h_1 h_2 h][h_1 h_2 h])$$

Thus, $z^{-1} t^{\delta}_{n-1,n-1}(z_+, z_-, z \mid [h_1 h_2 h][h_1 h_2 h])$ satisfies a generalized supermultiplicative inequality, and moreover, it is bounded by $\tau_d^{2n}[\max\{z_+, z_-, z\}]^{2n}$ (since all trees are bounded in this way). Consequently, the limit

$$\lim_{n\to\infty} \frac{1}{n} \log t^{\delta}_{n,n}(z_+, z_-, z \mid [h_1 h_2 h][h_1 h_2 h]) \tag{4.3}$$

exists and is finite as claimed.[19] Convexity of $\mathscr{F}(z_+, z_-, z \mid [h_1 h_2 h])$ can be shown by applying the Cauchy–Schwartz inequality to $t^{\delta}_{n,n}(z_+, z_-, z \mid [h_1 h_2 h][h_1 h_2 h])$. ∎

Next, notice that there are most popular values for $[h_1 h_2 h]$ in Eq. (4.3), and let these be $[h_1^* h_2^* h^*]$, and define the limiting free energy

$$\mathscr{F}(z_+, z_-, z) = \lim_{n\to\infty} \frac{1}{n} \log t^{\delta}_{n,n}(z_+, z_-, z \mid [h_1^* h_2^* h^*][h_1^* h_2^* h^*]) \tag{4.4}$$

Let the most popular values of $[h_r h_b h_a][b_r b_b b_a]$ in $t^{\delta}_{n,n}(z_+, z_-, z \mid [h_r h_b h_a][b_r b_b b_a])$ be $[h_r^* h_b^* h_a^*][h_r^* h_b^* h_a^*]$. The double concatenation in the proof of Theorem 4.1 now shows that

$$[t^{\delta}_{n,n}(z_+, z_-, z \mid [h_r^* h_b^* h_a^*][b_r^* b_b^* b_a^*])]^2 \\ \leqslant z^{-1}(2n+1)\, t^{\delta}_{2n+1,2n+1}(z_+, z_-, z \mid [h_r^* h_b^* h_a^*][h_r^* h_b^* h_a^*]) \\ \leqslant z^{-1}(2n+1)\, t^{\delta}_{2n+1,2n+1}(z_+, z_-, z \mid [h_1^* h_2^* h_a^*][h_1^* h_2^* h^*] \tag{4.5}$$

Thus

$$\limsup_{n\to\infty} \frac{1}{n} \log t^{\delta}_{n,n}(z_+, z_-, z \mid [h^*_r h^*_b h^*_a][b^*_r b^*_b b^*_a]) \leqslant \mathscr{F}(z_+, z_-, z) \qquad (4.6)$$

In addition, since $[h^*_r h^*_b h^*_a][b^*_r b^*_b b^*_a]$ are the most popular values,

$$\begin{aligned} &t^{\delta}_{n,n}(z_+, z_-, z \mid [h^*_1 h^*_2 h^*][h^*_1 h^*_2 h^*]) \\ &\qquad \leqslant t^{\delta}_{n,n}(z_+, z_-, z \mid [h^*_r h^*_b h^*_a][b^*_r b^*_b b^*_a]) \end{aligned} \qquad (4.7)$$

and thus

$$\mathscr{F}(z_+, z_-, z) \leqslant \liminf_{n\to\infty} \frac{1}{n} \log t^{\delta}_{n,n}(z_+, z_-, z \mid [h^*_r h^*_b h^*_a][b^*_r b^*_b b^*_a]) \qquad (4.8)$$

Equations (4.6) and (4.8) imply the following lemma:

Theorem 4.2.

$$\mathscr{F}(z_+, z_-, z) = \lim_{n\to\infty} \frac{1}{n} \log t^{\delta}_{n,n}(z_+, z_-, z \mid [h^*_r h^*_b h^*_a][b^*_r b^*_b b^*_a])$$

These results can finally be put together to prove existence of the limiting free energy.

Theorem 4.3. The limiting free energy

$$\mathscr{F}(z_+, z_-, z) = \lim_{n\to\infty} \frac{1}{n} \log t^{\delta}_{n,n}(z_+, z_-, z)$$

exists. Moreover, it is convex in all its arguments.

Proof. Notice that

$$\begin{aligned} &t^{\delta}_{n,n}(z_+, z_-, z \mid [h^*_r h^*_b h^*_a][b^*_r b^*_b b^*_a]) \\ &\quad \leqslant t^{\delta}_{n,n}(z_+, z_-, z) \\ &\quad = \sum_{[h_r h_b h_a]} \sum_{[b_r b_b b_a]} t^{\delta}_{n,n}(z_+, z_-, z \mid [h_r h_b h_b][b_r b_b b_a]) \\ &\quad \leqslant (2n)^{2d+2}\, t^{\delta}_{n,n}(z_+, z_-, z \mid [h^*_r h^*_b h^*_a][b^*_r b^*_b b^*_a]) \end{aligned}$$

since $[h_r h_b h_a]$ takes at most $(2n)^{d+1}$ distinct values. Existence of the free energy now follows from Theorem 4.1 and the squeeze theorem for limits. ▮

It is not difficult to see that there is a critical value of z where the two blocks interact to "adsorb" onto one another through the interface. In particular, observe that if $z \geqslant 1$, then

$$t^{\delta}_{n,n}(z_+, z_-, z) \geqslant t^{\delta}_{n,n}(0, 0, n)\, z^n \tag{4.9}$$

where only the term corresponding to the conformation with both blocks identical to one another (and both in the interface) was kept in the partition function, of the left. Since $t^{\delta}_{n,n}(0, 0, n) = t^{(d-1)}_n$ (the number of trees with n edges in $(d-1)$ dimensions), this shows that

$$\mathscr{F}(z_+, z_-, z) \geqslant \log \tau_{(d-1)} + \log z, \qquad \text{if} \quad z \geqslant 1 \tag{4.10}$$

The proof that there are phase boundaries relies on the above, and the following theorem.

Theorem 4.4. Suppose that $z \leqslant 1$. Then

$$\mathscr{F}(z_+, z_-, z) = \begin{cases} 2\log \tau_d + \log(z_+ z_-) \\ \qquad \text{for all} \quad z_+ > 1/z_c^+ \quad \text{and} \quad z_- > 1/z_c^+ \\ \log \tau_d + \mathscr{F}^+(1/z_-) + \log(z_+ z_-) \\ \qquad \text{for all} \quad z_+ > 1/z_c^+ \quad \text{and} \quad z_- < 1/z_c^+ \\ \log \tau_d + \mathscr{F}^+(1/z_+) + \log(z_+ z_-) \\ \qquad \text{for all} \quad z_+ < 1/z_c^+ \quad \text{and} \quad z_- > 1/z_c^+ \end{cases}$$

In addition, if $z = 1$ then

$$\mathscr{F}(z_+, z_-, 1) = \mathscr{F}^+(1/z_+) + \mathscr{F}^+(1/z_-) + \log(z_+ z_-)$$
$$\text{for all} \quad z_+ < 1/z_c^+ \quad \text{and} \quad z_- < 1/z_c^+$$

and if $z < 1$ then

$$\mathscr{F}(z_+, z_-, z) \leqslant \mathscr{F}^+(1/z_+) + \mathscr{F}^+(1/z_-) + \log(z_+ z_-)$$
$$\mathscr{F}(z_+, z_-, z) \geqslant \mathscr{F}^+(\sqrt{z}/z_+) + \mathscr{F}^+(\sqrt{z}/z_-) + \log(z_+ z_-)$$

if both $z_+ < 1/z_c^+$ and $z_- < 1/z_c^+$.

Proof. Let $t_n^+(v)$ be the number of positive trees with n edges and v visits, and $t_n^-(v) = t_n^+(v)$ be the number of negative trees with n edges and v visits. Observe in the first instance that

$$\begin{aligned} t_{n,n}^{\delta}(n, n, 0) &= t_n^+(1)\, t_n^-(1) = [t_n^+(1)]^2 \\ t_{n,n}^{\delta}(n, v_1, 0) &\geqslant t_n^+(1)\, t_n^-(n+1-v_-) \\ t_{n,n}^{\delta}(v_+, n, 0) &\geqslant t_n^+(n+1-v_+)\, t_n^-(1) \end{aligned} \tag{4.11}$$

In addition, if a diblock tree counted by $t_{n,n}^{\delta}(v_+, v_-, c)$ is cut in its root, and the two blocks are translated each one step away from the interface while new edges are inserted to reconnect the blocks to the root, the following inequality is found:

$$t_{n,n}^{\delta}(v_+, v_-, c) \leqslant t_{n+1,n+1}^{\delta}(n+1, n+1, 0) \tag{4.12}$$

and if only the positive or only the negative block is translated, then

$$t_{n,n}^{\delta}(v_+, v_-, c) \leqslant \begin{cases} t_{n+1,n}^{\delta}(n+1, v_-, 0) \\ t_{n,n+1}^{\delta}(v_+, n+1, 0) \end{cases} \tag{4.13}$$

Since $z \leqslant 1$, it follows that $t_{n,n}^{\delta}(z_+, z_-, z) \leqslant t_{n,n}^{\delta}(z_+, z_-, 1)$ so that

$$\begin{aligned} t_{n,n}^{\delta}(z_+, z_-, z) &\leqslant n^2 \sum_{v_+ v_- = 0}^{n+1} t_n^+(n+1-v_+)\, t_n^-(n+1-v_-)\, z_+^{v_+} z_-^{v_-} \\ &= n^2 t_n^+(1/z_+)\, t_n^-(1/z_-)[z_+ z_-]^{n+1} \end{aligned}$$

Take logarithms, divide by n and let $n \to \infty$. Then

$$\mathscr{F}(z_+, z_-, z) \leqslant \mathscr{F}^+(1/z_+) + \mathscr{F}^+(1/z_-) + \log(z_+ z_-) \tag{4.14}$$

Notice now that from Eq. (4.11) above,

$$t_{n,n}^{\delta}(z_+, z_-, z) \geqslant \sum_{v_+, v_- = 0}^{n} t_{n,n}^{\delta}(v_+, v_-, 0)\, z_+^{v_+} z_-^{v_-} \geqslant [t_n^+(1)]^2\, z_+^n z_-^n$$

where only those terms with zero contacts were kept. Thus, by taking logarithms, dividing by n and letting $n \to \infty$,

$$\mathscr{F}(z_+, z_-, z) \geqslant 2 \log \tau_d + \log(z_+ z_-)$$

which together with Eq. (4.14) and the fact that $\mathscr{F}^+(1/z) = \log \tau_d$ if $z > 1/z_c^+$ proves the first equality in the theorem.

Next, suppose that $z_- \leqslant 1/z_c^+$ and $z_+ \geqslant 1/z_c^+$. Then

$$\begin{aligned} t_{n,n}^{\delta}(z_+, z_-, z) &\geqslant \sum_{v_-=0}^{n} t_{n,n}^{\delta}(n, v_-, 0)\, z_+^n z_-^{v_-} \\ &= \sum_{v_-=0}^{n} t_n^+(1)\, t_n^-(n+1-v_-)\, z_+^n z_-^{v_-} \\ &= t_n^+(1)\, z_+^n\, t_n^-(1/z_-)\, z_-^{n+1} \end{aligned}$$

Taking logarithms, dividing by n, and letting $n \to \infty$ shows that

$$\mathscr{F}(z_+, z_-, z) \geqslant \log \tau_d + \mathscr{F}^+(1/z_-) + \log(z_+ z_-)$$

Since $\mathscr{F}^+(1/z_+) = \log \tau_d$ if $z_+ \geqslant 1/z_c^+$ in Eq. (4.14) above, this proves the second equation of the theorem. The third equation is proven following the above argument again, but with z_+ and z_- interchanged.

Lastly, consider the case that both $z_+ < 1/z_c^+$ and $z_- < 1/z_c^+$. A lower bound on $\mathscr{F}(z_+, z_-, z)$ can be obtained if only those diblock-trees with every visit a contact between the blocks are counted. In particular, since v_+, v_- and c satisfies the relation $2c + v_+ + v_- = 2n$ if all visits are contacts,

$$\begin{aligned} t_{n,n}^{\delta}(z_+, z_-, z) &\geqslant \sum_{v_+, v_-=0}^{n} t_n^+(n-v_+)\, t_n^-(n-v_-)\, z_+^{v_+} z_-^{v_-} \sqrt{z}^{2n-(v_+-v_-)} \\ &= t_n^+(\sqrt{z}/z_+)\, t_n^-(\sqrt{z}/z_-)(z_+ z_-)^n \end{aligned}$$

Thus

$$\mathscr{F}(z_+, z_-, z) \geqslant \mathscr{F}^+(\sqrt{z}/z_+) + \mathscr{F}^+(\sqrt{z}/z_-) + \log(z_+ z_-) \tag{4.15}$$

If $z = 1$, then together with Eq. (4.14) above this shows that

$$\mathscr{F}(z_+, z_-, 1) = \mathscr{F}^+(1/z_+) + \mathscr{F}^+(1/z_-) + \log(z_+ z_-)$$

if both $z_+ < 1/z_c^+$ and $z_- < 1/z_c^+$. ∎

Theorem 4.4 shows that $\mathscr{F}(z_+, z_-, z)$ is a non-analytic function if z_+ and of z_- for all fixed values of $z \leqslant 1$. The phase boundaries are particularly simple if $z = 1$; the two lines $z_+ = 1/z_c^+$ and $z_- = 1/z_c^+$ are adsorption transitions of the positive block and of the negative block, into the interface respectively; see Fig. 4.

If $z \leqslant 1$, then the situation is the same, but the arguments not as straight forward. Since $\mathscr{F}(z_+, z_-, z)$ is a non-analytic function if z_+ and

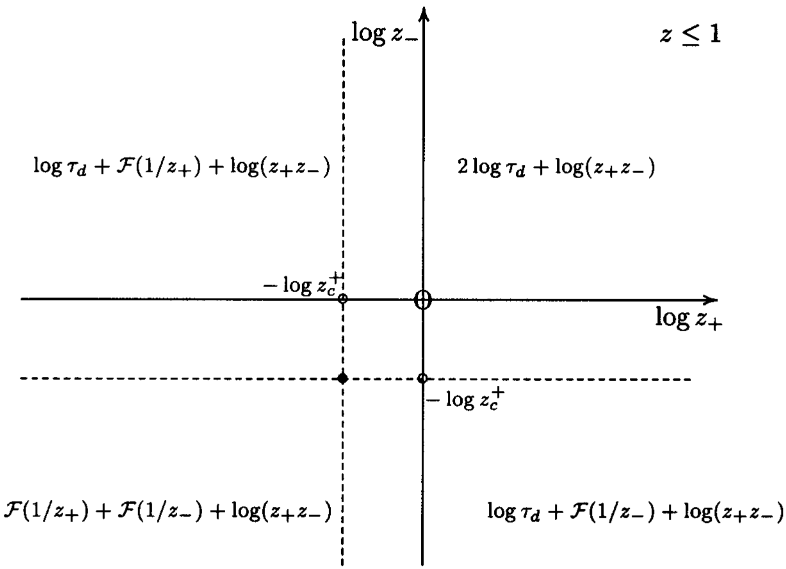

Fig. 4. The phase diagram of $\mathscr{F}(z_+, z_-, z)$ if $z \leqslant 1$. The location of the dashed critical curves in the third quadrant is uncertain, and it is also not known that there is a quadruple point, or two triple points, in this diagram.

of z_- for all fixed values of $z \leqslant 1$, it follows again that two critical lines (one corresponding to adsorption of the positive block, and the other to adsorption of the negative block) intersect in the (z_+, z_-)-plane (with $z < 0$). It follows immediately from Theorem 4.4 that parts of the curves are half-lines, meeting in the point $(z_+, z_-) = (1/z_c^+, 1/z_c^+)$; namely $z_+ = 1/z_c^+$ with $z_- \geqslant 1/z_c^+$, and $z_- = 1/z_c^+$ with $z_+ \geqslant 1/z_c^+$. Furthermore, the bounds on $\mathscr{F}(z_+, z_-, z)$ if $z_+ < 1/z_c^+$, $z_- < 1/z_c^+$ in Theorem 4.4 implies that the continuations of these half-lines are confined to the region $A \cup B$ where $A = \{(z_+, z_-) \mid \sqrt{z/z_C^+} \leqslant z_+ \leqslant 1/z_c^+$, and $z_- \leqslant 1/z_c^+\}$, and $B = \{(z_+, z_-) \mid \sqrt{z/z_c^+} \leqslant z_- \leqslant 1/z_c^+$, and $z_+ \leqslant 1/z_c^+\}$. It is in fact the case that the phase diagram in this case is also given by Fig. 4. This I demonstrate in Theorem 4.5.

Theorem 4.5. $\mathscr{F}(z_+, z_-, z)$ is independent of z for all $z \leqslant 1$.

Proof. Consider first the fact that $t^{\delta}_{n,n}(z_+, z_-, z)$ is non-decreasing with increasing z. Thus

$$t^{\delta}_{n,n}(z_+, z_-, z) \geqslant t^{\delta}_{n,n}(z_+, z_-, 0) \tag{4.16}$$

On the other hand, consider a tree T counted by $t^{\delta}_{n,n}(v_+, v_-, c)$. Separate T into a positive tree T_+ and a negative tree T_- by cutting it in the root. Define the top visit of T_+ as its lexicographic most visit, and the bottom visit of T_- as its lexicographic least visit. Translate T_+ and T_- such that the bottom visit of T_- coincide with the top visit of T_+, and join them into a new tree S rooted in this visit. Then S has no contacts in the membrane. Since each of T_+ and T_- has at most $n+1$ visits each, and since the root was present at most at $(n+1)^2$ positions (before the construction), it follows that

$$t^{\delta}_{n,n}(v_+, v_-, c) \leqslant (n+1)^4\, t^{\delta}_{n,n}(v_+, v_-, 0)$$

Multiplying by $z_+^{v_+} z_-^{v_-}$ and summing shows that for $z \leqslant 1$,

$$t^{\delta}_{n,n}(z_+, z_-, z) \leqslant (n+1)^4\, t^{\delta}_{n,n}(z_+, z_-, 0) \sum_{c=0}^{n} z^c \tag{4.17}$$

By taking logarithms, dividing by n and letting $n \to \infty$ in the inequalities in Eqs. (4.16) and (4.17), it follows that

$$\mathscr{F}(z_+, z_-, z) = \mathscr{F}(z_+, z_-, 0), \qquad \text{if} \quad z \leqslant 1$$

This completes the theorem. ▮

The density of contacts between the two blocks is defined by

$$\langle c \rangle = \frac{\partial}{\partial \log z} \mathscr{F}(z_+, z_-, z) \tag{4.18}$$

By Theorem 4.5 this is zero if $z < 1$, and the phase diagram is given by Fig. 4. On the other hand, Eq. (4.10) guarantees that $\mathscr{F}(z_+, z_-, z)$ will be dependent on z if z is large enough, for any finite values of (z_+, z_-), and so there is a transition where one block adsorbs into the visits of the other. The phase diagram can thus be described as follows: There exists a critical value of z, say $z_c(z_+, z_-)$, such that if $z < z_c(z_+, z_-)$, then the density of contacts between the two blocks is zero. There exists four phases in this regime, one delocalized phase where both blocks have zero densities of visits; two partially localized phases where either of the two blocks (but not both) has a density of visits; and finally a localised phase where both blocks are localised in the interface with a density of visits. Notice that the density of contacts between the two blocks is still zero in this phase as well. Next, if $z > z_c(z_+, z_-)$, then there are one or perhaps more, phases with a non-zero density of contacts. In analogy with the results in Eq. (1.7), one should expect that $z_c(z_+, z_-) > 1$ for all finite values of (z_+, z_-).

4. CONCLUSIONS

Perhaps the most interesting open question for trees at an interface is the conjecture that $z_c^{>} = 1$. If this turns out to be true, then there will be some implications for the models discussed above. For example, the localization-delocalization critical curves in Fig. 2 would meet in the origin, and attached trees would then be critical with respect to localization, and with respect to the delocalized $(+)$-phase and $(-)$-phase. By the way, if the above is correct, then the location of the critical curves c_- and c_+ in Fig. 2 is still an interesting question. Can it be shown that they are in the interior of the third quadrant of Fig. 2, and only intersects the axes in the origin? Theorem 2.3 shows that, if these curves are continuous at $z_+ = 0$ and $z_- = 0$, that there must be points on them in the interior of the third quadrant.

The existence and self-averaging properties of the limiting free energy of attached trees colored lexicographically at an interface was examined in Section 3. In addition, the presence of some transitions in this model was pointed out. In particular, there are $(+)$- and $(-)$-phases analogous to those encountered in the model in Section 2. However, it seems that there are phases with some colors on one side of the interface, and other colors on the opposite side. Such a phase is necessarily localized (as opposed to the $(+)$- and $(-)$-phases which are delocalized). While the arguments preceding Eq. (3.23) seems to indicate that increasing any one activity z_i^- associated with negative vertices will drive the model from a delocalized $(+)$-phase to a localized phase (in the lexicographic quenched ensemble), it is not obvious that there are more than one localized phase. Indeed, the fact that colors can be interchanged seems to suggest that there is only one such localized phase, and that the model will be driven into this phase if it has some large activities for positive vertices of a given color, and some large activities for negative vertices of a different color.

Lastly, the interaction of two branched polymers through a membrane was model by a pair of trees interacting via shared visits in the interface. In this case I show that there is an adsorption-like transition of one tree onto the visits of the other, regardless of the quality of the solvents on either sides of the membrane. In analogy with a positive tree adsorbing onto a plane (with critical activity $z_c^+ > 1$, see Eq. (1.7)), it seems that one should expect that the critical activity here is strictly bigger than one: $z_c(z_+, z_-) > 1$, but a proof for this fact is still outstanding.

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