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Proof of Gridlock in a Polymer Model

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It has been suggested that some lattice models of polymers, especially ones that incorporate more realistic excluded volume interactions extending to further neighbors, may be subject to gridlock. A model is defined to have the property of gridlock if it cannot melt at any temperature unless a density decrease is allowed. Classical theories of polymer melting are incompatible with the property of gridlock. This paper proves rigorously that a two-dimensional square-lattice model of polymer chains that have nearest-neighbor excluded volume interactions (called the X1S model) has the gridlock property. The proof uses elementary concepts from graph theory. Also, different interpretations of the X1S model are given in terms of real polymers. This leads to a discussion of a number of different classes of melting depending upon whether the intramolecular rotameric energies and the attractive intermolecular energies are antagonistic to or supportive of the melting transition.

KEY WORDS: Polymers; lattice model; gridlock; melting/crystallization phase transition; excluded volume interactions; semiflexible chains.

1. INTRODUCTION

It is generally acknowledged that modeling of the melting/crystallization equilibrium phase transition in long chain polymers such as polyethylene requires consideration of both the flexibility of the polymer and of the excluded volume intermolecular interaction. In contrast, intermolecular longer-range attractive interactions have been considered to be of "minor importance,"(1) because such interactions were not required in a classical calculation that yielded quite reasonable agreement with experiment. The classical theory(1) stood on two computational legs. One leg was a statistical approximation designed to describe the melt above the transition temperature, T_M. This approximation, which imposes a decoupling of chain

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conformational degrees of freedom from the excluded volume constraint, is being shown to be quantitatively inaccurate by Monte Carlo calculations on simple lattice models.(2,3) The other leg was the assumption that the system must remain in a thermodynamically negligible number of states when $T < T_M$, i.e., there is an "inactive low-temperature phase."(4) This assumption has been shown to be false for the same simple lattice models,(5–7) for which the classical calculations should be as valid (or invalid) as for any models.(8) A much fuller discussion of the classical theory and its failure is given in a recent review.(4)

The simple lattice models previously discussed would appear to be too easily disordered below T_M to be good models of polymer melting. Also, these models are not very faithful geometric representations of any real polymer chains. Slight differences in the details of lattice models can make a large difference in phase transition behavior, as is shown for four exactly solved two-dimensional models.(8,9) These exact results show that polymerlike models do not all belong to the same universality class. Thus far, there are no reliable identifiers of universality class for such models. Therefore, there is some motivation to consider more realistic models which are more likely to be in the same universality class as the particular polymer, e.g., polyethylene, that one wishes to study, and a start has been made in this direction.(4)

One way to construct more realistic lattice models is to represent the geometry of the polymer chains more nearly exactly. This requires abandoning the square and simple cubic lattices and, for polyethylene chains, it leads one to the four-coordinated three-dimensional tetrahedral, i.e., diamond lattice, with 1.54-Å bond lengths. Even more importantly, a realistic tetrahedral lattice model for polyethylene is not "simple" in the sense of previously considered models because each CH_2 monomer in the polyethylene polymer excludes from occupation by other CH_2 monomers, not only one lattice site, as in the "simple" models, but also several neighboring lattice sites.(4)

Our examination of more realistic nonsimple "further neighbor excluded volume" models led us to believe that they do indeed belong to a different class of models from the previously studied simple models. In particular, it seems that these models may be subject to *gridlock*; this is a new concept which means that the model becomes locked into a small set of conformational states, even at infinite temperature, unless the polymer chain density is allowed to decrease.(4) Unlike the simple square or cubic lattice models which disorder too easily, models with gridlock should remain much less chain conformationally active below T_M. At T_M the chain density decreases and many more conformationally disordered chain states become possible within the constraints of the excluded volume interactions. In this view of the melting/crystallization phase transition in polymers the density decrease at T_M is a necessary part of the transition in real polymers like polyethylene. In fact, a good deal of the enthalpy of melting (about 70% for polyethylene(10)) may come from the attractive intermolecular interactions. The intramolecular chain flexing energy, while important, is then not the whole story (amounting to less than 25% of the enthalpy of transition in polyethylene). This has led to the formulation of the hypothesis that intermolecular interactions play an essential role, not a minor role, in polymer melting.

The concept of gridlock has been pivotal in formulating the new hypothesis for polymer melting. However, it is not easy to prove that a given model has gridlock. This is partly because the three-dimensional diamond lattice models have several different kinds of symmetrically and rotamerically inequivalent states with maximum density.(4) It is also partly due to the difficulty of proving nonexistence, in this case the nonexistence of many states with maximal density. In contrast, it is easier to prove the existence of many such states for the simple models on the square, cubic, and even the diamond lattice. Fortunately, it is possible to prove rigorously that a two-dimensional lattice model of chains with nearest-neighbor excluded volume interactions (the X1S model) does indeed have gridlock, so the concept is not a vacuous one. The proof, which is presented in the next section, will be the primary result in this paper. Discussion of this lattice model in physical terms may also be of some interest and this is given in the last section.

2. PROOF OF GRIDLOCK FOR THE X1S MODEL

A chain model on the square lattice is considered in this paper. The excluded volume interactions consist of forbidding any two nonbonded monomers from occupying the same *or nearest-neighbor* lattice sites. This has been called the X1S model,(4) referring to excluded volume interactions with hard cores including up to 1st neighbor sites on the square lattice. In this notation the "simple" square lattice model is called X0S because occupancy of first neighbors is allowed; only the monomer site itself is excluded to additional occupancy. Figure 1 shows the densest state of packing the chains in the X1S model; it has a density, $\rho = 2/3$, of lattice sites occupied by the centers of monomers. Notice, in particular, that an array of parallel straight chains only has a density, $\rho = 1/2$. Further, notice that no single chain may occupy all four sites around a square because there would then be two nonbonded nearest-neighbor monomers; such a forbidden sequence of chain links, which is allowed in the X0S model, will be called a tight turn. We now proceed to prove that the X1S model has gridlock by

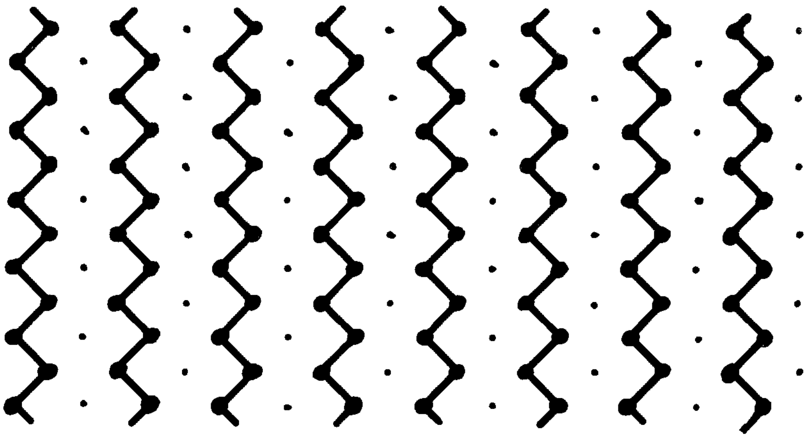

Fig. 1. The densest conformational state for the X1S model with number density $\rho = 2/3$. The lattice is the square lattice oriented at 45° to the usual x or y axis. Each unconnected light dot is a vacancy. Each heavy dot on a chain is a monomer. No pair of nonbonded monomers is a nearest neighbor. Only a small piece of a very large large lattice is shown.

proving that there are no other maximally dense states except for the one in Fig. 1 and its obvious five symmetrical equivalents.

Let us develop some notation. First, consider sites occupied by the centers of chain monomers; let n_F be the number of such *filled* sites for a given conformational state. Of those filled sites, some will be occupied by monomers attached to two colinear bonds; let the number of these *straight* sites be n_S. The other sites will be occupied by monomers attached to two noncolinear bonds which meet at right angles to form a corner; let n_C denote the number of these *corner* sites. Since we are interested in the limit of very long chains on very large lattices, chain ends are negligible. Therefore,

$$n_F = n_S + n_C \tag{1}$$

Next, we consider *vacant* sites, n_V in number. Again, ignoring chain ends one has

$$n_F + n_V = N \tag{2}$$

where N is the number of lattices sites. Each vacant site will be classified with two numbers, i and j, according to its local neighborhood, as shown in Fig. 2. This local neighborhood includes the four nearest-neighbor (NN) sites and also the four next-nearest-neighbor (NNN) sites to the central vacant site. The first number i in this classification scheme refers to the number of filled nearest-neighbor (NN) sites to the central vacant site being considered. The second number j in the classification scheme refers to the number of

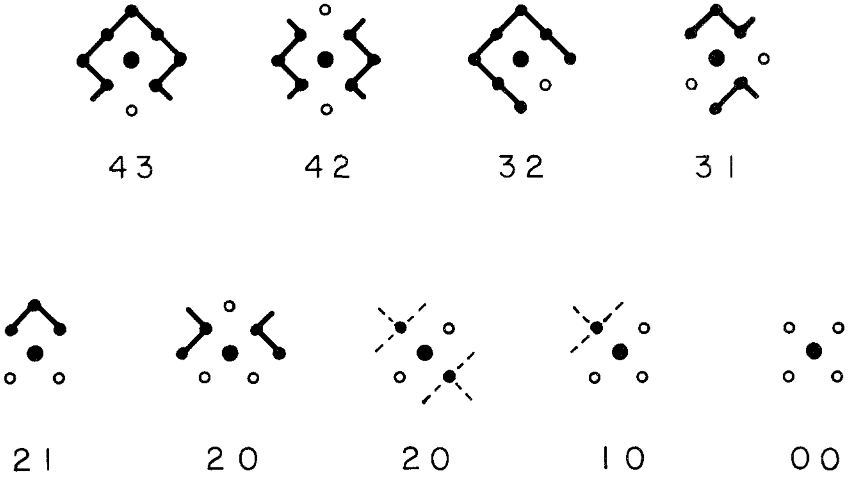

Fig. 2. Different kinds of vacant sites and their *ij* classifications. The first number *i* given for each type of vacant site is the number of filled nearest-neighbor sites and the second number *j* is the number of associated corner sites as defined in the text. The central vacant site being classified is designated by a large filled dot. Some other local sites that are necessarily empty in the X1S model are designated by an unfilled dot. Sites with no dot and with no polymer chain going through them may or may not be filled depending upon irrelevant continuations of the polymer chains shown or other polymer chains. Those figures with three dashed bonds incident upon a filled vertex represent several possibilities, each of which utilizes two of the three bonds so indicated, all of which have the same *ij* classification.

corner sites that are *associated* with the central vacant site; a corner site is defined to be *associated* with one (and only one) vacant site if the vacant site is diagonally opposite the corner site on that (unique) elementary square which has two sides occupied by the bonds incident to the corner site. Clearly, the only possible sites that can be associated corner sites to a central vacant site are NNN sites. Furthermore, every corner site is an associated corner site to one and only one of *its* four NNN.

One notices that not every combination[2] of i and j appears in Fig. 2. Only values of j appear that satisfy

$$\max i-1,0 \geqslant j \geqslant \max i-2,0 \tag{3}$$

where $0 \leqslant i \leqslant 4$. Although only the second inequality is essential to completion of the proof, it may be of some interest to prove both inequalities as an indication of the completeness of the classification scheme in Fig. 2. If

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[2] Each case shown in Fig. 2 is meant to include obvious symmetries. In addition, to obtain all the possibilities for the second member of the 20 class and the 10 class, take all combinations at each filled nearest-neighbor site of any two of the three bonds shown.

$i = 4$, then one NNN site must be unoccupied, requiring $j \leqslant 3$, because otherwise there would be an eight-bond polymer loop that completely surrounds the central vacant site and such closed loops are forbidden in the X1S model. If $i = 3$, then the two NNN sites adjacent to the vacant NN site cannot be associated corner sites, so $j \leqslant 2$. Together with the observation that one corner site ($j = 1$) requires at least two filled NN sites, this proves the inequality $\max i - 1, 0 \geqslant j$. To prove the second part of the inequality in (3), consider first $i = 3$. That unique filled NN site that is colinear with the vacant site and the only unfilled NN site must have a bond to at least one NNN site, which in turn must have a bond to the next NN site because it is also filled. Therefore, the NNN site is an associated corner and $j \geqslant 1$ if $i = 3$. If $i = 4$, then each filled NN site has at least one bond leading into an associated corner; since each associated corner has at most two such bonds adjacent to it, there must be at least $i/2 = 2$ associated corners. The cases $i = 0$, 1 and 2 are trivial since j need only be $\geqslant 0$. This completes the proof of (3).

From the completeness of the classification scheme for vacant sites it follows that for any chain state in the X1S model

$$n_V = \sum \sum n_{ij} \tag{4}$$

where n_{ij} is the number of vacant sites belonging to the ij class shown in Fig. 2, the first sum is over i from 0 to 4, and the second sum is over those values of j compatible with a given i according to (3). The second sum is also meant to go over all symmetrically inequivalent members of the same ij classes, an example being the two different members of the 20 class.

Another type of relation is obtained by considering the number, n_{VF}, of VF edges on the lattice between two sites, one of which is vacant and one of which is filled. Since each filled site has two such edges, in addition to the two polymer bonds, one has

$$n_{VF} = 2n_F \tag{5}$$

Also, by counting the VF edges adjacent to each vacant site one has

$$n_{VF} = \sum \sum i n_{ij} \tag{6}$$

where the summations, here and below, have the same limits as in (4). Combining (5), (6), and (1) yields

$$\sum \sum (i/2)\, n_{ij} = n_F = n_S + n_C \tag{7}$$

A similar kind of relation can also be established by counting the number of filled corner sites associated uniquely with each vacant site, namely,

$$n_C = \sum \sum j n_{ij} \tag{8}$$

It is also useful to display two relations which follow from the preceding ones and which do not require any additional graph theoretical concepts. First, subtracting (8) from (7) yields

$$n_S = \sum \sum (i/2) - jn_{ij} \tag{9}$$

Second, using (2), (5), (4), and (6), the total number of lattice sites, N, can be written as

$$N = n_V + n_F = n_V + (1/2)\, n_{VF} = \sum \sum \, [1 + (i/2)]\, n_{ij} \tag{10}$$

Let us now consider the volume of the system, synonymous with the size, N, of the lattice, which is required to accommodate a fixed amount, n_F, of polymer chains. From exploratory examination of a number of states it appeared that one might have the following basic inequality:

$$N \geqslant (3n_F + n_S)/2 \tag{11}$$

In terms of the volume, v, per monomer, (11) is equivalent to

$$v = \rho^{-1} = N/n_F \geqslant (3/2) + (1/2)(n_S/n_F) \tag{12}$$

This is indeed the case: proof of (11) follows from the use of (10), (7), and (9) to compute

$$2N - (3n_F + n_S) = \sum \sum \, (2 - i + j)\, n_{ij} = n_{43} + n_{32} + n_{21} + n_{10} + 2n_{00} \tag{13}$$

and the observation that, because of the second inequality in (3), the right-hand side of (13) is non-negative. From either (11) or (12) one sees that no state can be maximally dense unless $n_s = 0$. Also, (12) shows that $\rho_{\max} \leqslant 2/3$. From the explicit construction of the state in Fig. 1 it follows that $\rho_{\max} = 2/3$ as was asserted earlier.

To finish the proof of gridlock it suffices to show that there are only six symmetrically related states with $n_s = 0$ and with maximum density. First, observe that specifying the positions at a single lattice site of any two adjacent bonds in an $n_S = 0$ chain uniquely determines the conformation of that chain and its position on the lattice. Once one such chain is specified, each neighboring chain must also be uniquely positioned as closely as possible if maximum density is to be achieved.[3] There are six such states

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[3] Clearly, many states with $n_S = 0$ exist which do not have maximum density, although they are thermodynamically insignificant. Also, complete precision in this counting requires some specification of the length of the chains and/or the boundary conditions; the simplest case is periodic boundary conditions and the same even number of lattice sites in each direction for a lattice oriented as shown in Fig. 1.

because there are four ways to place a corner site at a given lattice site and there are two ways to keep the given lattice site vacant but to pass two $n_S = 0$ chains as closely as possible on either side of it.

DISCUSSION

As was mentioned in the Introduction, the primary motivation for consideration of the X1S model (excluded volume interactions extending to first neighbors on the square lattice) is that it can be proved clearly that this model has gridlock. Therefore, the concept of gridlock is not vacuous. It also provides a nice contrast to the much studied simple X0S model which does not have gridlock. However, no inference should be drawn that the X1S model is our preferred model for polymers; our preference for polyethylene remains with three-dimensional models with further neighbor interactions on the diamond lattice.(4)

Nevertheless, it is worth discussing briefly the strengths and weaknesses of the X1S model as a polymer model, especially since this discussion will illustrate some additional varieties of melting in chain models. To interpret the X1S model in terms of polyethylene[4] one must associate the various conformations of the X1S model chains with conformational sequences in polyethylene. Such an association, as with any two-dimensional model, is necessarily forced because the geometry is different. One has a further ambiguity for the X1S model because there are two possible ways to interpret the model, both with merits and demerits, which will be considered in turn.

The first way to interpret the X1S model in terms of polyethylene is the same as the identification used for the simple X0S model. A chain with all monomers lying on a straight line is called an all-trans chain. Whenever a chain makes a right angle, such a turn is identified as a gauche rotation which costs the higher energy ε. If a chain makes two successive left-hand turns (g^+g^+), then it forms a tight turn which forces two nonbonded monomers to be nearest neighbors; this is allowed in the simple X0S model but forbidden in the X1S model. In real polyethylene successive gauche rotations of opposite sense (g^+g^-) incur a substantial energy penalty, about 4ε, which is known as the pentane effect.(11) Although it is g^+g^+ sequences, not g^+g^- sequences, that are heavily penalized in the X1S model, the fact that one such sequence is penalized makes it a more realistic model for polyethylene than the X0S model. There are two disadvantages to this identification. The first is that a sequence of only three sites or two bonds determines whether the central site is trans or gauche, whereas in

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[4] It is possible that it is a better model for other polymers.

polyethylene a sequence of four methylenes is required. The second is that this identification requires the densest state to consist of all-gauche instead of all-trans chains.

The second way to interpret the X1S model overcomes the two disadvantages of the first way. This is done by declaring the zig-zag chain consisting of all corners to be the all-trans chain.[5] To identify a trans rotation in an arbitrary chain now requires examination of a sequence of three bonds, or four monomers, as in real polyethylene. The disadvantage of this identification is that conformational sequences are not isomorphic to those in polyethylene. For example, a trans bond can only be followed by a trans bond or by a gauche bond in a single way, not by a gauche bond in two ways. Also, not all gauche rotamers are symmetrically equivalent.

For the purposes of illustrating gridlock the second interpretation is preferable. In this interpretation the $T = 0$ K state consists of all-trans chains which, by maximizing density, minimizes both the conformational energy and the attractive van der Waals energy. As the temperature is raised the system would remain in a highly ordered nearly all-trans state with only a few defects.(4) In order for the chains to become conformationally disordered at melting would require the volume expansion necessary to circumvent the effect of gridlock. Therefore, the X1S model in this interpretation cannot conform to the classical theory.(1)

Nevertheless, the first interpretation also raises two interesting possibilities not usually considered. For the first possibility suppose that the conformational energy dominates the van der Waals attractive interaction[6] so that the $T = 0$ K state is the all-trans (straight chain) state, even though this does not minimize the attractive intermolecular energy. ($\rho = 1/2\rho_{\max}$.) In this case melting is driven, as usual, by the entropic contribution of disordered chains, but it may also be partially driven by the intermolecular interactions if the disordered states with gauche rotamers have greater density than the ordered states. That is, one might even have a volume decrease upon melting in such a model. For the second possibility suppose that the van der Waals attractive intermolecular interactions dominate the conformational energy so that the $T = 0$ K state consists of an array of parallel all-gauche chains which is the state shown in Fig. 1. In this case melting would be driven both by the entropic contribution of disordering chains, and also by the conformational energy. Usually, the conformational energy and the attractive van der Waals cohesive energy are both antagonistic to melting as in the second interpretation of the X1S model. But in this first interpretation of the X1S model the cohesive energy switches

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[5] The all-trans chain in real polyethylene is also a zig-zag chain.

[6] This is usually deemed to be the case for hydrocarbon chains.(12)

sides in the first case and the conformational energy switches sides in the second case.

It would appear that gridlock, including its various cases, should play a role in determining the different classes of polymer melting. Not all chain models fit into the same melting class and it is quite possible that real polymers, which encompass a great deal of variety, do not either. Attention should be paid to details of conformational energetics and how the chains can be packed together in condensed matter phases. Theories, such as the classical theories,(1) that are incapable of distinguishing these features and predict a single universal class of first-order melting(8) are therefore shown to be inadequate.

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