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Crystalline Ordering and Large Fugacity Expansion for Hard-Core Lattice Particles

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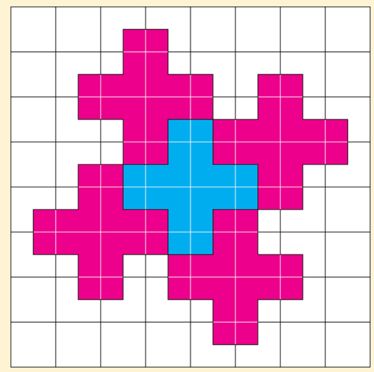
ABSTRACT: Using an extension of Pirogov−Sinai theory, we prove phase transitions, corresponding to sublattice orderings, for a general class of hard-core lattice particle systems with a finite number of perfect coverings. These include many cases for which such transitions have been proven. The proof also shows that for these systems the Gaunt−Fisher expansion of the pressure in powers of the inverse fugacity (aside from an explicit logarithmic term) has a nonzero radius of convergence.



■ INTRODUCTION

The study of order−disorder phase transitions for hard-core lattice particle (HCLP) systems has a long history (see, to name but a few, refs 1−7 and references therein). These are purely entropy-driven transitions, similar to those observed numerically and experimentally for hard spheres in the continuum.[8−11] Whereas a proof of the transition in the hard-sphere model is still lacking, there are several HCLP systems in which phase transitions have been proved.

One example is the hard diamond model on the square lattice (see Figure 1a), which is a particle model on $\mathbb{Z}^2$ with

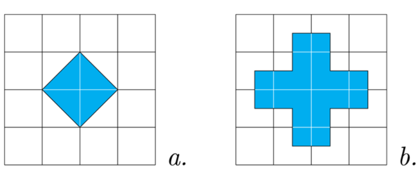


Figure 1. (a) A diamond on a square lattice. This system is equivalent to the nearest-neighbor exclusion model. (b) A cross on a square lattice. This system is equivalent to the third-nearest-neighbor exclusion model.

nearest-neighbor exclusion. The existence of a transition from a low-density disordered state, in which the density of occupied sites is the same on the even and odd sublattices, to a high-density ordered state, in which one of the sublattices is preferentially occupied, was proved by Dobrushin[12] using a Peierls-type construction. This transition had been predicted earlier using various approximations. In particular, Gaunt and Fisher[3] did an extensive study of this model using Padé approximants obtained from low- and high-fugacity expansions for the pressure, $p(z)$, to determine the location of a singularity on the positive z axis. They estimated that there is a transition at fugacity $z_t = 3.8$ and density $\rho_t = 0.37$, which is in good agreement with computer simulations.

Another example is that of hard hexagons on a triangular lattice. Following earlier numerical and approximate work, Baxter[4,13] obtained an exact solution of this system and found a transition at $z_t = \frac{1}{2}(5\sqrt{5} + 11) \approx 11.09$ and $\rho_t = \frac{1}{10}(5 - \sqrt{5}) \approx 0.28$. Further work, particularly by Joyce,[14] elaborated on this solution. Baxter's solution provides a full, albeit implicit, expression for the pressure $p(z)$ in the complex z and ρ planes, implying in particular that $p(z)$ is analytic for all $z \geq 0$ except at z_t. The transition at z_t is of second order, as is expected to be the case for diamonds. For $z > z_t$, this system has three ordered phases, corresponding to the three different perfect coverings.

Yet another HCLP model for which an order−disorder transition was shown to occur, with only a sketch of a proof,[15] is that of hard crosses on a square lattice (see Figure 1b). This model has 10 distinct perfect coverings (see Figure 2) and is conjectured[16] to have a first-order phase transition at $z_t \approx 39.5$. At this fugacity, the density jumps from $\rho_f \approx 0.16$ to $\rho_s \approx 0.19$. We shall use this model as an illustration of the type of system to which our analysis applies and for which we can prove

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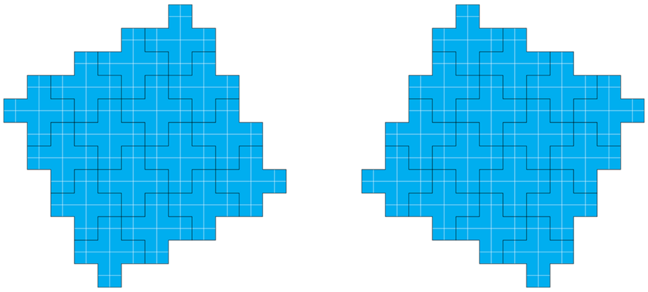

Figure 2. Perfect coverings of the cross model are obtained by translating these two configurations. In each panel there are five inequivalent translations, thus totaling 10 perfect coverings.

crystalline order at high fugacities and the convergence of the high-fugacity expansion.

The expansion in powers of $y \equiv z^{-1}$ was first considered by Gaunt and Fisher[3] specifically for the diamond model, but it has been used later for other HCLP systems.[14,16] As far as we know, there has been no study of the convergence of this series, though Baxter's explicit solution[4] for the hard hexagon model shows it to be so for that solvable model. This is in contrast to the low-fugacity expansion of the pressure $p(z)$ in powers of z, which dates back to Ursell[17] and Mayer.[18] This expansion was proven to have a positive radius of convergence in all dimensions by Groeneveld[19] for positive pair potentials and by Ruelle[20] and Penrose[21] for general pair potentials.

In this note, we sketch a proof that the radius of convergence of the high-fugacity expansion is positive for a certain class of HCLP systems in $d \geq 2$ dimensions (for details of the proof, see ref 22). The proof is based on an extension of Pirogov–Sinai theory[23,24] and implies the existence of phase transitions in these models. Unlike the low-fugacity expansion, the positivity of the radius of convergence does not hold for general HCLP systems: indeed, there are many examples in one and higher dimensions in which the coefficients in this expansion diverge in the thermodynamic limit.

■ THEORY

It is convenient for our analysis to think of these HCLPs as having a finite shape ω in physical space $\mathbb{R}^d$ and to impose the constraint that, when put on lattice sites x and y, the shapes do not overlap (e.g., for the nearest-neighbor exclusion on the square lattice, ω could be a diamond; see Figure 1*a*). Equivalently, one can think of each particle as occupying a finite collection of lattice sites. It should be noted that the choice of these shapes, or of the lattice points assigned to each particle, is not unique: two different shapes can translate to the same hard-core interaction. For instance, the nearest-neighbor exclusion on the square lattice can be obtained by taking diamonds or disks of radius r with $\frac{1}{2} < r < \frac{1}{\sqrt{2}}$.

Given a d-dimensional lattice Λ_∞ and a finite subset $\Lambda \subset \Lambda_\infty$, we define the grand-canonical partition function of the system at activity $z > 0$ on Λ, with some specified boundary conditions, as

$$\Xi_\Lambda(z) = \sum_{X\subset\Lambda} z^{|X|} \prod_{x\neq x'\in X} \varphi(x, x') \tag{1}$$

in which X is a particle configuration in Λ, $|X|$ is the number of particles, and, setting $\omega_x \equiv \{x + y, y \in \omega\}$, $\varphi(x, x') \in \{0, 1\}$ enforces the hard-core repulsion: it is equal to 1 if and only if $\omega_x \cap \omega_{x'} = \emptyset$. It should be noted that as a result of the hard-core interaction, the number of particles is bounded:

$$|X| \leq N_{\max} \leq |\Lambda| \tag{2}$$

where $|\Lambda|$ denotes the number of lattice sites in Λ. Our aim in this note is to prove that in certain cases the finite-volume *pressure* of the system, defined as

$$p_\Lambda(z) := \frac{1}{|\Lambda|} \log \Xi_\Lambda(z) \tag{3}$$

satisfies

$$p(z) := \lim_{\Lambda\to\Lambda_\infty} p_\Lambda = \rho_m \log z + f(y) \tag{4}$$

in which ρ_m is the maximum density in Λ (i.e., $\rho_m = \lim_{\Lambda\to\Lambda_\infty} N_{\max}/|\Lambda|$) and f is an analytic function of $y \equiv z^{-1}$ for small values of y. The expansion of f in powers of y is called the *high-fugacity expansion* of the system. It should be noted that, as is well-known, $p(z) \equiv \lim_{\Lambda\to\Lambda_\infty} p_\Lambda(z)$ is independent of the boundary conditions for all $z \geq 0$ (see, e.g., Ruelle[25]). This is not so for the correlation functions, which may depend on the boundary conditions and can also be shown to be analytic in y with the same radius of convergence as the high-fugacity expansion.

It is rather straightforward to express the pressure p_Λ as a power series in z (which converges for small values of z, thus earning the name "low-fugacity expansion"). Indeed, defining the *canonical* partition function, denoted by $Z_\Lambda(k)$, as the number of particle configurations with k particles, eq 1 can be rewritten as

$$\Xi_\Lambda(z) = \sum_{k=0}^{N_{\max}} z^k Z_\Lambda(k) \tag{5}$$

Substituting eq 3 into eq 5, we find that, formally,

$$p_\Lambda = \sum_{k=1}^{\infty} z^k b_k(\Lambda) \tag{6}$$

with

$$b_k(\Lambda) := \frac{1}{|\Lambda|} \sum_{n=1}^{k} \frac{(-1)^{n+1}}{n} \sum_{\substack{k_1,\cdots,k_n\geq 1\\ k_1+\cdots+k_n=k}} Z_\Lambda(k_1)\cdots Z_\Lambda(k_n) \tag{7}$$

As is well-known (see, e.g., Ruelle[25]), there is a remarkable cancellation that eliminates the Λ dependence from $b_k(\Lambda)$ when $\Lambda \to \Lambda_\infty$. This is readily seen by writing these coefficients in terms of *Mayer graphs*, which implies that $b_j(\Lambda)$ converges to b_j as $\Lambda \to \Lambda_\infty$ independent of the boundary condition. Furthermore, the radius of convergence $R(\Lambda)$ of eq 6 converges to $R > 0$, which for positive potentials (like those considered here) is equal to the radius of convergence R_∞ of $\sum_{j=1}^{\infty} b_j z^j$.[21]

■ RESULTS

The main idea of the high-fugacity expansion, due to Gaunt and Fisher,[3] is to perform a *low-fugacity* expansion for the *holes* of the system. In other words, instead of expressing the pressure p_Λ in terms of the number of *particle* configurations with k particles, we express it in terms of the number of *hole* configurations in the *absence* of k particles from perfect covering. To make this idea more precise, let us consider the

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example of nearest-neighbor exclusion (which corresponds to hard diamonds) on the square lattice.

Assume that Λ is a $2n \times 2n$ torus, so that Λ can be completely packed with diamonds. By the invariance of the system under translations, there are two perfect coverings, each of which contains $|\Lambda|/2$ particles. Let

$$Q_\Lambda(k) := Z_\Lambda\left(\frac{|\Lambda|}{2} - k\right) \quad (8)$$

denote the number of configurations that are *missing* k particles, in terms of which

$$\Xi_\Lambda(z) = 2z^{|\Lambda|/2} \sum_{k=0}^{\infty} \left(\frac{1}{2} z^{-k} Q_\Lambda(k)\right) \quad (9)$$

(we factor the 2 out because $Q_\Lambda(0) = 2$ and we wish to expand the logarithm in eq 3 around 1). We thus have, formally,

$$p_\Lambda = \frac{1}{|\Lambda|}\log 2 + \frac{1}{2}\log z + \sum_{k=1}^{\infty} y^k c_k(\Lambda) \quad (10)$$

where $y \equiv z^{-1}$ and

$$c_k(\Lambda) := \frac{1}{|\Lambda|}\sum_{n=1}^{k} \frac{(-1)^{n+1}}{n2^n} \sum_{\substack{k_1,\cdots,k_n \geq 1 \\ k_1+\cdots+k_n = k}} Q_\Lambda(k_1)\cdots Q_\Lambda(k_n) \quad (11)$$

The first nine terms of this expansion were computed by Gaunt and Fisher[3] for periodic boundary conditions. They found that, as in the low-fugacity expansion, these nine coefficients $c_k(\Lambda)$ converge to c_k as $\Lambda \to \Lambda_\infty$. However, there is no systematic way of exhibiting the cancellations needed for this convergence to hold for general HCLP systems. In fact, there are many simple examples where $c_2(\Lambda) \to \infty$ as $\Lambda \to \Lambda_\infty$. For instance, consider the nearest-neighbor exclusion in one dimension (which exactly maps to the one-dimensional monomer−dimer model). In the language of this paper, the model is characterized by $\Lambda_\infty = \mathbb{Z}$ and $\omega = (-1, 1) \subset \mathbb{R}$. It is easy to compute (e.g., using the transfer matrix technique) that the infinite-volume pressure of this model is

$$p = \log\left(\frac{1 + \sqrt{1 + 4z}}{2}\right) = \frac{1}{2}\log z + \log\left(\sqrt{1 + \frac{1}{4z}} + \frac{1}{2\sqrt{z}}\right) \quad (12)$$

Therefore, $p - \frac{1}{2}\log z$ (note that $\rho_m = \frac{1}{2}$) is not an analytic function of $y \equiv z^{-1}$ at $y = 0$ (though it is an analytic function of $\sqrt{y}$). For the n-nearest-neighbor exclusion in one dimension, $p - \rho_m \log z$ is analytic in $y^{1/n}$. Similar effects occur in higher dimensions as well, for instance in systems exhibiting columnar order at high fugacities.[26]

For systems whose pressure admits a convergent high-fugacity expansion, the partition function may not have any roots for large values of $|z|$, which implies that the Lee−Yang[27,28] zeros of such systems are confined within an annulus: denoting the radius of convergence of the low- and high-fugacity expansions by R and $\tilde{R}$, every Lee−Yang zero ξ satisfies

$$R \leq |\xi| \leq \tilde{R}^{-1} \quad (13)$$

Furthermore, it can easily be seen (by Krammers−Wannier duality) that systems with bounded repulsive pair potentials all have a convergent high-fugacity expansion, so their Lee−Yang zeros lie within an annulus.

Here we prove that for a class of HCLP systems that we call "nonsliding models" (which include the three models discussed above, i.e., the hard diamond, cross, and hexagon models), the function

$$f_\Lambda(y) := p_\Lambda - \rho_m \log z + o(1) \quad (14)$$

is analytic in a disk around $y = 0$ uniformly in $|\Lambda|$, in which $o(1) \to 0$ as $\Lambda \to \Lambda_\infty$. That is,

$$f_\Lambda(y) = \sum_{k=1}^{\infty} y^k c_k(\Lambda), \quad |c_k(\Lambda)| < \tilde{R}^k, \quad \lim_{\Lambda \to \Lambda_\infty} c_k(\Lambda) = c_k \quad (15)$$

for some $\tilde{R} > 0$, independent of $|\Lambda|$. We thus prove the validity of the Gaunt−Fisher expansion for nonsliding models. Our method of proof further shows that for such systems the high-fugacity phases exhibit crystalline order.

A precise definition of the notion of nonsliding will be given below. An example of a *sliding* model is the hard 2×2 square model on a square lattice: given a perfect covering, whole columns or rows of particles can slide without forming vacancies (see Figure 3). On the other hand, hard diamonds do *not* slide: the close-packed configurations are rigid. The same is true of hard crosses and hard hexagons as well as the nearest-neighbor exclusion on Z^d for any $d \geq 2$.

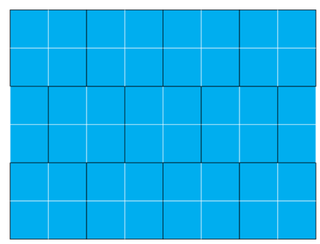

Figure 3. Hard 2×2 squares on the square lattice slide: whole columns or rows of particles can be moved without forming vacancies.

DISCUSSION

In this note, we will only give a detailed sketch of the proof. The full details can be found in ref 22.

Ultimately, the reasoning behind eq 15 is similar to that underpinning the convergence of the Mayer expansion (eq 6), so let us first discuss the Mayer expansion and, in particular, focus on the uniform boundedness of $b_k(\Lambda)$ defined in eq 7. For the sake of simplicity, we will consider periodic boundary conditions and take $|\Lambda|$ sufficiently larger than k. First of all, we note that $Z_\Lambda(k)$ is a polynomial in $|\Lambda|$ of order k with no constant term, and thus,

$$\frac{1}{|\Lambda|} Z_\Lambda(k_1)\cdots Z_\Lambda(k_n) \quad (16)$$

is a polynomial in $|\Lambda|$ of order $k - 1$. Therefore, in order for $b_k(\Lambda)$ to remain bounded in the $\Lambda \to \Lambda_\infty$ limit for $k > 1$, there must be a significant cancellation. For the purpose of illustration, consider

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$$b_2(\Lambda) = \frac{1}{|\Lambda|}\left(Z_\Lambda(2) - \frac{1}{2}Z_\Lambda(1)^2\right) \quad (17)$$

In the one-particle case, the particle can occupy any site in Λ, so $Z_\Lambda(1) = |\Lambda|$. In the two-particle case, the particles must not overlap. We can therefore write $Z_\Lambda(2)$ as the number of unconstrained configurations (excluding the cases in which particles coincide) minus the number of configurations in which the particles overlap. The former is equal to $\frac{1}{2}|\Lambda|(|\Lambda| - 1)$, and the latter is proportional to $|\Lambda|$. The $|\Lambda|^2$ term thus cancels out. This reasoning can be extended to all $b_k(\Lambda)$.

Following Gaunt and Fisher,[3] we construct the high-fugacity expansion in a similar way, but instead of counting particle configurations, we count hole configurations. To that end, we factor out $z^{\rho_m|\Lambda|}$ from the partition function, as in eq 9, thus giving each hole a weight $z^{-\rho_m}$. The most significant difference with the Mayer expansion is that the interaction between holes is not simply a hard-core repulsion, since the sites that are not empty must be covered by particles that in turn must satisfy the hard-core constraint. In particular, the connected components of the empty space may come in various shapes and sizes, but they are constrained by the fact that the overall empty volume is an integer multiple of the volume of each particle (see Figure 4). This implies that different connected components of the empty volume could in principle interact strongly, even if they are arbitrarily far from each other (see Figure 4b). If that were the case, then the $|\Lambda|^2$ terms in $c_2(\Lambda)$ would not cancel out, and the high-fugacity expansion would be ill-defined in the thermodynamic limit. This phenomenon will be called *sliding*.

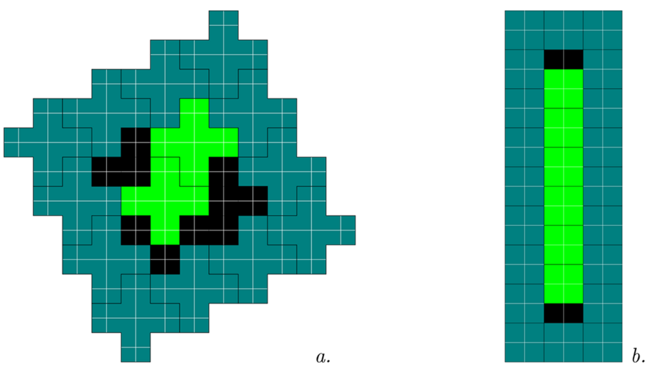

Figure 4. (a) A hole configuration for a system of hard crosses. There is no sliding in this model. (b) A hole configuration for a system of hard 2 × 2 squares on a square lattice (next-nearest-neighbor exclusion). There is sliding in this model. It should be noted that the central column corresponds to a configuration in the one-dimensional nearest-neighbor exclusion model, which, as discussed earlier, does not have an expansion in z^{-1}. Particles of different colors correspond to different phases: the colored subconfiguration can be extended to different perfect coverings (the color assignment is not unique).

In this paper, we will only consider models in which there is *no sliding*, a notion that we will now define precisely. First of all, in order to qualify as a nonsliding model, the system must admit only a *finite* number of distinct perfect coverings and must be such that any particle configuration is entirely determined by the location of the holes and the particles adjacent to them. In addition, whenever different locally close-packed phases coexist, the interface between the phases must contain a number of holes proportional to its length (see Figure 5). This condition is analogous to the *Peierls condition* in the standard Pirogov–Sinai theory.[23,24] This rules out situations similar to Figure 4b, in which the interface between the central column and the other two may be arbitrarily long while having only two holes. More precisely, a model is said to exhibit *no sliding* if, for every *connected* particle configuration $X \subset \Lambda$ that is *not* a subset of a perfect covering of Λ and for every configuration $Y \supset X$, there exists at least one empty site *neighboring* a particle in X (see Figure 5). It should be noted that with X fixed, there are many possible connected configurations Y that contain X, and we require that *every one* of them contain some empty space. The notions of *connectedness* and *neighbors* are inherited from the lattice structure, and a particle configuration X is said to be connected if the set of lattice sites that are covered by particles is connected.

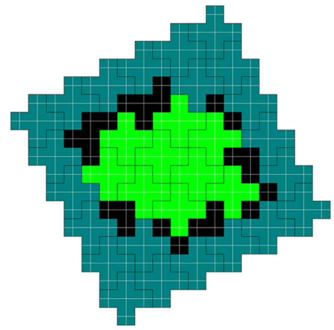

Figure 5. An interface between two different phases. The particles are colored according to the phase to which they belong (the coloring is not in general unique). There is empty space (shown in black) along the entire interface. This follows from the absence of sliding: for every connected collection of particles along the interface, there is empty space nearby.

In the absence of sliding, it is easy to see which holes are correlated. Indeed, consider the connected components of the union of the holes and their neighboring particles (see Figure 6). Each such component is called a *Gaunt–Fisher (GF) configuration*. The space that is not occupied by GF configurations is completely covered by particles, so, since there is no sliding, each of its connected components can be extended to a perfect covering of Λ. To each such component, we associate an index that specifies to which of the possible perfect coverings the configuration in the component can be extended. The interaction between GF configurations is then rather simple: distinct GF configurations must be disjoint, and each connected component of the complement of each GF configuration must be coverable by particles in a configuration that can be extended to the perfect covering specified by the index of the component. The latter interaction is thus mediated by the indices of the connected components of the complements of the GF configurations. We then completely remove this interaction, as described below.

Let us consider only the most external GF configurations, that is, those that do not lie inside any other GF configuration. To eliminate their interaction, we fix the boundary condition on Λ once and for all, so as to fix the index of the perfect covering on the outside. At this point, the constraint on each GF configuration is that it be compatible with the boundary condition, which is independent of the other GF configurations, thus eliminating the interaction between them. Now, the GF configurations may have holes (see Figure 6c), and other

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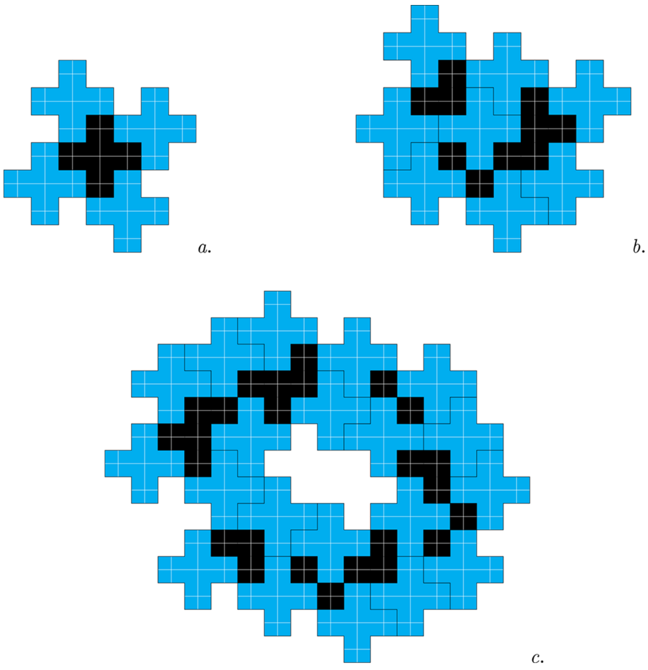

Figure 6. Example Gaunt−Fisher configurations. The empty space is colored black. Panel (b) corresponds to the configuration in Figure 4a, and panel (c) corresponds to that in Figure 5. The complement of these Gaunt−Fisher configurations can be entirely covered by crosses.

configurations may lie inside these holes. These would interact with the GF configurations that contain them. In order to eliminate these interactions, we make use of a technique from Pirogov−Sinai theory.[23,24] Namely, the partition function in each hole is a partition function on a smaller volume, with the boundary condition imposed by the index of the covering of the hole. In general, the partition function in a hole may depend on the boundary condition (see Figure 7), but this dependence is

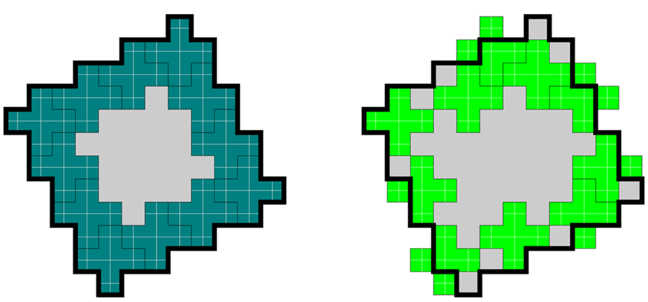

Figure 7. Two different boundary conditions for the hard cross model. The set Λ is outlined by the thick black line. The crosses that are drawn are those mandated by the boundary condition (the boundary condition stipulates that every cross that is in contact with the boundary must be of a specified phase), and the remaining available space in Λ is colored gray. The partition function in the left panel is $z^{16}(1 + 4y + 10y^2 + 8y^3 + y^4)$, whereas that in the right panel is $z^{16}(1 + 6y + 18y^2 + 48y^3 + 43y^4 + 13y^5 + y^6)$.

weak. Indeed, one can show that the ratio of the partition function with one boundary condition divided by that with another is at most exponential in the size of the *boundary* (whereas each partition function is exponential in the size of the *bulk*). Thus, at the price of an exponential factor in the size of the GF configuration, called the *flipping term*, we can pretend that the partition function in each hole has the same boundary condition as the entire space. At this point, the interaction between GF configurations simply states that they must not overlap. Since there is no sliding, each GF configuration therefore contains a number of holes that is proportional to its size, thus contributing a factor $z^{-c|\mathrm{size}|}$ to the partition function (from which, we recall, we have factored out $z^{-\rho_m|\Lambda|}$ so that each hole contributes $z^{-\rho_m}$), which outweighs the flipping term.

We have thus constructed a model of GF configurations that interact via a purely hard-core potential and have a very small effective fugacity. We then use a low-fugacity expansion to express the function f_Λ (eq 14) as a convergent series, following Kotecký and Preiss.[29] In addition, the effective fugacity of a GF configuration of volume $|V|$ is equal to the fugacity of the particles inside the configuration divided by $z^{\rho_m|V|}$. Furthermore, since the GF configuration contains empty space, the number of particles in the GF configuration is smaller than $\rho_m|V|$. Finally, since the volume obtained by removing the GF configuration from the lattice can be covered by particles, $\rho_m|V|$ is an integer. Therefore, the fugacity of a GF configuration is an analytic function of $y \equiv z^{-1}$, which implies that f_Λ is analytic in y uniformly in $|\Lambda|$.

CONCLUSIONS

In this paper, we have focused on the pressure p at large z. Other thermodynamic quantities can be computed from p or by a computation similar to that for p. We recover the average density $\bar{\rho}$ from the pressure by

$$\bar{\rho} = z\frac{\partial p}{\partial z} = -y\frac{\partial p}{\partial y} = \rho_m + \sum_{j=1}^{\infty} k c_k y^k \tag{18}$$

Since the pressure is independent of the boundary condition, it is the same in all phases, which implies that the average density is as well. In order to distinguish between phases, one could consider the local density $\rho(x)$ at x, which does depend on the phase. Thus, for diamonds on a square lattice, at large fugacities the local density at sites on the even sublattice would be different from that on the odd sublattice: in the even phase, the former would be close to 1, whereas the latter would be close to 0. In general, when there are n close-packed phases, there are n sublattices, and in each phase, the local density at one of the sublattices is close to 1 while the others are close to 0. The local density $\rho(x)$ can be expanded in powers of y using methods similar to those described in this paper. Similarly, one can expand higher-order correlation functions and find that when the series converges, the truncated correlation functions in a specified phase decay exponentially.

Here we have considered only HCLP systems that have a single shape. A natural extension would be to consider systems in which several types of particles of different shapes can coexist, provided that there is a finite number of perfect coverings and no sliding. In that case, different particles may have different fugacities, for instance, one might set $z_\alpha = \lambda_\alpha z$ and expand in z^{-1}. The qualitative behavior of the system might depend on the λ_α. Further extensions could be to consider more general pair potentials by, for instance, allowing for smooth interactions or for more general hard-core repulsions such as the Widom−Rowlinson[30] interaction.

If instead of overlap between the particles being forbidden, it were merely discouraged by replacing the hard-core potential by a strongly repulsive potential J, then using a technique similar to that sketched in this paper, one would expect to prove that the pressure is analytic in an intermediate regime z_0

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$< |z| \ll e^J$. This was shown for the soft diamond model by Braskamp and Kunz.[31]

The methods described here allow, in some cases, the continuum to be approached but not reached. For instance, in the cross model, one can make the lattice finer (or, equivalently, the crosses can be made thicker). However, the radius of convergence vanishes in the continuum limit. New ideas are needed to treat such a case.

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Notes

The authors declare no competing financial interest.

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