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Applications of the Yang–Lee–Ruelle Theory to Hard-Core Lattice Gases

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The grand-partition-function-zero method is applied to lattice systems of rigid molecules, based on the algebraic technique of Ruelle. Consideration of small collections of lattice molecules, through this approach, provides rigorous delineation of regions of the complex activity plane which are free of zeros of the grand partition function, and hence free of thermodynamic singularities. Two conjectures, as yet unproved, are offered, which greatly reduce the computational effort required in using the technique. A simple proof is provided for the absence of physical phase transitions in monomer–dimer systems, and bounds are obtained on the locations of the transitions of other lattice gases.

KEY WORDS: Lattice gas; phase transition; grand partition function; dimers; Ising model.

1. INTRODUCTION

Mathematically rigorous conclusions about the statistical behavior of systems of interacting molecules are quite limited in number and type. When exact results can be obtained, it seems the price inevitably is a loss in generality: a restriction to one dimension, the imposition of some asymptotic limit, the assumption of some specific form of intermolecular potential, and so on. The role played in statistical physics by many of these "models" should not be minimized, however, for they usually give rise to the important questions:

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How general is this result? How would the result be changed if the model were altered?

Essentially, this line of development has been followed over the past two decades by the theory of lattice statistics—more precisely, by the "Yang-Lee" theory of phase transitions in lattice systems.[1-5] The Yang-Lee approach to the subject of phase transition centers around the grand partition function $P(z)$ for a fintite system, with the activity regarded as a complex variable. For a finite system with a maximum density, $P(z)$ is necessarily only a polynomial and, hence, an entire function. But the thermodynamics of the system enters through the logarithmic function log P; consequently *zeros* of P spoil the analyticity of the thermodynamic functions and account for singularities, or phase transitions.

It is, of course, true that physically, the activity $z = \exp(\beta\mu)$ must be real and positive; here, $\beta = (kT)^{-1}$ and μ is the chemical potential. It is also true that the coefficients in the polynomial $P(z)$—since they are weighted Boltzmann factors—are also real and positive. It follows easily that for a finite system, the zeros of P cannot be on the positive real axis. What does not follow easily is what the zeros do as the system becomes infinite; they can sneak closer and closer to the positive real axis and wreak the havoc known as a phase transition.

For the square lattice ferromagnetic Ising model—already subdued by Onsager[6]—Lee and Yang showed in 1952 that the partition function zeros (pfz's) for the infinite lattice all reside on the unit circle in the complex z plane.[1] The real axis is thus sliced at $z = 1$ (corresponding to vanishing magnetic field) by the line of pfz's. All other physical activities (real and positive) are points of thermodynamic analyticity.

In the years following this discovery, it has been learned that the model can be generalized to some extent—as long as it stays essentially ferromagnetic—and the pfz's will dutifully stay on the unit circle. It has been learned that repulsive intermolecular interactions (switching to lattice-gas language) tend to draw the pfz's off the circle and toward the *negative* real axis.[7] But it has also been learned by other techniques[8-10],[3] that some "hard-core" systems demand a physical phase transition; so in these cases, also, the positive real activity axis must be menaced by pfz's. On the other hand, rigorous proofs have been obtained to demonstrate the *absence* of phase transitions in other hard-core systems—notably for the "monomer-dimer" problem.[11],[4]

The original paper of Lee and Yang contained a very important idea: that it might prove useful to associate different activities z_i with each lattice site. The advantage, basically, is that the partition function must be *linear* in

[3] See Ref. 10 for references to approximate techniques.

[4] Heilmann[12] has indicated a technique related to the present method.

each of these site activities, a great help mathematically. These activities can later all be set equal after the benefits of the linearity have been realized.

Asano[2] later added another valuable idea ("contractions") to the technique. Let each site be replaced (temporarily) by several surrogates, each interacting in only one "direction," and hence independent of each other. The surrogates are then successively identified (or contracted) until only the one "true" site remains. Asano's contribution, in effect, was the observation that sometimes it is possible to keep up with the changes in some properties of the partition function as the contractions proceed. We can thus more or less build a partition function for an interacting system from simpler, less interacting ones.

Finally, Ruelle[4]—assisted by a proof contributed by Dyson—blended these two ideas together and obtained a result of considerable generality for lattice gas systems. The essence of the theorem is a prescription for the calculation of regions of the complex activity plane which are free of pfz's, based on the molecular interactions postulated in the model. There are two intriguing aspects of Ruelle's theorem. The first is that any application of the theorem always yields a *rigorous* result (in the nature of a rigorous bound). The second is that the structure of the prescription injects into statistical mechanics the elements of complex analysis in a new and fundamental way.

In this paper, we will not need the full generality of the theorem, which permits interactions of any type. We will rather focus attention on hard-core lattice gas systems, for which every Boltzmann factor is either zero or one. This restriction will permit a simplification in the statement of the theorem, to which we now turn.

2. RUELLE'S THEOREM FOR HARD-CORE LATTICE GASES[4]

We let Λ denote the sites of some lattice, there being $|\Lambda| < \infty$ sites. Dimensionality is unimportant; nor need the lattice be "regular," so that we may have different types of sites and nonequivalent "bonds" between the sites. In fact, for our purposes, it is convenient to inscribe bonds between every pair of sites whose separation is less than the diameter σ of the (spherical) hard molecules postulated. Only for the "nearest-neighbor hard-core lattice gas," then, will our lattice appear conventional; if σ exceeds the second-neighbor distance, there will be additional lines drawn. In other words, every line stands for a *disallowed* configuration for a pair of molecules. And for hard-core molecules, the disallowed overlaps are the only interactions which must be considered.

Now, let the suffix α index a (finite) collection of subsets Λ_α of the lattice sites, together with all affixed bonds. The vertices (sites) of the subsets Λ_α are labeled—corresponding in some way to the vertices of Λ—but the subsets

themselves are not required to be congruent. If the collection of subsets Λ_α includes at least one subset site for each lattice site of Λ (and bond for bond), then the collection of subsets $\{\Lambda_\alpha\}$ is a "covering" of Λ. The subset sites are the "surrogates" in Asano's contraction scheme. It should be emphasized that every site and bond must be covered, and that many may well be multiply covered. It might be helpful in the latter case to think of the subset sites which multiply cover lattice site 3, for example, to be labeled 3a, 3b, 3c,... .

Associated with each covering set Λ_α, there is a (grand ensemble) partition function, a function of as many ($|\Lambda_\alpha|$) site activities z_i as there are vertices in Λ_α. (We are using the Yang–Lee notion of labeled site activities.) We will call this partition function simply P_α ; the multivariable-partition function for the entire lattice we call P_Λ. Also to be associated with each Λ_α is a collection of regions (some or all may be identical) of the complex plane, denoted $M_{\alpha,i}$, with some important properties:

1. $M_{\alpha,i}$ is closed [its complement $(\sim M_{\alpha,i})$ is open].
2. The origin 0 does not belong to $M_{\alpha,i}$ $(0 \notin M_{\alpha,i})$.

The third property is the crucial one, but we reserve it for inclusion in the theorem itself. Before stating the theorem, we hasten to mention that neither the choice of covering sets $\{\Lambda_\alpha\}$, nor the assignment of regions $M_{\alpha,i}$ $(1 \leqslant i \leqslant |\Lambda_\alpha|)$ is unique for a given lattice. This is where discretion and experience come into play: Some choices give better results than others.

Theorem (Ruelle). If the regions $M_{\alpha,i}$ are chosen (for each α) so that the requirement $z_i \in (\sim M_{\alpha,i})$ for all sites in Λ_α ensures that $P_\alpha \neq 0$, then the similar statement can be made for the entire lattice: $z_i \in (\sim R_i)$ for all sites in Λ ensures that $P_\Lambda \neq 0$, where R_i is the region of the complex plane given symbolically by the "set product"

$$R_i = -\prod_\alpha (-M_{\alpha,i}) \tag{1}$$

the product being over all values of α such that Λ_α contains a surrogate of site i. More precisely, the set R_i is the collection of numbers z which can be written as the product

$$z = -\prod_\alpha (-z_{\alpha,i}) \tag{2}$$

where $z_{\alpha,i} \in M_{\alpha,i}$ and the product is over the same values of α just mentioned.

Some cases can be handled by a "regular covering," by which we shall mean (a) all covering sets Λ_α are congruent, (b) all regions $M_{\alpha,i}$ are identical (simply M), and (c) each site belongs to the same number (s) of covering sets. We state the theorem under these conditions as a corollary.

Corollary. If $z_i \in (\sim M)$ for each i ensures that $P_\alpha \neq 0$ for each α, then $z_i \in (\sim R)$ for each i ensures that $P_\Lambda \neq 0$, where

$$R = (-)^{s+1} M^{**s} \tag{3}$$

We have introduced a special notation for the "set power" to emphasize the fact that M^{**s} is not just the collection of points z^s ($z \in M$), but rather all points of the form $\prod_i z_i$ ($z_i \in M$, $1 \leqslant i \leqslant s$).

For an outline of the proof of the theorem, we refer to Ruelle's original paper.[4] We limit ourselves here to a few general remarks and then turn to some applications. First, it should be recalled that P_Λ is not the usual grand partition function for the lattice at hand—not until all site activities z_i are set equal to some common value, $z_i = z$ for all i, at which point we call the function of one variable $P(z)$. Our primary goal is to know the values of z for which $P(z)$ vanishes. It should be noted clearly that the theorem cannot tell us this; it can at best tell us regions of the complex plane where $P(z)$ does *not* vanish and this is possible only if the intersection of the complements of the R_i's is not void. If this intersection (over *all* values of i),

$$S = \bigcap_i (\sim R_i) \tag{4}$$

is not empty, then we can conclude that $P(z) \neq 0$ throughout S. Any portion of the positive real axis which intersects S would then be free of any thermodynamic singularities.

It should also be noticed that the structure of the theorem requires the nonvanishing of each P_α as all z_i's wander *independently* throughout their allowed territories $(\sim M_{\alpha,i})$. This permits P_α to vanish (by cancellations) in "many more ways" than would be possible if the z_i's could be forced to be equal at this stage.

The determination of the region S free of pfz's is thus reduced to the following three steps:

1. Choose some collection of covering sets. Usually, congruent sets are easier to work with, as are smaller sets—but of course larger sets may give a better answer (larger S).

2. Write down the grand partition function (multivariable) for each type of covering set and discover (this is where the work enters) regions $M_{\alpha,i}$ so that $P_\alpha \neq 0$ if $z_i \in (\sim M_{\alpha,i})$.

3. Then determine the regions R_i according to the set product formula (this is often not easy either), and the pfz-free region $S = \bigcap_i (\sim R_i)$.

We turn now to some applications of the theorem.

3. NEAREST-NEIGHBOR HARD-CORE LATTICE GASES

A simple application of the corollary is both instructive and useful. We consider any regular lattice, with coordination number c; the hard molecules which are to reside at the lattice sites have diameter greater than the nearest-neighbor and less than the second-neighbor distance. For a regular covering, we choose the $(c \mid \Lambda \mid /2)$ nearest-neighbor pairs of sites (together with the bonds between them). For a representative set Λ_α, consider the pair of sites 1 and 2; for this pair of sites, the multivariable grand partition function for the postulated molecules is simply

$$P_\alpha = 1 + z_1 + z_2 \tag{5}$$

There is no $z_1 z_2$ term, due to the hard cores of the molecules.

Now, according to the prescription of the corollary, we wish to find a region M of the complex plane such that P_α will not vanish if neither z_1 nor z_2 are in M. A variety of choices is possible, but we will consider here only two. The first choice, which we denote by $M^{(1)}$, keeps z_1 and z_2 so small in absolute value that their sum cannot possibly be -1. Hence, we take $M^{(1)} = \{z: \mid z \mid \geqslant \frac{1}{2}\}$; that is, $M^{(1)}$ is the closed region exterior to a zero-centered circle of radius $\frac{1}{2}$. Clearly $z_1 \notin M^{(1)}$ and $z_2 \notin M^{(1)}$ ensures that $P_\alpha \neq 0$.

So far, the identity of the lattice has not entered. But we now must take into account the fact that this choice of covering sets covers each lattice site with c surrogates; that is, $s = c$. The region R, which must contain any pfz's for the entire lattice, is found from Eq. (3) to be given by the set-power $((-)^{c+1} M^{(1)**c}$. A zero-centered circular region (or its complement) is the easiest set to raise to a set-power. Even the phase factor $(-)^{c+1}$ is irrelevant; R is simply given by

$$R = \{z: \mid z \mid \geqslant 2^{-c}\} \tag{6}$$

and the pfz-free region S is the interior of a circle of radius 2^{-c}.

This result is easily obtained, and rigorous, but not very useful. It does not even prove for us that the linear hard-core lattice has no transition. Meeron's calculation[7] on systems of molecules with strictly repulsive forces produced the lower bound $z_b = \mid 2B_2 \mid^{-1}$ for any singularity, where B_2 is the usual second virial coefficient and the bound is on real, positive z. For the nearest-neighbor hard-core lattice gas, B_2 is $(c + 1)/2$ and hence Meeron's region of analyticity is $0 \leqslant z \leqslant (c + 1)^{-1}$, which is superior to the above bound for any lattice.

Another choice, $M^{(2)}$, is more fruitful. We take $M^{(2)}$ to be the (closed) half-plane

$$M^{(2)} = \{z: \mathrm{Re}(z) \leqslant a\} \tag{7}$$

where a is any negative real number greater than $-\frac{1}{2}$. Clearly, $\mathrm{Re}(P_a) > 0$ if $z_i \notin M^{(2)}$ and so P_a cannot vanish. The set-powers of $M^{(2)}$ are somewhat more difficult to compute, however, and this points up one of the difficulties of applying this theorem. Even for the set-square M^{**2}, it is not obvious how to determine the boundary of the region M^{**2}, and each case must be studied individually. For $M^{(2)}$, it may be shown that that boundary of $M^{(2)**2}$ is given by the "square of the boundary of $M^{(2)}$"; i.e., by points z of the form $z = z_1^2$, with $z_1 = a + it$ for any real t. This boundary line (including also the factor of -1) is given by

$$\mathrm{Re}(z) = -a^2 + t^2, \qquad \mathrm{Im}(z) = -2at \tag{8}$$

and is the boundary of the pfz-free region S for the linear lattice (see Fig. 1). Since the entire positive real axis is contained in S, we conclude that the linear lattice has no phase transition—as is well known.

For a lattice of coordination number four—such as the square lattice or diamond lattice—we must compute the boundary of the region

$$R = -M^{(2)**4} \tag{9}$$

Assuming that the boundary points of R arise from four points z_i on the line $z = a + it$, we can show that the four must in fact be identical, at least where the boundary crosses the real axis: let $R + iI$ denote the product

$$R + iI = z_1 z_2 z_3 z_4 \tag{10}$$

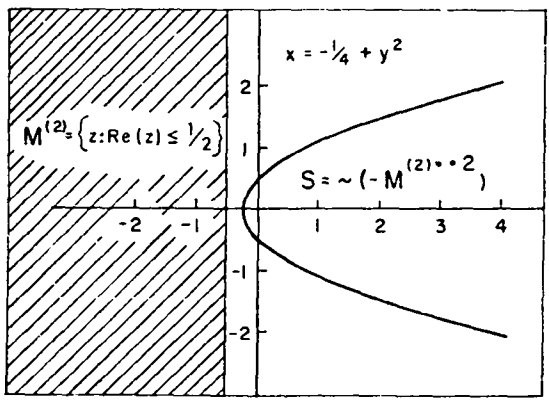

Fig. 1. Excluded region $M^{(2)}$ for nearest-neighbor hard-core lattice gas, with two-point covering sets. For coordination number $c = 2$ (linear lattice), the region S is free of zeros of the grand partition function.

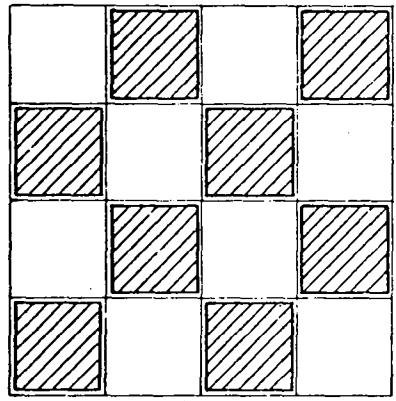

Fig. 2. Four-point covering sets for the hard-square lattice gas. Each site is represented by a surrogate corner of two covering squares.

and look for the extrema of R subject to $I = \text{const} = 0$. The Lagrange multiplier technique leads to the equations

$$\begin{aligned}
[a^2(t_2 + t_3 + t_4) - t_2t_3t_4](at_1 + \lambda) &= 0 \\
[a^2(t_1 + t_3 + t_4) - t_1t_3t_4](at_2 + \lambda) &= 0 \\
[a^2(t_1 + t_2 + t_4) - t_1t_2t_4](at_3 + \lambda) &= 0 \\
[a^2(t_1 + t_2 + t_3) - t_1t_2t_3](at_4 + \lambda) &= 0 \\
a^2(t_1 + t_2 + t_3 + t_4) - (t_1t_2t_3 + t_1t_3t_4 + t_1t_2t_4 + t_2t_3t_4) &= 0
\end{aligned} \tag{11}$$

One solution of these equations is $t_i = a$ for all i [and the Lagrange multiplier λ is $-a^2$]; this appears to be the only meaningful solution and gives $0 \leqslant z \leqslant \frac{1}{4} = z_b$ as the corresponding region of guaranteed analyticity on the positive real axis, for the best choice a—namely, $a = \frac{1}{2}$. This is slightly better than Meeron's bound of $\frac{1}{3}$, but still far short of the "experimental" location of the transition for the square lattice (at $z = 3.80$).[8]

The estimate can be improved by using judiciously chosen larger covering sets (and fewer of them). Fig. 2 shows a regular covering with square covering sets, containing two surrogates per lattice site. The partition function for one of the squares is

$$\begin{aligned}
P_a &= 1 + z_1 + z_2 + z_3 + z_4 + z_1z_3 + z_2z_4 \\
&= \xi_{13} + \xi_{24}
\end{aligned} \tag{12}$$

where

$$\begin{aligned}
\xi_{13} &= \tfrac{1}{2} + z_1 + z_3 + z_1z_3 \\
\xi_{24} &= \tfrac{1}{2} + z_2 + z_4 + z_2z_4
\end{aligned} \tag{13}$$

We force the nonvanishing of P_α by ensuring that $\mathrm{Re}(\xi_{13})$ and $\mathrm{Re}(\xi_{24})$ are both strictly positive. This we accomplish with the region $M^{(3)}$, which lies to the left of the line given by (see Fig. 3a)

$$y^2 = x^2 + 2x + \tfrac{1}{2} \tag{14}$$

We have, for example,

$$\mathrm{Re}(\xi_{13}) = \tfrac{1}{2} + x_1 + x_3 + x_1x_3 - y_1y_3 \tag{15}$$

using the obvious notation $z_i = x_i + iy_i$. But if $z_1 \in {\sim}M^{(3)}$ and $z_3 \in {\sim}M^{(3)}$,

$$\begin{aligned} |\, y_1y_3 \,|^2 &< (x_1^2 + 2x_1 + \tfrac{1}{2})(x_3^2 + 2x_3 + \tfrac{1}{2}) \\ &= x_1^2x_3^2 + 2x_1^2x_3 + 2x_1x_3^2 + 4x_1x_3 + \tfrac{1}{2}x_1^2 + \tfrac{1}{2}x_3^2 + x_1 + x_3 + \tfrac{1}{4} \\ &= |\, \tfrac{1}{2} + x_1 + x_3 + x_1x_3 \,|^2 - \tfrac{1}{2}(x_1 - x_3)^2 \\ &\leqslant |\, \tfrac{1}{2} + x_1 + x_3 + x_1x_3 \,|^2 \end{aligned} \tag{16}$$

It is easy to show that if x_1 and x_3 lie in $({\sim}M^{(3)})$, then $\frac{1}{2} + x_1 + x_3 + x_1x_3 > 0$. This, together with the inequality (16), establishes the conclusion $\mathrm{Re}(\xi_{13}) > 0$.

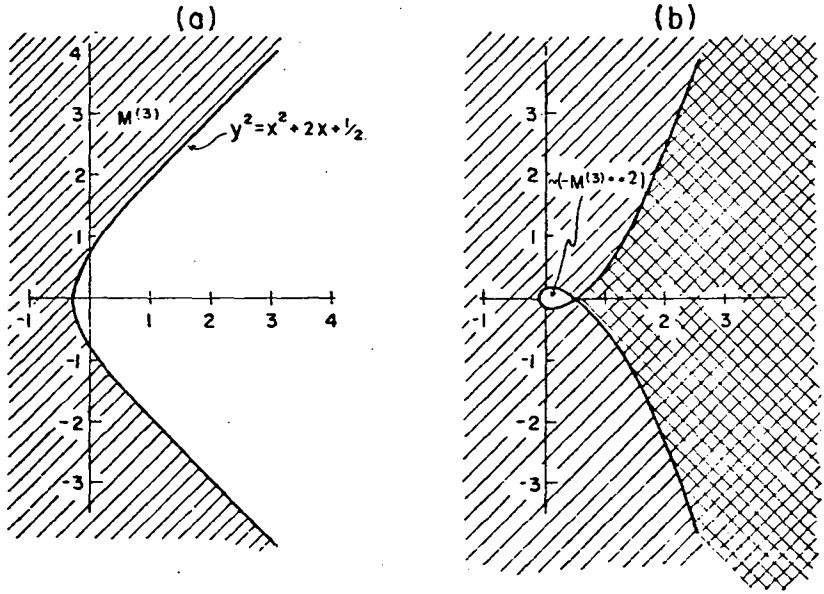

Fig. 3. (a) Excluded region $M^{(3)}$ for the four-point covering sets of Fig. 2. (b) Zero-free region of the infinite square lattice. Only the small almond-shaped region near the origin is rigorously guaranteed to be free of zeros of the partition function. The cross-hatched region is doubly covered by the (negative) set-square of $M^{(3)}$, and the shaded region is simply covered.

An analogous demonstration shows that $z_2 \in (\sim M^{(3)})$ and $z_4 \in (\sim M^{(3)})$ requires $\mathrm{Re}(\xi_{24}) > 0$ and hence P_α cannot vanish if each z_i satisfies $z_i \in (\sim M^{(3)})$. Since each site of the square lattice has two surrogates, it is now necessary to compute $R = -M^{(3)**2}$ to determine the pfz-free region $S = (\sim R)$. This is shown in Fig. 3b; again the boundary comes from the square of the points on the boundary of $M^{(3)}$. The region of analyticity has been extended to $z_b = \frac{1}{2}$.

4. FURTHER PROPERTIES AND SPECULATIONS

There are many details of the application of the Ruelle theorem which are not completely developed but about which some limited information is available, and for which some reasonable appearing speculations offer themselves. In this section, we wish at least to formulate the questions in a clear fashion and hopefully to project correctly a little beyond that which is known with unimpeachable rigor. The uncertainties and speculations all deal with the properties of the ("small") partition functions P_α for the covering sets Λ_α; we are thus dealing with finite questions for which answer should be obtainable.

As mentioned earlier, the form of the theorem permits the "excluded regions" $M_{\alpha,i}$ to be different for each site and each covering set, if desired. We shall, however, limit our inquiries to the simpler case where all are identical, $M_{\alpha,i} = M$; for ease of discussion, we will give a name to the complement of M, $N = \sim M$, for most of the discussion will center on this complement, N.

Thus, N is an open region free of pfz's for P_α, in the sense that $z_i \in N$ for all i ensures that $P_\alpha \neq 0$. An appropriate "set power" of N (actually of M), by virtue of the main theorem, will produce a pfz-free region of the true partition function P. It is thus desirable to make N maximal in some sense, and this leads us to the first conjecture: that there is, in fact, a maximal N. To this end, we first write P_α in a fairly symbolic way:

$$P_\alpha = 1 + \sum_{i=1}^{|\Lambda_\alpha|} z_i + \sum z_i z_j + \cdots + \sum \prod_{k=1}^{d_\alpha} z_{i_k} \tag{17}$$

The maximum number of molecules permitted by the hard-core exclusions is d_α.

Two observations about the finite polynomial P_α are clear. First, if each z_i is sufficiently small in modulus, say $|z_i| < \epsilon$, then the initial term (one) of Eq. (17) will dominate and P_α cannot vanish. Hence, N (which actually has not been defined unambiguously) should contain a circle of radius ϵ about the origin. (By the rules of the main theorem, N must contain the origin itself.) The second obvious statement about P_α is that, since it is real, positive, and

greater than one for z_i real and positive, it cannot vanish if each z_i has a sufficiently small argument, say $|\operatorname{Arg}(z_i)| < \delta$. Hence, N should also contain a sector of angle 2δ bisected by the positive real axis. (See Fig. 4.)

We can even give an estimate of ϵ, and in some cases δ. Since ϵ is small (compared to one), we can approximate Eq. (17) by its lowest-order terms,

$$P_\alpha \cong 1 + \sum_{i=1}^{|\Lambda_\alpha|} z_i \tag{18}$$

and obtain the estimate $\epsilon = |\Lambda_\alpha|^{-1}$.

We estimate δ for a class of coverings sets which we shall describe as "conjugated," a term we use only for nearest-neighbor exclusion problems. A conjugated set Λ_α is one which meets the requirement that the sites may be divided into two *equivalent* subsets ("sublattices") A and B; more precisely, each A site is neighbored entirely by B sites and conversely. Furthermore, there is a permutation Π of the integers $1,2,\ldots,|\Lambda_\alpha|$, which is composed entirely of 2-cycles and against which P_α is invariant. The permutation (reflection) Π would replace each site of sublattice A by one of sublattice B, but the net effect on the polynomial P_α would be nil. Clearly, $|\Lambda_\alpha|$ must be even.

For conjugated sets, the highest-order terms in P_α contain products of $d_\alpha = |\Lambda_\alpha|/2$ activities, and there are two such terms, one referring to A sites and the other to B sites. If each z_i has sufficiently large modulus, the polynomial P_α will be dominated by these two final terms; if also each z_i is "sufficiently real," these dominating terms will have positive real part and P_α will not vanish. We calculate an upper bound on the maximum argument δ, for large modulus, by considering the case

$$\begin{aligned} \operatorname{Arg}(z_i) &= \delta, \qquad i \in A \text{ sublattice} \\ \operatorname{Arg}(z_i) &= -\delta, \qquad i \in B \text{ sublattice} \end{aligned} \tag{19}$$

If $\delta = \pi/2d_\alpha = \pi/|\Lambda_\alpha|$, the two dominating terms will be pure imaginary

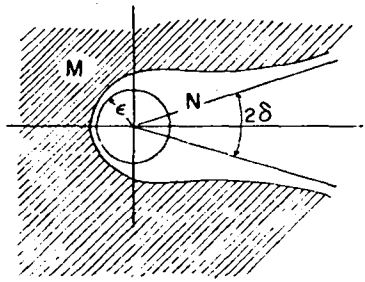

Fig. 4. General form of the zero-free region N for a finite-covering-set partition function P^0.

and will cancel, permitting (the highest-order terms of) P_α to vanish. We thus expect, for conjugated sets, that the region N will contain a sector of angle $2\pi/|\Lambda_\alpha|$ bisected by the positive real axis.

We combine the discussions of the preceding paragraphs into the following conjecture.

Conjecture 1. For any covering set Λ_α, we assume that a maximal open, pfz-free region N exists which contains the origin and the positive real axis; its boundary is assumed to be given by $x = \varphi(y)$, where φ is some single-valued function. For a conjugated set, asymptotically, $(|y| \to \infty)\varphi$ is given by $x = |y| \cot(\pi/|\Lambda_\alpha|)$.

It may be seen that the region $\sim M^{(3)}$ for the square covering sets (Fig. 3a) meets the conditions of the conjecture. Also meeting these conditions is the special case of the half-plane $\sim M^{(2)}$ conjured up for the two-point covering sets [Eq. (7)].

We now wish to make a stronger conjecture about the actual form of the boundary $x = \varphi(y)$ of the presumed extant region N, for conjugated sets. We have had no concern for the "true" zeros of the "small" partition functions P_α, where by a "true" zero we mean a pont z satisfying $P_\alpha(z, z, z, \ldots, z) = 0$. This equation has (at most) $|\Lambda_\alpha|$ solutions; all we can say about them is that certainly none of them can reside in the pfz-free region N. But our need is for the *region* N and solving for the *points* satisfying $P_\alpha(z, z, \ldots, z) = 0$ helps hardly at all in defining the maximal region N. What we need is an equation to solve for the boundary function φ; this equation is supplied by the next conjecture.

Conjecture 2. For a conjugated set, $x = \varphi(y)$ is one branch of the solution of

$$Q_\alpha(z) = 0 \tag{20}$$

where

$$Q_\alpha(z) = P_\alpha(z) \tag{21}$$

with

$$z_i = z, \qquad i \in A \text{ sublattice}$$
$$z_i = z^*, \qquad i \in B \text{ sublattice}$$

While we cannot prove this conjecture, it is supported by several observations. By their structure, Conjectures 2 and 1 concur in the asymptotic region $x, |y| \to \infty$. By the definition of conjugated sets, the imaginary part of Q_α automatically vanishes, since the permutation Π on the one hand replaces P_α by its complex conjugate and on the other hand leaves it unchanged.

While they were not derived in this way, the boundaries of the regions $M^{(2)}$ [Eq. (7)] and $M^{(3)}$ [Eq. (14)] follow most easily from the prescription given by Eqs. (20)–(21). It is of interest that, for 2-point covering sets considered by Ruelle for a general finite nearest-neighbor interaction, the correct region is given by Conjecture 2 *as long as the interaction is repulsive*—but the technique ceases to work when the interaction becomes attractive.

In any event, the boundary line given by Conjecture 2 is a rigorous outer bound on the maximal set N, since the rule does locate zeros of P_s—and none of them can be interior to N.

5. OTHER APPLICATIONS

We give now a few more applications of the theorem, some of them invoking Conjecture 2.

Continuing with the two-dimensional square lattice (nearest-neighbor) discussed in Section 3, we show that the use of larger and larger covering sets does not necessarily ensure better results. As shown in Fig. 5, the lattice may be covered by square-shaped covering sets of any integral edge length. Such covering sets seem attractive since(a) the covering sets are basically one-dimensional; (b) within a covering set, all sites are treated equivalently; and (c) each site of the lattice belongs to only two covering sets.

Even so, we have not succeeded in solving the general problem of determining a rigorous, maximal pfz-free region N as a function of covering set size. We have, however, solved a simpler problem: Using the crutch of Conjecture 2, we have determined the points of intersection of N with the imaginary axis. These points (they are, of course, a complex conjugate pair) map under the negative set-square function of Eq. (3) onto the positive real

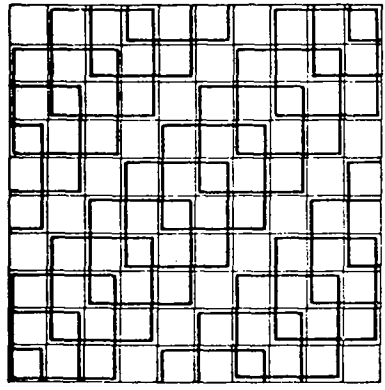

Fig. 5. Alternate covering of the square lattice.

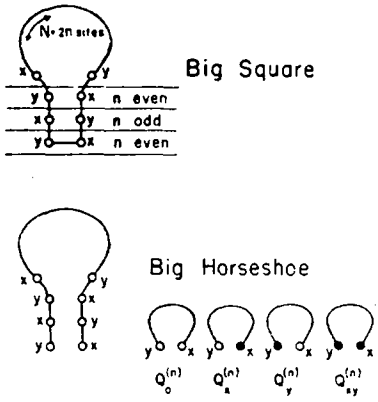

Fig. 6. Partition-function definitions for general covering of the square lattice.

axis and most likely determine the upper bound on the region of analyticity provided by these covering sets. It is true that other points on the boundary of N map under Eq. (3) onto the positive real axis—any two whose arguments add to π. Our strong feeling is that the minimum approach to the origin for positive numbers comes from the square of the purely imaginary points on the boundary of N; in any event, the "big square" covering sets can provide no better bound than that predicted by our assumptions.

We obtain a recursion relation for the Conjecture-2-partition-function $Q^{(n)}(z)$, where the number of sites in the big square is $2n$ (see Fig. 6 for notation). More particularly, we first obtain the "big-horseshoe" partition functions $Q_0^{(n)}$, $Q_x^{(n)}$, $Q_y^{(n)}$, $Q_{xy}^{(n)}$, where the subscripts portray the occupancy of the two sites at the ends of the horseshoe. We can then obtain $Q^{(n)}$ by joining the two ends (provided both are not occupied):

$$Q^{(n)} = Q_0^{(n)} + Q_x^{(n)} + Q_y^{(n)} \tag{22}$$

In terms of a column vector,

$$\mathbf{Q}^{(n)}(x, y) = \begin{pmatrix} Q_0^{(n)} \\ Q_x^{(n)} \\ Q_y^{(n)} \\ Q_{xy}^{(n)} \end{pmatrix} \tag{23}$$

the recursion formula is readily seen to be

$$\mathbf{Q}^{(n+1)} = \mathbf{K}\mathbf{Q}^{(n)} \tag{24}$$

where

$$\mathbf{K} = \begin{pmatrix} 1 & 1 & 1 & 1 \\ x & x & 0 & 0 \\ y & 0 & y & 0 \\ xy & 0 & 0 & 0 \end{pmatrix} \tag{25}$$

and x and y are, respectively, the activities of sublattice A and B molecules. The initial condition is

$$Q^{(1)} = \begin{pmatrix} 1 \\ x \\ y \\ 0 \end{pmatrix} \tag{26}$$

The general problem, then, is the resolution of Eq. (24), subject to the initial specification (26). The natural approach is through the diagonalization of **K**—which is possible even though **K** is not symmetric. The secular equation factors,

$$\begin{aligned} 0 &= \lambda^4 - (x + y + 1)\lambda^3 + xy(x + y + 1)\lambda - x^2y^2 \\ &= (\lambda^2 - xy)[\lambda^2 - (x + y + 1)\lambda + xy] \end{aligned} \tag{27}$$

from which the eigenvalues may be obtained simply enough. We have carried the problem forward only for the special case of

$$x = y^* = it \tag{28}$$

recommended to us by Conjecture 2. Here, t is a real number and the four eigenvalues are

$$\lambda = \begin{cases} t \\ -t \\ \lambda_- = (1 - \omega)/2 \\ \lambda_+ = (1 - \omega)/2 \end{cases} \tag{29}$$

with

$$\omega = (1 - 4t^2)^{1/2} \tag{30}$$

With t real, ω will be imaginary if $t > \frac{1}{2}$.

Since **K** is not symmetric, both the right and left eigenvectors must be determined. Equivalently, if the right eigenvectors are composed into a matrix **R** (which is nonsingular), the inverse of **R** may be calculated and its rows are the left eigenvectors; we call this matrix **L**.

We omit the tabulation of **R** and **L**, but they may be used to obtain

$$\begin{aligned} \mathbf{Q}^{(n+1)} &= \mathbf{K}^n \mathbf{Q}^{(1)} \\ &= \mathbf{R} \Lambda^n \mathbf{L} \mathbf{Q}^{(1)} \end{aligned} \tag{31}$$

where

$$\Lambda^n = \mathbf{diag}(t^n, (-t)^n, \lambda_-^n, \lambda_+^n) \tag{32}$$

While straightforward, these results fully displayed are rather cumbersome. The big-square partition function $Q^{(n)}$, defined by Eq. (22), collapses to a simple form, however. It is just

$$Q^{(n)} = \lambda_-^n + \lambda_+^n \tag{33}$$

where λ_+ and λ_- are given in Eqs. (29) and (30).

The intersections of the boundary of N with the imaginary axis are thus given by the roots of the equation

$$\lambda_-(t)^n + \lambda_+(t)^n = 0 \tag{34}$$

If we write $\omega = i\gamma$, where $\gamma = (4t^2 - 1)^{1/2}$ is real, Eq. (34) is equivalent to

$$\mathrm{Re}\,(1 + i\gamma)^n = 0 \tag{35}$$

or

$$\tan^{-1}\gamma = (2k + 1)\pi/2n \tag{36}$$

where k is an integer. The smallest value of γ, and hence of t, and hence the intersection nearest the origin, is given by setting $k = 1$. Thus, we have finally

$$(4t^2 - 1)^{1/2} = \tan(\pi/2n) \tag{37}$$

The solution of this equation for t gives intersection with the imaginary axis; hence t^2 is the apparent distance of closest approach of pfz-free region S to the origin on the positive real axis, so that the bound on analyticity is

$$\begin{aligned} z_b &= \tfrac{1}{4}[1 + \tan^2(\pi/2n)] \\ &= \tfrac{1}{4}\sec^2(\pi/2n) \end{aligned} \tag{38}$$

applicable for $n \geqslant 2$. For $n = 2$, this result agrees with that obtained earlier for the four-point covering set.

The unfortunate feature of this result is that the bound z_b becomes poorer and poorer as the size of the covering set increases. This statement is probably true regardless of the validity of Conjecture 2, although the strongest claim that can be made with certainty is that *for any n*, a completely rigorous bound z_b can be no larger than the one supplied by Conjecture 2.

One decided advantage of the present technique is that it is not limited in any way to two-dimensional lattices. The simple cubic lattice with nearest-neighbor exclusions will serve as an example of a three-dimensional system. Gaunt[9] has studied this hard-sphere lattice gas by series methods, concluding that its behavior is qualitatively similar to that of the square lattice. There is a phase transition—presumably of second order—near $z = 1.09$.

The circular region of analyticity referenced in Eq. (6) has radius $2^{-6} = 1/64$. The sixth set-power of the half-plane $M^{(2)}$ of Eq. (7), with $a = \frac{1}{2}$, should provide a better estimate. Taking the phase factor $(-)^7$ into account, we see that any point on the rays $\mathrm{Arg}(z) = \pm 5\pi/6$ will map onto the positive real axis—along with many other "points" $(z_1, z_2, \ldots, z_6)$ whose arguments add to $(2k + 1)\pi$, with k an integer, and which lie to the left of the line $\mathrm{Re}(z) = -\frac{1}{2}$. But the closest approach to the origin for positive numbers probably comes from the negative of the sixth power of the one point $(-1/2 \pm i/2\sqrt{3})$, which is 1/27.

This is an improvement by more than a factor of two, but still not very close to the "experimental" transition point. Another type of covering set is suggested by Fig. 7. Imagine the cubic lattice to be constructed by joining the smallest possible number of cubical building blocks—by gluing them together at the corners. Now imagine that the top, bottom, front, and back of each block is painted red—but not the sides. The red faces are the covering sets, and the four faces described suffice to include all of the edges of the blocks, and hence all of the "bonds" of the lattice.

The red faces are identical with the square covering sets studied at the end of Section 3, for which it was concluded that pfz's were confined to the region $M^{(3)}$ lying to the left of the line $y^2 = x^2 + 2x + \frac{1}{2}$. Now, each vertex of the simple cubic lattice belongs to four red faces, so the pfz's for the entire lattice are confined to $-M^{(3)**4}$. The points whose fourth powers lie on the negative real axis lie on the lines $y = \pm x$, which intersect the boundary of $M^{(3)}$ at the two points $\frac{1}{4} \pm \frac{1}{4}i$. With the minus sign taken into account, these points map onto the positive real axis, to yield the bound $z_b = 1/64$—worse than the bound resulting from the two-point covering sets!

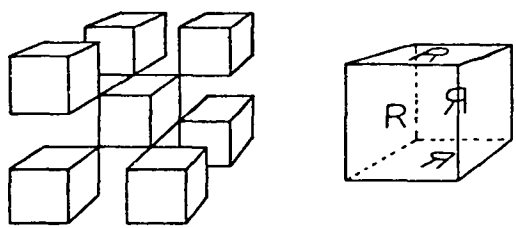

Fig. 7. Covering sets for the simple cubic lattice.

To make an improvement in the bound, we need to take the entire eight-point block as a representative covering set—although we are forced to invoke conjecture 2 in order to make any substantial progress. Under that assumption, the boundary that quarantines the pfz's is the line of zeros of

$$\begin{aligned} Q = & \ 1 \\ & + 4z + 4z^{*} \\ & + 6z^2 + 6z^{*2} + 4zz^{*} \\ & + 4z^3 + 4z^{*3} \\ & + z^4 + z^{*4} \\ = & \ (1 + 8x + 16x^2 + 8x^3 + 2x^4) \\ & - (8 + 24x + 12x^2)y^2 \\ & + 2y^4 \end{aligned} \tag{39}$$

The solution of $Q = 0$ that is nearest the origin is given by

$$y^2 = 2 + 6x + 3x^2 - [(7 + 40x + 80x^2 + 64x^3 + 16x^4)/2]^{1/2} \tag{40}$$

The region $M^{(4)}$ to the left of this line is presumed by conjecture 2 to contain all pfz's. Since each vertex of the simple cubic lattice belongs to two of the eight-point blocks, we are mainly interested in the negative set-square of $M^{(4)}$—especially its intersection with the positive real axis. One such point, and probably the closest to the origin, is the image of pure imaginary zeros of Q—that is, $\pm i[2 - (7/2)^{1/2}]^{1/2}$. The resulting real bound is

$$z_b = 2 - (7/2)^{1/2} = 0.129...$$

This bound represents another more-than-factor-of-two improvement in the previous best estimate of 1/27.

One further application we make deals with the "monomer–dimer problem."[10–12] For any lattice (coordination number c), a partial dimer covering can be visualized as a coloring of some of the bonds of the lattice, but no more than one bond incident at any vertex may be colored. (A vertex without even one incident bond painted is regarded as occupied by a monomer—each of the rest by half of a dimer.) Since the dimers reside, as it were, on the bonds of the original lattice, we may regard the midpoints of those bonds as the possible addresses of the dimeric molecules. We thus form an auxiliary lattice Λ' whose *sites* are those bond midpoints and whose *bonds* are connections between all new sites surrounding each old site (Fig. 8). These bonds of Λ' represent all dual occupancy exclusions of the dimer problem.[5]

[5] Professor J. Lebowitz pointed out the possibility of using what we have called the auxiliary lattice.[11]

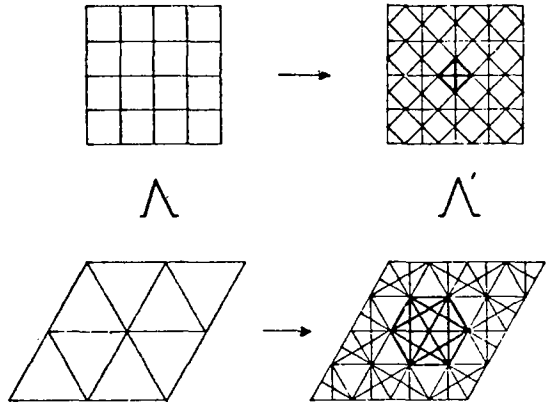

Fig. 8. Auxiliary lattices for the monomer–dimer problem.

The auxiliary lattice Λ' is thus a "cactus" formed by joining "stars" together at the vertices. The "stars" are actually complete graphs of order c and contain $E = c(c-1)/2$ edges, or bonds; each site of Λ' belongs to two stars. The obvious covering sets to employ are the stars themselves; the multivariable partition function for one star is just

$$P_\alpha = 1 + \sum_{i=1}^{c} z_i$$

since by the dimer rules no two may be simultaneously occupied. We may then use the region $M^{(2)}$ of Eq. (7) with $-c^{-1} < a < 0$ for the pfz-contaminated area. But the negative set-square of $M^{(2)}$ never quite reaches the positive reals, so there can be no singularity and no phase transition for any dimer problem. Since an external field would only change site activities by constant factors, this proof can easily be extended to include nonvanishing external (electric) fields—as long as no further intermolecular interaction is induced.

6. CONCLUSIONS

The Ruelle theorem is an extremely interesting application of complex analysis to the problem of locating singularities of lattice gas systems. The technique transforms exact properties of small, finite subsystems into exact bounds for the corresponding infinite system. Strictly speaking, the answers provided by the theorem are of the form: region thus-and-so of the complex plane contains no zeros of the grand partition function. We can thus prove the *absence* of singularities under certain restraints, but we cannot prove the *existence* of singularities. The theorem can be very powerful in some cases—

such as for the monomer–dimer problem, which is proven in general to be free of physical singularities.

For hard-molecule lattice systems which are presumed to possess phase transitions, the theorem can be used to determine bounds on the portion of the positive real activity axis that is free of singularities. The size and nature of the "covering sets" employed in applying the theorem determine the quality of the bound obtained. It is shown by counterexamples that increasing the size of the covering sets does not necessarily improve the bound.

The algebraic manipulations required to apply the theorem become more complicated as the size of the covering sets increases; the calculations required, however, are of a type new to statistical mechanics. Although not yet proven, Conjectures 1 and 2 are felt to be true and lighten considerably the computational burden for covering sets with sufficient symmetry.

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