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Phase Transition in a Lattice Gas of Hard Spheres with Second-Neighbor Exclusions on the Simple Cubic Lattice

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Using reflection positivity and the Peierls argument, we prove the existence of an ordered phase at sufficiently high activity for a lattice gas of hard spheres on the simple cubic lattice with first- and second-neighbor exclusions.

KEY WORDS: Phase transitions; lattice gas; Peierls' argument; reflection positivity.

1. INTRODUCTION

Lattice gases with hard-core interactions have been extensively studied as models for phase transitions.[1] For several different lattices,[2–6] phase transitions have been proved to exist in lattice gases of hard spheres or disks with first-neighbor exclusions. The lattice gas of hard disks with first-neighbor exclusions on the triangular lattice has been solved exactly by Baxter.[7] For all of the lattices considered, the transition appears to be second order when only first neighbors are excluded.[1]

Extending the range of the interaction in hard-core lattice gases to include second- or higher-neighbor exclusions tends to change the transition to first order.[1,8–13] The existence of a phase transition in lattice gas models with extended hard cores has been proved for the square lattice with first-, second-, and third-neighbor exclusions,[14] for the triangular lattice with exclusions extending any distance past first neighbors,[15] and for the body-centered cubic lattice with first- and second-neighbor exclusions.[16]

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In the present paper we prove that an ordered phase exists at sufficiently high activity in a lattice gas of hard spheres with first- and second-neighbor exclusions on the simple cubic lattice. The proof uses reflection positivity[17,18] combined with a generalized Peierls[19] argument.

2. REFLECTION POSITIVITY

Consider a simple cubic lattice Λ with cyclic boundaries given as

$$\Lambda = \{(a,b,c) : a,b,c = 0,1,\ldots,2M-1\} \tag{1}$$

The coordinates (x,y,z) are computed modulo $2M$ onto $0 \leqslant x,y,z < 2M$. This lattice is composed of four body-centered cubic (bcc) sublattices. One such sublattice is given as

$$\Lambda_1 = \{(a,b,c) : a,b,c \text{ are all even or all odd.}\} \tag{2}$$

The other three sublattices can be generated from Λ_1 by a unit translation in one of the three basis directions. Each square face of the unit cell in Λ has a vertex from each of the four bcc sublattices. A unit cell with center at r shall be called a cube C_r.

Consider next a lattice gas of hard spheres on Λ such that first- and second-neighbor sites on Λ are excluded from simultaneous occupancy. Let C be the set of allowed configurations on Λ. The grand canonical partition function is then given as

$$\Xi = \sum_{\xi \in C} e^{-H(\xi)/kT} \tag{3}$$

The Hamiltonian is given as $H(\xi) = -\mu|\xi|$, where μ is the chemical potential and $|\xi|$ is the number of spheres in the configuration ξ. For $\mu > 0$, the ground state for the system consists of a configuration in which any one of the four bcc sublattices is completely filled with spheres, the other three sublattices being vacant. In such a configuration, each cube has exactly two vertices occupied by spheres.

We define reflection planes $P_a^{\pm}$ for $0 \leqslant a \leqslant M-1$ as $P_a^- = \{(a,y,z) : y,z \in \mathbb{R}\}$ and $P_a^+ = P_{a+M}^-$. Similarly, we define reflection planes $P_b^{\pm}$ and $P_c^{\pm}$. The planes $P_a^{\pm}$ divide Λ into three disjoint regions:

$$\begin{aligned} \Lambda_a^+ &= \Lambda \cap \{(x,y,z) : M+a < x < 2M+a,\ y,z \in \mathbb{R}\} \\ \Lambda_a^- &= \Lambda \cap \{(x,y,z) : a < x < M+a,\ y,z \in \mathbb{R}\} \\ \Lambda_a^0 &= \Lambda \cap (P_a^- \cup P_a^+). \end{aligned} \tag{4}$$

There is a natural involution

$$\theta_a : (x,y,z) \to (2a-x,y,z) \tag{5}$$

which reflects the coordinates through the reflection planes $P_a^{\pm}$. Clearly $\theta_a \Lambda_1 = \Lambda_1$, each bcc sublattice being mapped onto itself by θ_a. If C_a^+ is the set of allowed molecular configurations on Λ_a^+ (and similarly for C_a^- and C_a^0), then $\theta_a C_a^{\pm} = C_a^{\mp}$ and $\theta_a C_a^0 = C_a^0$.

For any function $f: C \rightarrow \mathbb{C}$, we define $\theta_a f$ as

$$(\theta_a f)(\xi) = f(\theta_a(\xi)) \qquad \forall \xi \in C \tag{6}$$

We denote ξ as a triple $\xi = (\xi_a^-, \xi_a^0, \xi_a^+)$, where $\xi_a^{\pm} \in C_a^{\pm}$ and $\xi_a^0 \in C_a^0$. Let $F_a^+ = \{f: f(\xi) = f(\xi_a^0, \xi_a^+)\ \forall \xi \in C\}$. Then $\theta_a f(\xi) = f(\xi_a^0, \xi_a^-)$ if $f \in F_a^+$. We also define a set of functions F_a^- in an analogous fashion. It can be shown that[18]

$$\sum_{\xi \in C} \overline{f(\xi)}\, \theta_a f(\xi) \geqslant 0 \qquad \text{if} \quad f \in F_a^+ \cup F_a^- \tag{7}$$

The Hamiltonian can then be written as

$$H(\xi) = H_a^+(\xi) + \theta_a H_a^+(\xi) = H_a^-(\xi) + \theta_a H_a^-(\xi) \tag{8}$$

where $H_a^{\pm} \in F_a^{\pm}$ are given as

$$\begin{aligned} H_a^+(\xi) &= H_a(\xi_a^0, \xi_a^+) - H_a(\xi_a^0)/2 \\ H_a^-(\xi) &= H_a(\xi_a^-, \xi_a^0) - H_a(\xi_a^0)/2 \end{aligned} \tag{9}$$

Since the average value of a function $f: C \rightarrow \mathbb{C}$ is given as

$$\langle f \rangle = \Xi^{-1} \sum_{\xi \in C} f(\xi) e^{-H(\xi)/kT} \tag{10}$$

then Eqs. (8) and (10) give

$$\langle \bar{f} \theta_a f \rangle = \Xi^{-1} \sum_{\xi \in C} \overline{G^{\pm}(\xi)}\, \theta_a G^{\pm}(\xi) \tag{11}$$

where $G^{\pm}(\xi) = f(\xi)\exp[-H_a^{\pm}(\xi)/kT]$. If $f \in F_a^+ \cup F_a^-$, then Eqs. (7) and (11) yield

$$\langle \bar{f} \theta_a f \rangle \geqslant 0 \qquad \forall f \in F_a^+ \cup F_a^- \tag{12}$$

It then follows by a standard Cauchy–Schwartz proof that[18]

$$|\langle fg \rangle|^2 \leqslant \langle \bar{f} \theta_a f \rangle \langle \bar{g} \theta_a g \rangle \qquad \forall f \in F_a^+, \quad g \in F_a^- \tag{13}$$

Equation (13) will be used in the development of Section 3 to obtain an upper bound for the probability of the occurrence of other than a ground state configuration about a cube in Λ.

This bound will then be used in Section 4 to prove the existence of an ordered phase in the model at sufficiently large activity, $z = \exp(\mu/kT)$.

3. PROBABILITY OF THE OCCURRENCE OF DISORDERED CUBES

If, in a configuration $\xi \in C$ a cube C_r has two vertices occupied by a sphere, the cube is said to be a *ground state cube*. Otherwise the cube is said to be a *disordered cube*.

Let Q_r be the projection onto configurations in which C_r is a disordered cube; that is,

$$Q_r(\xi) = \begin{cases} 1 & \text{if } C_r(\xi) \text{ is a disordered cube} \\ 0 & \text{otherwise} \end{cases} \tag{14}$$

Let L be any nonempty set of cubes. Define

$$Q(L) = \prod_{r \in L} Q_r(\xi) \tag{15}$$

The probability P_L that L is a set of disordered cubes is then bounded as $P_L \leqslant g^{|L|}$, where

$$g = \max_L \langle Q(L) \rangle^{1/|L|} \tag{16}$$

Since $L = L_a^- \cup L_a^+$, where $L_a^\pm = L \cap (\Lambda_a^\pm \cup \Lambda_a^0)$, then $Q(L) = Q^+(L)Q^-(L)$, where $Q^\pm(L) = Q(L_a^\pm)$. Since $Q^+ \in F^+$ and $Q^- \in F^-$, Eq. (13) gives

$$\langle Q \rangle^2 \leqslant \langle Q^+ \theta_a Q^+ \rangle \langle Q^- \theta_a Q^- \rangle \tag{17}$$

Let

$$f(Q) = \begin{cases} Q^{1/|L|} & \text{if } |L| \neq 0 \\ 1 & \text{if } |L| = 0 \end{cases} \tag{18}$$

Then Eq. (17) becomes

$$f(Q) \leqslant f(Q^+ \theta_a Q^+)^{|L_a^+|/|L|} f(Q^- \theta_a Q^-)^{|L_a^-|/|L|} \tag{19}$$

If L_m maximizes $f(Q)$, then L_m also maximizes $f(Q^+ \theta_a Q^+)$. (Proof by contradiction.) Hence if $r \in L_m$, then $\theta_a r \in L_m$ as well. But since this is true for θ defined as a reflection through any pair of planes $P_a^\pm, P_b^\pm, P_c^\pm$, then L_m contains *all* the cubes in Λ. Hence $|L_m| = 8M^3$.

Let $H_i = -\mu i/8$ be the Hamiltonian restricted to a cube with i spheres at its vertices, where $i = 0, 1$, or 2. Then, for $\mu > 0$,

$$g \leqslant \left(\frac{9^{8M^3} (e^{-H_1/kT})^{8M^3}}{\Xi} \right)^{1/8M^3} \tag{20}$$

where the factor 9^{8M^3} is the maximum number of configurations about the $8M^3$ cubes. Since $\Xi > z^{2M^3}$, then

$$g < 9z^{-1/8} = 9\exp(-\mu/8kT) \tag{21}$$

Hence for $\mu > 0$, $g \to 0$ as $T \to 0$. This bound on g will be used in the next section to prove the existence of an ordered phase in the model for sufficiently high activity z.

4. PEIERLS' ARGUMENT

Since the notion of a contour is central to the Peierls argument, we shall now define what we shall mean by a contour in a configuration. A disordered cube in a configuration shall be said to be a contour segment. Two contour segments are said to be connected if they share a common face. A contour is said to be closed if each of its unconnected faces is shared by a ground state cube.

We showed in Section 3 that at sufficiently large activity z, the probability is high that a cubic region in a configuration is a ground state cube. We shall now use the Peierls argument to show that if a cube $C_r(\xi)$ is a ground state cube, then at sufficiently large z it is highly probable that another cube, $C_{r'}(\xi)$, at an arbitrary position r', is also a ground state cube belonging to the same ground state as $C_r(\xi)$. For $z > 1$, there are four translationally related ground states in which one of the four bcc sublattices is completely occupied by spheres.

Since in Section 3 we proved the probability a given cube is disordered is less than g, then the joint probability that $C_r(\xi)$ is a ground state cube and $C_{r'}(\xi)$ is a disordered cube is less than g as well. Because of the first- and second-neighbor exclusions, a ground state cube cannot share an edge or a side with a ground state cube belonging to a different ground state. As a consequence, if $C_r(\xi)$ and $C_{r'}(\xi)$ are ground state cubes belonging to different ground states, then either $C_r(\xi)$ or $C_{r'}(\xi)$ must be surrounded by a closed contour composed of $|L| \geqslant 18$ segments. The joint probability that $C_r(\xi)$ is a ground state cube and $C_{r'}(\xi)$ is either a disordered cube or a ground state cube belonging to a different ground state than does $C_r(\xi)$ is then less than

$$h = g + \sum_{|L| \geqslant 18} g^{|L|} n(|L|) S(|L|) \tag{22}$$

where an upper bound to g is given by Eq. (21). Here $n(|L|)$ is the maximum number of contours composed of $|L|$ segments which can be generated beginning at a certain cube C_{r_0}, and $S(|L|)$ is the maximum number of cubes enclosed by the contour L; that is, the maximum number of cubes C_{r_0} which need be considered for beginning a contour which encloses either C_r or $C_{r'}$.

To obtain an upper bound to $n(|L|)$, begin the contour with C_{r_0} together with any segments to which it is connected (through a face). This can be done in 5^6 ways if C_{r_0} is vacant and in $5^3 \cdot 2^3 \cdot 8$ ways if C_{r_0} contains one sphere. The factor 5 results since five types of (disordered) cube can share a face with a vacant face of C_{r_0}. The factor 2 results since an occupied face of C_{r_0} can be shared either by a (fixed) disordered cube or by no disordered cube. The factor 8 results since there are eight ways to realize a cube occupied by one sphere. Hence there are $189 \cdot 5^3$ ways to begin the contour in this fashion.

Number successively the cubes of Λ. To continue the contour, add any new segments attached to the segment of the growing contour which has the lowest number associated with it. This can be done in at most 5^5 ways. The process is terminated when the growing contour contains $|L|$ segments. Hence $n(|L|) < 189 \cdot 5^3 \cdot 5^{5(|L|-1)}$.

Since at most three sides of a given segment are not connected to other segments, then an upper bound to $S(|L|)$ is given as twice the volume of a sphere having a surface area equal to one half the surface area of $|L|$ cubes, where the volume of a cubic segment is taken as the unit of volume. A simple calculation gives $S(|L|) \leqslant (3/\pi)^{1/2}|L|^{3/2}$. Equation (22) then becomes

$$h < f(z) = 9z^{-1/8} + \sum_{|L| \geqslant 18} 8|L|^{3/2}(9 \cdot 5^5 z^{-1/8})^{|L|} \tag{23}$$

which converges if $z > 9^8 \cdot 5^{40}$.

The joint probability $P(z)$ that $C_r(\xi)$ and $C_{r'}(\xi)$ are both ground state cubes belonging to the same ground state is then bounded as

$$P(z) > (1 - 9z^{-1/8})(1 - f(z)) \tag{24}$$

Let z_0 be the positive real solution of the equation

$$(1 - 9z_0^{-1/8})(1 - f(z_0)) = 1/2 \tag{25}$$

If $z > z_0$, then $P(z) > 1/2$, and an ordered phase exists in which one bcc sublattice of the simple cubic lattice is predominantly occupied by spheres. We have therefore proved the existence of an ordered phase in the model for sufficiently large activity z.

Since four translationally related Gibbs states correspond to this ordered phase, and since the Gibbs state for such systems is unique at low activity, then there is an order–disorder transition in the model.[20] (Numerical estimates[9] indicate that the transition is probably first order and occurs at an activity $z \simeq 1.6$.)

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REFERENCES

1. L. K. Runnels, in *Phase Transitions and Critical Phenomena*, Vol. II, C. Domb and M. Green, eds. (Academic, New York, 1972), p. 305.
2. R. L. Dobrushin, *Funct. Anal. Appl.* **2**:292, 302 (1968).
3. O. J. Heilmann, *Nuovo Cimento Lett.* **3**:95 (1972).
4. O. J. Heilmann, *Commun. Math. Phys.* **36**:91 (1974).
5. L. K. Runnels, *Commun. Math. Phys.* **40**:37 (1975).
6. O. J. Heilmann, *J. Phys. A* **13**:1803 (1980).
7. R. J. Baxter, *J. Phys. A* **13**:L61 (1980).
8. J. Orban and A. Bellemans, *J. Chem. Phys.* **49**:363 (1968).
9. J. Orban, *Chem. Phys. Lett.* **3**:702 (1969).
10. L. K. Runnels, J. R. Craig, and H. R. Streiffer, *J. Chem. Phys.* **54**:1234 (1971).
11. A. Bellemans and R. K. Nigam, *Phys. Rev. Lett.* **16**:1038 (1966).
12. B. R. Riemenschneider and D. A. Huckaby, *J. Chem. Phys.* **58**:3940 (1973).
13. J. Orban, *J. Phys. A* **15**:L501 (1982).
14. O. J. Heilmann and E. Praestgaard, *J. Phys. A* **7**:1913 (1974).
15. O. J. Heilmann and E. Praestgaard, *J. Stat. Phys.* **9**:23 (1973).
16. D. A. Huckaby, *Phys. Rev. B* **20**:1208 (1979).
17. J. Fröhlich, R. B. Israel, E. H. Lieb, and B. Simon, *J. Stat. Phys.* **22**:297 (1980).
18. O. J. Heilmann and E. H. Lieb, *J. Stat. Phys.* **20**:679 (1979).
19. R. Peierls, *Proc. Cambridge Philos. Soc.* **32**:477 (1936).
20. See, e.g., Ya. G. Sinai, *Teoria Fazovyh Perekhodov* (Russian) (Nauka, Moscow, 1980).