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Phase Transitions in Lattice Gases of Hard-Core Molecules Having Two Orientations

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A number of hard-core lattice gases in which a lattice site can be occupied by a molecule in either of two possible orientations are proved to undergo order–disorder phase transitions. Examples include lattice gases of trigonal planar molecules on a triangular lattice, tetrahedral molecules on a body-centered cubic lattice, and linear molecules on a square lattice.

KEY WORDS: Lattice gas; lattice statistics; hard core.

1. INTRODUCTION

Hard-sphere lattice gases with first-neighbor exclusions have been proved to exhibit order–disorder phase transitions in two and three dimensions.[1–4] A lattice gas of hard, cross-shaped pentamers on a square lattice, equivalent to a hard-disk lattice gas with first-, second-, and third-neighbor exclusions on a square lattice, has been shown to exhibit an order–disorder phase transition.[5] Lattice gases of hard-core dimers have been shown to have no phase transitions in one, two, or three dimensions.[6,7]

A multicomponent lattice gas in which unlike molecules are excluded from occupying either the same site or a pair of first-neighbor sites has been shown to undergo a "demixing" transition.[8–10]

A number of hard-core molecular lattice gases in which the lattice sites can be occupied by a molecule having either of two possible orientations are shown in Sections 2 and 3 to exhibit order–disorder phase transitions.

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2. PHASE TRANSITIONS IN TWO-ORIENTATION LATTICE GASES

Pirogov and Sinai[11] proved that certain Ising models on d-dimensional cubic lattices, $d \geqslant 2$, at some magnetic field value have different equilibrium states depending on whether the system has the outer boundary spins all $(+)$ or all $(-)$. Hence these Ising models undergo phase transitions.

Consider a d-dimensional lattice Λ composed of two sublattices, such that the C first neighbors of sites on one sublattice are sites on the other sublattice. Runnels[4] showed that a hard-sphere lattice gas on Λ with first-neighbor exclusions can be transformed to a one-component lattice gas on one sublattice having finite-range interactions. The resulting lattice gas was shown to be equivalent to an Ising model on a cubic lattice, which was in turn shown to satisfy the conditions of the Pirogov–Sinai theorem if $C > 2$ on the original lattice Λ. The original hard-sphere lattice gas on Λ was therefore demonstrated to have a phase transition if $C > 2$ and $d \geqslant 2$.

Let us now define an *n-orientation lattice gas* as a lattice gas in which a lattice site can be occupied by a molecule in any one of n equivalent orientations, such that C sites, the sites depending on the orientation of the molecule, are thereby excluded from simultaneous occupation by another molecule. Lattice gases of hard spheres are examples of 1-orientation lattice gases.

Consider the lattice Λ formed by "splitting" each lattice site of a 2-orientation lattice gas into two separate sites, the occupancy of each of the two sites so formed being equivalent to occupancy of a site on the original lattice by a molecule in a certain one of the two possible orientations. The 2-orientation lattice gas is then equivalent to a 1-orientation lattice gas on the "split" lattice Λ.

If Λ is composed of two sublattices (which can be viewed as cubic lattices) such that occupancy of a site on one of the two sublattices excludes simultaneous occupancy of C sites on the other sublattice, and such that the C sites excluded by any site can be superimposed by a suitable space group operation upon the C sites excluded by any other such site, then the proof of Runnels[4] ensures the existence of a phase transition for the 1-orientation lattice gas on the split lattice. Hence the equivalent 2-orientation lattice gas has a phase transition as well.

3. EXAMPLES

We shall consider examples of 2-orientation hard-core molecular lattice gases in which the center of a molecule on the lattice must occupy a lattice site, the bonds of the molecule pointing toward neighboring lattice sites. No more than one bond may occupy the space between any two neighboring lattice sites, and no more than one molecule may occupy a single lattice site.

The lattice of such a 2-orientation lattice gas can be split into the lattice Λ of an equivalent 1-orientation lattice gas by the procedure described in Section 2.

For the examples we shall consider, Λ will be composed of two sublattices, which can be viewed as cubic lattices, such that a molecule occupying a site on one sublattice excludes $C > 2$ sites on the other sublattice. The exclusions of a site on either sublattice can, by a suitable space group operation, be superimposed on the exclusions of any other site on the sublattice. The development of Section 2 is then sufficient to prove the existence of an order–disorder phase transition for these 2-orientation lattice gases.

The first example is a 2-orientation lattice gas of trigonal planar molecules on a triangular lattice. The split lattice Λ of the equivalent 1-orientation lattice gas is composed of two triangular sublattices. Molecules in one orientation occupying sites of the 2-orientation lattice gas correspond to molecules occupying one of the two sublattices. One sublattice, completely filled, is illustrated in Fig. 1. A unit cell of an equivalent cubic lattice is outlined on the sublattice in Fig. 1.

The sites of one sublattice can be imagined to lie directly "below" the sites of the other. A molecule on one sublattice excludes four sites of the other sublattice, the site directly below it and the three sites toward which the bonds of the molecule occupying the site point. The exclusions of a site on one sublattice are translates of the exclusions of any other site on the sublattice. Since $C = 4$, the development of Section 2 ensures that the model has a phase transition. This transition has been previously located numerically.[12]

If a site of the 2-orientation lattice gas above can be simultaneously occupied by one molecule in each orientation, the model is then isomorphic to the hard-sphere lattice gas with first-neighbor exclusions on a hexagonal lattice. Since $C = 3$, Section 2 proves this model also has a phase transition, a fact which has been proven previously.[3,4] The transition for this model has also been located numerically.[13]

Consider next a lattice gas of tetrahedral molecules on a body-centered

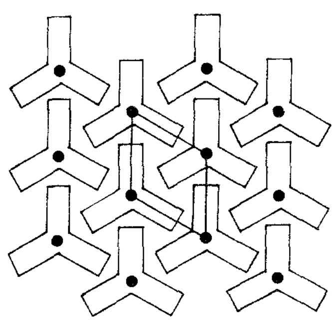

Fig. 1. Completely filled triangular sublattice of the split lattice Λ of a 1-orientation lattice gas equivalent of the 2-orientation lattice gas of trigonal planar molecules on a triangular lattice. The sublattice can be viewed as a cubic lattice having a unit cell as outlined.

cubic lattice. The split lattice Λ of the equivalent 1-orientation lattice gas is composed of two body-centered cubic sublattices. This example is similar to the first in that molecules occupying sites on one sublattice correspond to molecules in one orientation in the original 2-orientation lattice gas. Each sublattice can be viewed as a cubic lattice with primitive vectors **a**, **b**, and **c**, which are given in terms of the primitive vectors **x**, **y**, and **z** of the body-centered cubic sublattice of Λ as $\mathbf{a} = \mathbf{x}$, $\mathbf{b} = \mathbf{y}$, and $\mathbf{c} = (1/2)(\mathbf{x} + \mathbf{y} + \mathbf{z})$.

A molecule on one sublattice excludes five sites on the other sublattice, the site directly "below" it and the four sites toward which the bonds of the molecule point. The exclusions of a site on either sublattice are translates of exclusions of any other site on the sublattice. Since $C = 5$, the model has a phase transition.

If a site can be simultaneously occupied by one molecule in each orientation, then $C = 4$ and the model is equivalent to the hard-sphere lattice gas with first-neighbor exclusions on the diamond lattice. Section 2 ensures a transition for this model as well, a fact which has been proven previously.[3,4]

The last example we shall consider is a lattice gas of linear molecules on a square lattice. The split lattice Λ of the equivalent 1-orientation lattice gas is composed of two square sublattices. A molecule occupying a site of one sublattice excludes three sites of the other sublattice from simultaneous occupancy, the site directly "below" the center of the molecule and the two sites toward which the bonds of the molecule point. A filled sublattice of Λ is illustrated in Fig. 2. A unit cell of a corresponding cubic lattice is outlined on the sublattice in Fig. 2. The exclusions of one site on a sublattice are related to the exclusions of any other site on the sublattice by a combination of a translation and a rotation. Since $C = 3$, the model has an order–disorder phase transition. The existence of this transition has also been proved using the Dobrushin technique.[1,14]

If a site can be simultaneously occupied by one molecule in each orientation, the model is equivalent to the hard-sphere lattice gas in one dimension with first-neighbor exclusions ($C = 2$), which has no phase transition.

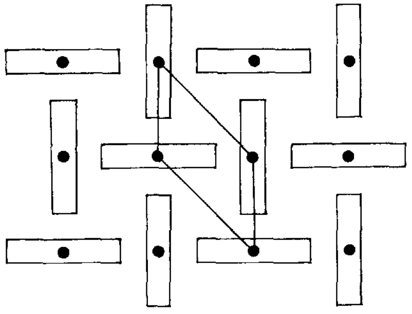

Fig. 2. Completely filled square sublattice of the split lattice Λ of a 1-orientation lattice gas equivalent of the 2-orientation lattice gas of linear molecules on a square lattice. The sublattice can be viewed as a cubic lattice having a unit cell as outlined.

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