Phase transition in a bcc lattice gas of hard spheres with second-neighbor exclusions

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The Peierls argument is used to prove that an ordered phase exists at sufficiently high activity for a body-centered cubic lattice gas of hard spheres with first- and second-neighbor exclusions.

I. INTRODUCTION

Solid-fluid phase transitions in molecular systems at high temperatures share some essential features with order-disorder transitions which occur in model systems of molecules having only hard-core interactions. In particular, hard-core systems have no solid-fluid critical points, and the transition pressure is strictly proportional to the transition temperature.[1]

The lattice gas, a model system in which the molecules are restricted to lattice sites, has been extensively studied as a model for phase transitions. Hard-core lattice gases in which only first-neighbor sites are excluded from simultaneous occupancy are not particularly realistic models for melting, for any order-disorder transition which occurs does not appear to be first order.[2] Extending the exclusions to more distant neighbors (corresponding to a smaller lattice grid) seems in several cases to effectively change the transition to first order.[2–6]

A number of lattice gases with first-neighbor hard-core interactions have been proved to exhibit order-disorder phase transitions.[7–12] Lattice gases of hard disks on the triangular lattice with exclusions extending to more distant neighbors have also been shown to undergo phase transitions.[13] Numerical methods have been used to locate the transition in this model for exclusions which extend through several neighbors.[3,4] In addition, a lattice gas of hard disks on the square lattice with exclusions extending through third neighbors has been proved to undergo a phase transition.[14] This transition has also been located numerically.[5]

In the present work we shall consider a body-centered cubic (bcc) lattice gas of hard spheres in which both first and second neighbors are excluded. Using the Peierls approach we shall prove that an ordered phase exists for this model at sufficiently large activity z. This lattice gas should provide a fairly good model for the melting of a simple substance at high temperatures and pressures, for the ordered phase is a cubic close-packed structure, and numerical results[6] indicate the transition is probably of the first-order type.

II. DEFINITION OF A CONTOUR IN A CONFIGURATION

Since the notion of a contour plays a central role in the Peierls argument, we shall first define what we shall mean by a contour in a configuration.

The bcc lattice is composed of two simple cubic sublattices, each of which is composed of two face-centered cubic (fcc) sublattices. The lattice is also composed of tetrahedra having one vertex from each of the fcc sublattices. One such tetrahedron is illustrated in Fig. 1. Two of the edges of each tetrahedron are of second-neighbor length and connect two vertices from the same simple cubic sublattice. Each of the other four edges connects a vertex

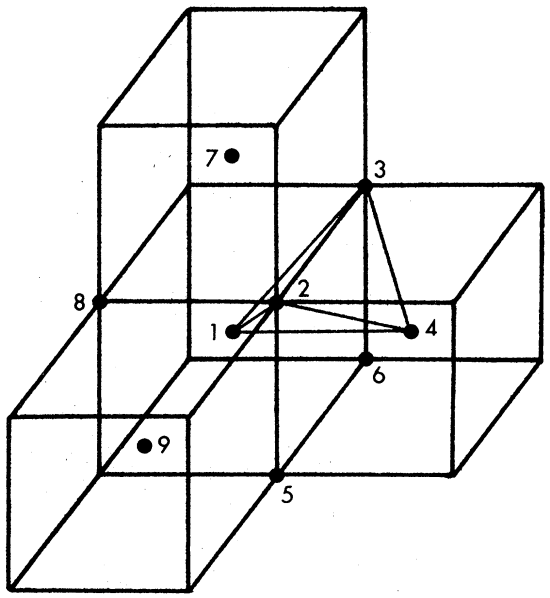

FIG. 1. A tetrahedron with vertices 1, 2, 3, and 4 is illustrated together with other sites of a bcc lattice which are referred to in the text. Each such tetrahedron contains one vertex from each of the four fcc sublattices of the bcc lattice.

from each of the two simple cubic sublattices and is of first-neighbor length. (These tetrahedra have also been used in connection with a Peierls argument for the existence of an ordered phase in a model for water.[15])

In the present model, any one of the fcc sublattices can be completely occupied at closest packing, thereby forming an ordered structure P_α, $\alpha = 1, 2, 3,$ or 4. A tetrahedron in a configuration will be said to belong to P_α if and only if the vertex of the tetrahedron which belongs to fcc sublattice α is occupied. Otherwise, the tetrahedron is vacant and will be said to constitute a contour segment.

Two contour segments will be said to be connected if they share a face or a common edge of first-neighbor length. Two contour segments which share an edge of second-neighbor length [as do tetrahedra (1,2,3,4) and (1,4,5,6) in Fig. 1] belong to the same contour, for they also each share a face with a third contour segment [tetrahedron (1,2,4,5) in Fig. 1]. A simply connected set of contour segments constitutes a contour. A contour will be said to be closed if it does not intersect the outer boundary of the lattice. A contour will be said to be an outer contour if it is not enclosed by another contour.

It may be helpful at this point to construct a mental picture of the structure of a closed contour. Since each tetrahedron has a vertex from each of the four fcc sublattices, then two occupied tetrahedra which share a face must belong to the same fcc structure P_α. Hence a simply connected surface of an ordered structure P_α is composed of tetrahedral faces each of which is shared internally by a tetrahedron of P_α and externally by a contour segment. These contour segments form a connected enclosure of P_α. A contour is composed of a union of enclosures and other segments which do not belong to an enclosure, all of which are mutually connected.

III. PEIERLS ARGUMENT

If N_α is the number of sites which have an ordered structure P_α in a configuration on a lattice Λ having $|\Lambda|$ sites, then as discussed by Dobrushin,[7] there is an order-disorder transition in the thermodynamic limit ($|\Lambda| \to \infty$) if $\langle N_\alpha \rangle / |\Lambda| > 1/p$, independent of $|\Lambda|$, where p is the number of ordered structures which can be superimposed by the operation of an element of the space group of the lattice, and where the thermal average is taken only over configurations in which the outer boundary is composed of the ordered structure P_α.

In the present model, if the boundary is occupied by one of the $p = 4$ fcc structures P_α, then all sites not belonging to P_α are enclosed by a closed contour which is also an outer contour. Then, for any such configuration,

$$|\Lambda| - N_\alpha \leq {\sum_{L=24}^{\infty}}' N(L) \sum_{j=1}^{m(L)} X_L^{(j)} , \tag{1}$$

where $N(L)$ is the maximum number of sites which can be enclosed by a contour of L segments, $m(L)$ is the maximum number of types of closed contours of L segments, and

$$X_L^{(j)} = \begin{cases} 1 & \text{if contour } j \text{ is present} \\ & \text{in the configuration} \\ 0 & \text{otherwise} . \end{cases} ,$$

Since the border is occupied by structure P_α, and since the interior could be filled with structure P_α, where each interior sphere of P_α occupies a vertex from each of 24 tetrahedra, then the interior must contain some multiple of 24 tetrahedra. Hence a closed outer contour and its interior must contain a multiple of 24 tetrahedra. Since the interior of a contour can be filled with the ordered structures which border its interior surfaces, and since these structures would each occupy a multiple of 24 tetrahedra, then it follows that any closed outer contour must be composed of some multiple of 24 contour segments. (The same argument holds for inner contours since their exterior is bordered by one ordered structure.) L in Eq. (1) is therefore restricted to multiples of 24.

We now proceed to obtain an upper bound to $m(L)$. Not all contours can be generated by adding to a growing contour segments which share faces with the contour, for a pair of segments which share an edge of first-neighbor length are not necessarily also connected through a set of faces. This can occur only if exactly two faces of each of the two connected segments are shared by occupied tetrahedra. [For example, in Fig. 1, segments (1,2,3,4) and (1,2,8,9) are not necessarily connected through a set of faces if and only if sites 7 and 5 are both occupied. Moreover, as is apparent from Fig. 1, this is the only manner in which a segment can share more than one face with occupied tetrahedra, all other cases being forbidden due to the exclusion of second-neighbor occupancy.]

To obtain an upper bound to $m(L)$ we first number successively the tetrahedra of Λ. To generate all the possible contours of L segments, we pick an arbitrary tetrahedron t, the contour segments which share a face with t, and any segment which is connected to t by a first-neighbor edge but which is not necessarily connected to t through a set of faces. These are the only types of connected segments which must be considered in order to generate all contours.

There are five ways in which three or four contour segments can each share a face with t. As shown above, there are four ways in which only two segments each share a face with t. In the latter case, a third segment shares a first-neighbor edge with t and

is not necessarily connected through a set of faces to t. Hence there are nine ways to begin the contour generation in this manner.

We then continue the contour by adding all new segments which are connected as above to the segment t' of the growing contour which has the smallest number associated with it. Each step of this process can be done in one way if t' is connected to the contour by only one edge. If t' is connected to the contour by a face, there are four ways in which three or four segments can each share a face with t', and there are two ways in which two segments can each share a face with t'. In the latter case, a third segment shares a first-neighbor edge with t' but is not necessarily connected through a set of faces to t'. Thus each step of the continuation can be done in at most six ways. The process is terminated when the contour contains L segments.

Since each segment is connected to at least three other segments, the last three segments t' from which the contour is continued add no new segments to the contour. Hence there are less than $9(6)^{L-4}$ contours which contain t. Since there are less than $6|\Lambda|$ tetrahedra in Λ, then

$$m(L) < 9(6)^{L-3}|\Lambda|/L \ , \tag{2}$$

the division by L resulting since the choice of the first segment is arbitrary.

We shall now obtain an upper bound to $N(L)$. Since each contour segment has one vertex from each of the four fcc sublattices, then no more than one face of a contour segment can be shared with a single ordered structure P_α. Hence no more than one face of each segment of a closed outer contour can be shared with outer structure P_α. Therefore a closed contour of L segments can have no more sites interior to the contour than can a three-dimensional sphere with volume V and surface SL, where S is the surface area of a face of a contour segment which has a volume V_0. Since a site interior to a contour is a vertex of 24 tetrahedra enclosed by the contour, each tetrahedron having four vertices, then $N(L) \leq \frac{1}{6}(V/V_0)$. A simple computation then gives

$$N(L) \leq (\tfrac{1}{24})(8/\pi^2)^{1/4}L^{3/2} < (\tfrac{1}{24})L^{3/2} \ . \tag{3}$$

We now proceed to obtain an upper bound to $\langle X_L^{(J)}\rangle$, where the average is only over configurations in which the outer boundary is occupied by P_α. Let λ be the set of all configurations which contain a contour $\mathfrak{L}$, which is an outer contour of length L. With each configuration $C \epsilon \lambda$ we associate a configuration $C^* \epsilon \lambda^*$ (this association is 1–1 correspondence) generated in the following manner. Let T_r be a unit translation which converts structure P_r to structure P_α. Translate by T_r all P_r, $r \neq \alpha$, regions (together with their interiors) which border $\mathfrak{L}$. Then replace all contour segments of $\mathfrak{L}$ with tetrahedra of type P_α. The result is to form a configuration C^* such that $N_C^* - N_C = \frac{1}{24}L$, where N_C is the number of spheres in configuration C. The division by 24 results since each sphere is shared by 24 tetrahedra.

Hence

$$\langle X_L^{(\mathfrak{L})}\rangle = \frac{\sum_{C\epsilon\lambda} z^{N_C}}{\sum_{C} z^{N_C}} \leq \frac{\sum_{C\epsilon\lambda} z^{N_C}}{\sum_{C^*\epsilon\lambda^*} z^{N_{C^*}}} = z^{-L/24} \ . \tag{4}$$

Combining Eqs. (1)–(4), we obtain

$$1 - \frac{\langle N_\alpha\rangle}{|\Lambda|} < (24^{-3/2}) \sum_{n=1}^{\infty} n^{1/2}(6^{24}z^{-1})^n \ , \tag{5}$$

which converges if $z > 6^{24}$. Let z_0 be the positive real solution of the equation

$$24^{-3/2} \sum_{n=1}^{\infty} n^{1/2}(6^{24}z_0^{-1})^n = \tfrac{3}{4} \ . \tag{6}$$

Then $\langle N_\alpha\rangle/|\Lambda| > \frac{1}{4}$ if $z \geq z_0$, proving the existence of an ordered phase for sufficiently large activity, z.

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