The Thermodynamic Phases of a Triangular Lattice Gas.

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by

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ABSTRACT

The temperature-dependent phase equilibrium of simple classical molecules has been studied, using a model based on the two-dimensional triangular lattice.

"Lattice gases" have been studied because they resemble real, dense fluid systems while presenting considerably simpler computational problems. The problem of a statistical theory of equations of state and phase transitions has always interested chemists and physicists, both from the practical viewpoint of seeking a workable theory of properties of matter (such as a theory of liquids) and also from the more academic viewpoint of understanding the discontinuities associated with phase transitions.

The system under investigation here has an intermolecular potential which includes a hard core extending up to and including first- and second-neighbor sites and with third-neighbor attractions. Repulsive, but finite, third-neighbor interactions are considered also. Fourth- and higher-neighbor interactions are assumed to be zero. Momentum and kinetic energy are not discussed; only the configurational properties are investigated.

The transfer matrix method (EFM) is used for lattices of infinite length and finite circumference up to 14 sites. Results which are exact for finite systems are used to infer the probable existence of a phase transition in the infinite two-dimensional array.

At low temperatures and attractive interactions, a first-order phase transition joins a phase of low density (gas-like) to a
solid-like phase of nearly close-packed density. At low temperatures
and repulsive interactions, a phase diagram similar to that of helium
is indicated. This diagram joins two "liquid"-like phases to solid and
gas phases. Like helium, the stable phase of the model at low tempera-
ture and pressure is one of the "liquids", and for similar reasons of
"order". On the other hand, there are notable differences between the
phase diagram for this model and that of helium.

Comparisons are made of transition parameters calculated from
an asymptotic law at low temperatures with parameters generated by the
transfer matrix method. Comparisons are also made with athermal (hard
core) systems studied in other laboratories. In general, comparisons
are good.
I. INTRODUCTION

A "lattice gas" is a system of molecules, each of which is located on one of a set of equivalent, distinguishable lattice sites.\(^1\) Any spaces not occupied by molecules of this one type are left vacant, and are called holes. The molecular shape required to fill the total space at close packing depends on the particular lattice employed and on the range of the postulated interactions. Hence, particles on the simple triangular lattice tend to be hexagons, as shown in Fig. 1. Evidently, particles on the triangular lattice correspond more closely in shape to discs than for other two-dimensional lattices.

The lattice gas is a version of a simple statistical model known as the Ising model. The model consists of a regular lattice of sites in one, two, or three dimensions in which each site can be occupied in a manner A or a manner B. The statistical problem is then to compute the thermodynamic properties of the system by an enumeration of the various possible configurations, giving each configuration its proper weight. This simple model can lead to phase transitions and therein lies its greatest interest.

Lattice gases have been studied because they vaguely resemble real, dense fluid systems while presenting considerably simpler computational problems. The goal of a statistical theory of equations of state and phase transitions has always interested physicists and chemists. The interest arises from the practical point of view of seeking a workable theory of properties of matter, such as a theory of liquids, and also from the more academic viewpoint of understanding the occurrence of discontinuities in thermodynamic functions associated with phase transitions.\(^2\)
Figure 1  Molecules on the Triangular Lattice. The molecules are shown as hexagons. The actual physical requirements is a size sufficient to exclude simultaneous occupancy of first- and second-nearest-neighbor sites with a finite interaction (attractive or repulsive) at the third-neighbor distance. Interactions are neglected between molecules separated by greater than third-nearest-neighbor distances. For a molecule with its center on ♦, a first-neighbor is represented by △, a second-neighbor by ○, and a third-neighbor by ◆.
Δ - First Neighbor
○ - Second Neighbor
● - Third Neighbor
One of the most interesting and significant properties of lattice gas systems is their ability to show first- and second-order phase transitions. First-order phase transitions are the usual changes of state accompanied by a latent heat and discontinuous changes in entropy and density. Second-order phase transitions are constant entropy and density processes with anomalous behavior in compressibility, specific heat or coefficient of expansion. Since \((\partial^2 G / \partial P^2)_T\) = \((\partial V / \partial P)_T\), a discontinuity in this second derivative implies a discontinuity in the isothermal compressibility. Also, \((\partial^2 G / \partial T^2)_p = -(\partial S / \partial T)_p = -c_v / T\) and a discontinuity in this quantity implies a discontinuity in the specific heat at constant pressure. The mixed second derivative, \((\partial^2 G / \partial P \partial T)\) is equal to \((\partial^2 V / \partial T)\) and a discontinuity in this implies a discontinuity in the coefficient of expansion. Ehrenfest named the transition, where one or more of the second derivatives of the free energy is discontinuous, a transition of the second order. Some examples of second-order phase transitions include the change from ferromagnetism to paramagnetism at the Curie point, and the transition of a superconductor to the normal state.

In recent years, systems of interacting molecules at moderate and high densities have been studied in the lattice approximation by two methods: the series technique and the exact finite method (EFM). It is hoped that both techniques will ultimately lead to the same results. At first, the molecular interactions investigated by both methods were restricted to hard centrosymmetric repulsions. More recently, the potentials postulated have included finite interactions (attractions) extending beyond the hard core. It is now considered established that the symmetric hard core "lattice gases" undergo a
single phase transition as do their continuum hard sphere and disc analogs. The transition resembles the equilibrium between a solid and a supercritical fluid.\textsuperscript{13} The lattice model transition is of second order for small molecules (nearest neighbor range of the hard core), but generally of first order for greater molecular size. Bellemans\textsuperscript{12} and co-workers have indicated that the appearance of a third phase (liquid-like) can result when regions of finite attraction are added to the intermolecular potential.

The system under consideration here is the two-dimensional triangular lattice gas with third-neighbor finite attractions (or repulsions) and first- and second-neighbor infinite repulsions (Fig. 1). It is assumed that no two molecules may have their centers on nearest-neighbor sites, or next-nearest-neighbor sites, or on the same site (thus retaining the excluded volume effect) but simultaneous occupation of the third-neighbor sites results in a pair-interaction potential energy, \( w \). Both positive (repulsive) and negative (attractive) values of \( w \) are studied. Fourth- and higher-neighbor interactions are assumed to be zero. Momentum and kinetic energy are not discussed, so that only the configurational properties are investigated. One of Bellemans' studies\textsuperscript{11} concerned itself with two special cases of this model: "Case B" with \( w = 0 \), and "Case C" with \( w/kT = +\infty \).
II. METHOD

The general procedure used has been discussed elsewhere at length\textsuperscript{7,8,13} but is reviewed here with emphasis on the additional development required by the presence of the finite interactions. The two-dimensional arrays employed are of infinite length and finite width. It has been shown by Runnels\textsuperscript{7} that a strict transition for a class of lattice gas models can only be the limiting behavior for lattices of infinite width. One should remember that functions which would be singular for the infinite two-dimensional system would be characterized by sharp "breaks", whereas the corresponding functions obtained for the semi-infinite two-dimensional lattice would be continuous, but with regions of large curvature. Results which would be exact for finite systems can be used only to infer the probable existence of a phase transition in the infinite two-dimensional array.

The EFM used in this investigation employs the calculation of thermodynamic parameters in the grand canonical ensemble for lattices of infinite length having a finite circumference of $M$ sites. The reduced pressure $p/kT$ is given in the grand ensemble by

$$\frac{p}{kT} = (2M)^{-1} \ln \lambda_1$$  \hspace{1cm} (1)

where $\lambda_1$ is the dominant eigenvalue of the Kramers-Wannier transfer matrix $P(z, \zeta)$. The intensive variables of $P$ are the molecular activity $z = \exp (\mu/kT)$ and a temperature variable $\zeta = \exp(-w/kT)$, where $w$ is the finite interaction (attraction or repulsion) between two molecules separated by the third-neighbor distance.

The elements of the transfer matrix $P_{ij}$ correspond to permissible configurations $\psi_i$ and $\psi_j$ of adjacent double rings of sites; each
double ring may contain up to $M/2$ molecules per ring, with the restriction that no two molecules may occupy nearest-neighbor or second-neighbor sites due to the hard cores of the molecules. The basic building unit must be taken as a double ring of sites because of the extended range of the postulated interaction. A molecule with center on row 1 can interact with a molecule on row 3, but these positions reside in adjacent double rings [rows (1,2) and rows (3,4)]. The matrix element, $P_{ij}$, is an activity-weighted Boltzmann factor describing the interaction between states $\psi_i$ and $\psi_j$ on adjacent double rows:

$$P_{ij} = \epsilon_{ij} \frac{1}{2}(n_i + n_j) d_{ij} \frac{1}{2}(t_i + t_j),$$

where the quantity $\epsilon_{ij}$ has the value of zero if states $\psi_i$ and $\psi_j$ are not compatible and one if they are compatible. The states $\psi_i$ and $\psi_j$ are compatible if there is no infinite repulsion between any molecule in state $\psi_i$ and any molecule in state $\psi_j$, when the two configurations occupy adjacent double rows. The quantity $d_{ij}$ is the number of third-neighbor pairs of molecules between states $\psi_i$ and $\psi_j$, $n_i$ is the number of molecules present in configuration $\psi_i$, and $t_i$ is the number of third-neighbor pairs within $\psi_i$. Equivalently, we may write

$$P_{ij} = \begin{cases} \frac{n_{ij} d_{ij} + t_{ij}}{2}, & \psi_i \text{ and } \psi_j \text{ compatible,} \\ 0, & \psi_i \text{ and } \psi_j \text{ incompatible} \end{cases}$$

where $n_{ij} = 1/2(n_i + n_j)$, and $t_{ij} = 1/2(t_i + t_j)$.

In terms of the eigenvector, $v$, (and its transpose $v^T$) corresponding to the dominant eigenvalue of $P$, the density of molecules is given by
\[ \rho = (2M)^{-1} \left( \frac{\partial \ln \lambda_1}{\partial \ln z} \right) \zeta \]

\[ = \left( \frac{z}{2M \lambda_1} \right)^T \left( \frac{\partial P}{\partial z} \right) v \]  \hspace{1cm} (4)

which reduces to\(^{14}\):

\[ \rho = (2M)^{-1} \Sigma_i v_i^2 \]  \hspace{1cm} (5)

To complete the description, some thermal property must be computed in addition to the essentially mechanical properties \( p/kT \) and \( \rho \). The most convenient is a reduced energy density, \( \epsilon \), which is the configurational energy per site in units of \( w \); thermodynamics and eqns. (1) and (3) show this to be given by\(^{13,14}\):

\[ \epsilon = (2M \lambda_1)^{-1} \Sigma_i v_i^2 \]  \hspace{1cm} (6)

where the "energy matrix", \( E \), is defined by

\[ E_{ij} = \rho_{ij} (d_{ij} + t_{ij}) \]  \hspace{1cm} (7)

Since the energy density is basically a two-particle property, it must remain in the operator form (6) with no simplification analogous to equation (5) for the one-particle property of density.\(^{13}\)

The full matrix, \( E \), has not actually been used, but rather a smaller matrix which takes advantage of the effectively dihedral symmetry of the lattice and the fact that the dominant eigenvector belongs to the totally symmetric representation of the dihedral group, \( D_M \).\(^7\)

Even values of the circumference \( M \) up to 14 sites have been studied, as well as certain odd values of \( M \), especially 7. The thermodynamic behavior corresponds to \( M \) infinite and may be approached by constructing matrices with increasing values of \( M \). In order to reach
the close packed configurations with third-neighbor exclusions (large, positive \( w/kT \)) as \( z = \exp(\mu/kT) \) goes to infinity, \( M \) must be a multiple of 7. Likewise, for second neighbor exclusions (the hard core), \( M \) must be a multiple of 2, so that ideally we should like lattices with widths of 14, 28, 42,... As a practical matter, 14 was the largest width accessible; due to the necessity of double-ring referencing, an actual width of 14 sites is effectively a 28 site problem.

The computational procedure was essentially the same as described by Runnels, Salvant, and Streiffer. The data used in this study was generated by a computer program written in MAP for the IBM 7040. In the present work, the following procedure was followed by the program:

1. Read as input the lattice width, temperature (actually \( w/kT \)), range of chemical potential, and the increment between successive values of \( x = \mu/kT \).

2. Determined the allowed double-ring states \( \psi \) with the cylindrical boundary conditions.

3. For each value of \( z = \exp(\mu/kT) \) and \( \zeta = \exp(-w/kT) \):
   a. Computed the transfer matrix \( P \) and the energy matrix \( E \).
   b. Computed the dominant eigenvalue of \( P \) and the corresponding eigenvector.
   c. Calculated and printed the pressure, density, and energy density from equations (1), (5), and (6), respectively.

4. Obtained output data in the form of punched cards for use in subsequent work (numerical analysis) and for graphical display on a Calcomp X-Y plotter.
III. SURVEY OF RESULTS

Typical "raw" data obtained from the computer program are shown in Figs. 2 and 3, showing number density and energy density as functions of $x = \mu/kT$. Also determined from the eigenvalue is the reduced pressure $\Gamma = p/kT$, which necessitates the elimination of the activity to determine $\Gamma$ as a function of density. Shown in Fig. 4 is the resulting equation of state.

An examination of Figs. 2, 3, and 4, should provide a reliable guide to the probable behavior of the doubly infinite lattice, even though we know, as has been stated previously, that sharp singularities can occur only for a lattice of infinite circumference and length. An examination of these plots seems to indicate that besides a gaseous phase of low density, there is a tendency to structures with densities of $1/7$, $1/6$, and $1/4$ for nearly all of the lattices studied. The corresponding molecular arrangements are shown in Figs. 5, 6, 7, and 8. While it is true that for certain lattice widths, some of the structures cannot be drawn, it is felt that for the infinite lattice no such problems would exist.

It is quite apparent that at low temperatures and attractive interactions a first-order phase transition joins a phase of low density, hereafter referred to as Phase I, with a solid-like phase of nearly close-packed density ($\rho \approx 1/4$), hereafter referred to as Phase IV. The athermal $\zeta = 0$ curve shows a transition that is rather accurately estimated to be at $\mu/kT = 1.76$, $p/p_0kT = 1.95$, where $p_0 = 1/4$. This is in good agreement with Bellemans' case B, corresponding to exclusion up to second neighbors, for which he reports $\mu/kT = 1.750 \pm 0.005$, and $p/p_0kT = 1.94 \pm 0.01$. We will return to such comparisons later when the
Figure 2a-2i  Number Density of the Triangular Lattice Gas, M = 4, 5, 6, 7, 8, 9, 10, 12, and 14. The curve marked 0 is the case of the vanishing third-neighbor interaction (or infinite temperature). The other isotherms represent changes of 0.2 in the temperature parameter w/kT; those to the left of the 0 isotherm correspond to attractive third-neighbor interactions and those to the right represent repulsive interactions. It should be noted that for most of the lattice widths, the temperature parameter w/kT = 0.3 is also included, except for M = 4, where w/kT = -0.3 is included.
\[ \frac{\rho}{\rho_0} \]

\[ \mu / kT \]

\[ M = 8 \]
Figure 3a-3i  Energy Per Site in Units of \( w \), \( M = 4, 5, 6, 7, 8, 9, 10, 12, \) and 14. These isotherms correspond to those in Figs. 2 and 4. The points of maximum curvature were used to define the co-existing "phases" for each width \( M \) and for each temperature.
Energy/site vs $\mu/kT$ for $M = 14$. The graph shows the relationship between energy per site and the chemical potential scaled by temperature.
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p/kT

M = 14
Figure 5  Molecules on the Triangular Lattice with $M = 14$ and $\rho = 1/7$ (typical of Phase II).
\[ \rho = \frac{1}{7} \]

\[ M = 14 \]
Figure 6  Molecules on the Triangular Lattice with $M = 14$ and $\rho = 1/6$ (straight chain, Phase III).
\[ \rho = \frac{1}{6} \]

\[ M = 14 \]
Figure 7  Molecules on the Triangular Lattice with $M = 14$ and $\rho = 1/4$ (Phase IV).
\[ \rho = \frac{1}{4} \]

\[ M = 14 \]
Figure 8  Molecules on the Triangular Lattice with $M = \frac{14}{7}$ and $\rho = \frac{1}{6}$ ("snake"-like structure, Phase III).
\[ \rho = \frac{1}{6} \]

\[ M = 14 \]
the phase diagram is discussed. It is quite clear that the addition of
the attractive third-neighbor interactions has not led to the appearance
of a third (liquid-like) phase at low temperatures.

On the other hand, at all temperatures studied with repulsive
interactions, a transition from a phase with a density \( \approx 1/6 \) (Phase III)
to a solid-like phase (Phase IV) is indicated (Figs. 2 and 4). It is
clear, however, from Fig. 2, that there is a continuity of phase between
the present Phase III and the gaseous Phase I just discussed. At very
low temperatures (and repulsive interactions) there is evidence of a
transition from a phase with a density \( \approx 1/7 \) (Phase II) to the phase
with density \( \approx 1/6 \). In addition, close examination of the equation of
state for \( M = 14 \) indicates a transition from a high density "gas" phase
to Phase II; Fig. 2 requires that we refer to this gas as Phase I.
Bellemans\(^{11}\) has indicated that for his Case C (infinite third-neighbor
repulsion) there is a transition between a phase with density approxi­
mately 90% of that of our Phase II and one with the density of Phase II.
It occurs at \( \mu/kT = 4.5-5.0 \) and \( p/p_0 kT = 4.5-5.0 \), where \( p_0 = 1/7 \) for the
third-neighbor exclusion case, and must correspond to this low tempera­
ture transition visible for \( M = 14 \).

It is thus evident that the general behavior of the system is
completely different for the two possible types of third-neighbor inter­
actions. For attractive interactions, there is, at any temperature,
precisely one transition from fluid to solid. This is very similar to
the square lattice case studied by Runnels, Salvant, and Streiffer,\(^{13}\)
and leaves us only the task of delineating the coexistence curve as
accurately as possible.

For repulsive third-neighbor interactions, on the other hand,
the thermodynamic behavior is considerably more complicated. There are
several coexistence curves to be explored, and the basic topology of the phase diagram must be worked out.
IV. CHARACTERIZATION OF THE TRANSITIONS

For a quantitative description of phase transitions, where possible, we prefer to rely on the trends in behavior as the circumference of the lattice increases. In the past, it has been noted that two trends are very useful in exploring probable singularities. The first involves a systematic study of the slopes of the "vertical" portions of the density profiles, such as shown in Fig. 2. For a real system which undergoes a first-order phase transition, a plot of density vs. chemical potential would show a discontinuity at the transition chemical potential. The derivative of the density with respect to chemical potential would be infinite at the transition. In our system of finite width, which cannot undergo a strict phase transition, we have defined a transition chemical potential as one which corresponds to the maximum first derivative of the density with respect to chemical potential at constant temperature.

It is commonly found that the location \( x_0 = \mu/kT \) of the maximum slope and the pressure \( \Gamma(x_0) = p/kT \) at that point, drift only slightly with increasing width.\(^{13,14}\) It is relatively easy to establish convincing extrapolations of \( x_0 \) and \( \Gamma(x_0) \) with some function of \( M \), such as \( M^{-\alpha}, \alpha > 0 \). By this means, one can determine the chemical potential and pressure at the transition with considerable accuracy for each value of the temperature parameter, \( w/kT \), remembering that by considering \( w \) to be constant, we can vary the temperature by changing the dimensionless ratio, \( w/kT \).

Characterizing the order of the transition is usually much more difficult. Here again, trends in the behavior with increasing
width are studied whenever possible. What one wants to know is whether, in the limit \( M \to \infty \), a strictly vertical slope of the isotherms in Figs. 2 and 3 is achieved at a single point or over some range of positive length. In previous studies\(^{13,14} \) of lattice gases using the EFM, the densities of the coexisting phases were defined as the densities at the interpolated points of maximum and minimum second derivative of the density with respect to chemical potential. For a first-order transition, these points will reach two different limits as \( M \to \infty \). These limits should correspond to the densities of the two phases involved in the particular transition. On the other hand, for a second-order "continuous" transition, the points will coalesce at an inflection point.

According to Runnels,\(^{13} \) one could perhaps better define the coexisting phases at each lattice width and temperature as the points of maximum curvature of the energy density profile. The energy density profiles (Fig. 3) for the most part behave qualitatively like the number densities, but since they involve a two-particle property rather than a one-particle property, they should be more sensitive to subtle configurational changes. From the two values of \( x = \mu/kT \) determined from \( \left| \frac{\partial^2 e}{\partial x^2} \right|_{\text{max}} \) the corresponding number densities are obtained by interpolation. We have used this definition of the coexisting phases.

To carry out this program, each of the basic thermodynamic properties, \( \Gamma, \rho, \) and \( \varepsilon \), was regarded as a function of \( x = \mu/kT \) and fitted with a "cubic spline" function.\(^{13,15} \) This is a sequence of segments of cubic functions, the various coefficients being determined so that when the segments are joined together the approximating function is continuous and has continuous first- and second-derivatives everywhere. From the spline function approximate first- and second-
derivatives are readily available, and the spline itself may be used for interpolation once the critical values of \( x \) are determined from the derivatives. This numerical analysis was accomplished by the same FORTRAN program as used with the square lattice.\(^{13}\)

The transition values of \( x_0 \) and \( \Gamma(x_0) \) for the infinite lattice were obtained from extrapolations of the finite width parameters as described above, whenever possible. The widths 6, 8, 10, 12, and 14 were included in the analysis of most of the transitions, although in many cases the data for \( M = 6 \) and \( M = 8 \) could not be included (Fig. 9). Only the widths 7 and 14 could be used for the transition on the repulsion side between Phase II and Phase III (Fig. 10), due to the packing requirements of Phase II. The extrapolation function, \( M^{-2.44} \) seemed to generate sufficiently linear correlations in the majority of cases. Our best estimates of these transition values of \( \mu/kT \) and \( p/kT \) for the infinite lattice may be found in Tables I and II. The error estimates in a study of this sort can hardly be more than educated guesses.

The values of \( \rho \) and \( \epsilon \) at the transitions were determined using the different extrapolation function, \( M^{-0.75} \), for all cases where extrapolation was possible.\(^{16}\) Since these densities (number and energy) are higher order properties than the chemical potential and pressure, somewhat reduced confidence should be placed in these values. Our best estimates of these densities, however, are plotted in Fig. 11 against the temperature variable, \( w/kT \) (positive and negative values), for the equilibrium between solid (Phase IV) and "gas" (Phase I or Phase III). The most important single feature which can be learned from this figure with a glance, is that this transition is first-order under all conditions.

The various plateaus discernible in Fig. 11 can, for the most part, be rationalized. A reduced density equal to one \( (\rho/\rho_0 = 1) \)
Figure 9  Transition Parameters for Triangular Lattice Gas. Although there is no theoretical justification for extrapolations of this type, they appear to be reasonable methods for refined predictions of the parameters for the infinite lattice. The transition values for $\mu/kT$ and $p/kT$ are obtained for $w/kT = 0.6$ using the extrapolation function $M^{-\alpha}$ with $\alpha = 2.44$ and the widths $M = 8, 10, 12, \text{ and } 14.$
Figure 10  Transition Parameters for Triangular Lattice Gas. The transition values for $\mu/kT$ and $p/kT$ are obtained for $w/kT = 2.4$ using $M^{-\alpha}$ with $\alpha = 2.44$ and the widths $M = 7$ and 14.
Figure 11  Number and Energy Densities, Extrapolated Values for the Transition from Phase of Low Density (Intermediate Density in the Repulsive Region) to Solid Phase. This phase transition is certainly of first-order for all the temperatures investigated. The dashed lines are the limiting behavior at very low temperature (see Appendix A).
### TABLE I
TRANSITION PARAMETERS FOR THE INFINITE LATTICE IN THE ATTRACTIVE REGION

<table>
<thead>
<tr>
<th>$w/kT$</th>
<th>$\mu/kT$</th>
<th>$p/kT$</th>
<th>$p/w$</th>
</tr>
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<tbody>
<tr>
<td>0</td>
<td>1.778</td>
<td>0.488</td>
<td>$\infty$</td>
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<tr>
<td>-0.2</td>
<td>0.625</td>
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<td>-0.00547</td>
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</table>

a. Uncertainties in $\mu/kT$ and $p/kT$ for all cases are estimated to be $\pm 0.01$.

b. Based on even widths studied.
TABLE II
TRANSITION PARAMETERS FOR THE INFINITE LATTICE IN THE REPULSIVE REGION

<table>
<thead>
<tr>
<th></th>
<th>&quot;Gas&quot; = Solid b</th>
<th>Gas = Liquid c</th>
<th>Liquid = Liquid d</th>
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<td>Phase III = Phase IV</td>
<td>Phase I = Phase II</td>
<td>Phase II = Phase III</td>
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<td>w/kT</td>
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<td>(p/kT)</td>
<td>(p/w)</td>
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<tr>
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<td>0.488</td>
<td>(\infty)</td>
</tr>
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<tr>
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<td>6.998</td>
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<td>1.110</td>
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a. Uncertainties in \(\mu/kT\) and \(p/kT\) for all cases are estimated to be \(\pm 0.01\)
b. Based on even widths studied.
c. Based only on width 14.
d. Based on widths 7 and 14.
represents the close-packed structure. Equivalent to that the energy density plateau is 0.75, the energy per site for the close-packed system (see Appendix A). The plateau at \( p/p_0 = 0.67 \) is indicative of one of the polymorphic "liquid"-like phases (see Figs. 6 and 8). What is perhaps not so obvious is the plateau in the low energy densities near \( \varepsilon = 0.33 \). The theoretical treatment in Appendix A predicts an energy density of \( 1/6 \), where \( p_0 = 1/6 \), as do Figs. 6 and 8. It is, however, possible to imagine that the chains could "condense" pairwise, thus increasing the energy per site by a factor of two. The density could remain virtually the same (see Fig. 6), if the space between double chains were not filled in. In general, rather subtle structural modifications can have a considerably larger effect on the energy than on the density.

Data for the larger lattices were extremely difficult to obtain, due to overflows in arithmetic operations. Scaling of the various parameters helped, but the running time to determine each point became excessive. A more fundamental difficulty was the greatly accentuated finite width dependence of the transition parameters at the very "strong" singularity\(^{13} \) between gas and solid at low temperature and negative \( w \). To solve this problem, one could conceivably work with lattices of much greater width, but this would only magnify the problems of computer capacity and time. Completely overcoming these difficulties was not essential in this treatment, due to the availability of approximate closed-form solutions of the equilibria between the various phases (see Appendix A). Also, a great deal of data was available from \( w/kT \) values amenable to the present treatment.
V. THE PHASE DIAGRAMS

The phase diagram for the attractive region is quite straightforward and is shown in Fig. 12a, along with a comparative diagram for argon, Fig. 12b. To scale the pressure for comparison with real systems, Fig. 12a shows $\Gamma = p/kT$ multiplied by 4, which is the square of the third-neighbor distance, the product being called $P^*$. The corresponding factor for argon is taken to be $r^*^3$, where $r^*$ is the separation at the minimum of the Lennard-Jones potential determined for argon. Even when scaled by the molecular volume (area), the pressure parameter $P^*$ is too low for the model system by more than an order of magnitude, as was the case with the square lattice gas reported by Runnels, Salvant, and Streiffer.13

The phase diagram for the repulsive region has been determined from the several transitions studied, and is shown in Fig. 13. There are two "liquid"-like forms (Phase II, $\rho \approx 1/7$, and Phase III, $\rho \approx 1/6$) in equilibrium with each other, and, under proper conditions, with a gaseous phase (Phase I) or a solid phase (Phase IV, $\rho \approx 1/4$). That there is a triple point connecting Phases II, III, and IV is suggested at temperatures just beyond the lowest temperature ($w/kT = 2.6$) studied for the repulsive interactions. A gas-"liquid" critical temperature is indicated at approximately $w/kT = 1.8$; at higher temperatures the gaseous phase compresses continuously until the crystallization transition occurs.

Utilization has been made of the theoretical treatment of Appendix A to extend the Phase II-to-Phase IV equilibrium line and of Bellemans'10 third-neighbor Case C to extend the equilibrium line joining Phase I with Phase II. The closed form approximation in Appendix A shows in the low temperature limit that $p/w = 1$ (Eqn. A26), which indicates
Figure 12a  The Phase Diagram for the Infinite Lattice in the Attractive Range of Temperatures Studied. The pressure variable has been scaled with the molecular area for the model and with $r^*^S$ for argon. ▲ refers to Bellemans' second-neighbor case.
Figure 12b The Phase Diagram for Argon. The $r^*$ is the pair separation at the minimum ($-\epsilon_{6-12}$) of the Lennard-Jones potential determined for argon.
2.0

(a) Solid Gas

\[ T^* = \frac{kT}{(-w)} \]

(b) Argo

\[ \epsilon_{6-12}/k = 119.8^\circ K \]

\[ r = 3.822 \text{ Å} \]

\[ P^* = \frac{4p}{kT} \]

\[ P^* = \frac{P_r^3}{kT} \]

Critical point

Fluid

Solid

Triangular Lattice Gas
The Phase Diagram for the Infinite Lattice in the Repulsive Range of Temperatures Studied. At low temperatures and repulsive interactions, a phase diagram similar to that of helium (see Fig. 14) is indicated. This diagram joins two "liquid"-like phases to solid and gas phases. Like helium, the stable phase of the model at low temperature and pressure is one of the "liquids", and for similar reasons of "order". On the other hand, there are notable differences between this model and that of helium. The equilibrium line between Phases II and III was extended using the theoretical data of Appendix A. The equilibrium between Phases I and II was extended to include Bellemans' Case C.
that the solid-"liquid" (Phase II) equilibrium line should intercept the ordinate \( p/w \) at 1.0. Bellemans' prediction of a transition for his third-neighbor Case C of a transition at \( p/p_0kT = 4.6 \pm 0.2 \) (where \( p_0 = 1/7 \)) indicates that the ratio \( p/w \) approaches zero for our coexisting Phases I and II at low temperatures (since \( p/T \) remains finite).

The additional phase diagram, Fig. 14, is included to show the relationship between pressure and temperature in a different light by using the reduced pressure, \( \Gamma = p/kT \) for ordinate; \( \Gamma \) has the advantage of being able to remain finite and nonzero in the limits \( T \to 0 \) and \( T \to \infty \). The same general features are apparent in this version of the phase diagram as in the preceding diagram. That there is a triple point connecting Phases II, III, and IV, is strongly suggested somewhere just beyond \( w/kT = 2.6 \) as in Fig. 13. Furthermore, the transition predicted by Bellemans'\(^\text{12}\) for his second-neighbor Case B should correspond to our model at infinite temperature; this is so indicated for at high temperatures the slope of the equilibrium line approaches the value of \( p/kT \) that Bellemans discovered for his hard sphere Case B.

A schematic phase diagram for helium (Fig. 15) is included in order to illustrate the surprising comparison with our model. The similarities between the diagram for the triangular lattice (with repulsive intermolecular potential) and that for helium, suggest that somehow similar kinds of ordering phenomena are at work in both cases. In each instance, there are two "liquid" forms which can be in equilibrium with each other or with a gaseous or a solid phase. One triple point in our model (II-III-IV) is reasonably well defined. On the basis of our computations, we indicate no phase boundary between I and III; \( \text{i.e.,} \) they are different conditions of the same phase. A short coexistence line
Figure 14 The Phase Diagram with Both the Attractive and Repulsive Ranges Included. Correlation is indicated with the second- and third-neighbor models of Bellemans and coworkers.\textsuperscript{12} The symbol $\Delta$ refers to Bellemans' second-neighbor case, and the symbol $\Delta$ to his third-neighbor case. The dashed line joins our data to Bellemans' third-neighbor case.
Figure 15  The Phase Diagram for Helium (Schematic).
Solid

1.76°, 29.6 atm

Q

k

< / >

CD

Liquid

Helium I

CRITICAL POINT

P 5.2°, 2.26 atm

Liquid

Helium II

Gas

2.17°, 38 atm

Temperature, °K

Pressure, P
projecting from a triple point near $w/kT = 1.8$ on the boundary with Phase II is not altogether out of the question, however, and would render the diagram more similar topologically to that of helium.

A somewhat trickier problem involves the appearance of another slight jump in the density near $\mu/kT \approx 13$ and most apparent for the $w/kT = 2.4$ and $2.2$ isotherms in Fig. 2, $M = 14$. If this persisted at higher values of $M$, there would be a small spur on the II-III coexistence curve of the phase diagram of Fig. 13. We do not feel there to be sufficient evidence at this stage to warrant the claim of an additional phase, although its existence should be regarded possible.
VI. CONCLUSIONS AND DISCUSSION

The principle qualitative features indicated by the study of this model are: (1) the transition observed for \( w/kT = 0 \) (\( T = \infty \)) noted by Runnels and Combs and Bellemans among others, remains at all temperatures investigated for both attractive and repulsive interactions, although it undergoes modifications as \( w/kT \) changes; (2) there is no indication of an intermediate "liquid"-like phase in the presence of third-neighbor attractive interactions; (3) there is, however, evidence of a transition between a gaseous phase and a "liquid"-like phase for repulsive interactions and very low temperatures, which represents the third-neighbor hard sphere transition of Bellemans; (4) furthermore, there is another transition from this phase to a different "liquid" phase at temperatures less than about \( (1.8 \, k/w)^{-1} \) and greater than about \( (2.6 \, k/w)^{-1} \). This latter temperature, \( (2.6 \, k/w)^{-1} \), is approximately that of a triple point connecting the two "liquid"-like phases and the solid phase. The higher temperature, \( (1.8 \, k/w)^{-1} \), partakes of the properties of a gas-liquid critical temperature.

The character of the one transition present under all conditions is changed little when the third-neighbor interaction, superimposed on the first- and second-neighbor hard core, is finite and repulsive. The transition is shifted to higher activities, but remains first-order (Fig. 11). The transition in the attractive region should be regarded as a sublimation equilibrium between a gas and a solid; in the repulsive region the equilibrium is between the solid and the "liquid" (or the supercritical "gas"). In the limit \( T \to \infty \) for both attractive and repulsive interactions, the behavior becomes that of the second-neighbor hard core gas. In the limit \( T \to 0 \) for repulsive but finite interactions, the behavior approaches that of the third-neighbor hard core gas.
It is interesting to speculate why there is no gas-liquid equilibrium in the attractive range. Apparently any arrangement of molecules that is low in energy must be an ordered one and low in entropy also; hence, any maneuvering for free energy is precluded. When the gas condenses, it goes all the way to the solid phase. As with the square lattice gas, we have a fairly clear idea from the work of Bellmans and coworkers\textsuperscript{11} how such a lower density equilibrium would have developed. Referring to Fig. 2, it would have grown out of the broad region of negative curvature. This region becomes more pronounced with increasing $w/kT$ but does not constitute a genuine phase transition, interrupting the rapid rise of the density profiles, until reaching the repulsive region.

The missing liquid phase in the attractive region may be discussed in another way: in terms of the low-order virial coefficients (see Appendix B). Attempts to locate the gas-liquid critical point by use of the standard simultaneous equations leads to a predicted negative critical density -- clearly not reasonable and indicative that we are not likely to have a liquid phase for this kind of molecular potential.

Perhaps the interaction potential is too simple and provides only one unique ordered structure to which both a decrease of temperature and an increase in pressure tend to bring the system. On the other hand, if we allow the third-neighbor interactions to become repulsive, there are several indications of at least two intermediate ordered structures between the gas-like phase and the close-packed structure, one with a density of $1/7$, and the other with a density of $1/6$ as previously shown (Figs. 5 and 6). An examination of the plot of density $\text{vs. } \mu/kT$ (Fig. 2) indicates in the repulsive region that there can be three successive jumps
in the density. At low enough temperatures, the system should condense into a phase corresponding to the structure of minimum energy (Phase II). Although this phase has a smaller density \( \rho \approx 1/7 \) than the other ordered structures (\( \rho \approx 1/6 \) and \( \rho \approx 1/4 \)) its compressibility is small. Increasing its density must mean increasing its energy and its entropy at the same time. But it is also true that "random" gaseous configurations of lower density would also be expected to have higher entropy and energy than Phase II, which accounts for the striking appearance of the \( M = 14 \) energy density profile at very low temperatures.

It is the existence of this Phase II that results in the thermodynamic similarities between our model system and helium. Each has a phase which is (a) intermediate in density between the gas and the crystalline solid, and (b) lower in entropy than either. Thus it is this phase (Phase II or superfluid helium) that is stable at \( T = 0 \) and pressure \( > 0 \) -- unless the pressure is sufficiently high to stabilize the solid relative to the exceptional, zero entropy phase.

The model studied demonstrates that lattice models of hard core molecules may present several phase transitions and even rather realistic phase diagrams with appropriate intermolecular interaction potentials. Such models are simpler to consider than the more realistic systems of Lennard-Jones molecules with continuous coordinates, for example, and are for that reason alone worthy of attention for simulating the equation of state of actual substances.
APPENDIX A

THE LOW TEMPERATURE LIMIT - A THEORETICAL TREATMENT

If we assume the equilibrium:

Phase I (low density gas) = Phase IV (high density solid) at very low temperatures (and \( w < 0 \)), we can readily calculate the transition parameters. The low density phase is an ideal lattice gas with pressure and chemical potential given by

\[
p_I/kT = -\ln(1 - \rho_I) \quad (A1)
\]
\[
\mu_I/kT = \ln[\rho_I/(1 - \rho_I)] \quad (A2)
\]
in terms of the gas density \( \rho_I \). These follow from setting the entropy of \( N_I = \rho_I B \) molecules on \( B \) sites equal to \( k \ln(\rho_I) \) and the configurational energy equal to zero.

The high density solid phase would have entropy given approximately by \( k \ln(\frac{B}{N_{IV}}) \) and energy by \( (6N_{IV} - 3B/4)w \). This would be true only near the close-packed density. The assumption is that all configurations result from the removal of \( N_{IV} \) molecules from the close-packed lattice, with no rearrangement of the remaining molecules. The expression for the configurational energy \( (6N_{IV} - 3B/4)w \) comes from:

\[
[\frac{6(B/4)}{2} - 6(B/4 - N_{IV})]w
\]

by reference to Fig. 7, it can be noted that the total number of occupied sites for the close-packed structure is \( B/4 \) and that each molecule has six neighbors. Since \( w \) represents the interaction between two molecules at third-neighbor distances, the first term must be divided by 2 in order to count each interaction only once. Furthermore, one must subtract the number of interactions lost because of "holes" \( (B/4 - N_{IV}) \). The above
expressions for entropy and energy give

\[ p_{IV}/kT = 3w/4kT - 1/4 \ln(1 - 4\rho_{IV}) \]  \hspace{2cm} (A3)

\[ \mu_{IV}/kT = 6w/kT + \ln[4\rho_{IV}/(1 - 4\rho_{IV})] \]  \hspace{2cm} (A4)

where \( \rho_{IV} = N_{IV}/B \) is the density of the solid. Equilibrium is determined by equating the pressures of the two phases and the chemical potentials of the two phases to give simultaneous transcendental equations for \( \rho_I \) and \( \rho_{IV} \). For this case, we have written only the zeroth order -- in \( \rho_I \) and \( (1 - 4\rho_{IV}) \) -- form of the equation:

\[ \ln \rho_I = 6w/kT - \ln(1 - 4\rho_{IV}) \]  \hspace{2cm} (A5)

\[ 0 = 3w/4kT - 1/4 \ln(1 - 4\rho_{IV}) \]  \hspace{2cm} (A6)

These equations are solved for the densities, and then the common chemical potential and pressure. The limiting values of these parameters are, in this approximation,

\[ \rho_I = \exp(3w/kT) = 1 - 4\rho_{IV} \]  \hspace{2cm} (A7)

\[ \mu/kT = 3w/kT \]  \hspace{2cm} (A8)

\[ p/kT = \exp(3w/kT) \]  \hspace{2cm} (A9)

The transition parameter \( p/kT \) is calculated, using equation (A9), for the transition from Phase I (gas) to Phase IV (solid) at all temperatures studied. These pressures are tabulated in Table III along with the values obtained using the transfer matrix method. At low temperatures, they are seen to be in good agreement.

Similarly, for the transition between the intermediate polymorphic "liquid"-like Phase III \( (\rho_0 = 1/6) \) and the solid Phase IV \( (\rho_0 = 1/4) \):
### TABLE III

COMPARISON OF TRANSITION $p/kT$ CALCULATED FROM THE ASYMPTOTIC LAW (APPENDIX A) WITH THE EFM $p/kT$

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<th>Attraction Phase I = Phase IV$^a$</th>
<th>Repulsion Phase III = Phase IV$^b$</th>
<th>Phase II = Phase III$^c$</th>
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<td>$p/kT$ (Calc.)</td>
<td>$p/kT$ (EFM)</td>
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<td>----------------</td>
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a. Calculated from $p/kT = \exp 3w/kT$.
b. Calculated from $p/kT = w/kT + 0.3$.
c. Calculated from $p/kT = w/kT - 0.6$. 
\[ \frac{P_{III}}{kT} = \frac{w}{6kT} - \frac{1}{6} \ln(1 - \frac{6\rho_{III}}{B}) \quad (A10) \]
\[ \frac{\mu_{III}}{kT} = \frac{w}{kT} - 0.6 - \ln\left[\frac{(1 - 6\rho_{III})/6\rho_{III}}{1 - \rho_{III}}\right] \quad (A11) \]

These follow from setting the energy equal to \((2N_{II} - B/6)w\), as explained in the previous case, and the entropy equal to \(k \ln\left(\frac{B/6}{N_{III}}\right) + k(0.6N_{III})\). The additional entropy indicated by the \(k(0.6N_{III})\) term is necessary to account for the several "snake"-like structures that can be drawn (Fig. 8). This is somewhat similar to "communal" or "fluctuation" entropy, where interchange of identical molecules would produce no change in configuration, but fluctuations in position which do not interchange will produce a contribution to the entropy. This is often difficult to calculate, and in most cases resort is made to some, hopefully intelligent, guesswork. The factor \(k(0.6N_{III})\) has been added after the fact, but seems generally reasonable. Equations (A5), (A4), (A10), and (A11) are used to determine equilibrium by equating the pressures of the two phases and the chemical potentials of the two phases as before to give:

\[ -\ln(1 - 6\rho_{III}) = 5w/kT + 1.8 \quad (A12) \]
\[ -\ln(1 - 4\rho_{IV}) = w/kT + 1.2 \quad (A13) \]
\[ \mu/kT = 7w/kT + 1.2 \quad (A14) \]
\[ p/kT = w/kT + 0.3 \quad (A15) \]

Again, the transition parameter \(p/kT\) is calculated, using equation (A15), this time for the transition from Phase III \((\rho_0 \approx 1/6)\) to Phase IV \((\rho_0 \approx 1/4)\). Table III shows the agreement of these values with those obtained using the transfer matrix method.

In exactly the same fashion, the transition from Phase II \((\rho_0 \approx 1/7)\) to Phase III \((\rho_0 \approx 1/6)\) gives
\[ \frac{p_{II}}{kT} = -\frac{1}{7} \ln(1 - 7\rho_{II}) \]  
\hspace{2cm} (A16)

and

\[ \frac{\mu_{II}}{kT} = \ln\left[\frac{7\rho_{II}}{(1 - 7\rho_{II})}\right] \]  
\hspace{2cm} (A17)

Eqns. (A16) and (A17) follow from setting the entropy of Phase II equal to \( k \ln(B/7) \) and the configurational energy equal to zero (see Fig. 5). Equating the pressures of Phase II and Phase III and the chemical potentials of Phase II and Phase III, gives:

\[ -\ln(1 - 6\rho_{III}) = 5w/kT - 3.6 \]  
\hspace{2cm} (A18)

\[ -\ln(1 - 7\rho_{II}) = 7w/kT - 4.2 \]  
\hspace{2cm} (A19)

\[ \frac{\mu}{kT} = 7w/kT - 4.2 \]  
\hspace{2cm} (A20)

\[ \frac{p}{kT} = \frac{w}{kT} - 0.6. \]  
\hspace{2cm} (A21)

A check of the plot of \( \epsilon \) vs. \( \frac{\mu}{kT} \) in Fig. 3 reveals this to be a good approximation for \( -\frac{w}{kT} = -2.0 \), but the correlation drops off with higher negative values of \( -\frac{w}{kT} \). It can be seen in Fig. 3 that the spacing between the transitions for incremented values of \( -\frac{w}{kT} \) does not remain constant. Furthermore, Table III shows the limited agreement of the \( \frac{p}{kT} \) parameters calculated from Equation (A21), and those obtained from EFM.

A similar treatment of the equilibrium between the "liquid"-like Phase II (\( \rho_0 \approx 1/7 \)) and the solid Phase IV, utilizing Equations (A3) and (A16) leads to

\[ -\ln(1 - 7\rho_{II}) = 7w/kT \]  
\hspace{2cm} (A22)

\[ -\ln(1 - 4\rho_{IV}) = w/kT \]  
\hspace{2cm} (A23)

\[ \frac{\mu}{kT} = 7w/kT \]  
\hspace{2cm} (A24)

\[ \frac{p}{kT} = \frac{w}{kT} \]  
\hspace{2cm} (A25)

\[ \frac{p}{w} = 1 \]  
\hspace{2cm} (A26)
Equation (A26) was used to extend the solid = liquid \((\rho_0 \approx 1/7)\) line to the intercept at 1.0 on the ordinate \((p/w)\) of the phase diagram (Fig. 14).

An attempt to develop an approximate theoretical treatment for a possible transition between Phase I \((\rho_0 \approx 0)\) and Phase II \((\rho_0 \approx 1/7)\) yielded the following equations:

\[ \ln(1 - \rho_I) = \frac{1}{7} \ln(1 - 7\rho_{II}) \]  
\[ \ln \rho_I/(1 - \rho_I) = \ln 7\rho_{II}/(1 - 7\rho_{II}) \]

for which there is no meaningful solution. It should be pointed out that the energies of these two phases is zero. This indication that there is not supposed to be a transition from Phase I to Phase II is substantiated by the lack of any evidence to that effect from the "experimental data."
APPENDIX B

THE GAS LIQUID CRITICAL TEMPERATURE FROM THE TRUNCATED VIRIAL SERIES

The gas-liquid critical temperature (if it exists) can often be estimated rather well from the truncated virial series

\[ \frac{p}{kT} = \rho + B_2(T)\rho^2 + B_3(T)\rho^3. \]  \hspace{1cm} (B1)

At the critical temperature \((\frac{\partial p}{\partial \rho})_{T_c} = (\frac{\partial^2 p}{\partial \rho^2})_{T_c} = 0\) which leads to \(B_2(T_c) = 3B_3(T_c)\), an implicit equation for the critical temperature. The virial coefficients \(B_2\) and \(B_3\) have been evaluated for this model using abstract graph theory; the results are:

\[ B_2 = 13/2 - 3f \]  \hspace{1cm} (B2)

\[ B_3 = 97/3 - 30f + 6f^2 - 4f^3 \]  \hspace{1cm} (B3)

where \(f = \exp(-w/kT) - 1 \geq -1\). The equation \(B_2(T_c) = 3B_3(T_c)\) yields

\[ 12f^3 - 9f^2 + 5f - 219/4 = 0 \]  \hspace{1cm} (B4)

upon substitution of Equations (B2) and (B3). The only real solution of this equation is \(f = 1.014\), for which \(-w/kT = 0.7\). In itself, this is not unreasonable, but if one derives an expression for the critical density from (B1) above, and the relation that at the critical temperature \((\frac{\partial p}{\partial \rho})_{T_c} = (\frac{\partial^2 p}{\partial \rho^2})_{T_c} = 0\), the critical density would be negative. Finding the first and second derivatives and setting them equal to zero gives the following simultaneous equations:

\[ 1 + 2B_2(T_c)\rho_c + 3B_3(T_c)\rho_c^2 = 0 \]  \hspace{1cm} (B5)

\[ 2B_2(T_c)\rho_c' + 6B_3(T_c)\rho_c = 0 \]  \hspace{1cm} (B6)
where $T$ and $\rho$ are the variables. The solution is

$$\rho_c = -\frac{B_2(T_c)}{3B_3(T_c)},$$ \hspace{1cm} (B7)

which is negative if $B_2$ and $B_3$ are evaluated at $f = 1.014$. 
REFERENCES


16. The use of different extrapolation functions for ρ's on the one hand, and μ/kT and p/kT on the other, has been observed previously, but never explained.


VITA

Jon Robert Craig was born in Mill Run, Pennsylvania. He attended elementary school in Normalville, Pennsylvania, and graduated from Connellsville, Pennsylvania High School. He received a B.S. degree from West Virginia Wesleyan with a double major in Chemistry and Biology and a minor in French. He received a teaching certificate after spending one year at California State College, California, Pennsylvania, and a M. Litt. in Zoology from the University of Pittsburgh, Pittsburgh, Pennsylvania. Currently, he is a candidate for the Doctor of Philosophy degree in Chemistry at Louisiana State University and is employed in the Physical Science Department of California State College, California, Pennsylvania.
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Title of Thesis: The Thermodynamic Phases of a Triangular Lattice Gas

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Date of Examination:

July 2, 1970