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THE VIRIAL EQUATION OF STATE FOR HARD PARTICLES
ON TWO-DIMENSIONAL LATTICES

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By
Janis Ellen Clymer, B.S., M.S.

****

The Ohio State University
1983

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CHAPTER I
INTRODUCTION

The Monte Carlo technique as previously applied to the problem of phase transitions for hard particles\(^1\) indicates that there is a transition, but the nature of the transition is not well understood. It is desired to examine this system in greater detail in hopes of gaining a better understanding of the nature of the thermodynamics of hard particles. Since the continuum problem is difficult to handle, a "lattice gas" will be examined instead. This model, first introduced by Lee and Yang in 1952,\(^2\) is particularly useful in that it allows the formulation of the grand partition function in terms of a transfer matrix. A lattice gas is a system represented by particles situated on a lattice. At each lattice site there may be a particle or no particle. Chapter II shows how a transfer matrix can be constructed to contain the details of a particular lattice. This transfer matrix is then used to calculate the grand partition function, from which all of the thermodynamics of the system can be obtained.

If the transfer matrix is formulated such that its elements are powers of the square root of the fugacity, \(z\), \(1\)
then the grand partition function is obtained as a polynomial in \( z \). By expanding the log of the grand partition function as a power series in \( z \), the pressure and the number density can also be obtained as polynomials in \( z \) (see section III.5), and \( z \) can be eliminated between these two polynomials to obtain the virial equation of state.

In chapter III the one-dimensional lattice is examined in detail. It is possible to obtain the equation of state analytically in closed form. In section III.2, the zeroes of the grand partition function are calculated for both attractive and repulsive interactions, from which it is shown that there can be no transition in either case for the one-dimensional lattice.

For two-dimensional lattices, the transfer matrices involved are larger and analytical solutions are not known in general. A computer is thus used to construct the transfer matrix and calculate the grand partition function and the expressions for the pressure and number density as power series in \( z \). Lagrange's theorem is then used to eliminate \( z \) to obtain the equation of state.

This method is superior to the Monte Carlo technique in that it is not a statistical approach, so no statistical errors are introduced. Further, the transfer matrix and the inversion of the expressions for the pressure and
number density to obtain the equation of state can be handled by machine algebraically. Exact results can thus be obtained for finite lattices, and these results are then extrapolated to predict the behavior of infinite lattices. Moreover, it is possible to determine to what degree the results for finite lattices are accurate for infinite lattices. (See section IV.4.) Therefore, exact results can be obtained for the first several virial coefficients for various types of lattices for the infinite case. The first eight virial coefficients for the square, triangular and union jack lattices, and the first three coefficients for the hexagonal lattice are obtained here. Any lattice structure can be treated by this method if a suitable choice for the transfer matrix is made.

To summarize, in this thesis, an algebraic method to obtain exactly the first few terms of the virial equation of state for a lattice gas of hard particles using a computer is developed. This represents a first step in a larger effort to understand the thermodynamics of hard particles.
CHAPTER II
THE TRANSFER MATRIX

Consider an m-site periodic one-dimensional lattice in which no two particles are allowed to occupy adjacent sites. The system can be viewed as hard rods confined to a ring. If each particle is assigned a statistical weight \( z^* \), then a transfer matrix \( A \) describing the configuration of two adjacent sites \( i, i+1 \) can be constructed. The symbol \( \dagger \) will be used to indicate the presence of a particle, while \( \dagger \) represents no particle. Using \( \sigma_i \) as the state variable of the \( i^{th} \) site, the transfer matrix can be written as

\[
\begin{array}{ccc}
A_{\sigma_i \sigma_{i+1}} & \sigma_{i+1} = \dagger & \sigma_{i+1} = \dagger \\
\sigma_i = \dagger & 1 & \sqrt{z} \\
\sigma_i = \dagger & \sqrt{z} & 0 \\
\end{array}
\]

or

\[
A = \begin{pmatrix} 1 & \sqrt{z} \\ \sqrt{z} & 0 \end{pmatrix} \quad (1)
\]

\( *z \) is the fugacity and is defined as \( e^{\mu B/\lambda^d} \), where \( d \) is the dimension of the system and \( \lambda \) the thermal wavelength, \( \lambda = h/(2\pi mkT)^{\frac{1}{2}} \).
The grand partition function can then be expressed as

$$2_m = \sum_{\sigma_i = \uparrow, \downarrow} A_{\sigma_1 \sigma_2} A_{\sigma_2 \sigma_3} \ldots A_{\sigma_m \sigma_1}$$

or

$$2_m = \text{Tr} A^m$$

where the sum is over all configurations, with the case of two particles being adjacent disallowed by the zero entry in A and statistical weights accounted for by the terms containing $\sqrt{z}$.

This method can easily be extended to two dimensions. Suppose one wishes to find the grand partition function for an mxn lattice. First construct all the allowed configurations for a one-dimensional lattice with m sites. The elements of the transfer matrix can then be obtained by comparing the two one-dimensional configurations. If a pair of configurations are allowed to be adjacent, the matrix element is $z^{p/2}$, where $p$ is the total number of particles contained in the two configurations; if the pair is not allowed, the matrix element is zero. (The dimension of the transfer matrix for an mxn lattice is equal to the total number of allowed configurations for a one-dimensional lattice with m sites; i.e. the sum of all the coefficients of powers of $z$ in $2_m$.) The grand partition function for the mxn lattice is then found by calculating the trace of this matrix raised to
the $n^{th}$ power.

i.e. \[ 2_{mn} = \text{Tr} \left[ \left[ A_m(z) \right]^n \right] \] (4)

Different types of lattice structures can be treated simply by changing the conditions which determine whether or not a particular pair is allowed to be adjacent. In this work, square, hexagonal, triangular and union jack lattices are examined.

Three dimensional lattices can be treated by comparing neighboring pairs of two-dimensional lattices to obtain the transfer matrix. In fact, this method can in principle be used to calculate the grand partition function for any size or type of lattice, provided that the structure of the lattice is known. In practice, the calculations are limited by the availability of computer time and space to handle manipulations of very large matrices.

In some instances, one wishes to know simply the total number of allowed configurations for a particular lattice. This total can be obtained by setting $z=1$ in all of the previous discussion. The transfer matrix then contains only ones and zeroes and the product $A_{d_1} A_{d_2} A_{d_3} \cdots A_{d_m} d_1$ is one for allowed configurations and zero for those that are not allowed. The expression (2) then becomes a simple enumeration of all allowed configurations with the result
that

$$\Omega_m = \text{Tr} A^m$$

(5)

for the one-dimensional case, or for the two-dimensional case,

$$\Omega_{mxn} = \text{Tr} [(A_m)^n]$$

(6)

This is useful, for instance, in determining the total number of allowed configurations for a one-dimensional lattice in order to construct the transfer matrix for the corresponding two-dimensional lattice, or for calculating the entropy of an equivalent Ising spin system.
CHAPTER III
THE ONE-DIMENSIONAL LATTICE

III.1: The Grand Partition Function and the Equation of State

As an example of the application of the transfer matrix method to a specific problem, consider a one-dimensional lattice in which adjacent particles interact with energy $\epsilon$. The transfer matrix for this lattice is

$$A = \begin{pmatrix} 1 & \sqrt{z} \\ \sqrt{z} & zu \end{pmatrix}$$

(10)

(where $u = e^{-\beta \epsilon}$).

Diagonalization of $A$ yields the eigenvalue equation

$$\lambda^2 - (1+uz)\lambda + (u-1)z = 0$$

(11)

with eigenvalues

$$\lambda_{\pm} = \frac{1+uz \pm \sqrt{(1-uz)^2 + 4z}}{2}$$

(12)
The grand partition function for an \( m \)-site lattice is then

\[
\mathcal{Z}_m = \text{Tr} \, \lambda^m = \lambda_+^m + \lambda_-^m \tag{13}
\]

The thermodynamics of this system can be obtained from

\[
\beta P = \lim_{m \to \infty} \frac{1}{m} \ln \mathcal{Z}_m \tag{14}
\]

and

\[
\rho = z \frac{\partial}{\partial z} (\beta P) \tag{15}
\]

Substitution of (13) into (14) yields

\[
\beta P = \ln \lambda_+ \tag{16}
\]

or, from (12),

\[
\beta P = \ln \left(1 + uz + \frac{\sqrt{(1-uz)^2 + 4z}}{2}\right) \tag{17}
\]

Then, from (15),

\[
\rho = \frac{1}{2} \left[ 1 + \frac{uz-1}{\sqrt{(1-uz)^2 + 4z}} \right] \tag{18}
\]

Elimination of \( z \) between (17) and (18) yields (after some algebra - see Appendix A):
From this expression, it can be shown that \( \frac{\partial P}{\partial V} \bigg|_\beta < 0 \); see appendix B. This implies that phase transition does not occur.

This expression can now be examined to obtain the P-V diagram for various values of \( \epsilon \). Four cases will be considered.

**Case 1:** \( \epsilon = 0 \) (free particles)

If \( \epsilon = 0 \), \( u = 1 \) and (19) becomes

\[
e^\beta P = \frac{1}{1-\beta}
\]

or, in terms of the specific volume, \( v = 1/\beta \),

\[
e^\beta P = \frac{v}{v-1}
\]

Figure 1 shows the P-V diagram for this case. Note that \( v_{min} = 1 \) as expected for free particles. Evidently no phase transition occurs.

Notice that (21) can be rewritten as

\[
\beta P = -\ln(1-\frac{1}{v})
\]

The virial expansion can then be easily obtained for all \( v > 1 \). Expanding (22), using \( \ln(1+z) = z - \frac{1}{2}z^2 + \frac{1}{3}z^3 + \cdots \), one obtains
Figure 1

P-V Diagram for 1-D Lattice with $\varepsilon=0$
The first order term gives the ideal gas behavior.

Case 2: $\epsilon = \infty$; hard rods (particles cannot be adjacent)

If $\epsilon = \infty$, $u = 0$ and (19) becomes

$$e^\beta P = 1 + \frac{2\rho}{1 - 2\rho + \sqrt{(2\rho - 1)^2}}$$

(24)

Since $\nu \geq 2$ (see below), $\rho \leq \frac{1}{2}$; so the positive square root of $(2\rho - 1)^2$ is $(1 - 2\rho)$. Thus (24) becomes

$$e^\beta P = \frac{\nu - 1}{\nu - 2}$$

(25)

The P-V diagram for this case is shown in figure 2. The diagram is similar to the previous one except that $v_{\text{min}} = 2$, indicating that each particle occupies a length of two units. That is, no two particles can be adjacent. For this case, the virial expansion, valid for all $\nu > 2$ is

$$e^\beta P = \frac{1}{\nu} - \frac{3}{2}(\frac{1}{\nu})^2 + \frac{7}{2}(\frac{1}{\nu})^3 - \frac{15}{4}(\frac{1}{\nu})^4 + \ldots$$

(26)

As before, the first order term gives the ideal gas behavior. Again phase transition is absent.

Case 3: $\epsilon < 0$ (attractive interaction)

Use the example $\epsilon = -1$, so that $u = e^\beta$ and (19) becomes
Figure 2

P-V Diagram for 1-D Lattice with $\xi=\infty$
Case 4: \( \epsilon > 0 \) (repulsive interaction)

Consider \( \epsilon = 1 \). Then \( u = e^{-\beta} \) and (19) becomes

\[
\beta P = \ln \left[ \frac{2}{1 - \frac{2}{v} + \sqrt{(2v-1)^2(1-e^{2\beta})+e^{2\beta}}} + 1 \right]
\]

The P-V diagrams for attractive and repulsive interactions are shown in figures 3 and 4 respectively.

III.2: Zeroes of the Grand Partition Function

In order to determine whether or not phase transitions exist in general for the one-dimensional lattice, it is useful to examine the zeroes of the grand partition function. Let \( z_1, z_2, \ldots, z_m \) be the zeroes of \( \lambda_m \). Then

\[
\lambda_m = (1 - \frac{z}{z_1}) (1 - \frac{z}{z_2}) \ldots (1 - \frac{z}{z_m});
\]

and from (14), the pressure can be written as

\[
P_m = \frac{1}{\beta m} \left[ \ln(1 - \frac{z}{z_1}) + \ln(1 - \frac{z}{z_2}) + \ldots + \ln(1 - \frac{z}{z_m}) \right].
\]

For \( z = z_1, z = z_2, \ldots, z = z_m \), this function is undefined. As \( m \to \infty \), if any of these singular points lies on the positive real axis, then a phase transition is expected at that point.

For the one-dimensional case, using (12) and (13), one has

\[
\lambda_m = \left(1 + u z + \sqrt{(1 - u z)^2 + 4 z^2}\right)^m + \left(1 + u z - \sqrt{(1 - u z)^2 + 4 z^2}\right)^m
\]
Figure 3

P-V Diagram for 1-D Lattice with $\epsilon < 0$
Figure 4

P-V Diagram for 1-D lattice with $\epsilon > 0$
Setting $z_m=0$, this becomes

$$\frac{1+uz+\sqrt{(1-uz)^2+4z}}{1+uz-\sqrt{(1-uz)^2+4z}} = (-1)^m = e^{\imath \alpha_n}$$  \hspace{1cm} (30)

where \( \alpha_n = \frac{(2n+1)n}{m} \) \hspace{1cm} (n=0,1,2,...,m-1)  \hspace{1cm} (31)

Consider the following cases:

**Case 1:** \( 1+uz=0 \Rightarrow z=-1/u \). Then (12) becomes

$$\lambda_\pm = \pm \sqrt{1 - \frac{1}{u}}$$  \hspace{1cm} (32)

(So $z_m=0$ for all odd $m$ and $z_m=0$ for even $m$ provided $u=1$.)

In this case, $z$ is a negative real number (since $u>0$) and is on the circle of radius $1/u$.

**Case 2:** \( 1+uz \neq 0 \). Then (with the subscript on $\alpha$ suppressed)

$$e^{\imath \alpha} = 1 + \frac{\sqrt{(1-uz)^2 + 4z(1+uz)^2}}{1 - \sqrt{(1-uz)^2 + 4z(1+uz)^2}}$$  \hspace{1cm} (33)

or,

$$\left(\frac{1-uz}{1+uz}\right)^2 + \frac{4z}{(1+uz)^2} = \frac{e^{\imath \alpha} - 1}{e^{\imath \alpha} + 1}$$  \hspace{1cm} (34)

Simplifying, (34) becomes

$$\left(\frac{1-uz}{1+uz}\right)^2 + \frac{4z}{(1+uz)^2} = -\tan^2(\alpha/2)$$  \hspace{1cm} (35)
which can be written in quadratic form as

\[ u^2z^2 + 2uz[1+2\cos^2(\alpha/2)(\frac{1}{u}-1)] + 1 = 0 \]  (36)

Now make the substitutions:

\[ x=uz \]  (37)

and \[ y = 1 + 2\cos^2(\alpha/2)(\frac{1}{u}-1) \]  (38)

so that (36) becomes

\[ x^2 + 2yx + 1 = 0 \]  (39)

For repulsive interaction, \( \epsilon > 0 \Rightarrow u < 1 \), so that \( \frac{1}{u} > 1 \) and \( y \geq 1 \). Let \( y = \cosh^\gamma \), with \( \gamma > 0 \). Then (39) has solutions

\[ x = -e^{\pm \gamma} \]  (40)

or \[ z = \frac{1}{u} e^{\pm \gamma} \]  (41)

Since both terms in (38) are positive in this case, the maximum value of \( y \), and of \( \cosh^\gamma \) is given by setting \( \cos^2(\alpha/2)=1 \) in that equation. One then obtains
So the roots of the grand partition function for $\epsilon > 0$ are on the negative real axis and are between the limits $-\frac{1}{u}e^{\pm \gamma}$ with $\gamma$ specified by (42).

Now examine the temperature dependence of these limits. As $T \to 0$ (or $\epsilon \to \infty$ for any value of $T$), $\beta \to \infty$, $u = e^{-\beta \epsilon} \to 0$ and $\frac{1}{u} \to \infty$. Also, from (42), $\cosh \gamma \to \infty$ so $\gamma \to \infty$. Thus $\frac{1}{u}e^{-\gamma} \to \infty$.

In order to evaluate $\frac{1}{u}e^{-\gamma}$, note that

$$e^\gamma = \cosh \gamma + \sinh \gamma = \cosh \gamma + \sqrt{\cosh^2 \gamma - 1}$$

Substituting from (42) into (43), one obtains

$$e^\gamma = \left[ \frac{2}{u} - 1 + \sqrt{\frac{4}{u^2}(1-u)} \right]$$

Therefore,

$$\frac{1}{u}e^{-\gamma} = \frac{1}{u} \frac{-1}{\left[ \frac{2}{u} - 1 + \sqrt{\frac{4}{u^2}(1-u)} \right]} = \frac{-1}{\left[ 2-u + \sqrt{4(1-u)} \right]}$$

So $\lim_{u \to 0} \frac{1}{u}e^{-\gamma} = \frac{1}{4}$. Thus the roots for this case are distributed along the negative real axis between $-\infty$ and $-\frac{1}{4}$.

As $T$ increases, the range of roots becomes gradually
smaller until for $T=\infty$, $\beta = 0$ and $u = e^\beta e = 1$. Thus $\cosh y = 1$ and $y = 0$. Then $\frac{1}{u} e^{\frac{i y}{u}} = -1$. All roots then coincide at $z = -1$ for this case. (See figure 5.)

For attractive interaction, $\xi < 0 \Rightarrow u > 1$, so that $\frac{1}{u} < 1$ and $\gamma < 1$. In this case, it is useful to let $\gamma = -\cos \theta$.

The solutions of (39) are then

$$x = e^{\pm i \theta}$$

or

$$z = \frac{1}{u} e^{\pm i \theta}$$

So the zeroes lie on a circle of radius $\frac{1}{u}$. But the entire circle is not occupied. If the identity, $\cos \theta = 2 \cos^2(\theta/2) - 1$, is substituted into (38), one obtains

$$1 - 2\cos^2(\theta/2) = 1 - 2\cos^2(\alpha/2)(1 - \frac{1}{u})$$

or

$$\cos(\theta/2) = \pm \sqrt{\frac{u-1}{u}} \cos(\alpha/2)$$

It is evident from (31) that $\alpha$ is in the range from 0 to $2\pi$, so for $m = \infty$, $\cos(\alpha/2)$ is in the range from 1 to -1. Therefore, $\cos(\theta/2)$ is limited by

$$-\sqrt{\frac{u-1}{u}} \leq \cos(\theta/2) \leq \sqrt{\frac{u-1}{u}}$$

and $\theta/2$ is limited by
Figure 5

Zeroes of the One-dimensional Grand Partition Function

for ε > 0
\[ \pi - \cos^{-1}\left(\sqrt{\frac{u-1}{u}}\right) \geq \theta/2 \geq \cos^{-1}\left(\sqrt{\frac{u-1}{u}}\right) \]  

Examining the temperature dependence, one finds that for \( T=0, \, \beta=\infty \), so \( u=\exp{\beta E} = \infty \) and \( \frac{1}{u}=0 \). Also, from (51) and (50), one obtains \( \theta/2=0, \pi \); \( \theta=0,2\pi \). So the circle on which the zeroes lie has zero radius and the entire circle is occupied.

As \( T \) increases, the radius gradually increases and \( \theta \) becomes larger. As \( u \) goes from \( \infty \) to 1, \( \frac{u-1}{u} \) goes from 1 to 0; \( \frac{u-1}{u} \) will always be <1. So \( \theta \) is always >0. Hence, in this case as in the repulsive case, the grand partition function can have no zeroes on the positive real axis. Therefore no transition is possible at any finite temperature.

At \( T=\infty, \, \beta=0 \), \( u=1 \) and \( \frac{1}{u}=1 \). And from (50), \( \theta=\pi \); so for \( T=\infty \), all roots are again located at \( z=-1 \). (See figure 6.) This is the same as the result obtained for the repulsive case for \( T=\infty \).

It should be noted that the fact that the zeroes are on a circle for the attractive interaction is a special case of the circle theorem of Lee and Yang. Unlike the proof of the circle theorem, the proof here is valid only for the one-dimensional case.

III.3: Finite 1-D hard Rods - Grand Partition Function and Virial Expansion

In order to illustrate how the transfer matrix can be used to calculate the virial expansion for a finite lattice, consider once again the case on one-dimensional hard rods,
Figure 6
Zeroes of the One-dimensional Grand Partition Function
for $\xi<0$
for which the transfer matrix is

\[
A = \begin{pmatrix}
1 & \sqrt{z} \\
\sqrt{z} & 0 \\
\end{pmatrix}
\]  

(52)

The grand partition function is then calculated from

\[
Z_m = \text{Tr} A^m.
\]

The resulting coefficients of the powers of \(z\) in \(Z_m\) for \(m=1-10\) are given in table 1. Notice that \(Z_m\) can be written in the form

\[
Z_m = 1 + f(z)
\]

so that

\[
p^r = \frac{1}{m} \ln [1 + f(z)]
\]

(54)

The expansion

\[
\ln[1+f(z)] = f(z) - \frac{f^2(z)}{2} + \frac{f^3(z)}{3} - \ldots
\]

(55)

can then be used to obtain \(p^r\) as a polynomial in \(z\). It has been shown\(^6\) that for any value of \(m\), the coefficients of this expansion will be identical to those for \(m=\infty\) up to \(z\) to the \((m-1)\)th power. This is verified in table 2 which shows the coefficients of \(z^p\) in the expansion for \(p^r\) for \(m=1-5\) and \(p=1-5\). (Notice that the first \(m-1\) terms in the \(m\)th row are identical to the corresponding terms in the following row.) The particle density, \(\rho\), can be readily calculated from the polynomial obtained for \(p^r\) using

\[
\rho = z^{3/2} (p^r)
\]

(56)
Table 1
Number of Allowed Configurations of \( k \) Particles on \( m \) Sites on a \( 1 \times m \) Periodic Lattice

<table>
<thead>
<tr>
<th>( k )</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>4</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>5</td>
<td>5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>6</td>
<td>9</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>1</td>
<td>7</td>
<td>14</td>
<td>7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>8</td>
<td>20</td>
<td>16</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>1</td>
<td>9</td>
<td>27</td>
<td>30</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>1</td>
<td>10</td>
<td>35</td>
<td>50</td>
<td>25</td>
<td>2</td>
</tr>
</tbody>
</table>
Results for this expansion are given in table 3. Evidently this expansion will be accurate to the same power of \( z \) as the expansion for \( \beta P \).

The virial expansion can, in principal, be obtained by solving the polynomial representing \( \beta P \) for \( z \) and substituting back into the polynomial for \( \rho \). However, this becomes tedious in practice if terms of order higher than \( z^3 \) are needed. A direct inversion of the functions can be accomplished via Lagrange's theorem, which will be discussed later in connection with two-dimensional lattices.
Table 2

Coefficients of Expansion of $\frac{1}{m} \ln 2^m$

in terms of $z$ for 1-D Lattice

<table>
<thead>
<tr>
<th>$m$</th>
<th>$z^1$</th>
<th>$z^2$</th>
<th>$z^3$</th>
<th>$z^4$</th>
<th>$z^5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>-1</td>
<td>$\frac{4}{3}$</td>
<td>-2</td>
<td>$\frac{16}{5}$</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>$\frac{3}{2}$</td>
<td>3</td>
<td>$\frac{27}{4}$</td>
<td>$\frac{81}{5}$</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>$\frac{3}{2}$</td>
<td>$\frac{10}{3}$</td>
<td>$\frac{17}{2}$</td>
<td>$\frac{116}{5}$</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>$\frac{3}{2}$</td>
<td>$\frac{10}{3}$</td>
<td>$\frac{35}{4}$</td>
<td>25</td>
</tr>
</tbody>
</table>

Table 3

Coefficients of Expansion of $p$

in terms of $z$ for 1-D Lattice

<table>
<thead>
<tr>
<th>$m$</th>
<th>$z^1$</th>
<th>$z^2$</th>
<th>$z^3$</th>
<th>$z^4$</th>
<th>$z^5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>-2</td>
<td>4</td>
<td>-8</td>
<td>16</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>-3</td>
<td>9</td>
<td>-27</td>
<td>81</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>-3</td>
<td>10</td>
<td>-34</td>
<td>116</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>-3</td>
<td>10</td>
<td>-35</td>
<td>125</td>
</tr>
</tbody>
</table>
CHAPTER IV
TWO-DIMENSIONAL LATTICES

IV.1: The Grand Partition Function

The method of the previous chapter can easily be extended to two dimensions. For the two-dimensional lattices, however, general analytic solutions are not known. Hence the computer is used extensively to obtain the desired results. We consider here only hard particles.

For finite one-dimensional hard rods, a program has been written to raise the matrix

\[ A = \begin{pmatrix} 1 & 1 \\ 0 & 1 \end{pmatrix} \]  

(57)

to the \( m \)th power, then add the diagonal elements to get \( \text{Tr} \ A^m = \Omega_m \). This is the total number of allowed configurations for a one-dimensional periodic lattice. It is also the dimension of the transfer matrix for an \( mn \) two-dimensional lattice. Results for \( m=2-20 \) are given in table 4.
### Table 4

**Number of Allowed Configurations**

for a One-dimensional Periodic Lattice

<table>
<thead>
<tr>
<th>Number of Sites (m)</th>
<th>$\Omega_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>4</td>
<td>7</td>
</tr>
<tr>
<td>5</td>
<td>11</td>
</tr>
<tr>
<td>6</td>
<td>18</td>
</tr>
<tr>
<td>7</td>
<td>29</td>
</tr>
<tr>
<td>8</td>
<td>47</td>
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<tr>
<td>9</td>
<td>76</td>
</tr>
<tr>
<td>10</td>
<td>123</td>
</tr>
<tr>
<td>11</td>
<td>199</td>
</tr>
<tr>
<td>12</td>
<td>322</td>
</tr>
<tr>
<td>13</td>
<td>521</td>
</tr>
<tr>
<td>14</td>
<td>843</td>
</tr>
<tr>
<td>15</td>
<td>1364</td>
</tr>
<tr>
<td>16</td>
<td>2207</td>
</tr>
<tr>
<td>17</td>
<td>3571</td>
</tr>
<tr>
<td>18</td>
<td>5778</td>
</tr>
<tr>
<td>19</td>
<td>9349</td>
</tr>
<tr>
<td>20</td>
<td>15127</td>
</tr>
</tbody>
</table>
In order to obtain $gP(\rho)$ for two-dimensional lattices, it was at first thought that it would be necessary to calculate $\beta_P(z)$ and $\varphi(z)$ for each particular value of $z$ and compile extensive tables of these results. The corresponding values of $\beta_P$ and of $\varphi$ for each value of $z$ would then be examined in hopes of obtaining an expression for $\beta_P$ as a function of $\varphi$. This would have to be done for many values of $z$ for each $m$ and $n$, and would be a very tedious process.

After a considerable amount of initial frustration, however, a much better method was developed. One can compute $L_{m\times n}(z) = \text{Tr} \, A_m^n$ as a polynomial in $z$ by computer if one uses as elements of $A$ not numbers but polynomials of $z^{1/2}$. Each element of $A$ is stored in the computer as a linear array of numbers that are coefficients of the polynomials of $z^{1/2}$. This method will now be described in detail.

Consider first the case of the square lattice. The dimension of the transfer matrix for the $m\times n$ lattice is obtained from table 4. The computer is then used to construct all possible configurations of a $1\times m$ lattice. That is, all possible strings of $m$ entries, where each entry is either $-1$ (representing a particle) or $+1$ (representing no particle) are constructed. Those strings in which two $-1$'s are adjacent are then deleted. The
remaining strings are then arranged as \( \Omega_m \) columns of +1's and -1's. This \( mx\Omega_m \) array is called \( \mu \).

The machine then compares adjacent sites for a pair of allowed configurations of the \( 1 \times m \) lattice. That is, \( \mu(i,j) \) is compared to \( \mu(i,k) \) for all values of \( i \). If two adjacent -1's are found for any value of \( i \), then the matrix element \( A_m(j,k) \) of the two-dimensional transfer matrix is zero. If no adjacent -1's are found, then the machine must count the total number of particles contained in both columns \( (j \) and \( k \) in order to determine the power of \( z^{\frac{k}{2}} \) for the matrix element \( A_m(j,k) \). To see how this is accomplished, let

\[
\begin{align*}
\text{n}_+ &= \text{the number of +1's contained in columns } j \text{ and } k \text{ of } \mu \\
\text{n}_- &= \text{the number of -1's contained in columns } j \text{ and } k \text{ of } \mu
\end{align*}
\]

(59)

If all elements of columns \( j \) and \( k \) of \( \mu \) are summed, the result can be defined as

\[
\text{SUM} = n_+ - n_-
\]

(60)

But the total number of elements in these two columns must be \( 2m \). So

\[
n_+ + n_- = 2m
\]

(61)
Solving (92) and (93) for \( n_\_ \) yields

\[
n_\_ = m - \frac{\text{SUM}}{2}
\]  

(62)

Since each particle contributes a factor of \( z^{\frac{1}{2}} \), the power of \( z \) for \( A_m(j, k) \) will be \( n_\_/2 \). A third dimension of \( A_m \) is used to store the coefficients of the powers of \( z^{\frac{1}{2}} \), which will range from 0 to \( m \). Now \( A_m \) appears as an \( \Omega_m \times \Omega_m \) matrix with elements that are monomials of the form \( z^{n_\_/2} \), and powers of \( A_m \) can be calculated by computer if care is taken to keep track of the coefficients of the various powers of \( z^{\frac{1}{2}} \). The grand partition function is then found by taking the trace of \( A_m \) to the \( n^{\text{th}} \) power. It will be a polynomial in \( z \).

For the triangular lattice, essentially the same procedure is followed except that in addition to comparing the \( i^{\text{th}} \) element of each pair of columns \( j \) and \( k \) of \( \mu \) for all values of \( i \), the \((i+1)^{\text{st}}\) element of \( k \) must be compared to the \( i^{\text{th}} \) element of \( j \) as well, because of the diagonal bonds in the triangular lattice. (See figure 7.)

For the union-jack lattice, diagonal bonds exist in both directions (see figure 8). So in addition to the comparisons made for the triangular lattice, the \((i-1)^{\text{st}}\) element of \( k \) and the \( i^{\text{th}} \) element of \( j \) must also be compared.

For the hexagonal lattice the process is somewhat more complicated. Because this lattice does not exhibit translational invariance over one lattice spacing (see figure 9),
Figure 7

Two-dimensional Triangular Lattice
Figure 8

Two-dimensional Union-Jack Lattice
Figure 9

Two-dimensional Hexagonal Lattice
it is necessary to construct two matrices $A_m(j,k)$ and $B_m(j,k)$. The elements of $A_m$ represent comparison of columns $l-1$ and $l$ in figure 9; the elements of $B_m$ represent comparison of columns $l$ and $l+1$.

The matrix $A_m$ is constructed in a manner similar to that for the square lattice, except that in comparing $\mu(i,j)$ to $\mu(i,k)$, adjacent -1's will be allowed if $i$ is even. In constructing $B_m$, adjacent -1's will be allowed if $i$ is odd.

After obtaining $A_m$ and $B_m$ in this way, these two matrices are multiplied to obtain a matrix $C_m$, and the grand partition function for an $mxn$ hexagonal lattice is given by, for $n$ even,

$$Z_{mxn} = \text{Tr} \left[ C_m(z) \right]^{n/2}$$

(63)

### IV.2: Zeroes of the Grand Partition Function

After computing the coefficients of $z^n$ in $Z_{mxn}$, a root finding procedure was used to calculate the zeroes of the grand partition function. For small lattices (of all types) the zeroes were found to be distributed along the negative real axis. As the lattice size increases, complex roots appear and they seem to migrate toward the positive side. It seems reasonable that if the lattice size becomes large enough, the zeroes will
eventually approach the positive real axis, indicating a transition. However, for large lattices, $\lambda_{mxn}$ becomes a polynomial of high order and the root finding procedure becomes increasingly less reliable. Hence the validity of the results obtained for larger lattices is somewhat questionable and no easily discernible pattern of the zeroes can be found. Therefore it is impossible to say anything about the thermodynamic behavior at this time.

IV.3: Pressure and Density Expansions

Once the coefficients of $z$ in $\lambda_{mxn}$ have been found, the pressure can be obtained. For the two-dimensional case, (34) becomes, following the notations used in the one-dimensional case,

\[
(\beta V)_{mxn} = \frac{1}{mn} \ln [1 + f(z)_{mxn}]
\] (64)

The first three coefficients in (64) can be obtained analytically. Let $\bar{N}=mxn$ and write the grand partition function as

\[
\lambda_{\bar{N}} = 1 + q_1 z + q_2 z^2 + \ldots
\] (65)
so that

\[ f(z) = q_1 z + q_2 z^2 + \ldots \]  

(66)

Expanding (64), one has

\[(\beta p)_N = \frac{1}{N} \left[ (q_1 z + q_2 z^2 + \ldots)^2 \right] + \ldots \]  

(67)

or

\[(\beta p)_N = \left( \frac{q_1}{N} \right) z + \frac{1}{N} \left( q_2 - \frac{q_1^2}{2} \right) z^2 + \frac{1}{N} \left( q_3 - q_1 q_2 + \frac{q_1^3}{3} \right) z^3 + \ldots \]  

(68)

But from (65) it is evident that \( q_1 \) is the number of allowed configurations which contain one particle. Since this one particle can occupy any of the \( N \) sites available, \( q_1 = N \). Similarly, \( q_2 \) is the number of allowed configurations which contain two particles. In order to evaluate \( q_2 \), define \( p \) to be the number of nearest neighbors for a particular lattice and notice that once a site has been chosen for the first particle, the number of sites available for the second particle is reduced by \( p + 1 \) (the site chosen and its \( p \) nearest neighbors). That is, there will be \( N - (p + 1) \) sites available for the second particle. So the number of allowed configurations containing two particles is \( N(N - p - 1) \). To take care of correct Boltzmann
counting in the q's, the classical particles are treated as identical. So the actual number of distinct allowed configurations containing two particles is

\[ q_2 = \frac{N(N-p-1)}{2} \]  \hspace{1cm} (69)

Notice that \( q_1 \) depends only on the size of the lattice and is completely independent of the type of lattice; and \( q_2 \) depends on both the lattice size and the number of nearest neighbors, but does not depend on the topology of the lattice. It will now be seen that \( q_3 \) depends on all three of these factors.

Now examine \( q_3 \). The total number of distinct configurations of three particles on \( N \) sites (for all types of lattices) is \( \frac{N(N-1)(N-2)}{6} \). But only those configurations for which no two particles are adjacent are allowed. Thus there are two classes of non-allowed configurations:

I. those configurations for which two of the particles are adjacent and the third is located such that it is not adjacent to either of the other two

II. those configurations for which all three particles are clustered together

The number of type I and type II configurations is different for different types of lattices.

First examine the square lattice and count the number of type I configurations. For each of the \( N \) sites there are
4 adjacent sites (p=4). So the number of distinct ways to place two particles adjacent to one another is \(\frac{4N}{2}\) (since the two particles can be interchanged) or \(2N\). There are then \(N-8\) remaining sites which the third particle can occupy without being adjacent to either of the other two. (See figure 10.) So the number of type I configurations is \(2N(N-8)\).

In order to count the number of type II configurations, notice that for each site there are 6 different ways to cluster three particles about that site. (See figure 11.) So the total number of type II configurations for the square lattice is \(6N\).

Now examine the hexagonal lattice, first count the number of type I configurations. For this lattice \(p=3\), so the number of distinct ways to place two particles adjacent to one another is \(\frac{3N}{2}\). There are then \(N-6\) remaining sites for the third particle. (See figure 12.) So the number of type I configurations for the hexagonal lattice is \(\frac{3N}{2}(N-6)\).

Figure 13 shows that for the hexagonal lattice, there are 3 different ways to cluster three particles about any of the \(N\) sites. So the number of type II configurations for this lattice is \(3N\).

Examination of these results reveals that one can write a general expression for \(q_3\) which applies to both square and hexagonal lattices. The number of type I configurations can be written as \(\frac{Np(N-2p)}{2}\), and the number of
\( \bullet \) = particle

\( x \) = site which is unoccupied but unavailable for the 3\textsuperscript{rd} particle

\textit{total number of unavailable sites} = 8

\textbf{Figure 10}

\textit{Square Lattice}

\textit{Cluster of Two Particles}
\* = particle

number of type II configurations = 6

Figure 11
Square Lattice
Clusters of Three Particles
• = particle

x = site which is unoccupied but unavailable for the 3\textsuperscript{rd} particle

\text{total number of unavailable sites} = 6

\textbf{Figure 12}

Hexagonal Lattice

Cluster of Two Particles
\* = particle

number of type II configurations = 3

Figure 13

Hexagonal Lattice

Clusters of Three Particles
type II configurations is \( \frac{N_p(p-1)}{2} \). Therefore,

\[
q_3 = \frac{N(N-1)(N-2)}{6} - \frac{N_p(N-2p)}{2} - \frac{N_p(p-1)}{2}
\]

(for square and hexagonal lattices)

Using a procedure similar to that used for the square
and hexagonal lattices, and examining figures 14 and 15,
one can see that for the triangular lattice, the number of
type I configurations is \( \frac{6N}{2}(N-10) \), or \( \frac{N_p(N-p-4)}{2} \); and the
number of type II configurations is \( 11N \), or \( \frac{N(N-14)}{2} \).

In order to determine the number of type I configur­
ations for the union-jack lattice, two cases must be con­
sidered. In the first case, the two particles which are
clustered together are joined by either a vertical or a
horizontal bond. In this case the total number of sites
unavailable for the third particle is 12 (see figure 16a),
and the number of possibilities for this type of cluster
of two particles is \( \frac{4N}{2} \). So the number of type I config­
urations for this case is \( \frac{4N}{2}(N-12) \).

In the second case, the two particles which are clus­
tered together are joined by a diagonal bond. For this
case, the number of sites unavailable for the third par­
ticle is 14 (see figure 16b), and the number of clusters
of this type is also \( 4N \). So the number of type I config­
urations for this case is \( \frac{4N}{2}(N-14) \). So the total number
• = particle

x = site which is unoccupied but unavailable for the 3rd particle

total number of unavailable sites = 10

Figure 14
Triangular Lattice
Cluster of Two Particles
All configurations shown for the square lattice are also included, so the total number of type II configurations = 11.

Figure 15

Triangular Lattice

Clusters of Three Particles
(a) number of unavailable sites = 12

(b) number of unavailable sites = 14

• = particle

x = site which is unoccupied but unavailable for the 3rd particle

Figure 16

Union-jack Lattice

Clusters of Two Particles
of type I configurations for the union-jack lattice is
\[ \frac{4N-12}{2} + (N-14) \], or \[ \frac{N-12}{2} + (N-14) \].

From figure 17, it is evident that the number of type II configurations for the union-jack lattice is 20N, or \[ \frac{5P}{2}N \].

Now, adding the number of type I configurations (for both cases) to the number of type II configurations for the union-jack lattice, one finds that the expression obtained for the total number of disallowed configurations for this lattice is exactly the same as that for the triangular lattice. Hence a general expression can be written which applies to both the triangular and the union-jack lattice. That is

\[ q_3 = \frac{N(N-1)(N-2)}{6} - \frac{N-4}{2} + N\left(\frac{5P-4}{2}\right) \]  \hspace{1cm} (71)

(for triangular and union-jack lattices)

Putting these results back into (68), one obtains

\[ (BF)_N = z - (\frac{P+1}{2})z^2 + \left[ \frac{P(P+1)}{2} + \frac{1}{2} \right]z^3 \]  \hspace{1cm} (72)

(for square and hexagonal lattices)

and

\[ (BF)_N = z - (\frac{P+1}{2})z^2 + \left[ \frac{P(P-1)}{2} + \frac{13}{3} \right]z^3 \]  \hspace{1cm} (73)

(for triangular and union-jack lattices)
All configurations shown for the square and triangular lattices are also included, so the total number of type II configurations = 20.

Figure 17
Union-jack Lattice
Clusters of Three Particles
These two expressions can be combined to obtain a single expression which is valid for all four lattices (see appendix C):

\[ \beta \mathcal{P} = \frac{1}{2} \left( v + \frac{1}{2} \right) z^2 + \frac{1}{36} (2p^3 - 21p^2 + 193p - 254) z^3 \]  

(74)

It can be observed from these equations that the first coefficient in \((\beta \mathcal{P})^n\) is always one, and the second and third coefficients can be obtained if the lattice structure is known. The values obtained from (74) are given at the bottoms of tables 7 thru 9. These theoretical values are seen to agree with the calculated values obtained for finite lattices in all those cases where the values for finite lattices are predicted to agree with those for infinite lattices (see section IV.4).

This method can also be applied to the one-dimensional problem simply by setting \(n=1\) in the previous discussion, so that \(N=m\). Table 1 verifies that \(q_1 = N = m\). Also, if \(p=2\) is substituted into (69), the values obtained for \(q_2\) agree with those given in table 1. The values of \(q_3\) for the one-dimensional lattice should be given by (70) since there are no diagonal bonds in this case. Again the theoretical results can be seen to agree with those given in table 1.

If a factor of \(u\) is included in the transfer matrix for each pair of interacting particles as in section III.1, the calculations are much more complicated, but the procedure is essentially the same, and results can then be obtained for
lattices with general nearest neighbor interaction. Values for \( q_1 \) thru \( q_4 \) for the square lattice have been obtained by Majid and Yang.\(^9\)

As \( n \) increases, the calculation of the coefficients of \( z^n \) by this method becomes increasingly more cumbersome. However, the computer can be used to obtain powers of \( f_{mxn}(z) \) from \( g_{mxn}(z) \) and to compute \( (\beta P)_{mxn} \) directly from (55) and (64). Since \( (\beta P)_{mxn} \) is a polynomial in \( z \), its derivative with respect to \( z \) can also be calculated by computer; thus the number density is easily obtained from (56).

**IV.4: Theorem on the Accuracy of the Pressure Expansion**

D. Sherrill and C.P. Yang\(^10\) have shown that for one-dimensional lattices and for higher dimensional symmetric lattices, \( (\beta P)_{kxmxn} = (\beta P)_{kxmxn} \) up to terms of order \( z^{n-1} \). This result can be generalized to include non-symmetric lattices as well. Without loss of generality we shall prove the following theorem:

**Theorem:** For any two-dimensional lattice, symmetric or non-symmetric, \( (\beta P)_{mxn} \) agrees with \( (\beta P)_{mxn} \) up to terms of order \( z^{n-1} \).
In order to prove this theorem, one must first examine the proof of the theorem for symmetric lattices (see again ref. 10). That proof involves diagonalization of $A$ to obtain the two largest eigenvalues of $A$. For non-symmetric lattices, as for symmetric lattices, in the limit of small $z$, $A$ is of the form

$$A = \begin{pmatrix}
1 & z^{1/2} & z^{1/4} & \cdots & z^{1/2n} & 0 & \cdots & 0 \\
\vdots & z^{1/2} & \vdots & \ddots & \vdots & \vdots \\
0 & \vdots & \vdots & \ddots & z^{1/2} \\
0 & \vdots & \vdots & \ddots & \vdots & z^{1/2} \\
0 & \vdots & \vdots & \ddots & \vdots & \vdots & \ddots & 0 \\
0 & \vdots & \vdots & \ddots & \vdots & \vdots & \ddots & \ddots & 0 \\
0 & \vdots & \vdots & \ddots & \vdots & \vdots & \ddots & \ddots & \ddots & 0 \\
\end{pmatrix} \tag{75}$$

The diagonalization of $A$ for non-symmetric $A$ can proceed in exactly the same manner as for symmetric $A$, since this process does not depend on the symmetry of the matrix. However, for symmetric $A$, the eigenvalues are all real and so is the largest eigenvalue, $\lambda_1$. For non-symmetric $A$, it is not obvious that $\lambda_1$ is real, so a proof is necessary.

The proof can be accomplished via Perron's theorem, which states that if $A$ is an irreducible matrix with the $i,j$th element, $a_{ij} \geq 0$, for all $i,j$, and if $\lambda_1, \ldots, \lambda_n$ are the eigenvalues of $A$, then $\varphi = \max |\lambda_n|$ is an eigenvalue of
A and has multiplicity one. Since the elements of $A$ are either 0 or powers of $z^k$, it is clear that $a_{ij} \geq 0$. It is necessary to show that $A$ is irreducible.

A matrix $A$ is said to be irreducible if for all pairs $p$ and $q$, there is some set of indices $i_1, \ldots, i_r$, such that

$$a_{p, i_1} a_{i_1, i_2} \cdots a_{i_{r-1}, i_r} a_{i_r, q} \geq 0$$

(76)

If the first configuration is chosen to be the one which contains no particles, then any other configuration is allowed next to the first one. That is, for $z > 0$,

$$a_{p, i_1} \geq 0 \quad \text{for all } p$$

(77)

$$a_{q, i_1} \geq 0 \quad \text{for all } q$$

(78)

These conditions satisfy (76) for $r=1$, with $i_1=1$, so $A$ is irreducible. Therefore by Perron's theorem (see above), $A$ does possess a positive eigenvalue, $\lambda_1$, which is greater than or equal to the absolute value of any other eigenvalue.

Now, from (77) and (78).

$$a_{ij}^2 > 0 \quad \text{for all } i, j$$

(79)

According to a variation of Perron's theorem, which
states that if A is a matrix with all $a_{ij} > 0$, then A has a positive eigenvalue, $\rho$, of multiplicity one with $\rho > |\lambda_1|$ for all other eigenvalues $\lambda_i$ of A. Since $A^2$ has been shown to satisfy the condition for this more restricted form of the theorem, it is evident that $A^2$ has a maximum, positive, non-degenerate eigenvalue that is strictly greater than all the other eigenvalues of $A^2$. But if $\lambda_1, \lambda_2, \ldots, \lambda_d$ are the eigenvalues of A, then $\lambda_1^2, \lambda_2^2, \ldots, \lambda_d^2$ are the eigenvalues of $A^2$. Thus if $\lambda_1^2$ is the maximum eigenvalue for $A^2$, then $\lambda_1$ is the maximum eigenvalue for A, and there can be no other eigenvalue of A whose absolute value is equal to that of $\lambda_1$. That is, A does possess a real, positive, non-degenerate eigenvalue $\lambda_1$, such that $|\lambda_1| > |\lambda_i|$ for all $i \neq 1$.

Now that a real, positive $\lambda_1$ has been shown to exist, it is evident that this must be the same $\lambda_1$ obtained by Sherrill and Yang (ref. 10) for symmetric A. That is

$$\lambda_1 = 1 + mz + \text{higher order terms} \quad (80)$$

and all other eigenvalues are of order $z$ or higher. Following now the procedure used for symmetric lattices, one has

$$\f{SP}_{mxn} = \frac{1}{mn} \ln \left( \sum_{i=1}^{d} \lambda_i^m \right) \quad (81)$$

The quantity $\left( \sum_{i=1}^{d} \lambda_i^m \right)$ on the right hand side of (81) is evidently real since $\text{Tr}A^m = \sum_{i=1}^{d} \lambda_i^m$ is real and greater than one.
Now (81) can be rewritten as

\[(\beta P)_{mxn} = \frac{1}{mn} \ln \left( \frac{\lambda_1^n}{1 + \sum_{i=2}^{d} \frac{\lambda_i}{\lambda_1} n} \right) \]  

or \[(\beta P)_{mxn} = \frac{1}{m} \ln \lambda_1 + \frac{1}{mn} \ln \left[ 1 + \sum_{i=2}^{d} \frac{\lambda_i}{\lambda_1} n \right] \]

As for the symmetric case, the first term in (83) is \((\beta P)_{mx\infty}\) since the other terms go to zero as \(n\to\infty\); and since each ratio \(\lambda_1/\lambda_i\) in (83) is of order \(z\) or higher, the correction to the infinite lattice term is of order \(z^n\) or higher. This completes the proof of the theorem.

The triangular lattice is an example of a system with a non-symmetric transfer matrix. The theorem above is illustrated by table 5, which shows the coefficients of the powers of \(z\) in \((\beta P)_{mxn}\) for \(m=4\) and \(n=2-12\). (Note the agreement between the first \(n-1\) terms of the \(n^{th}\) row with the corresponding terms of the following row.)

Since the theorem also applies if \(n\) is held constant and \(m\) is varied, \((\beta P)_{mxn}\) will be identical to \((\beta P)_{m\infty n}\) for terms up to \(z^{m-1}\). This is illustrated for square, triangular, union-jack and hexagonal lattices in tables 6 thru 9 respectively, which give results for \((\beta P)_{m\infty}\) for \(m=2-9\) for square; triangular; and union-jack lattices,
Table 5
Coefficients of Series Expansion in \( z \) for \((\text{BP})_{mxn}\)
for a 4xn Triangular Lattice
\((m=3-12)\)

<table>
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<tr>
<th>( mn )</th>
<th>( z^1 )</th>
<th>( z^2 )</th>
<th>( z^3 )</th>
<th>( z^4 )</th>
<th>( z^5 )</th>
<th>( z^6 )</th>
<th>( z^7 )</th>
<th>( z^8 )</th>
<th>( z^9 )</th>
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Table 6

Coefficients of Series Expansion in $z$ for $(\beta P)^{m_{\infty}}$

for an $m_{\infty}$ Square Lattice

(m=2-9 and $m=\infty$)

<table>
<thead>
<tr>
<th>$m_{\infty}$</th>
<th>$z^1$</th>
<th>$z^2$</th>
<th>$z^3$</th>
<th>$z^4$</th>
<th>$z^5$</th>
<th>$z^6$</th>
<th>$z^7$</th>
<th>$z^8$</th>
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<td>10</td>
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Table 7
Coefficients of Series Expansion in $z$ for $(\beta P)_{m\infty}$
for an $m\infty$ Triangular Lattice

$$(m=2-9 \text{ and } m=\infty)$$

<table>
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<th>$z^4$</th>
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Table 8
Coefficients of Series Expansion in $z$ for $(8P)^{mx^\infty}$

for an $mx^\infty$ Union-Jack Lattice

$(m=2-9$ and $m=\infty$)

<table>
<thead>
<tr>
<th></th>
<th>$z^1$</th>
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<th>$z^3$</th>
<th>$z^4$</th>
<th>$z^5$</th>
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Table 9

Coefficients of Series Expansion in \( z \) for \((\beta P)_{m \rightarrow \infty}\)

for an \( m \rightarrow \infty \) Hexagonal Lattice

\((m=2-8 \text{ and } m=\infty)\)

<table>
<thead>
<tr>
<th>( m )</th>
<th>( z^1 )</th>
<th>( z^2 )</th>
<th>( z^3 )</th>
<th>( z^4 )</th>
<th>( z^5 )</th>
<th>( z^6 )</th>
<th>( z^7 )</th>
<th>( z^8 )</th>
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</thead>
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<td>( 4 \times \infty )</td>
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<td>-2</td>
<td>4.83</td>
<td>-13</td>
<td>46.2</td>
<td>-229.17</td>
<td>1233.14</td>
<td>-5652</td>
</tr>
<tr>
<td>( 6 \times \infty )</td>
<td>1</td>
<td>-2</td>
<td>6.33</td>
<td>-26</td>
<td>82.2</td>
<td>162.5</td>
<td>-6064.36</td>
<td>71878</td>
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<tr>
<td>( 8 \times \infty )</td>
<td>1</td>
<td>-2</td>
<td>6.33</td>
<td>-24.5</td>
<td>104.7</td>
<td>-649.92</td>
<td>6162.64</td>
<td>-63319.5</td>
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<tr>
<td>( \infty \times \infty )</td>
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<td>-2</td>
<td>6.33</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
and for $m=2,4,8$ for the hexagonal lattice. (only even values of $m$ and $n$ are treated for the hexagonal lattice, since the periodicity requirement cannot be imposed for odd values of $m$ and $n$.) According to the theorem, these results should be accurate for the infinite case up to terms of order $z^8$ for square, triangular and union-jack lattices. For the hexagonal lattice, since the results for the $8x8$ lattice are obtained from $Tr C^4$ (see equation 63), accuracy should be to order $z^3$.

The coefficients of powers of $z$ in the expansion for the number density are given in tables 10 thru 13. Since $\rho = z^{d/dz}(\phi P)$, it is obvious that these expressions will be accurate to the same power of $z$ as the corresponding expressions for $\phi P$.

**IV.5: The Virial Expansion**

For the two-dimensional lattice, the polynomials in $z$ for $\phi P$ and will contain many terms; hence the expression for $\phi P$ in terms of $\rho$ cannot be obtained directly. However, using LaGrange's theorem (see appendix D), it is possible to obtain the expression

$$\phi P = \sum_{n=1}^{\infty} \frac{\rho^n}{n!} \left[ (\frac{d}{dz})^{n-1} \frac{1}{\rho} \right]_{z=0}$$

which is the virial equation of state. Since $\frac{\rho}{z}$ has been obtained as a polynomial in $z$, derivatives of the inverse
Table 10

Coefficients of Series Expansion for $(\rho)_{mx\infty}$
for an $mx\infty$ Square Lattice

$m=2-9$

<table>
<thead>
<tr>
<th></th>
<th>$z^1$</th>
<th>$z^2$</th>
<th>$z^3$</th>
<th>$z^4$</th>
<th>$z^5$</th>
<th>$z^6$</th>
<th>$z^7$</th>
<th>$z^8$</th>
</tr>
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<tbody>
<tr>
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<td>-96</td>
<td>501</td>
<td>-2668</td>
<td>14407</td>
<td>-78592</td>
</tr>
<tr>
<td>3x∞</td>
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<td>-5</td>
<td>30</td>
<td>-193</td>
<td>1286</td>
<td>-8754</td>
<td>60460</td>
<td>-421985</td>
</tr>
<tr>
<td>4x∞</td>
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<td>-5</td>
<td>31</td>
<td>-208</td>
<td>1456</td>
<td>-10457</td>
<td>76392</td>
<td>-564848</td>
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<td>5x∞</td>
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<td>-5</td>
<td>31</td>
<td>-209</td>
<td>1475</td>
<td>-10715</td>
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<tr>
<td>6x∞</td>
<td>1</td>
<td>-5</td>
<td>31</td>
<td>-209</td>
<td>1476</td>
<td>-10738</td>
<td>79752</td>
<td>-601385</td>
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<tr>
<td>7x∞</td>
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<tr>
<td>8x∞</td>
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<td>1476</td>
<td>-10739</td>
<td>79780</td>
<td>-601904</td>
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<tr>
<td>9x∞</td>
<td>1</td>
<td>-5</td>
<td>31</td>
<td>-209</td>
<td>1476</td>
<td>-10739</td>
<td>79780</td>
<td>-601905</td>
</tr>
</tbody>
</table>
Table 11
Coefficients of Series Expansion for $(\phi)_{mx^\infty}$
for an $mx^\infty$ Triangular Lattice

$(m=2-9)$

<table>
<thead>
<tr>
<th></th>
<th>$z^1$</th>
<th>$z^2$</th>
<th>$z^3$</th>
<th>$z^4$</th>
<th>$z^5$</th>
<th>$z^6$</th>
<th>$z^7$</th>
<th>$z^8$</th>
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<tr>
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<td>40</td>
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<td>-14784</td>
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<td>$4x^\infty$</td>
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<td>-46780</td>
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<td>58</td>
<td>-519</td>
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<tr>
<td>$9x^\infty$</td>
<td>1</td>
<td>-7</td>
<td>58</td>
<td>-519</td>
<td>4856</td>
<td>-46780</td>
<td>460027</td>
<td>-4593647</td>
</tr>
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</table>
Table 12
Coefficients of Series Expansion for \((\rho)_{m \times \infty}\)
for an \(m \times \infty\) Union-Jack Lattice
\((m=2-9)\)

<table>
<thead>
<tr>
<th>(m\times\infty)</th>
<th>(z^1)</th>
<th>(z^2)</th>
<th>(z^3)</th>
<th>(z^4)</th>
<th>(z^5)</th>
<th>(z^6)</th>
<th>(z^7)</th>
<th>(z^8)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>40</td>
<td>-280</td>
<td>2016</td>
<td>-14784</td>
<td>109824</td>
<td>-823680</td>
</tr>
<tr>
<td>3(\times\infty)</td>
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<td>-9</td>
<td>90</td>
<td>-945</td>
<td>10206</td>
<td>-112266</td>
<td>1250964</td>
<td>-1407345</td>
</tr>
<tr>
<td>4(\times\infty)</td>
<td>1</td>
<td>-9</td>
<td>97</td>
<td>-1114</td>
<td>13211</td>
<td>-159798</td>
<td>1959273</td>
<td>-24262144</td>
</tr>
<tr>
<td>5(\times\infty)</td>
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<td>97</td>
<td>-1133</td>
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<tr>
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<td>97</td>
<td>-1133</td>
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<td>2245761</td>
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<tr>
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<td>-174579</td>
<td>2246154</td>
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<tr>
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<td>97</td>
<td>-1133</td>
<td>13856</td>
<td>-174579</td>
<td>2246154</td>
<td>-29351493</td>
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</tbody>
</table>
Table 13
Coefficients of Series Expansion for \((\varphi)_{\infty}^{\infty}\)
for an \(m\infty\) Hexagonal Lattice
(\(m=2-8\))

<table>
<thead>
<tr>
<th>(m)</th>
<th>(z^1)</th>
<th>(z^2)</th>
<th>(z^3)</th>
<th>(z^4)</th>
<th>(z^5)</th>
<th>(z^6)</th>
<th>(z^7)</th>
<th>(z^8)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2(x\infty)</td>
<td>1</td>
<td>-6</td>
<td>40</td>
<td>-280</td>
<td>2016</td>
<td>-14784</td>
<td>109824</td>
<td>-82360</td>
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<tr>
<td>4(x\infty)</td>
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<td>-52</td>
<td>231</td>
<td>-1375</td>
<td>8632</td>
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<tr>
<td>6(x\infty)</td>
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<td>523.5</td>
<td>-3899.5</td>
<td>43138.5</td>
<td>-506556</td>
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</table>
of this function can be calculated by computer and the coefficients of \( \rho^n \) in (84) can be calculated. It can be shown (see appendix E) that the virial expansion is accurate to the same number of terms as the expressions for the pressure and number density. The first eight virial coefficients for the square, triangular and union-jack lattices are given in tables 14 thru 16 respectively, and the first three coefficients for the hexagonal lattice are given in table 17.
Table 14

Virial Expansion
Square Lattice

<table>
<thead>
<tr>
<th>n</th>
<th>coefficient of $\varphi^n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>2.50</td>
</tr>
<tr>
<td>3</td>
<td>4.33</td>
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<tr>
<td>4</td>
<td>4.25</td>
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<td>5</td>
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<tr>
<td>6</td>
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<td>-113.26</td>
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<td>-527236.05</td>
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Table 15
Virial Expansion
Triangular Lattice

<table>
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<tr>
<th>n</th>
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<tbody>
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<td>2</td>
<td>3.5</td>
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<tr>
<td>3</td>
<td>10.34</td>
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<td>4</td>
<td>28.96</td>
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<td>81.76</td>
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<tr>
<td>n</td>
<td>coefficient of $p^n$</td>
</tr>
<tr>
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<td>-------------------</td>
</tr>
<tr>
<td>2</td>
<td>4.5</td>
</tr>
<tr>
<td>3</td>
<td>16.34</td>
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<tr>
<td>4</td>
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<tr>
<td>7</td>
<td>2612.84</td>
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<tr>
<td>8</td>
<td>-25665503.42</td>
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</table>
### Table 17

**Virial Expansion**

**Hexagonal Lattice**

<table>
<thead>
<tr>
<th>n</th>
<th>Coefficient of $\rho^n$</th>
</tr>
</thead>
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<td>2.00</td>
</tr>
<tr>
<td>3</td>
<td>3.33</td>
</tr>
</tbody>
</table>
In this thesis, a method to calculate algebraically the first few virial coefficients for hard particles on a lattice gas has been described. At the present time, it is inconvenient to process the transfer matrices for \( m > 9 \). However, it should be remembered that this limitation is due to practical rather than theoretical considerations. Three-dimensional lattices can also be treated by this method if sufficient storage on the computer can be obtained. With rapidly expanding computer technology, calculations for three-dimensional lattices are likely to be feasible in the very near future.

There are several other areas of related research suggested by this work which are either under current investigation or could be investigated at some future time:

(1) The difference in the \( z^n \) power between the \( (\beta P)_{m\times n} \) and \( (\beta P)_{m\times \infty} \) expansions can now be obtained exactly for square and triangular lattices for hard particles. This means that one additional term in the virial expansion can be obtained. Other lattices are under investigation.
(2) One can ask the question of whether or not this method can be extended to include lattices with arbitrary interaction. Expansions are possible at the present time for square and triangular lattices. Again, other lattices are under investigation.

(3) What is the region of convergence of the $\phi P$ expansion for the series in $z$ and for the series in $\rho$?

(4) Using the particle-hole symmetry for hard particles, an expansion in terms of $\frac{1}{z}$ can be obtained. What is the region of convergence of this series?

(5) The $\frac{1}{z}$ expansion can also be investigated for general interaction.

(6) The possibility of obtaining approximate calculations for much larger lattices than the ones treated here is now under investigation. By this method, some higher virial coefficients could be obtained approximately.

(7) One could examine in more detail the distribution of zeroes of the grand partition function in hopes of gaining more information about transitions.
BIBLIOGRAPHY


5. ibid


7. Argonne National Labs, Subroutine Library, Department of Applied Mathematics


9. Majid and Yang, private communication


12. ibid, p. 181

13. ibid, p. 178


15. ibid, p. 43


APPENDIX A

Derivation of Equation 19

Equation (17) can be rewritten as

\[ \sqrt{(1-uz)^2 + 4z} = 2e^{\beta P} - 1 - uz \]  \hspace{1cm} (85)

Squaring both sides, simplifying, and solving for \( z \), this becomes

\[ z = \frac{e^{\beta P} - e^{2\beta P}}{u-ue^{\beta P}-1} \]  \hspace{1cm} (86)

from which one can obtain

\[ 1 + uz = \frac{u-1-ue^{2\beta P}}{u-1-ue^{\beta P}} \]  \hspace{1cm} (87)

Now, if the radical in (18) is replaced by the expression on the right hand side of (85), the result is

\[ \varphi = \frac{e^{\beta P} - 1}{2e^{\beta P} - (1+uz)} \]  \hspace{1cm} (88)

Substitution from (87) into (88) yields
This can be written as a quadratic equation in $e^{BP}$:

$$u(1-\rho)e^{2BP} + [(1-2\rho) - 2u(1-\rho)]e^{BP} + (1-\rho)(u-1) = 0$$  \hspace{1cm} (90)$$

Applying the quadratic formula to solve for $e^{BP}$, one obtains

$$e^{BP} = 1 + \frac{2\rho - 1 \pm \sqrt{(2\rho - 1)^2 (1-u) - u}}{2u(1-\rho)} \hspace{1cm} (91)$$

Multiplying numerator and denominator of the second term in (91) by $2\rho - 1 \mp \sqrt{(2\rho - 1)^2 (1-u) + u}$, one obtains

$$e^{BP} = 1 + \frac{(2\rho - 1)^2 - [(2\rho - 1)^2 (1-u) + u]}{2u(1-\rho)(2\rho - 1) \pm 2u(1-\rho)\sqrt{(2\rho - 1)^2 (1-u) + u}} \hspace{1cm} (92)$$

After expanding and simplifying, (92) reduces to

$$e^{BP} = 1 + \frac{2\rho}{1-2\rho \pm \sqrt{(2\rho - 1)^2 (1-u) + u}} \hspace{1cm} (93)$$

Since $e^{BP} \geq 1$, the second term in (93) must be non-negative in order for the result to be physically reasonable.

Examine the denominator of that term when the negative sign
is used. In this case

\[
\text{DEN} = 1 - 2\varphi - \sqrt{(2\varphi - 1)^2(1-u)+u} = 1 - 2\varphi - \sqrt{(2\varphi - 1)^2 + 4\varphi(1-\varphi)} \tag{94}
\]

But the specific volume, \(v\), must be \(\geq 1\); so \(0 \leq \varphi \leq 1\) and \(1 - \varphi \geq 0\). Thus, for small \(\varphi\),

\[
\sqrt{(2\varphi - 1)^2 + 4\varphi(1-\varphi)} > 12\varphi - 1 \tag{95}
\]

which makes \(\text{DEN} < 0\). This will make \(P\) negative, from (93).

Thus it is seen that only the positive root yields physically reasonable results, so the negative root is discarded. The result is equation (19).
APPENDIX B

Proof that \( \frac{\partial P}{\partial v} < 0 \)
(one-dimensional lattice)

Substituting \( \rho = \frac{1}{v} \) into (19), one obtains

\[
P = \frac{1}{\beta} \ln \left[ 1 + \frac{2}{v} + \frac{2-v}{v} \sqrt{(2-v)(1-u)+uv} \right]
\]  

(96)

or, after some algebra,

\[
P = \frac{1}{\beta} \ln \left[ \frac{v + \sqrt{(2-v)^2(1-u)+uv^2}}{v-2 + \sqrt{(2-v)^2(1-u)+uv^2}} \right]
\]  

(97)

The derivative of \( P \) with respect to \( v \) is then

\[
\left( \frac{\partial P}{\partial v} \right)_\beta = \frac{2}{\beta} \cdot \frac{1}{(v+\sqrt{\ldots})(v-2+\sqrt{\ldots})} \cdot \frac{[1+(2-v)(u-1)+uv]}{\sqrt{\ldots}}
\]  

(98)

(where \( \sqrt{\ldots} = \sqrt{(2-v)^2(1-u)+uv^2} \))

or, simplifying,

\[
\left( \frac{\partial P}{\partial v} \right)_\beta = \frac{2}{\beta} \cdot \frac{v-2+\sqrt{\ldots} + 2u}{(v-2+\sqrt{\ldots})(v+\sqrt{\ldots})}
\]  

(99)
Now $\beta > 0$, so $-2/\beta < 0$. Also since $v > 0$, and since only the positive root is being used (see appendix A), the second and third terms in the denominator of the second fraction in (99) are positive. The third term in the numerator of the second fraction is also $> 0$, since $u = e^{-\beta \epsilon}$ is always $> 0$. Thus in order for $(\frac{\partial k}{\partial v})_{\beta}$ to be $< 0$, it remains to show that

$$v-2 + \sqrt{(2-v)^2(1-u)+uv^2} > 0 \quad (100)$$

If $v-2 > 0$, (100) is obviously satisfied. If $v-2 < 0$, then it is necessary to show that

$$\sqrt{(2-v)^2(1-u)+uv^2} > 2-v \quad (101)$$

Since both sides of (101) are now positive, (101) is equivalent to

$$(2-v)^2(1-u)+uv^2 > (2-v)^2 \quad (102)$$

But simplification of (102) yields $v > 1$, which is always required, so the proof is completed.
APPENDIX C

Derivation of Equation 74

It is desired to consolidate the results of (72) and (73) to obtain an expression for \((\beta P)_N\) which applies to all four types of lattices. The first two terms of (72) and (73) are identical, so it is necessary only to find an expression for the coefficient of \(z^3\) which will apply to both cases. In order to do this, assume the coefficient of \(z^3\) is a cubic expression in \(p\) of the form

\[ap^3 + bp^2 + cp + d\] \hspace{2cm} (96)

For the square lattice, substitution of \(p=4\) into (72) shows that the coefficient of \(z^3\) must be \(19/3\); and for the hexagonal lattice, substitution of \(p=3\) into (72) yields \(31/3\) for the coefficient of \(z^3\). Similarly, substitution of \(p=6\) and \(p=8\) into (73) yields \(58/3\) and \(97/3\) as the coefficients of \(z^3\) for the triangular and union-jack lattices respectively. Putting these results back into (96) one obtains

\[81a + 27b + 9c + 3d = 19 \quad \text{(hexagonal lattice)} \hspace{2cm} (97)\]
\[192a + 48b + 12c + 3d = 31 \quad \text{(square lattice)} \hspace{2cm} (98)\]
\[648a + 108b + 18c + 3d = 58 \quad \text{(triangular lattice)} \hspace{2cm} (99)\]
\[1536a + 192b + 24c + 3d = 97 \quad \text{(union-jack lattice)} \hspace{2cm} (100)\]
A simultaneous solution for $a$, $b$, $c$, and $d$ in equations (97) through (100) can be obtained via Cramer's rule. The results are: $a = 1/15$; $b = 21/30$; $c = 193/30$; $d = -127/15$.

Thus the coefficient of $z^2$ in (74) becomes

$$\frac{1}{30}(2p^3 - 21p^2 + 193p - 254)$$

(101)
APPENDIX D

Lagrange's Theorem

Consider the area A bounded by the contours C and \( c \) as shown in figure 18. Teixeira's theorem states that if:

1. \( f(z) \) is analytic in A and on C and \( c \)
2. \( \theta(z) \) is analytic within C
3. \( x \) is in A
4. \( \theta(z) = 0 \) at \( z = a \) (only root within C)
5. \( |\theta(z)| > |\theta(x)| \) for \( z \) on C
6. \( |\theta(z)| < |\theta(x)| \) for \( z \) on \( c \),

then

1. \( \theta(z) - \theta(x) \) has a single root at \( z = x \)

and

\[
f(x) = \frac{1}{2\pi i} \left[ \oint_C \frac{f(z)\theta'(z)dz}{\theta(z) - \theta(x)} - \oint_c \frac{f(z)\theta'(z)dz}{\theta(z) - \theta(x)} \right]
\]  \hspace{1cm} (102)

Notice that for \( z \) on C,

\[
\frac{1}{\theta(z) - \theta(x)} = \sum_{n=0}^{\infty} \frac{\theta^n(x)}{\theta^{n+1}(z)}
\]  \hspace{1cm} (103)

and for \( z \) on \( c \),
Figure 18
Diagram for Teixeira's Theorem
Then \( f(x) \) can be written in the form

\[
f(x) = \sum_{n=0}^{\infty} A_n \theta^n(x) + \sum_{n=1}^{\infty} B_n \theta^{-n}(x)
\]

(105)

where

\[
A_n = \frac{1}{2\pi i} \oint_C \frac{f(z)\theta'(z)dz}{\theta^{n+1}(z)}
\]

(106)

and

\[
B_n = \frac{1}{2\pi i} \oint_C f(z)\theta'(z)\theta^{n-1}(z)dz
\]

(107)

Now consider the special case where \( f(z) \) is analytic within \( C \). Then \( B_n = 0 \) and (105) becomes

\[
f(x) = \sum_{n=0}^{\infty} A_n \theta^n(x) = \sum_{n=0}^{\infty} \frac{1}{2\pi i} \oint_C \frac{f(z)\theta'(z)}{\theta^{n+1}(z)} \theta^n(x)
\]

(108)

Now from (106) one obtains
\[ A_0 = \frac{1}{2\pi i} \oint_C \frac{f(z)}{z-a} \, dz = f(a) \] (109)

Now, in order to evaluate \( A_n \) for \( n \neq 0 \), notice that
\[ -\frac{1}{n} e^{-nf'} + f \frac{\theta'}{e^{n+1}} = \frac{d}{dz} \left( f \frac{e^{-n}}{\theta} \right) \] (110)

So (106) becomes
\[ A_n = \frac{1}{2\pi i} \oint_C \, dz \left\{ -\frac{d}{dz} \left[ f \frac{e^{-n}}{\theta} \right] + \frac{1}{n} e^{-n} f' \right\} \] (111)

The integral of the first term is zero since \( f(z) \) and \( \theta(z) \) are analytic on \( C \), and (111) becomes
\[ A_n = \frac{1}{2\pi i n} \oint_C \, dz \frac{f^*(z)dz}{e^{n}(z)} \] (112)

Now let
\[ \theta(z) = \theta_1(z)(z-a) \] (113)

Then
Taking the \((n-1)\)st derivative of (109) with respect to \(a\), one obtains

\[
\left( \frac{d}{da} \right)^{n-1} f(a) = \frac{(n-1)!}{2\pi i} \oint_C \frac{f(z)dz}{(z-a)^n}
\]

Comparing (114) and (115), it can be seen that

\[
A_n = \frac{1}{n!} \left( \frac{d}{da} \right)^{n-1} \left[ \frac{f'(a)}{\theta_1^n(a)} \right]
\]

Substituting back into (108), one obtains

\[
f(x) = f(a) + \sum_{n=1}^{\infty} \frac{\theta^n(x)}{n!} \left( \frac{d}{da} \right)^{n-1} \left[ \frac{f'(a)}{\theta_1^n(a)} \right]
\]

This is Lagrange's theorem. For \(a=0\), (117) becomes

\[
f(x) = f(0) + \sum_{n=1}^{\infty} \frac{\theta^n(x)}{n!} \left( \frac{d}{da} \right)^{n-1} \left[ \frac{f'(a)}{\theta_1^n(a)} \right]_{a=0}
\]

Now, in order to obtain the desired expression, (84), for \(\Phi\) as a function of \(\rho\), it is necessary to make the following substitutions:

\[
x \rightarrow z
\]

\[
f(z) \rightarrow \Phi(z)
\]

\[
\theta(z) \rightarrow \rho(z)
\]

\[
a \rightarrow 0
\]
Then \( f(0) = 0 \) and

\[
\frac{1}{\theta_1(z)} = \frac{z}{\rho(z)} \quad (119)
\]

Also, \( \rho = z \frac{d}{dz}[\beta \rho(z)] \) implies that

\[
f'(z) = \frac{d}{dz}[\beta \rho(z)] = \frac{\rho}{z} \quad (120)
\]

So

\[
f'(a) \frac{1}{\theta_1^a(a)} = \left( \frac{a}{\rho} \right)^{n-1} \quad (121)
\]

and (118) becomes (after changing dummy variables)

\[
\beta \rho = \sum_{n=1}^{\infty} \frac{\rho^n}{n! \left[ \frac{d}{dz} \right] (z)_{z=0}^{n-1} \left( \frac{z}{\rho} \right)^{n-1}} \quad (122)
\]

which is the desired expression.
APPENDIX E

Proof that the Virial Expansion is Accurate to the same number of terms as the expressions for the Pressure and Number Density

The pressure and number density are of the form:

\[ \beta P = a_1 z + a_2 z^2 + a_3 z^3 + \ldots \]  \hspace{1cm} (123)

and

\[ \rho = \frac{d}{dz}(\beta P) = a_1 z + 2a_2 z^2 + 3a_3 z^3 + \ldots \] \hspace{1cm} (a_1 = 1) \hspace{1cm} (124)

It is desired to obtain \( \beta P \) as a polynomial in \( \rho \). That is

\[ \beta P = \sum_{n=1}^{\infty} a_n \rho^n = \sum_{n=1}^{\infty} b_n \rho^n = \sum_{n=1}^{\infty} b_n (\sum_{k=1}^{n} k a_k z^k)^n \] \hspace{1cm} (125)

Expansion of (125) yields

\[ a_1 z + a_2 z^2 + a_3 z^3 + \ldots = b_1 (a_1 z + 2a_2 z^2 + 3a_3 z^3 + \ldots) \]
\[ + b_2 (a_1 z + 2a_2 z^2 + 3a_3 z^3 + \ldots)^2 \]
\[ + b_3 (a_1 z + 2a_2 z^2 + 3a_3 z^3 + \ldots)^3 \]
\[ + \ldots \] \hspace{1cm} (126)
Equating coefficients of the same powers of $z$ on both sides of (126), one obtains,

\[ a_1 = b_1a_1 \quad (127) \]
\[ a_2 = 2b_1a_2 + b_2a_1^2 \quad (128) \]
\[ a_3 = 3b_1a_3 + 4b_2a_1a_2 + b_3a_1^3 \quad (129) \]
\[ \vdots \]
\[ a_n = nb_1a_n + \ldots + b_na_1^n \quad (130) \]

Equations (127) thru (130) can be solved to obtain $b_1, b_2, \ldots, b_n$ in terms of $a_1, a_2, \ldots, a_n$. But for any particular value of $n$, the expression for $b_n$ will contain only $a_1$ thru $a_n$.

So $\beta P(\rho)$ is accurate to the same number of terms as $\beta P(z)$ and $\rho(z)$. 