LANGEBERG, John Carl, 1944-
THE PROPERTIES, CONCENTRATIONS AND EFFECTS
OF VACANCIES IN HARD SPHERE AND RIGID DISK
SOLIDS.

Rice University, Ph.D., 1971
Chemistry, physical

University Microfilms, A XEROX Company, Ann Arbor, Michigan
RICE UNIVERSITY

The Properties, Concentrations and Effects of Vacancies in Hard Sphere and Rigid Disk Solids

by

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A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

Doctor of Philosophy

Thesis Director's signature:

Rox B. McAllan

Houston, Texas

December 1970
ACKNOWLEDGMENTS

I first wish to thank the late Dr. Zevi W. Salsburg whose guidance and encouragement made this thesis possible.

Dr. George V. Bettoney deserves a special note of thanks for many helpful discussions and suggestions and for assistance with the material presented in Chapter 2. To me he was my official, unofficial research advisor.

I thank Dr. Rex B. McLellan for many helpful discussions and suggestions, especially concerning the material in Chapter 3, and for becoming my research advisor after Dr. Salsburg's death.

The financial support of the Robert A. Welch Foundation, through Grants C-281 and C-055, and the National Science Foundation, through Grant GP-9240, is gratefully acknowledged.

Other people whom I wish to thank include: Dr. Howard Thames for helpful discussions concerning the operation of the Rice Computer, Larry Masinter for working out excellent programs for the evaluation of cell cluster integrals on the Burroughs Computer, Dr. Walter G. Rudd for helpful discussions, Dr. Bruce N. Miller for helpful discussions, and Mrs. Dorothy Butler for her time, patience and the great job she did in typing this thesis.
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CHAPTER 1. CELL CLUSTER ANALYSIS AND
THE HELMHOLTZ FREE ENERGY OF FORMATION OF VACANCIES IN HARD SPHERE SOLIDS

INTRODUCTION

In order to calculate the Helmholtz free energy of a \( v \)-dimensional
(\( v = 2 \) or 3) system of \( N \) rigid disks or spheres of diameter \( \sigma \) in a
volume \( V \) at temperature \( T \), it is useful to have an approximation scheme,
which if carried out to an order equivalent to the number of spheres
in the system, will converge to the exact free energy. Such a scheme
although not unique is provided by cell cluster theory. Eq. (1.1)
gives the Helmholtz free energy \( F_N^v \) for our system derived from cell
cluster theory.\(^1\)

\[
(1.1) \quad \frac{F_N^v}{NkT} \sim \nu \ln(\lambda/\sigma) - \nu \ln(\tau - 1) + C + D(\tau - 1) + E(\tau - 1)^2 + \cdots
\]
\[\tau + 1\]

Here \( k \) is Boltzmann's constant, \( \lambda = (h^2/2\pi mkT)^{\frac{1}{4}} \) is the mean thermal
de Broglie wavelength, \( \tau = V/V_0 \) is the reduced volume of a system of
volume \( V \), close-packed volume \( V_0 \), at temperature \( T \), and \( C, D \) and \( E \) are
appropriate numerical constants.

There is no proof that the sequence of approximations to the
Helmholtz free energy which arise when we go to higher and higher orders
in the cell cluster scheme converges. However, if we consider all of
its applications in recent years from which a convergence or non-
convergence might be implied, in all cases a reasonable convergence is
indicated.\(^2\) These applications include the analysis of a one-dimensional
system\(^1\), a two-dimensional triangular harmonic lattice\(^3\), the tunnel
model\(^4\), and the hard square solid\(^5\), as well as other results for two
and three-dimensional hard sphere systems.
In its lowest order approximation the cell cluster scheme makes an Einstein type approximation and considers individual spheres or disks in the system. The particle (sphere or disk) considered is allowed to freely move about its lattice site while all other particles in the system are rigidly fixed on their lattice sites. \( F_{1,1} \) the Helmholtz free energy associated with this single sphere or disk is calculated using Eq. (1.2).

\[
(1.2) \quad F_{1,1} = -kT \ln Q_{1,1}
\]

\( Q_{1,1} \) is the one-particle rigid disk or sphere partition function which is proportional to the \( \nu = 2 \) or 3 dimensional area in which the center of the movable disk or sphere is free to move. The boundaries of this volume are dictated by the fixed nearest neighbors of the movable disk or sphere. This volume is described most easily in the two dimensional case of a hexagonal lattice of rigid disks, here it corresponds to area \( A \) depicted in Fig. 2, Chapter 2. \( Q_{1,1} \) for this case is given by Eq. (1.3)

\[
(1.3) \quad Q_{1,1} = \lambda^{-2} \int_{A} \prod_{d=1}^{6} H(|\mathbf{r} - \mathbf{R}_d| - \sigma) \delta_{\mathbf{r}}
\]

Here \( \mathbf{r} \) is the position vector of the movable disk and \( \mathbf{R}_d \) is the position vector of nearest neighbor lattice site \( d \) with the lattice site of the movable disk taken as the origin. \(|\mathbf{r} - \mathbf{R}_d|\) is the distance between the centers of the movable disk and the fixed nearest neighbor disk on lattice site \( d \). \( \lambda = (h^2/2\pi mkT)^{1/2} \), the mean thermal de Broglie wavelength and \( H(|\mathbf{r} - \mathbf{R}_d| - \sigma) \) is the unit step function defined as follows
\( H(\frac{r - R_d}{\zeta} - \sigma) = \begin{cases} 
0 & \text{for } \frac{|r - R_d|}{\zeta} < \sigma \\
1 & \text{for } \frac{|r - R_d|}{\zeta} \geq \sigma .
\end{cases} \)

The Helmholtz free energy of the system under consideration can now be approximated by

\( F_N \approx N F_{1,1} = - N k T \ln Q_{1,1} . \)

This neglects interaction effects and surface effects. Surface effects can be neglected since they make a negligible contribution to the total result. When we consider a two dimensional system, the surface effects are proportional to \( N^{1/2} \); when we consider a three dimensional system, they are proportional to \( N^{2/3} \). Both of these numbers are negligible compared to \( N \) when \( N \) is very large as it is in the systems we consider. In order to take the interaction effects into account, larger clusters of movable, contiguous particles are considered. A particular cluster of particles will be denoted by \( \ell,t \) where \( \ell \) is the number of spheres or disks in the cluster and \( t \) denotes the particular geometrical arrangement of these particles. The calculation of \( Q_{\ell,t} \) for higher order clusters must consider the correlated motion between the particles comprising the cluster in contrast to that of the clusters of type \( 1,t \).

If we now consider the two particle cluster associated with a system of \( N \) rigid disks on a two dimensional hexagonal lattice, the Helmholtz free energy of this cluster can be approximated by

\( F_{2,1} \approx 2 F_{1,1} . \)
A correction factor $w_{2,1}$ accounting for the correlated motion in the cluster 2,1 which Eq. (1.6) does not consider is defined as

$$w_{2,1} = F_{2,1} - 2F_{1,1} = -kT\ell_n \ln \left( \frac{q_{2,1}}{(q_{1,1})^2} \right).$$

We also now define in general

$$w_{1,t} = F_{1,t}.$$  

We now introduce $Y_{2,1}$ where

$$Y_{2,1} = \exp \left[ -\frac{w_{2,1}}{kT} \right] = \frac{q_{2,1}}{(q_{1,1})^2}$$

and define in general

$$Q_{1,t} = Y_{1,t}.$$  

$Y_{2,1}$ is useful, as can be seen from Eq. (1.9), in that upon taking minus its natural logarithm we get the correction factor $w_{2,1}/kT$. Higher order $Y_{t,t}$'s will be useful in the same sense.

Continuing with our two particle cluster example we note that the cluster 2,1 can be placed on a trigonal, two dimensional array of lattice points in 3 N different ways. Therefore the second approximation to the Helmholtz free energy in the cell cluster scheme is given by Eq. (1.11)

$$F_N \approx NF_{1,1} + 3Nw_{2,1}.$$  

In general we can say that the Helmholtz free energy of our $v$-dimensional system can be written as $NF_{1,1}$ plus a series of $w_{t,t}$'s multiplied
by a number $g_{\ell,t}$ which gives the number of different ways the cluster $\ell,t$ can be placed on the lattice of the system divided by $N$. Hence, using Eq. (1.8), we write

\begin{equation}
F_N = N \sum_{\ell,t} g_{\ell,t} w_{\ell,t}
\end{equation}

If $\ell$ is summed from 1 to $N$ in Eq. (1.12) and $t$ is summed over all of its possible values for each value of $\ell$, then Eq. (1.12) is an exact expression for the Helmholtz free energy of our system.

We can now write an equation analogous to Eq. (1.12) for the cluster $\ell,t$

\begin{equation}
F_{\ell,t} = \sum_{i=1}^{\ell-1} \sum_{j=1}^{T_i} C_{i,j}(\ell,t) w_{i,j} + w_{\ell,t}
\end{equation}

in which $C_{i,j}(\ell,t)$ is the number of subclusters of type $i,j$ contained in the cluster $\ell,t$, and $w_{i,j}$, as before, is the correction factor for subcluster $i,j$. $T_i$ is the number of different geometrical arrangements of the $i$ particles in the subcluster contained in the cluster $\ell,t$. In the case $i=\ell$, $T_1=1$ corresponding to arrangement $t$; hence this term is simply $w_{\ell,t}$. For example $F_{3,11} = 3w_{1,2} + 2w_{2,4} + w_{3,11}$ (see Table 1-1 for the clusters corresponding to the $\ell,t$ designations). From Eq. (1.13) we see that the $w_{\ell,t}$ are defined by

\begin{equation}
w_{\ell,t} = F_{\ell,t} - \sum_{i=1}^{\ell-1} \sum_{j=1}^{T_i} C_{i,j}(\ell,t) w_{i,j}
\end{equation}
Upon using a general form of Eq. (1.9), we have

\[(1.15) \quad Y_{\mathcal{L},t} = \exp \left[ - \frac{w_{\mathcal{L},t}}{kT} \right]. \]

Now using Eq. (1.14), we find

\[(1.16) \quad Y_{\mathcal{L},t} = Q_{\mathcal{L},t} \prod_{i=1}^{\mathcal{L}-1} \prod_{j=1}^{T_i} Y_{i,j} \exp(-c_{i,j}(\mathcal{L},t)). \]

We can write the partition function corresponding to cluster \( \mathcal{L},t \) as

\[(1.17) \quad Q_{\mathcal{L},t} = Y_{\mathcal{L},t} \prod_{i=1}^{\mathcal{L}-1} \prod_{j=1}^{T_i} Y_{i,j} \exp(-c_{i,j}(\mathcal{L},t)). \]

The partition function for the entire system is

\[(1.18) \quad Q_N = \prod_{\mathcal{L}=1}^{N} \prod_{t} Q_{\mathcal{L},t}. \]

from Eqs. (1.12) and (1.15).

Now that the general cell cluster technique has been explained, it is important to understand how we define \( I_{\mathcal{L},t} \) the numerical value of cluster \( \mathcal{L},t \). \( I_{\mathcal{L},t} \) is represented by an integral over a volume defined by a product of unit step functions.

The form of \( I_{\mathcal{L},t} \) can be derived from the corresponding \( Q_{\mathcal{L},t} \) for the cluster. In the one particle cluster case in a system of rigid disks \( Q_{1,1} \) is given by

\[(1.19) \quad Q_{1,1} = \lambda^{-2} \int_{\mathcal{A}} 6 \prod_{d=1}^{6} H(\left| r - \mathcal{R}_d \right| - \sigma) \delta r \]

as previously explained.
When the lattice approaches its closest possible packing $|\vec{r} - \vec{R}_d|$ can be expanded as follows using a Taylor's series expansion

$$
(1.20) \quad |\vec{r} - \vec{R}_d| \approx |\vec{R}_d| + \left( -\frac{\vec{R}_d}{|\vec{R}_d|}\right) \cdot \vec{r} = a - \vec{w}_d \cdot \vec{r}
$$

where $a$ is the smallest distance between lattice sites and where

$$
(1.21) \quad \vec{w}_d = \frac{\vec{R}_d}{|\vec{R}_d|} = \frac{\vec{R}_d}{a}.
$$

The $\vec{w}_d$ are unit vectors pointing in the direction of the lattice points corresponding to the six, fixed, nearest neighbor disks with the origin taken as the lattice point of the movable disk. The $\vec{w}_d$ can be expressed in Cartesian coordinates.

$$
(1.22) \quad \vec{w}_d = C_{1d}\vec{i} + C_{2d}\vec{j}.
$$

The vectors $\vec{i}$ and $\vec{j}$ are the unit vectors along the $x$ and $y$ Cartesian axes respectively, and $C_{1d}$ and $C_{2d}$ are constants satisfying the condition

$$(C_{1d})^2 + (C_{2d})^2 = 1$$

since $\vec{w}_d$ is a unit vector. Similarly $\vec{r}$ can be expressed as

$$
(1.23) \quad \vec{r} = x\vec{i} + y\vec{j}
$$

where $x$ and $y$ are the small Cartesian components of the displacement of the movable disk off its lattice site. Using these Cartesian forms for $\vec{w}_d$ and $\vec{r}$, the argument of a representative unit step function becomes

$$
(1.24) \quad a - \sigma - \vec{w}_d \cdot \vec{r} = a - \sigma - C_{1d}x - C_{2d}y.
$$
If we now divide through by $a - \sigma$ and introduce the reduced coordinates

$$(1.25) \quad x' = x / \sigma t \quad y' = y / \sigma t$$

where

$$(1.26) \quad t = a / \sigma - 1$$

Eq. (1.24) becomes

$$(1.27) \quad 1 - \frac{w_4 - r}{a - \sigma} = 1 - C_1 d^x' - C_2 d^y' .$$

The transformation to reduced coordinates introduces a multiplicative factor of $o^{2^2}$ into Eq. (1.19).

An appropriate set of oblique coordinates $(z_1, z_2)$ given in Eq. (1.28)

$$(1.28) \quad z_1 = x' \quad z_2 = -(1/2)x' + (\sqrt{3}/2)y'$$

can now be introduced which reduce Eq. (1.27) to a form in which the coefficients of $z_1$ and $z_2$ are either 1, 0 or -1. Hence the arguments of the unit step functions now have the form

$$(1.29) \quad 1 - e_1 d^z_1 - e_2 d^z_2$$

where $e_1 d$ and $e_2 d$ have the values 1, 0 or -1. Upon transforming to oblique coordinates, the integral Eq. (1.19) must be multiplied by the appropriate Jacobian given by Eq. (1.30) to give the correct volume

$$(1.30) \quad J(z_1, z_2) = \begin{vmatrix} 1 & 0 \\ 1/\sqrt{3} & 2/\sqrt{3} \end{vmatrix} = 2/\sqrt{3} .$$
Eq. (1.19) now has the form

\begin{equation}
Q_{1,1} = 2/\sqrt{3} \lambda^{-2} \sigma^2 \int \prod_{d=1}^6 \mathcal{H}[1 - e_{1d}z_1 - e_{2d}z_2] \delta z_1 \delta z_2 .
\end{equation}

We define

\begin{equation}
I_{1,1} = \int \prod_{d=1}^6 \mathcal{H}[1 - e_{1d}z_1 - e_{2d}z_2] \delta z_1 \delta z_2 .
\end{equation}

An analogous procedure is followed for higher order clusters, the only difference being that we will have more unit step functions and more variables over which we are integrating. In any case, the resultant equations of lines in the arguments of the unit step functions, together with the requirement that each of these arguments be greater than or equal to zero, defines the volume of integration for the cluster under consideration.

By knowing the arguments of the unit step functions corresponding to a particular cluster, the numerical value of that cluster can be determined using a computer program developed by Rudd, Masinter, et al.

For all clusters other than those in the class 1,t, the corresponding $W_{\lambda,t}$'s and $Y_{\lambda,t}$'s are defined as functions of the ratios of $Q_{\lambda,t}$'s which reduce to functions of the ratios of the corresponding $I$'s. So it is really the $I$'s which we are interested in calculating, and they are listed in the following tables.

The three dimensional clusters in the F.C.C. and H.C.P. lattices are evaluated in a way analogous to that described above. The forms of the $w$'s and $z$'s as well as the Jacobians involved have been presented elsewhere in detail.\textsuperscript{8,9}
THE CALCULATION OF THE HELMHOLTZ FREE ENERGY OF VACANCIES

The cell cluster technique can be used to calculate the Helmholtz free energy of formation of vacancies in the two and three dimensional systems of rigid disks and spheres under consideration. In hard sphere systems such as these in which there is no potential other than that allowing no overlap of spheres, there are no interaction forces which would introduce a non-zero energy of formation of vacancies in the system. This means that what we are actually calculating here is $T$ times the entropy of formation of a vacancy in our system since $F = E - TS = -TS$ in these cases. An equation analogous to Eq. (1.12) needs to be derived which expresses the Helmholtz free energy of a system containing a mono- or divacancy.

A monovacancy is introduced into a perfect lattice system by moving a disk or sphere from the interior of the system to its surface. Here as before we neglect surface effects. The net change in the system is the introduction of a monovacancy and the increase in the number of lattice sites from $N$ to $N+1$. The introduction of a divacancy into the system is defined in an analogous way; it increases the number of lattice sites from $N$ to $N+2$.

The introduction of a vacancy into the lattice decreases the number of perfect lattice clusters in the system in two ways. It is decreased by the number of different ways the cluster under consideration can be made to lie on at least one of the lattice sites of the vacancy. Secondly, the number is decreased by the number of different ways the cluster under consideration can be placed on the lattice so that at least one of its component particles is adjacent to the vacancy. When a monovacancy is under consideration, the former number will be denoted by $\beta_{l,t}$ and the
latter by \( \gamma_{\lambda, t} \). For a divacancy the former number is \( \delta_{\lambda, t} \) and the latter \( \varepsilon_{\lambda, t} \). The Helmholtz free energy of a system of \( N \) lattice points into which a monovacancy has been introduced can be written as

\[
F_{N+1}^V = \sum_{\lambda, t} \left\{ [(N+1)g_{\lambda, t} - \beta_{\lambda, t} - \gamma_{\lambda, t}] \omega_{\lambda, t} + \gamma_{\lambda, t} \omega_{\lambda, t} \right\}
\]

where the first term under the summation sign is the perfect lattice clusters' contribution to the Helmholtz free energy and the last term is the contribution of those clusters adjacent to the monovacancy. \( \gamma_{\lambda, t} \) is the number of different ways the cluster \( \lambda, t \) which is adjacent to a vacancy can be placed on the lattice so that it is adjacent to the vacancy. An analogous equation can be written for a system containing a divacancy

\[
F_{N+2}^{2V} = \sum_{\lambda, t} \left\{ [(N+2)g_{\lambda, t} - \delta_{\lambda, t} - \varepsilon_{\lambda, t}] \omega_{\lambda, t} + \varepsilon_{\lambda, t} \omega_{\lambda, t} \right\}.
\]

We now define the Helmholtz free energy associated with the formation of a vacancy in our system as

\[
\Delta F^V = F_{N+1}^V - F_N.
\]

We now consider an application of this equation; the calculation of the Helmholtz free energy of formation of a monovacancy in a system of \( N \) rigid disks on a two dimensional hexagonal lattice. Using Eq. (1.12) and the notation given in Table 1-1, we can write out \( F_N \) considering up to and including three particle clusters as follows:

\[
F_N = NF_{1, 2} + 3N\omega_{2, 4} + 3N\omega_{3, 11} + 6N\omega_{3, 12} + 2N\omega_{3, 13}.
\]
Using Eq. (1.33) and Table 1-1, $F^V_{N+1}$ is as given in Eq. (1.37)

\begin{align*}
F^V_{N+1} &= (N-6)F_{1,2} + 6F_{1,1} + 3(N-9)w_{2,4} + 6w_{2,1} + 12w_{2,2} \\
&+ 6w_{2,3} + 3(N-11)w_{3,11} + 6w_{3,1} + 12w_{3,2} + 12w_{3,3} \\
&+ 6(N-12)w_{3,12} + 12w_{3,4} + 24w_{3,5} + 6w_{3,6} + 12w_{3,7} \\
&+ 6w_{3,8} + 2(N-11)w_{3,13} + 12w_{3,9} + 6w_{3,10} .
\end{align*}

We notice that $l,t$ is summed over only those values given in Table 1-1. There are more values of $l,t$ to be summed over in the defect containing lattice because there are more different types of clusters in this lattice than in the perfect lattice.

Subtracting Eq. (1.36) from Eq. (1.37) we get

\begin{align*}
\Delta F^V &= 6(F_{1,1} - F_{1,2}) + 6(w_{2,1} - w_{2,4}) + 12(w_{2,2} - w_{2,4}) \\
&+ 6(w_{2,3} - w_{2,4}) - 3w_{2,4} + 6(w_{3,1} - w_{3,11}) + 12(w_{3,2} - w_{3,11}) \\
&+ 12(w_{3,3} - w_{3,11}) - 3w_{3,11} + 12(w_{3,4} - w_{3,12}) + 24(w_{3,5} - w_{3,12}) \\
&+ 6(w_{3,6} - w_{3,12}) + 12(w_{3,7} - w_{3,12}) + 6(w_{3,8} - w_{3,12}) \\
&- 12w_{3,12} + 12(w_{3,9} - w_{3,13}) + 6(w_{3,10} - w_{3,13}) - 4w_{3,13} .
\end{align*}

The final numerical result for $\Delta F^V/kT$ is given in Table 1-2, where it is broken up into its component contributions from one, two, and three particle clusters.
COLUMN HEADINGS USED IN TABLE 1-1 AND FOLLOWING TABLES

$\beta_{\ell,t}$ - the number of different ways the perfect lattice cluster $\ell,t$
    can be placed on the lattice so that it lies on the lattice site
    of a monovacancy.

$\gamma_{\ell,t}$ - the number of different ways perfect lattice cluster $\ell,t$
    can be placed on the lattice so that at least one of its component disks
    or spheres is adjacent to a monovacancy.

$\gamma^v_{\ell,t}$ - the number of different ways the cluster $\ell,t$
    incorporating a monova-
    cancy can be placed adjacent to a monovacancy.

$\delta_{\ell,t}$ - the number of different ways the perfect lattice cluster $\ell,t$
    can be placed on the lattice so that it lies on at least one of the
    lattice sites of a divacancy.

$\epsilon_{\ell,t}$ - the number of different ways perfect lattice cluster $\ell,t$
    can be placed on the lattice so that at least one of its component disks
    or spheres is adjacent to a divacancy.

$\epsilon^v_{\ell,t}$ - the number of different ways the cluster $\ell,t$
    incorporating a mono-
    or divacancy can be placed adjacent to a divacancy.

$\epsilon_{\ell,t}$ - the number of different ways perfect lattice cluster $\ell,t$
    can be placed on the perfect lattice divided by the number of lattice
    sites $N$. 
TABLE 1-1

Rigid Disk Clusters in a Hexagonal Lattice

**Perfect Lattice Clusters**

<table>
<thead>
<tr>
<th>$\beta(\mathcal{L},t)$</th>
<th>Cluster Graph*</th>
<th>$\mathcal{L},t$</th>
<th>$I_{\mathcal{L},t}$</th>
<th>$w_{\mathcal{L},t}$</th>
<th>$e_{\mathcal{L},t}$</th>
<th>$Y_{\mathcal{L},t}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>1,2</td>
<td>3.00000000000</td>
<td>-1.098612289</td>
<td>1</td>
<td>6</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>2,4</td>
<td>9.04166666667</td>
<td>-0.004618946</td>
<td>3</td>
<td>24</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>3,11</td>
<td>26.9916666667</td>
<td>0.009546582</td>
<td>3</td>
<td>30</td>
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<td>18</td>
<td></td>
<td>3,12</td>
<td>27.255555556</td>
<td>-0.000182616</td>
<td>6</td>
<td>60</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>3,13</td>
<td>27.5583333333</td>
<td>-0.006611265</td>
<td>2</td>
<td>18</td>
</tr>
</tbody>
</table>

**Clusters Surrounding a Vacancy**

<table>
<thead>
<tr>
<th>Cluster Graph</th>
<th>$\mathcal{L},t$</th>
<th>$I_{\mathcal{L},t}$</th>
<th>$w_{\mathcal{L},t}$</th>
<th>$Y_{\mathcal{L},t}^V$</th>
</tr>
</thead>
<tbody>
<tr>
<td>•---•••</td>
<td>3,1</td>
<td>32.387500000</td>
<td>0.004232921</td>
<td>6</td>
</tr>
<tr>
<td>•---•</td>
<td>3,2</td>
<td>32.241666667</td>
<td>0.004877377</td>
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</tr>
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<td>0.005415991</td>
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<tr>
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<td>12</td>
</tr>
<tr>
<td>•---•</td>
<td>3,5</td>
<td>32.486111111</td>
<td>-0.002675658</td>
<td>24</td>
</tr>
<tr>
<td>Cluster Graph</td>
<td>$l,t$</td>
<td>$I_{l,t}$</td>
<td>$\frac{\psi_{l,t}}{kT}$</td>
<td>$\gamma_{l,t}$</td>
</tr>
<tr>
<td>---------------</td>
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<td>-------------</td>
</tr>
<tr>
<td><img src="image1" alt="Cluster 1" /></td>
<td>3,6</td>
<td>33.090277778</td>
<td>-0.002190976</td>
<td>6</td>
</tr>
<tr>
<td><img src="image2" alt="Cluster 2" /></td>
<td>3,7</td>
<td>39.790277778</td>
<td>-0.000907125</td>
<td>12</td>
</tr>
<tr>
<td><img src="image3" alt="Cluster 3" /></td>
<td>3,8</td>
<td>47.152777778</td>
<td>0.010881045</td>
<td>6</td>
</tr>
<tr>
<td><img src="image4" alt="Cluster 4" /></td>
<td>3,9</td>
<td>33.681944444</td>
<td>-0.011425957</td>
<td>12</td>
</tr>
<tr>
<td><img src="image5" alt="Cluster 5" /></td>
<td>3,10</td>
<td>41.240277778</td>
<td>-0.015223644</td>
<td>6</td>
</tr>
<tr>
<td><img src="image6" alt="Cluster 6" /></td>
<td>1,1</td>
<td>3.500000000</td>
<td>-1.252762968</td>
<td>6</td>
</tr>
<tr>
<td><img src="image7" alt="Cluster 7" /></td>
<td>2,1</td>
<td>10.791666667</td>
<td>-0.027398974</td>
<td>6</td>
</tr>
<tr>
<td><img src="image8" alt="Cluster 8" /></td>
<td>2,2</td>
<td>10.750000000</td>
<td>-0.023530497</td>
<td>12</td>
</tr>
<tr>
<td><img src="image9" alt="Cluster 9" /></td>
<td>2,3</td>
<td>12.916666667</td>
<td>-0.052992530</td>
<td>6</td>
</tr>
</tbody>
</table>

* denotes rigid disk
o denotes vacancy
TABLE 1-2

One, Two and Three Particle Contributions to $\Delta F^V/kT$

of a Monovacancy in a Lattice of Rigid Disks

<table>
<thead>
<tr>
<th>Order of Clusters</th>
<th>Contribution to $\Delta F^V/kT$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-0.924904079</td>
</tr>
<tr>
<td>2</td>
<td>-0.640003450</td>
</tr>
<tr>
<td>3</td>
<td>-0.276090357</td>
</tr>
<tr>
<td>1,2,3</td>
<td>-1.840997886</td>
</tr>
</tbody>
</table>
Figure 1: Areas accessible to the centers of the rigid disks in cluster 3,7 showing the boundary conditions approximated by straight lines as they are in the high density limit and expressing them in terms of oblique coordinates.
FIG. 1
Following an analogous procedure, we can calculate the Helmholtz free energies of formation of a monovacancy and a divacancy in the three-dimensional face-centered-cubic (F.C.C.) and hexagonal-close-packed (H.C.P.) lattices. First we consider the F.C.C. lattice. The F.C.C. lattice is formed by stacking two-dimensional hexagonal lattices above one another in the packing scheme abcabc⋯. Using Eq. (1.12) and the notation and values given in Table 1-3, we can write out \( F_N \) as follows

\[
(1.39) \quad F_N = NF_{1,3} + 6NW_{2,12} .
\]

The corresponding expression for \( F_{N+1}^V \) from Table 1-3 and Eq. (1.33) is

\[
(1.40) \quad F_{N+1}^V = (N - 12)F_{1,3} + 12F_{1,1} + (6N - 108)W_{2,12} + 48W_{2,1} + 24W_{2,2} + 24W_{2,3} + 12W_{2,4} .
\]

The Helmholtz free energy of formation of a monovacancy in the F.C.C. lattice is then found by subtracting Eq. (1.39) from Eq. (1.40) which gives Eq. (1.41).

\[
(1.41) \quad \Delta F^V = 12(F_{1,1} - F_{1,3}) + 48(W_{2,1} - W_{2,12}) + 24(W_{2,2} - W_{2,12}) + 24(W_{2,3} - W_{2,12}) + 12(W_{2,4} - W_{2,12}) .
\]

Again using Table 1-3, the Helmholtz free energy of a F.C.C. lattice of \( N \) spheres containing a divacancy is
Key to Notation Used in Cluster Graphs in Table 1-3 and Following Tables

- denotes sphere or disk in base plane
x " " 1 plane above base plane
o " " 1 plane below base plane
Δ " " 2 planes above base plane
□ " " 2 planes below base plane
+ " vacancy in base plane
- " " 1 plane below base plane
# " " 1 plane above base plane
TABLE 1-3

Rigid Sphere Clusters in the F.C.C. Lattice

**Perfect Lattice Clusters**

<table>
<thead>
<tr>
<th>$\varepsilon_{\ell,t}$</th>
<th>$\delta_{\ell,t}$</th>
<th>Cluster Graph</th>
<th>$\lambda_{\ell,t}$</th>
<th>$L_{\ell,t}$</th>
<th>$W_{\ell,t}/kT$</th>
<th>$E_{\ell,t}$</th>
<th>$U_{\ell,t}$</th>
<th>$S_{\ell,t}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>2</td>
<td>•</td>
<td>1,3</td>
<td>4.0000000000</td>
<td>-1.38629436</td>
<td>1</td>
<td>12</td>
<td>1</td>
</tr>
<tr>
<td>154</td>
<td>19</td>
<td>••</td>
<td>2,12</td>
<td>15.566666667</td>
<td>0.02745685</td>
<td>6</td>
<td>108</td>
<td>12</td>
</tr>
</tbody>
</table>

**Clusters Adjacent to Mono- and Divacancies**

<table>
<thead>
<tr>
<th>Cluster Graph</th>
<th>$\lambda_{\ell,t}$</th>
<th>$L_{\ell,t}$</th>
<th>$W_{\ell,t}/kT$</th>
<th>$U_{\ell,t}$</th>
<th>$S_{\ell,t}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1,1</td>
<td>4.3333333333</td>
<td>-1.46633707</td>
<td>12</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>1,2</td>
<td>5.0000000000</td>
<td>-1.60943791</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2,1</td>
<td>16.9972222222</td>
<td>0.01958150</td>
<td>48</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>2,2</td>
<td>16.8694444444</td>
<td>0.02712746</td>
<td>24</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>2,3</td>
<td>18.2597222222</td>
<td>0.02797647</td>
<td>24</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>2,4</td>
<td>17.0111111111</td>
<td>0.01876470</td>
<td>12</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>2,5</td>
<td>21.3000000000</td>
<td>0.01706791</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2,6</td>
<td>21.0333333333</td>
<td>0.02966650</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2,7</td>
<td>19.730555556</td>
<td>0.01356380</td>
<td>8</td>
<td></td>
</tr>
</tbody>
</table>
TABLE 1-3 (Continued)

<table>
<thead>
<tr>
<th>Cluster Graph</th>
<th>$l,t$</th>
<th>$I_{l,t}$</th>
<th>$w_{l,t}/kT$</th>
<th>$V_{l,t}$</th>
<th>$V_{l,t}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2,8</td>
<td>19.88611111</td>
<td>0.00571072</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2,9</td>
<td>19.86666667</td>
<td>0.00668999</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2,10</td>
<td>25.50000000</td>
<td>-0.01980263</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2,11</td>
<td>18.28194444</td>
<td>0.02676021</td>
<td>2</td>
<td></td>
</tr>
</tbody>
</table>

* Those values not listed are equal to zero

TABLE 1-4

One and Two Particle Cluster Contributions to $\Delta F/kT$ of a Monovacancy and a Divacancy in a Three Dimensional F.C.C. Lattice

**Monovacancy**

<table>
<thead>
<tr>
<th>Order of Cluster</th>
<th>Contribution to Respective $\Delta F/kT$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-0.96051248</td>
</tr>
<tr>
<td>2</td>
<td>-0.47775653</td>
</tr>
<tr>
<td>1 + 2</td>
<td>-1.43826901</td>
</tr>
</tbody>
</table>

**Divacancy**

<table>
<thead>
<tr>
<th>Order of Cluster</th>
<th>Contribution to Respective $\Delta F/kT$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-2.01317210</td>
</tr>
<tr>
<td>2</td>
<td>-1.22646828</td>
</tr>
<tr>
<td>1 + 2</td>
<td>-3.23964038</td>
</tr>
</tbody>
</table>
(1.42) \[ F_{N+2}^{2v} = (N - 18)F_{1,3} + 14F_{1,1} + 4F_{1,2} + (6N - 161)w_{2,12} \]
\[ + 60w_{2,1} + 24w_{2,2} + 20w_{2,3} + 14w_{2,4} + 8w_{2,5} + 8w_{2,6} \]
\[ + 8w_{2,7} + 4w_{2,8} + 4w_{2,9} + 2w_{2,10} + 2w_{2,11} . \]

The Helmholtz free energy of formation of a divacancy in the F.C.C. lattice is found by subtracting Eq. (1.39) from Eq. (1.42) which gives

(1.43) \[ \Delta F_{2v} = 14(F_{1,1} - F_{1,3}) + 4(F_{1,2} - F_{1,3}) + 60(w_{2,1} - w_{2,12}) \]
\[ + 24(w_{2,2} - w_{2,12}) + 20(w_{2,3} - w_{2,12}) + 14(w_{2,4} - w_{2,12}) \]
\[ + 8(w_{2,5} - w_{2,12}) + 8(w_{2,6} - w_{2,12}) + 8(w_{2,7} - w_{2,12}) \]
\[ + 4(w_{2,8} - w_{2,12}) + 4(w_{2,9} - w_{2,12}) + 2(w_{2,10} - w_{2,12}) \]
\[ + 2(w_{2,11} - w_{2,12}) - 7w_{2,12} . \]

The numerical values of \( \Delta F/V/kT \) and \( \Delta F_{2v}/kT \) are given in Table 1-4 where they are also broken up into one and two particle cluster contributions.

We now consider the H.C.P. lattice. This lattice is formed by stacking two-dimensional hexagonal lattices above one another in the packing scheme abab... Using Table 1-5 we first write out the expression for \( F_N \)

(1.44) \[ F_N = NF_{1,5} + 3NW_{2,41} + 3NW_{2,42} . \]
Using Table 1-5, \( F^V_{N+1} \) is given by

\[
(1.45) \quad F^V_{N+1} = (N - 12)F_{1,5} + 12F_{1,1} + (3N - 54)w_{2,41} + (3N - 54)w_{2,42} + 6w_{2,1} + 6w_{2,2} + 6w_{2,3} + 3w_{2,4} + 3w_{2,5} + 6w_{2,6} + 12w_{2,7} + 12w_{2,8} + 12w_{2,22} + 12w_{2,23} + 12w_{2,24} + 6w_{2,25} + 12w_{2,26}
\]

Subtracting Eq. (1.44) from Eq. (1.45) we find that for the H.C.P. lattice \( \Delta F^V \) is given by

\[
(1.46) \quad \Delta F^V = 12(F_{1,1} - F_{1,5}) + 6(w_{2,1} - w_{2,41}) + 6(w_{2,2} - w_{2,41}) + 6(w_{2,3} - w_{2,41}) + 3(w_{2,4} - w_{2,41}) + 3(w_{2,5} - w_{2,41}) + 6(w_{2,6} - w_{2,41}) + 12(w_{2,7} - w_{2,41}) + 12(w_{2,8} - w_{2,41}) + 12(w_{2,22} - w_{2,42}) + 12(w_{2,23} - w_{2,42}) + 12(w_{2,24} - w_{2,42}) + 6(w_{2,25} - w_{2,42}) + 12(w_{2,26} - w_{2,42})
\]

The H.C.P. lattice contains two types of divacancies, one with its two component monovacancies in the same plane -- the \((a,a)\) type, and one with them in different planes -- the \((a,b)\) type. Again using Table 1-5 and Eq. (1.34), we can write down \( F^V_{N+2} \) for the type \((a,a)\) divacancy as follows.
\[ F_{N+2}^{2 \nu}(a, a) = (N - 18) F_{1,5} + 14 F_{1,1} + F_{1,2} + 2 F_{1,3} + F_{1,4} \]
\[ + (3N - 81) w_{2,41} + 6 w_{2,1} + 6 w_{2,2} + 6 w_{2,3} + 2 w_{2,4} + 2 w_{2,5} \]
\[ + 4 w_{2,6} + 12 w_{2,7} + 16 w_{2,8} + 2 w_{2,9} + 2 w_{2,10} + 2 w_{2,11} + 2 w_{2,12} \]
\[ + 2 w_{2,13} + 4 w_{2,14} + 4 w_{2,15} + 4 w_{2,16} + (3N - 84) w_{2,42} \]
\[ + 12 w_{2,22} + 12 w_{2,23} + 12 w_{2,24} + 8 w_{2,25} + 16 w_{2,26} + 4 w_{2,27} \]
\[ + 4 w_{2,28} + 2 w_{2,29} + 2 w_{2,30} + 4 w_{2,31} + 2 w_{2,32}. \]

Subtracting Eq. (1.44) from Eq. (1.47) we obtain

\[ \Delta F_{N+2}^{2 \nu}(a, a) = 14(F_{1,1} - F_{1,5}) + (F_{1,2} - F_{1,5}) + 2(F_{1,3} - F_{1,5}) \]
\[ + (F_{1,4} - F_{1,5}) + 6(w_{2,1} - w_{2,41}) + 6(w_{2,2} - w_{2,41}) \]
\[ + 6(w_{2,3} - w_{2,41}) + 2(w_{2,4} - w_{2,41}) + 2(w_{2,5} - w_{2,41}) \]
\[ + 4(w_{2,6} - w_{2,41}) + 12(w_{2,7} - w_{2,41}) + 16(w_{2,8} - w_{2,41}) \]
\[ + 2(w_{2,9} - w_{2,41}) + 2(w_{2,10} - w_{2,41}) + 2(w_{2,11} - w_{2,41}) \]
\[ + 2(w_{2,12} - w_{2,41}) + 2(w_{2,13} - w_{2,41}) + 4(w_{2,14} - w_{2,41}) \]
\[ + 4(w_{2,15} - w_{2,41}) + 4(w_{2,16} - w_{2,41}) - 5 w_{2,41} \]


+ 12(w_{2,22} - w_{2,42}) + 12(w_{2,23} - w_{2,42}) + 12(w_{2,24} - w_{2,42})

+ 8(w_{2,25} - w_{2,42}) + 16(w_{2,26} - w_{2,42}) + 4(w_{2,27} - w_{2,42})

+ 4(w_{2,28} - w_{2,42}) + 2(w_{2,29} - w_{2,42}) + 2(w_{2,30} - w_{2,42})

+ 4(w_{2,31} - w_{2,42}) + 2(w_{2,32} - w_{2,42}) - 6w_{2,42}.

For a type (a,b) divacancy we have using Table 1-5

\[
F^{2\nu}_{N+2}(a,b) = (N - 18)F_{1,5} + 14F_{1,1} + 4F_{1,3} + (3N - 84)F_{2,41}
\]

+ 8w_{2,1} + 8w_{2,2} + 8w_{2,3} + 2w_{2,4} + 4w_{2,5} + 6w_{2,6} + 12w_{2,7}

+ 12w_{2,8} + 2w_{2,17} + 4w_{2,18} + 4w_{2,19} + 4w_{2,20} + 4w_{2,21}

+ (3N - 77)F_{2,42} + 12w_{2,22} + 8w_{2,23} + 16w_{2,24} + 6w_{2,25}

+ 2w_{2,33} + 4w_{2,34} + 4w_{2,35} + 4w_{2,36} + 4w_{2,37} + 4w_{2,38}

+ 4w_{2,39} + 4w_{2,40}.

Subtracting Eq. (1.44) from Eq. (1.49) we get
(1.50) \[ \Delta F^{2v}(a,b) = 14(F_{1,1} - F_{1,5}) + 4(F_{1,3} - F_{1,5}) + 8(w_{2,1} - w_{2,41}) \]

\[ + 8(w_{2,2} - w_{2,41}) + 8(w_{2,3} - w_{2,41}) + 2(w_{2,4} - w_{2,41}) \]

\[ + 4(w_{2,5} - w_{2,41}) + 6(w_{2,6} - w_{2,41}) + 12(w_{2,7} - w_{2,41}) \]

\[ + 12(w_{2,8} - w_{2,41}) + 2(w_{2,17} - w_{2,41}) + 4(w_{2,18} - w_{2,41}) \]

\[ + 4(w_{2,19} - w_{2,41}) + 4(w_{2,20} - w_{2,41}) + 4(w_{2,21} - w_{2,41}) \]

\[ -6w_{2,41} + 12(w_{2,22} - w_{2,42}) + 8(w_{2,23} - w_{2,42}) + 16(w_{2,24} - w_{2,42}) \]

\[ + 6(w_{2,25} - w_{2,42}) + 2(w_{2,33} - w_{2,42}) + 4(w_{2,34} - w_{2,42}) \]

\[ + 4(w_{2,35} - w_{2,42}) + 4(w_{2,36} - w_{2,42}) + 4(w_{2,37} - w_{2,42}) \]

\[ + 4(w_{2,38} - w_{2,42}) + 4(w_{2,39} - w_{2,42}) + 4(w_{2,40} - w_{2,42}) - 5w_{2,42} \].

The numerical values of Eqs. (1.46), (1.48) and (1.50) are given in Table 1-6 where they are broken up into one and two particle cluster contributions.
TABLE 1-5

Rigid Sphere Clusters in the H.C.P. Lattice

**Perfect Lattice Clusters**

<table>
<thead>
<tr>
<th>Cluster Graph</th>
<th>( l, t )</th>
<th>( I_{l,t} )</th>
<th>( w_{l,t}/kT )</th>
<th>( e_{l,t} )</th>
<th>( \gamma_{l,t} )</th>
<th>( \beta_{l,t} )</th>
<th>( \varepsilon_{l,t} )</th>
<th>( \delta_{l,t} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1,5</td>
<td>4.000000000</td>
<td>-1.38629436</td>
<td>1</td>
<td>12</td>
<td>1</td>
<td>18</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>2,41</td>
<td>15.566666667</td>
<td>0.02745685</td>
<td>3</td>
<td>54</td>
<td>6</td>
<td>76</td>
<td>78</td>
</tr>
<tr>
<td></td>
<td>2,42</td>
<td>15.57234226</td>
<td>0.02709231</td>
<td>3</td>
<td>54</td>
<td>6</td>
<td>78</td>
<td>72</td>
</tr>
</tbody>
</table>

**Clusters Surrounding Monovacancies and Divacancies in the H.C.P. Lattice**

<table>
<thead>
<tr>
<th>Cluster Graph</th>
<th>( l, t )</th>
<th>( I_{l,t} )</th>
<th>( w_{l,t}/kT )</th>
<th>( \gamma_{l,t} )</th>
<th>( e_{l,t} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1,1</td>
<td>4.333333333</td>
<td>-1.46633707</td>
<td>12</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>1,2</td>
<td>5.555555556</td>
<td>-1.71479843</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1,3</td>
<td>5.000000000</td>
<td>-1.60943791</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>1,4</td>
<td>4.777777778</td>
<td>-1.56397554</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2,1</td>
<td>17.011111111</td>
<td>0.01876470</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>2,2</td>
<td>16.994444444</td>
<td>0.01974494</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>2,3</td>
<td>17.000000000</td>
<td>0.01941809</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>2,4</td>
<td>18.72407407</td>
<td>0.00286406</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>2,5</td>
<td>17.91296291</td>
<td>0.04714950</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>Cluster Graph</td>
<td>$\ell, t$</td>
<td>$I_{\ell, t}$</td>
<td>$w_{\ell, t}/kT$</td>
<td>$\gamma_{\ell, t}$</td>
<td>$c_{\ell, t}^v$</td>
</tr>
<tr>
<td>--------------</td>
<td>----------</td>
<td>--------------</td>
<td>-----------------</td>
<td>-----------------</td>
<td>---------------</td>
</tr>
<tr>
<td>x x x</td>
<td>2, 6</td>
<td>18.25972222</td>
<td>0.02797647</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>x x</td>
<td>2, 7</td>
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TABLE 1-6

The Numerical Values of $\Delta F^V/kT$, $\Delta F^{2v}(a,a)/kT$ and $\Delta F^{2v}(a,b)/kT$
for the H.C.P. Lattice

$\Delta F^V/kT$

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<td>-1.45384179</td>
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$\Delta F^{2v}(a,a)/kT$

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<td>2</td>
<td>-1.29806343</td>
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<td>1 + 2</td>
<td>-3.37113367</td>
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$\Delta F^{2v}(a,b)/kT$

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DISCUSSION

The calculations presented in this chapter show that for rigid sphere systems near close packing monovacancies and divacancies are more stable in a H.C.P. lattice than in a F.C.C. lattice. The (a,b) type divacancy in the H.C.P. lattice is the most stable divacancy of those considered.

The Helmholtz free energy of formation of a vacancy in our system divided by kT is equal to minus the entropy of formation of the vacancy divided by k since the energy of formation of a vacancy is zero in our system. Therefore, we have actually been comparing the entropies of formation of the vacancies considered to determine their relative stabilities.

The entropy of formation of a monovacancy has been determined experimentally in many metals and in solid argon. For the metals this entropy lies in the range of about 1 to 2.4 k\textsuperscript{10}. For solid argon it is larger, with most of the determined values lying in the range of 4.0 to 6.0 k\textsuperscript{11}. Our calculated value is about 1.45 k.

The experimental values for the entropies of formation of divacancies in metals are roughly twice those for monovacancies.\textsuperscript{12} Our calculated values for this entropy vary from about 3.24 to 3.46 k.
REFERENCES


5. Ibid, pp. 75-76.


CHAPTER 2. THE CONCENTRATION OF VACANCIES IN A HARD SPHERE SOLID

INTRODUCTION

The equilibrium concentration of monovacancies and divacancies in a $v$-dimensional rigid sphere system at high density has previously been calculated in order to find their effect on the free energy of the system.\(^1\) The following asymptotic series gives the Helmholtz free energy per sphere in such a system

\[
(2.1) \quad \frac{F_N}{NkT} \sim \nu \ell n(\lambda/\sigma) - \nu \ell n(\tau-1) + C + D(\tau-1) + E(\tau-1)^2 + \cdots
\]

where $k$ is Boltzmann's constant, $\lambda = \left( \frac{\hbar}{2\pi m k T} \right)^{1/2}$ is the mean thermal de Broglie wavelength for spheres of mass $m$, $\sigma$ is the diameter of the spheres, $\tau = V/V_0$ is the reduced volume of a system of volume $V$ with close packed volume $V_0$, and $T$ is the absolute temperature. $C$, $D$ and $E$ are appropriate numerical constants and $N$ is the number of spheres in the system.\(^1\) It was shown that the concentration of monovacancies $m_1/M$, where $m_1$ is the number of monovacancies and $M$ is the number of lattice sites in the system, is proportional to the essentially singular function $\exp[-2/(\tau-1)]$. Hence $m_1/M$ vanishes faster than any positive power of $(\tau-1)$, and referring to the previous work\(^1\), we find that monovacancies as well as the less numerous polyvacancies can make no contribution to the Helmholtz free energy described by Eq. (2.1).

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In this chapter formal expressions for equilibrium constants between monovacancies and polyvacancies are calculated. No interaction forces are assumed to exist between the vacancies. It is shown that previous results did not include all terms of a given order. We find that curvature corrections which produce first order terms in the Helmholtz free energy produce zeroth order terms in the vacancy concentrations. These results do not change the previous results on the Helmholtz free energy but are important when the primary consideration is vacancy concentration. An example, the derivation of the concentration of monovacancies in a rigid disk solid in the limit of close packing considering one particle clusters, is given. Finally, the appropriate constants are evaluated, considering through two particle clusters, and expressions are written out for the concentration of mono- and divacancies in the F.C.C. and H.C.P. lattices in the close packed limit.
THEORY

If we let \( m_{j,\ell} \) represent the number of vacancies in our system that are made up of \( j \) adjacent monovacancies and that are arranged in a configuration denoted by \( \ell \), then the concentration of these vacancies is given by \( m_{j,\ell}/M \). \( M \) is the total number of lattice sites in the system and is given by

\[
(2.2) \quad M = N + \sum_{j=1}^{J} \sum_{\ell} j \ m_{j,\ell}
\]

where \( N \) is the total number of spheres on the lattice.

\( M - \sum_{j=1}^{J} \sum_{\ell} (j-1) \ m_{j,\ell} \) is the total number of spheres and vacancies which are to be distributed on the \( M \) lattice sites. The number of different ways in which these spheres and vacancies can be arranged on the \( M \) lattice sites is given by \( W \) where

\[
(2.3) \quad W = \left[ \frac{M - \sum_{j=1}^{J} (j-1) \ m_{j,\ell}}{\prod_{j=1}^{J} \ m_{j,\ell}!} \right] \prod_{\ell} \frac{(g_{j,\ell})^{m_{j,\ell}}}{m_{j,\ell}!}
\]

\( g_{j,\ell} \) is the number of different orientations of the \((j,\ell)\)th type of vacancy on the lattice. Upon taking the natural logarithm of Eq. (2.3), using Stirling's formula and carrying through the algebra, we find

\[
(2.4) \quad \ln W = \sum_{j=1}^{J} \sum_{\ell} \left[ m_{j,\ell} \ln g_{j,\ell} - m_{j,\ell} \ln \frac{m_{j,\ell}}{M} + m_{j,\ell} \right]
\]
This is the entropy of mixing of the spheres with all the different types of vacancies which comprise the system. We have used the assumption that the concentration of spheres is much greater than the sum of the concentrations of all the different types of vacancies. This means we can neglect interactions between vacancies and drop terms of order \( m_j \ell / M \).

We can now derive the concentrations of vacancies and polyvacancies in a solid of \( v \)-dimensional spheres.

The partition function can be written as

\[
(2.5) \quad Q = W\lambda^{-\nu N}(k_{0,1})^N(k_{1,1})^{m_1,1}(k_{2,1})^{m_2,1}\ldots
\]

which makes the assumption that there is no interaction between vacancies.

The partition function of a perfect lattice of \( N \) spheres is \( \lambda^{-\nu N}k_{0,1}^N \) where \( k_{0,1} \) is the effective free volume in which the center of a sphere completely surrounded by other spheres in the lattice can move about.

Hence \( k_{0,1} \) has the leading term of order \((a - \sigma)^{\nu} = \sigma^{\nu} t^{\nu}\), which is an approximation to the free volume and which has the right dimensionality.

The variable \( t = a/\sigma - 1 \), where \( a \) is the smallest distance between lattice sites (see Fig. 1). \( k_{0,1} \) has the form

\[
(2.6) \quad k_{0,1}(t) = \sigma^{\nu}C_{0,1}\left[t^{\nu} + b_1^{(0,1)}t^{\nu+1} + b_2^{(0,1)}t^{\nu+2} + \ldots\right]
\]

where \( C_{0,1}, b_1^{(0,1)} \) and \( b_2^{(0,1)} \) are constants depending on the value of \( \nu \) and the symmetry of the lattice.

The higher order \( K \)'s, the \( K_{j,\ell} \), are correction factors brought about through the introduction of a vacancy of type \((j, \ell)\) into the perfect lattice.
In two- or three-dimensional systems \( K_{1,1} \) has the form

\[
(2.7) \quad K_{1,1} = C_{1,1} [1 + B_1^{(1,1)} t + B_2^{(1,1)} t^2 + \ldots]
\]

where \( C_{1,1}, B_1^{(1,1)}, \) and \( B_2^{(1,1)} \) are again constants depending on the value of \( v \), and the symmetry of the lattice. Some \( K_j, \ell \)'s corresponding to higher order vacancies in \( v = 3 \) systems have the same form as \( K_{1,1} \): \( K_{2,1} \) is of this form in a \( v = 3 \) system. All other vacancies of a higher order than monovacancies in \( v = 2 \) or 3 systems are assumed to have \( K_j, \ell \)'s which are of the form of some convergent power series in \( t \). This assumption is made because we certainly do not expect the introduction of a very small concentration of higher order vacancies (such as divacancies into a \( v = 2 \) system or trivacancies into a \( v = 3 \) system) into a large rigid disk or sphere system in the limit of close packing to cause its thermodynamic properties to diverge.

We now use the above form of the partition function to calculate the concentration of \( (c,d) \) type vacancies by minimizing the free energy with respect to the concentration of the \( (c,d) \) type vacancies. We have

\[
(2.8) \quad - \frac{F}{kT} = \ell nQ = \ell nW - \nu \ell n\lambda + N \ell nK_{0,1} + \sum_{j, \ell} m_{j, \ell} \ell nK_{j, \ell}(t).
\]

The \( t \) variable and the \( m_{j, \ell} \) variables are connected by the two relations:

\[
(2.9) \quad \begin{align*}
(a) \quad V &= \alpha a^v M \\
(b) \quad M &= N + \sum_{j=1} \sum_{\ell} j m_{j, \ell}
\end{align*}
\]

where \( V \) is the volume of the system, \( M \) is the total number of lattice sites, and \( \alpha \) is a constant depending on the symmetry and dimensionality of the lattice. We now differentiate \( \ell nQ \) holding \( T \) and \( V \) constant, and set the result equal to zero:
\[
(2.10) \quad \frac{\partial \ln Q}{\partial m_{c,d}} \bigg|_{T,V} = \frac{\partial \ln W}{\partial m_{c,d}} + N \frac{\partial \ln K_{0,1}}{\partial t} \frac{\partial a}{\partial M} \frac{\partial a_{c,d}}{\partial M} + \ln k_{c,d} + \sum_{j=1}^{m} \sum_{l} \frac{\partial \ln K_{j,l}}{\partial t} \frac{\partial a}{\partial M} \frac{\partial a_{c,d}}{\partial M} = 0
\]

From Eq. (2.4) we have

\[
(2.11) \quad \frac{\partial \ln W}{\partial m_{c,d}} = -\ln \frac{m_{c,d}}{M} + \ln g_{c,d}
\]

Upon substitution into Eq. (2.10) and then solving for the number of 
(c,d)th type vacancies we have

\[
(2.12) \quad p_{c,d} = \frac{m_{c,d}}{M} = g_{c,d} K_{c,d} \exp \left[ \frac{\partial t}{\partial a} \frac{\partial a}{\partial M} \frac{\partial M}{\partial m_{c,d}} \right] \left( N \frac{\partial \ln K_{0,1}}{\partial t} + \sum_{j=1}^{m} \sum_{l} \frac{\partial \ln K_{j,l}}{\partial t} \frac{\partial a}{\partial M} \frac{\partial a_{c,d}}{\partial M} \right).
\]

Since

\[
(2.13) \quad (a) \quad \frac{\partial M}{\partial m_{c,d}} = c
\]

and

\[
(b) \quad g_{1,1} = 1
\]
\[ P_{c,d} = g_{c,d} \left[ \frac{K_{c,d}}{K_{1,1}^c} \right] P_{1,1}^c \]  

This gives us the expected form for the equilibrium constant

\[ \frac{P_{c,d}}{P_{1,1}^c} = K_{c,d} = g_{c,d} \frac{K_{c,d}}{K_{1,1}^c} \]

This expression requires only that the interaction between vacancies be small so that Eqs. (2.4) and (2.5) are valid.

As the above equation shows, the most important quantity in the theory of vacancies is the concentration of monovacancies. This is given by the equation

\[ P_{1,1} = K_{1,1} \exp \left[ \frac{\partial t}{\partial a} \frac{\partial a}{\partial M} \left( N \frac{\partial \ln K_{0,1}}{\partial t} + \sum_{j=1}^{m} \sum_{k=1}^{m} \frac{\partial \ln K_{j,k}}{\partial t} \right) \right]. \]

Using

\[ t = (a-v)/\sigma \quad \text{and} \quad V = aa^\gamma M \]

we have

\[ \frac{\partial t}{\partial a} \frac{\partial a}{\partial M} = \frac{1}{\sigma (\frac{a}{vM})} = \frac{(1 + t)}{vM}. \]

Hence,

\[ P_{1,1} = K_{1,1} \exp \left[ - \frac{(t + 1)}{vM} \left( N \frac{\partial \ln K_{0,1}}{\partial t} + \sum_{j=1}^{m} \sum_{k=1}^{m} \frac{\partial \ln K_{j,k}}{\partial t} \right) \right] \]
This can be simplified considerably if the summation can be dropped from the exponential. This is possible by our assumption that $m_j, \xi/r$ are very small and may be neglected in comparison to 1 if $\partial \ln K_j / \partial t$ is finite. This finiteness is given by our assumption of the form of the higher order $K_j, \ell$'s. The formula now becomes

$$P_{1,1} = K_{1,1} \exp \left[ - \frac{(t + 1)}{v} \frac{\partial \ln K_{0,1}}{\partial t} \right].$$

A more explicit expression for $P_{1,1}$ can be obtained through the use of Eq. (2.6) for $K_{0,1}$;

$$\frac{\partial \ln K_{0,1}}{\partial t} = \frac{v}{t} \left[ 1 + \frac{1}{v} B_1(0,1) t + \ldots \right],$$

hence

$$P_{1,1} = K_{1,1} \exp \left[ - \left( 1 + \frac{B_1(0,1)}{v} \right) \right] \exp \left[ - \frac{1}{t} \right]$$

to zeroth order in $t$.

Most theoretical and experimental results are expressed in terms of the reduced volume, $\tau = V/V_o$, where $V_o$ is the volume at close packing. In terms of the $t$ variable this is

$$\tau = \frac{a \gamma}{a_0 \gamma} = (1 + t)^\nu.$$

This can be solved for $1/t$ in terms of $(\tau - 1)$,

$$\frac{1}{t} = \frac{\nu}{(\tau - 1)} + \frac{\nu - 1}{2} + O(\tau - 1).$$
This gives for \( p_{1,1} \) in terms of \((\tau - 1)\),

\[
(2.24) \quad p_{1,1} = K_{1,1} \exp \left[ - \frac{v + \frac{1}{2} + \frac{B_1^{(0,1)}}{v}}{2} \right] \exp \left[ - \frac{v}{\tau - 1} \right].
\]

The argument of the exponential has been expanded only to zeroth order in \( t \) or \( \tau - 1 \), so the result is only good to zeroth order in \( t \). To be consistent all the \( K_{j,\ell} \)'s, except \( K_{0,1} \), only have to be calculated to zeroth order in \( t \).

In order to utilize previous calculations of curvature corrections\(^2\), namely of \( D \), we again need to consider the expression for the partition function of a perfect lattice

\[
(2.25) \quad Q = \lambda^{-\nu N} \frac{K_{0,1}^N}{N}.
\]

The explicit form of \( K_{0,1} \) is given by Eq. (2.6). Hence

\[
(2.26) \quad \ln Q = -\nu \ln \lambda + \nu \ln c + \nu \ln t + \ln c_{0,1}
\]

\[
+ N \ln (1 + B_1^{(0,1)} t + B_2^{(0,1)} t^2 + \cdots).
\]

It follows that

\[
(2.27) \quad \frac{F_N}{N K T} = -\frac{\ln Q}{N} = \nu \ln \lambda - \nu \ln c - \nu \ln t - B_1^{(0,1)} t - \ln c_{0,1}
\]

where we have expanded the last term in Eq. (2.26) to only first order.
We now need to express $t$ in terms of $\tau - 1$, which again can be done by solving Eq. (2.22). We find:

$$
(2.28) \quad t = \frac{1}{v} (\tau - 1) - \frac{1}{2} \frac{(v-1)}{v} (\tau - 1)^2 + \cdots.
$$

Hence

$$
(2.29) \quad \ln t = \ln v + \ln(\tau - 1) - \frac{(v-1)}{2v} (\tau - 1).
$$

Now Eq. (2.27) becomes

$$
(2.30) \quad \frac{F_N}{NKT} = v\ln \left(\frac{1}{\sigma}\right) - v\ln(\tau - 1) + (v\ln v - \ln c_{0,1})
$$

$$
+ \left[\frac{v - 1}{2} - \frac{B_1^{(0,1)}}{v}\right] (\tau - 1) + \cdots.
$$

Upon comparing this with Eq. (2.1) we find that

$$
(2.31) \quad (a) \quad C = (v\ln v - \ln c_{0,1}) , \quad (b) \quad D = \frac{v - 1}{2} - \frac{B_1^{(0,1)}}{v}.
$$

If we now consider the first part of the exponential in Eq. (2.24) we see

$$
(2.32) \quad -\frac{v + 1}{2} - \frac{B_1^{(0,1)}}{v} = (D - v).
$$

Hence Eq. (2.24) becomes

$$
(2.33) \quad P_{1,1} = K_{1,1} \exp[D - v] \exp\left[-\frac{v}{(\tau - 1)}\right].
$$
Figure 2: An arrangement of disks on a trigonal lattice showing a monovacancy. The figures A and B are, respectively, the one-particle cell cluster theory free volume available to the centers of the movable disks under consideration, surrounded by six and five fixed nearest neighbor disks.
AN EXAMPLE USING ONE PARTICLE CELL CLUSTER THEORY

The derived equations so far have not really assumed a specific approximation for their evaluation. In this section the one particle cell cluster model\(^2\) will be used to calculate some of those \(K_{j,k}'s\) to which we ascribed a definite form in the last section. The first application will be to a system of rigid disks on a trigonal lattice (see Fig. 2). The first term in the cell cluster expansion is the one particle (disk) cluster term. This term is the product of all possible single disk configuration integrals, one corresponding to each disk in the solid. Each configuration integral is calculated using the assumption that all of the other disks, aside from the one under consideration, are locked on their lattice sites. Each integral is then a measure of the free volume in which the center of the disk under consideration is free to move. In a hard disk solid containing monovacancies there are different types of one particle clusters as shown in Fig. 2.

If there are \(N\) disks and \(m_1\) monovacancies on the lattice, there are \(N-6m_1\) disks with configuration integral \(Q_0\), and \(6m_1\) with configuration integral \(Q_1\). The partition function for this system is therefore

\[
Q = \lambda^{-2N} W(N,m_1) Q_0^{N-6m_1} Q_1^{6m_1}. \tag{2.34}
\]

This can be put in the form

\[
Q = \lambda^{-2N} W(N,m_1) Q_0^N \left( \frac{Q_1}{Q_0} \right)^{6m_1}. \tag{2.35}
\]

Upon comparing Eq. (2.35) with Eq. (2.4) we find

\[
Q_0,1 = Q_0, \quad (b) \quad K_{1,1} = \left( \frac{Q_1}{Q_0} \right)^{6}. \tag{2.36}
\]
The configuration integrals \(Q_0\) and \(Q_1\) both approach zero as \(t^2\). Hence for this case, \(K_{0,1}\) has a leading term proportional to \(t^2\), and \(K_{1,1}\) has a leading term equal to a constant.

When we calculate the \(Q\)'s explicitly we find

\[
(2.37) \quad K_{0,1} = Q_0 = \sigma^2 t^2 \sqrt[3]{2} (1 + \frac{1}{9} t + \cdots)
\]

\[
(2.38) \quad K_{1,1} = \left(\frac{Q_1}{Q_0}\right)^6 = \left(\frac{7}{6}\right)^6 + \cdots
\]

It is evident from Eqs. (2.14) and (2.19) that in obtaining the leading asymptotic value for the concentration as \(t\) approaches zero, it is only necessary to obtain the leading term in the asymptotic expansion of \(K_{c,d'}\) where \(c,d \neq 0,1\). However, the exponential factor in the concentration expression involves the derivative of \(K_{0,1}\) with respect to \(t\). Therefore, it is necessary to obtain not only the leading term in the asymptotic expansion for \(K_{0,1}\), but the linear term as well. The linear term of \(K_{0,1}\) can be calculated by approximating the circular boundary of the free volume with a parabola, \(y = (1/2)x^2\), as shown in Fig. 3 or by expanding the exact equation for the collision circle boundary. When integrated, both of these give the first order correction term \(\frac{1}{9} t\). \(Q_1\) without curvature corrections is simply the area of the hexagon plus a triangle which has an area of \(\frac{1}{6}\) of that of the hexagon. Hence \(K_{1,1}\) is \(\left(\frac{7}{6}\right)^6\) dropping all curvature corrections.

This gives finally for the concentration of monovacancies

\[
(2.39) \quad p_{1,1} = \left(\frac{7}{6}\right)^6 \exp\left[-\frac{3}{2} - \frac{1}{18}\right] \exp\left[-\frac{2}{(\tau - 1)}\right]
\]
Figure 3: This figure represents one-twelfth of the free volume available to the center of a movable disk of diameter $\sigma$ in a perfect trigonal lattice of fixed disks. The lattice spacing is $\sigma(t+1)$. The shaded area is one-twelfth of the curvature correction for this disk or one-particle cluster.
This concentration can be compared with the previous result of Salsburg et al.\(^1\) which gave

\[
(2.40) \quad P_{1,1} = \left(\frac{7}{6}\right)^6 \exp \left[-\frac{2}{\tau - 1}\right].
\]

This concentration of monovacancies is larger than our result by a factor of about 4.7.

**THE CONCENTRATIONS OF MONO- AND DIVACANCIES IN THE F.C.C. AND H.C.P. LATTICES**

We now evaluate those \(K_{j,\ell}\)'s, considering through two particle clusters, necessary in the calculations of the concentrations of mono- and divacancies in the F.C.C. and H.C.P. lattices. We then write out the expressions for these concentrations utilizing values of \(D\) which have been calculated previously.\(^2\) The cluster notation used here is the same as that used in Chapter 1.

We first consider the F.C.C. lattice. Using Eqs. (1.41) and (1.15) we can write down an expression for \(K_{1,1}\).

\[
(2.41) \quad K_{1,1} = \begin{bmatrix}
Q_{1,1} & Y_{2,1}^{12} & Y_{2,2}^{48} & Y_{2,3}^{24} & Y_{2,4}^{12} \\
Q_{1,3} & Y_{1,108}^{24} & Y_{2,12}^{24}
\end{bmatrix}
\]

since the following relation holds

\[
(2.42) \quad \Delta F^V/kT = -\ell nK_{1,1}.
\]

Similarly by using Eqs. (1.43) and (1.15) we can derive the expression for \(K_{2,1}\)
\[(2.43)\]

\[
K_{2,1} = \begin{bmatrix}
Q_{1,1}^{14} Q_{1,2}^{60} y_{2,1}^{20} y_{2,2}^{14} y_{2,3}^{8} y_{2,4}^{8} y_{2,5}^{8} y_{2,6}^{8} y_{2,7}^{8} y_{2,8}^{8} y_{2,9}^{8} y_{2,10}^{8} y_{2,11}^{8} \\
Q_{1,3}^{18} y_{2,12}^{161} y_{2,12}^{161}
\end{bmatrix}.
\]

The numerical value of these \(K\)'s are given in Table 2-1.

The expressions for \(K_{1,1}, K_{2,1}^{(a,a)}\) and \(K_{2,1}^{(a,b)}\) corresponding to a mono-vacancy and the two types of divacancies in the H.C.P. lattice are derived from Eqs. \((1.46), (1.48)\) and \((1.50)\) respectively and are given by Eqs. \((2.44), (2.45)\) and \((2.46)\) respectively.

\[(2.44)\]

\[
K_{1,1} = \begin{bmatrix}
Q_{1,1}^{12} y_{2,1}^{6} y_{2,2}^{6} y_{2,3}^{6} y_{2,4}^{3} y_{2,5}^{6} y_{2,6}^{3} y_{2,7}^{12} y_{2,8}^{12} y_{2,22}^{12} y_{2,23}^{12} \\
Q_{1,5}^{54} y_{2,24}^{54} y_{2,41}^{54} y_{2,42}^{54}
\end{bmatrix}
\]

\[(2.45)\]

\[
K_{2,1}^{(a,a)} = \begin{bmatrix}
Q_{1,1}^{14} Q_{1,2}^{6} Q_{1,3}^{6} Q_{1,4}^{12} y_{2,1}^{6} y_{2,2}^{6} y_{2,3}^{6} y_{2,4}^{2} y_{2,5}^{2} y_{2,6}^{2} y_{2,7}^{12} y_{2,8}^{12} y_{2,22}^{12} y_{2,23}^{12} \\
Q_{1,5}^{61} y_{2,41}^{61} y_{2,42}^{64}
\end{bmatrix}
\]

\[\times y_{2,10}^{2} y_{2,11}^{2} y_{2,12}^{2} y_{2,13}^{2} y_{2,14}^{4} y_{2,15}^{4} y_{2,16}^{4} y_{2,17}^{12} y_{2,22}^{12} y_{2,23}^{12} y_{2,24}^{12} y_{2,25}^{8} \]

\[\times y_{2,26}^{16} y_{2,27}^{4} y_{2,28}^{2} y_{2,29}^{2} y_{2,30}^{4} y_{2,31}^{4} y_{2,32}^{2} \]
(2.46) \( K_{2,1}^{(a,b)} = 
\begin{bmatrix}
Q_{1,1}^{14} & Q_{1,3}^{4} & Y_{2,1}^{8} & Y_{2,2}^{8} & Y_{2,3}^{8} & Y_{2,4}^{2} & Y_{2,5}^{4} & Y_{2,6}^{6} & Y_{2,7}^{12} & Y_{2,8}^{12} & Y_{2,18}^{4} & Y_{2,19}^{4} & Y_{2,20}^{4} & Y_{2,21}^{4} \\
Q_{1,5}^{18} & Y_{2,41}^{84} & Y_{2,42}^{77}
\end{bmatrix} 
\times Y_{2,22}^{12} Y_{2,23}^{8} Y_{2,24}^{16} Y_{2,25}^{c} Y_{2,26}^{c} Y_{2,27}^{c} Y_{2,28}^{c} Y_{2,29}^{c} Y_{2,30}^{c} Y_{2,31}^{c} Y_{2,32}^{c} Y_{2,33}^{c} Y_{2,34}^{c} Y_{2,35}^{c} Y_{2,36}^{c} Y_{2,37}^{c} Y_{2,38}^{c} Y_{2,39}^{c} Y_{2,40}^{c}
\)

The numerical values for the constants \( K_{1,1} \), \( K_{2,1}^{(a,a)} \), and \( K_{2,1}^{(a,b)} \) are given in Table 2-1.

Using the values of \( D \) calculated previously\(^2\), Eqs. (2.14) and (2.33), and values of \( g_{c,d} \) given in Tables 1-3 and 1-5, we can now write out expressions for the concentrations of the above considered types of vacancies in the F.C.C. and H.C.P. systems. These expressions are given in Table 2-2.
TABLE 2-1

<table>
<thead>
<tr>
<th>Type of Lattice</th>
<th>Constant</th>
<th>Numerical Value of Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>F.C.C.</td>
<td>$K_{1,1}$</td>
<td>4.2133962</td>
</tr>
<tr>
<td></td>
<td>$K_{2,1}$</td>
<td>25.5245410</td>
</tr>
<tr>
<td>H.C.P.</td>
<td>$K_{1,1}$</td>
<td>4.2795240</td>
</tr>
<tr>
<td></td>
<td>$K_{2,1}(a,a)$</td>
<td>29.1115112</td>
</tr>
<tr>
<td></td>
<td>$K_{2,1}(a,b)$</td>
<td>31.8807899</td>
</tr>
</tbody>
</table>

TABLE 2-2

<table>
<thead>
<tr>
<th>Type of Lattice</th>
<th>$P_{c,d}$</th>
<th>Expression for $P_{c,d}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>F.C.C.</td>
<td>$P_{1,1}$</td>
<td>$0.366507 \exp\left(-\frac{3}{\tau - 1}\right)$</td>
</tr>
<tr>
<td></td>
<td>$P_{2,1}$</td>
<td>$1.158803 \exp\left(-\frac{6}{\tau - 1}\right)$</td>
</tr>
<tr>
<td>H.C.P.</td>
<td>$P_{1,1}$</td>
<td>$0.366306 \exp\left(-\frac{3}{\tau - 1}\right)$</td>
</tr>
<tr>
<td></td>
<td>$P_{2,1}(a,a)$</td>
<td>$0.639859 \exp\left(-\frac{6}{\tau - 1}\right)$</td>
</tr>
<tr>
<td></td>
<td>$P_{2,2}(a,b)$</td>
<td>$0.700726 \exp\left(-\frac{6}{\tau - 1}\right)$</td>
</tr>
</tbody>
</table>
DISCUSSION

In this paper we calculated the concentrations of vacancies in hard sphere systems. Particular care was taken in making expansions which provided slightly different results than previously reported. In particular, curvature corrections, which appear only to first order in the free energy expansion, appear to zeroth order in the concentrations of the vacancies. They produce about a 5% change in concentrations for hard disks. The surprising thing about this is that at high density where all available volumes are very small and are bounded effectively by planes, the curvature corrections are still present to zeroth order. We don't really have a physical intuition as to why this strange behavior occurs.

The numerical calculations of this chapter show that for a system of rigid spheres near close packing the concentration of mono- and di-vacancies is greater in the H.C.P. lattice than in the F.C.C. lattice.

Since solid argon, which has an F.C.C. crystal structure, is probably the closest simulation to our system in nature, we first compare our theoretically derived concentrations with those found experimentally in solid argon. The experimentally determined monovacancy concentrations \( (p_{1,1}) \) in the temperature range of 60 to 83.78°K (argon's triple point) range from a low of about \( 2.5 \times 10^{-5} \) at 60°K to a high of about \( 2 \times 10^{-3} \) at 83.78°K. Our derived equation giving the concentration of monovacancies in a F.C.C. crystal lattice gives concentrations in this range for values of \( \tau \) which correspond to values of \( \ell / \sigma \) in the range of 1.10 at 60°K to 1.16 at 83.78°K. Using the molar volumes of argon at these
two temperatures, we can calculate values for \( \sigma \), the effective diameter of an argon atom. We find that \( \sigma = 3.47 \) Å at 60°K and \( \sigma = 3.33 \) at 83.78°K. Both of these values agree with experimental values for argon's atomic diameter.\(^5\)

No experimental data on the concentrations of divacancies \( (P_{2,1}) \) for solid argon was found; it is calculated to be about \( 2.6 \times 10^{-5} \) from our equation. However, such experimental data is available for many metals. Using the experimentally determined concentrations of mono- and divacancies in the F.C.C. metals, copper, silver and gold at their melting point temperatures\(^6\), we calculated the effective diameters of these metallic atoms.\(^7\) From the experimental data we found that concentrations of mono- and divacancies are generally about an order of magnitude smaller in these metals at their melting points than in solid argon at its triple point. The calculated diameters of the metallic atoms turn out to be small usually by about a factor of 2. Hence, the agreement of our equations is not nearly as good with these metallic systems as it is with solid argon.
REFERENCES


CHAPTER 3. THE EFFECT OF MONOVACANCIES
ON THE ELASTIC PROPERTIES OF RIGID DISK SOLIDS

INTRODUCTION

There are two possible methods utilizing cell cluster theory to calculate the elastic stiffness constants of a rigid disk crystal in the high density limit. One method\(^1\) involves the equating of coefficients in two different expressions for the Helmholtz free energy of the system; one expression being the phenomenological Helmholtz free energy involving the system's strains and elastic stiffness constants, and the other being an analogous expression derived from the cell cluster theory expansion of the partition function of the system, where the numerical values of the clusters are expressed as functions of the strains. To carry out the evaluation of all the elastic constants using this method involves the evaluation of the same clusters in different strain fields as a function of the strains involved. This means the evaluation of many clusters is necessary; a tedious job, especially when two or three particle clusters are considered.

The method used in this paper is simpler in principle in that it first involves evaluating the second derivative of the Helmholtz free energy, again expressed in terms of cell cluster theory, with respect to the strains, and then setting the strains equal to zero (see Eq. (3.1)).

\[
(3.1) \quad c_{ijkl} = \frac{1}{A} \left( \frac{\partial^2 F}{\partial \eta_{ij} \partial \eta_{kl}} \right)_{\eta = 0}
\]

A is the area to which our system is confined.

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Although some of the integrals involved in this derivation are complicated, once they are evaluated, most are repeated in the evaluation of other constants. The obvious advantage of this method is that the actual evaluation of clusters as a function of particular strains is not necessary.

The consideration of a small concentration of monovacancies in the lattice involves the development of a slightly different treatment, however, many aspects of the perfect lattice treatment are used unchanged or only slightly modified.

We hope to extend the mathematical treatment developed in this paper to find the effect of monovacancies on the elastic stiffness constants of the three-dimensional face-centered-cubic and hexagonal-close-packed lattices of hard spheres.

GENERAL THEORY

We first examine an unstrained two-dimensional, hexagonal lattice of \( N \) identical rigid disks whose centers are confined to an area \( A \) in a plane. Let \( A \) be covered by a regular hexagonal array of \( M \) points, where the integer \( M \) is limited to the values

\[
N \leq M \leq N_{\text{max}};
\]

\( N_{\text{max}} \) is the maximum number of disks which may be placed with their centers in \( A \) in a regular hexagonal array.\(^2\)
Using cell cluster theory we can approximate the free energy of the system of disks described above by

\[ F_N \approx N F_{(1,1)} \]  \hspace{1cm} \text{(3.5)}

where

\[ F_{(1,1)} = - kT \ln Q_{(1,1)} \]  \hspace{1cm} \text{(3.6)}

\( F_{(1,1)} \) represents the Helmholtz free energy of a movable disk in a lattice of \( N-1 \) disks fixed on their lattice sites. The free area available to such a disk can be realized by considering only its six fixed neighbors, see Fig. 4. \( Q_{(1,1)} \) is the partition function for this movable disk and is given by

\[ Q_{(1,1)} = (\lambda^2)^{-1} \int_\mathbb{R}^{6} H(|r-R_d| - \sigma) \, dr \]  \hspace{1cm} \text{(3.7)}

Here \( r \) is the position vector of the center of the movable disk and \( R_d \) is the position vector of lattice site \( d \) with the lattice site of the movable disk taken as the origin. Hence, \(|r-R_d|\) is the magnitude of the distance from the center of the movable disk to lattice site \( d \).

Therefore, the canonical partition function for the \( N \) disks in area \( A \) at temperature \( T \) becomes

\[ Q_N \approx \left[ Q_{(1,1)}^{2N} \right]^{N} = (\lambda^{2N})^{-1} \left[ \int_\mathbb{R}^{6} H(|r-R_d| - \sigma) \, dr \right]^{N} \]  \hspace{1cm} \text{(3.8)}

Hence

\[ F_N \approx N kT \ln(\lambda^2) - N kT \ln \left[ \int_\mathbb{R}^{6} H(|r-R_d| - \sigma) \, dx \, dy \right] \]  \hspace{1cm} \text{(3.9)}
For such a system the Helmholtz free energy $F_N(T,V)$ is given by

$$F_N(T,V) = -kT \ln Q_N$$

where $Q_N$ is the canonical partition function which is given by

$$Q_N = (\lambda^{2N})^{-1} \int \cdots \int_A \prod_{i<j=1}^N H(ij) \, dr_1 \cdots dr_N$$

where

$$\lambda = (\hbar^2/2\pi mkT)^{\frac{1}{2}},$$

the mean thermal de Broglie wavelength,

$$H(ij) = H(\left| r_{ij} \right| - \sigma)$$

and

$$H(ij) = \begin{cases} 
0 & \left| r_{ij} \right| < \sigma \\
1 & \left| r_{ij} \right| \geq \sigma 
\end{cases}$$

$H(ij)$ is the unit step function, and

$$dr_i = dx_i dy_i.$$

Because each disk is confined to the area closely surrounding its lattice site by its neighbors as the closest possible packing is approached, there are $N!$ indistinguishable ways of interchanging the disks on the lattice sites; therefore the customary $N!$ in the denominator of Eq. (3.3) has been eliminated.

$|r_{ij}|$ denotes the distance between the centers of disks $i$ and $j$, $k$ is Boltzmann's constant, $\hbar$ is Planck's constant, $\sigma$ is the diameter of the disks, and $m$ is the mass of a disk.
Figure 4: An arrangement of disks on a hexagonal lattice. The figure A represents the one-particle cell cluster theory free volume available to the center of a disk surrounded by six fixed nearest neighbor disks numbered according to a convention which we will use throughout this paper. The vectors \( \mathbf{R}_2 \) and \( \mathbf{r} \) are respectively a lattice vector locating the lattice site of disk 2, and the position vector of the movable disk, both of which use the lattice site of the movable disk as their origin.
If we now introduce the effect of a strain upon the lattice, it is expedient to define a new set of strain coordinates \((v, w)\), corresponding to \((x, y)\) in the unstrained lattice. We also introduce a set of vectors \(\{\mathbf{a}_1, \mathbf{a}_2\}\) to describe the strained lattice corresponding to \((i, j)\), which we use for the unstrained lattice. \(\{\mathbf{a}_1, \mathbf{a}_2\}\) are not unit vectors, nor are they orthogonal, see Fig. 5. We define \(\{\mathbf{a}_1, \mathbf{a}_2\}\) such that in the limit of zero strain they become equal to \(\{i, j\}\), that is

\[
\lim_{\eta \rightarrow 0} \{\mathbf{a}_1, \mathbf{a}_2\} = \{i, j\}
\]

where \(\eta\) represents the two-dimensional strain tensor. It therefore follows that

\[
\lim_{\eta \rightarrow 0}(v, w) = (x, y)
\]

Similarly if we denote the coordinates of lattice site \(i\) by \((V_i, W_i)\) in the strained lattice, and by \((X_i, Y_i)\) in the unstrained lattice, it follows that

\[
\lim_{\eta \rightarrow 0}(V_i, W_i) = (X_i, Y_i)
\]

The isothermal elastic constants are given by

\[
C_{ijkl} = \frac{1}{A} \left( \frac{\alpha^2 F_N}{\beta \eta_{k\ell} \eta_{ij}} \right)_{\eta = 0} = \frac{2V}{3Na^2} \left( \frac{\beta^2 F_N}{\beta \eta_{p} \eta_{q}} \right)_{\eta = 0}
\]

where we define \(\eta_{ij}\) by

\[
\eta_{ij} = \frac{1}{2} (\mathbf{a}_i \cdot \mathbf{a}_j - \delta_{ij})
\]
Figure 5: The unit vectors $\hat{i}$ and $\hat{j}$ and the corresponding strained system vectors $a_1$ and $a_2$. 
Finally we have replaced the double subscripts of the strains by single subscripts using the well-known convention

(3.15) \quad (11) \leftrightarrow 1 \quad (22) \leftrightarrow 2 \quad (12) = (21) \leftrightarrow 6

so that p,q = 1,2 or 6 for two dimensions. This notation will be used whenever it is convenient to do so.

From Eq.(3.13) it is clear that we need to express $F_N$ as a function of the strains. In order to do this, we first express the Helmholtz free energy Eq.(3.9) in terms of strained coordinates. The Jacobian for the transformation from Cartesian to strained coordinates is found as follows:

Let

(3.16) \quad x = r_1 = v a_{1x} + w a_{2x} = s_1 a_{1x} + s_2 a_{2x}

(3.17) \quad y = r_2 = v a_{1y} + w a_{2y} = s_1 a_{1y} + s_2 a_{2y}

where we have replaced v and w by $s_1$ and $s_2$ respectively to simplify notation and where

$$
\begin{align*}
 a_{1x} &= a_{1x}^i \\
 a_{2x} &= a_{2x}^i \\
 a_{1y} &= a_{1y}^j \\
 a_{2y} &= a_{2y}^j
\end{align*}
$$

Hence the Jacobian is given as follows: \textsuperscript{5}
\[
J(\nu, \omega) = \det \begin{bmatrix}
\frac{\partial r_1}{\partial s_1} & \frac{\partial r_1}{\partial s_2} \\
\frac{\partial r_2}{\partial s_1} & \frac{\partial r_2}{\partial s_2}
\end{bmatrix} = \det \begin{bmatrix}
\frac{\partial r_1}{\partial s_1} & \frac{\partial r_1}{\partial s_2} \\
\frac{\partial r_2}{\partial s_1} & \frac{\partial r_2}{\partial s_2}
\end{bmatrix} = \sqrt{\det \begin{bmatrix}
\frac{\partial r_1}{\partial s_1} & \frac{\partial r_1}{\partial s_2} \\
\frac{\partial r_2}{\partial s_1} & \frac{\partial r_2}{\partial s_2}
\end{bmatrix} \det \begin{bmatrix}
\frac{\partial r_k}{\partial s_1} & \frac{\partial r_k}{\partial s_2}
\end{bmatrix}}
\]

\[
= \sqrt{\det \left[ \sum_{i=1}^{2} a_{ij} a_{i1} \right]} = \sqrt{\det \left[ a_j \cdot a_{i} \right]} = \sqrt{\det \left[ 2n_{ij} + \delta_{ij} \right]}
\]

Therefore in terms of strained coordinates Eq. (3.9) becomes

\[
(3.19) \quad F_N \cong NkT ln(\lambda^2) - NkT ln \left[ \left( \det [2n_{ij} + \delta_{ij}] \right)^{\frac{1}{2}} \int_{\lambda}^{\lambda} H(r-R_d) |r-R_d| - \sigma \right] \delta \nu \delta \omega
\]

To express the configurational integral as a function of the strains, we notice that,

\[
(3.20) \quad H(\lambda) = H(\lambda^2 - \sigma^2)
\]

and

\[
(3.21) \quad |r-R_d|^2 = (r-R_d) \cdot (r-R_d)
\]

\[
= (v_{d_{11}} + w_{d_{21}} - v_{d_{12}} - w_{d_{22}}) \cdot (v_{d_{11}} + w_{d_{21}} - v_{d_{12}} - w_{d_{22}})
\]

After multiplying this out and evaluating the dot products of the strained lattice vectors using Eq. (3.14) we find

\[
(3.22) \quad |r-R_d|^2 = (2n_1 + 1)(v-v_{d})^2 + (2n_2 + 1)(w-w_{d})^2 + 4n_6(v-v_{d})(w-w_{d})
\]
Upon dividing through by \( \sigma^2 \) the r.h.s of Eq. (3.20) becomes

\[
(3.23) \quad \frac{1}{\sigma^2} \left[ (2n_1 + 1)(v - v_d)^2 + (2n_2 + 1)(w - w_d)^2 + 4\eta_6(v - v_d)(w - w_d) \right] - 1 \equiv H(C_d)
\]

Now Eq. (3.19) becomes

\[
(3.24) \quad P_N = NkT \ln(\lambda^2) - \frac{NkT}{2} \ln \left( \det \left[ 2n_{ij} - \delta_{ij} \right] \right) - NkT \ln \left( \prod_{d=1}^{6} H(C_d) \delta v \delta w \right)
\]

Using Eq. (24) we proceed to evaluate the elastic constants. First letting \( D = \det[2n_{ij} - \delta_{ij}] \), we consider the term involving the determinant

\[
(3.25) \quad \frac{\partial D}{\partial n_{ij}} \bigg|_{n=0} = 2\delta_{ij}
\]

\[
(3.26) \quad \frac{\partial^2 D}{\partial n_{ij} \partial n_{kl}} \bigg|_{n=0} = 4\delta_{ij}\delta_{kl} - 4\delta_{il}\delta_{jk}
\]

\[
(3.27) \quad \left[ \frac{\partial}{\partial n_{ij}} \left( \frac{NkT}{2} \ln D \right) \right]_{n=0} = \frac{NkT}{2} \left( \frac{1}{D} \frac{\partial D}{\partial n_{ij}} \right)_{n=0}
\]

so

\[
(3.28) \quad \left( \frac{\partial}{\partial n_{kl}} \left[ \frac{NkT}{2D} \frac{\partial D}{\partial n_{ij}} \right] \right)_{n=0} = - \left[ \frac{NkT}{2D} \left( \frac{\partial D}{\partial n_{ij}} \right) \left( \frac{\partial D}{\partial n_{kl}} \right) \right]_{n=0} + \left[ \frac{NkT}{2D} \left( \frac{\partial^2 D}{\partial n_{kl} \partial n_{ij}} \right) \right]_{n=0}
\]

\[
= 2NkT \left( \delta_{ij}\delta_{kl} + \delta_{ij}\delta_{kl} - \delta_{il}\delta_{jk} \right) = -2NkT \delta_{ij}\delta_{jk}
\]
The contributions from the term arising from the Jacobian to the elastic constants are as given in Table 3-1.

Now we proceed to evaluate the second derivative with respect to the strains of the last term in Eq. (3.24).

First we let

\[
\int \prod_{d=1}^{6} H(C_d) \delta v \delta w = Q_{(1,1)} = Q
\]

so we have

\[
\frac{\partial}{\partial \eta_p} (-NkT \epsilon_n Q) = -\frac{NkT}{Q} \frac{\partial Q}{\partial \eta_p}
\]

where \( p = 1,2 \) or 6

and

\[
\left( \frac{\partial}{\partial \eta_q} \left[ -\frac{NkT}{Q} \left( \frac{\partial Q}{\partial \eta_p} \right) \right] \right)_{\eta=0} = \left[ \frac{NkT}{Q^2} \left( \frac{\partial Q}{\partial \eta_p} \frac{\partial Q}{\partial \eta_q} \right) - \frac{NkT}{Q} \frac{\partial^2 Q}{\partial \eta_q \partial \eta_p} \right]_{\eta=0}
\]

In Eqs. (30) and (31)

\[
\left( \frac{\partial Q}{\partial \eta_p} \right)_{\eta=0} = \int \int \sum_{d=1}^{6} \delta(C_d) \left( \frac{\partial C_d}{\partial \eta_p} \right)_{\eta=0} = \int \int \prod_{d=1}^{6} H(C_d) \delta v \delta w
\]

and
<table>
<thead>
<tr>
<th>Elastic Constant</th>
<th>Contribution of Jacobian in units of $\frac{2\sqrt{3}kT}{3a^2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_{11}$</td>
<td>-2</td>
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<tr>
<td>$c_{22}$</td>
<td>-2</td>
</tr>
<tr>
<td>$c_{66}$</td>
<td>0</td>
</tr>
<tr>
<td>$c_{16} = c_{61}$</td>
<td>0</td>
</tr>
<tr>
<td>$c_{26} = c_{62}$</td>
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</tr>
</tbody>
</table>

TABLE 3-2

<table>
<thead>
<tr>
<th>$n_p$</th>
<th>Value of $\left(\frac{\partial C_a}{\partial n_p}\right)_{n=0}^*$</th>
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</thead>
<tbody>
<tr>
<td>$n_1$</td>
<td>$2x_{a_1}^2$</td>
</tr>
<tr>
<td>$n_2$</td>
<td>$2y_{a_2}^2$</td>
</tr>
<tr>
<td>$n_6$</td>
<td>$4x_{a_6}y_{a_6}$</td>
</tr>
</tbody>
</table>

* Where each of these values represents six different values depending on $a$. 
\begin{equation}
- \left( \frac{\partial^2 Q}{\partial \eta \partial \eta} \right)_{\eta=0} = - \int \sum_{a=1}^{6} \delta^i (C_a) \left( \frac{\partial C_a}{\partial \eta} \right) \frac{\partial C_a}{\partial \eta} \prod_{d=1}^{6} H(C_d) \right]_{\eta=0} \delta \nu \delta \omega
\end{equation}

\begin{equation}
- \int \sum_{a=1}^{6} \delta^i (C_a) \left( \frac{\partial C_a}{\partial \eta} \right) \sum_{b=1}^{6} \delta^j (C_b) \left( \frac{\partial C_b}{\partial \eta} \right) \prod_{d=1}^{6} H(C_d) \right]_{\eta=0} \delta \nu \delta \omega
\end{equation}

We now consider \[ \left( \frac{1}{Q} \frac{\partial Q}{\partial \eta} \right)_{\eta=0} \] in detail; using Eq. (3.34) we see that,

\begin{equation}
\left[ \frac{1}{Q} \frac{\partial Q}{\partial \eta} \right]_{\eta=0} = \int \sum_{a=1}^{6} \delta \left[ \frac{(v-V_a)^2}{\sigma^2} + \frac{(w-W_a)^2}{\sigma^2} - 1 \right] \left( \frac{\partial C_a}{\partial \eta} \right) \prod_{d=1}^{6} H \left[ \frac{(v-V_d)^2}{\sigma^2} + \frac{(w-W_d)^2}{\sigma^2} - 1 \right] \delta \nu \delta \omega
\end{equation}

Now since

\begin{equation}
\frac{(v-V_a)^2}{\sigma^2} + \frac{(w-W_a)^2}{\sigma^2} - 1 = \frac{|r-R_a|^2}{\sigma^2} - 1
\end{equation}

and

\begin{equation}
\delta (x^2 - c^2) = \frac{1}{2c} \left[ \delta (x + c) + \delta (x - c) \right]
\end{equation}

Eq. (3.34) becomes
\[ (3.37) \quad \int_0^\lambda \int \sum_{a=1}^{6} \delta \left( \frac{|r-R_a|}{\sigma} - 1 \right) \left( \frac{\partial C_a}{\partial \eta_p} \right)_{\eta=0}^{d=1} \prod_{d=1}^{6} \frac{H \left( \frac{|r-R_d|}{\sigma^2} - 1 \right)}{\delta \phi d} \delta \delta \omega \]

As we approach the high density limit in which the disks approximate close packing, the following expansion of the magnitude of the distance between the movable disk and its \( d \)th nearest neighbor is valid,

\[ (3.38) \quad |r - R_d| = a + (-R_d/a) \cdot r + \cdots = a - w_d \cdot r \]

where \( w_d = R_d/a \), and letter \( a \) is the distance between nearest lattice sites.

In the high density limit only the first two terms need be considered. The use of the first two terms of this expansion is equivalent to replacing the circular collision boundary between the movable disk and fixed nearest neighbor disk \( d \) by a tangent line to that boundary perpendicular to the lattice vector extending from the movable disk's lattice site \( i \) to lattice site \( d \) (see Fig. 6). The boundary lines of a movable disk in a perfect hexagonal lattice of fixed disks depicts a hexagon.

In the high density limit Eq. (3.37) can then be written as

\[ (3.39) \quad \int_0^\lambda \int \sum_{a=1}^{6} \delta (\phi_a) \left( \frac{\partial C_a}{\partial \eta_p} \right)_{\eta=0}^{d=1} \prod_{d=1}^{6} \frac{H (\phi_d) \delta x \delta y}{\delta \phi d} \]

\[ = \frac{1}{Q} \left[ \frac{\partial Q}{\partial \eta_p} \right]_{\eta=0}^{d=1} \]

\[ = \frac{6}{\Pi} \frac{H (\phi_d) \delta x \delta y}{\delta \phi d} \int_0^\lambda \int \sum_{d=1}^{6} H (\phi_d) \delta x \delta y \]
Figure 6: The collision circle boundaries imposed by the six fixed neighboring disks of a movable disk in a hexagonal lattice and the corresponding inscribed one-particle free area. Also shown is the high density approximation to this area, a hexagon. The sides of the hexagon are lines drawn tangent to the collision circles and perpendicular to the lattice vector of the corresponding disk with the lattice site of the movable disk taken as the origin.
where

\[(3.40) \quad \phi_a = \alpha / \sigma - 1 - \omega \cdot r / \sigma \]

where subscript \(a\) is not to be confused with full sized \(a\) which is defined above.

We now define

\[(3.41) \quad t = \alpha / \sigma - 1 \]

and divide the arguments of the delta and unit step functions by \(t\).

Also we define the reduced variables

\[(3.42) \quad x' = \frac{x}{\sigma t} \quad y' = \frac{y}{\sigma t} \quad z = \frac{r}{\sigma t} \]

Now Eq. (3.39) becomes

\[(3.43) \quad \left[ \frac{1}{Q} \frac{\partial G}{\partial \eta_p} \right]_{\eta=0} = \frac{1}{2\pi} \int_0^6 \left[ \sum_{a=1}^6 \delta(\phi_a') \left( \frac{\partial C}{\partial \eta_p} \right) \right] \prod_{d=1}^6 H(\phi_d') \delta x' \delta y' \]

where

\[(3.44) \quad \phi_a' = 1 - \omega \cdot z \]

and where we have used the relation

\[(3.45) \quad \delta(cx) = (1/|c|) \delta(x). \]

The derivative \(\left( \frac{\partial C}{\partial \eta_p} \right)_{\eta=0}\) in the high density limit is just a quadratic
function of the coordinates of the six nearest neighbor disks surrounding
the movable disk. Consider \( p=1 \) as an example. From Eq. (3.23) we see

\[
(3.46) \left( \frac{\partial C_a}{\partial \eta_1} \right)_{\eta=0} = \frac{2(v - v_a)^2}{\sigma^2}
\]

\[
(3.47) \lim_{t \to 0} \frac{2(v - v_a)^2}{\sigma^2} = \frac{2(x - x_a)^2}{\sigma^2} = \frac{2(\sigma x' - \sigma x_a)^2}{\sigma^2} = 2X_a^2
\]

where

\[
(3.48) \quad X_a' = \frac{X_a}{\sigma}
\]

Hence \( \left( \frac{\partial C_a}{\partial \eta} \right)_{\eta=0} \) can have three values depending on \( p \) (see Table 1-2).

Proceeding with Eq. (3.43), it is now convenient to introduce the oblique
coordinates

(a) \( z_1 = x' \)

(b) \( z_2 = -(1/2)x' + (\sqrt{3}/2)y' \)

Therefore

\[
(3.49) \quad J(z_1, z_2) = \det \begin{bmatrix} 1 & 0 \\ 1/\sqrt{3} & 2/\sqrt{3} \end{bmatrix} = 2/\sqrt{3}
\]

The area of the hexagon described by the denominator in Eq. (3.43) is
\( 2\sqrt{3} \), so now Eq. (3.43) becomes upon transforming to oblique coordinates
TABLE 3-3

\[ w^a \cdot z \]

\[ w^1 \cdot z \]
Cartesian Coordinates
\[ x' \]
\[ z_1 \]
\[ 1 - z_1 \]

\[ w^2 \cdot z \]
\[ (1/2)x' + (\sqrt{3}/2)y' \]
\[ z_1 + z_2 \]
\[ 1 - z_1 - z_2 \]

\[ w^3 \cdot z \]
\[ -(1/2)x' + (\sqrt{3}/2)y' \]
\[ z_2 \]
\[ 1 - z_2 \]

\[ w^4 \cdot z \]
\[ -x' \]
\[ -z_1 \]
\[ 1 + z_1 \]

\[ w^5 \cdot z \]
\[ -(1/2)x' - (\sqrt{3}/2)y' \]
\[ -z_1 - z_2 \]
\[ 1 + z_1 + z_2 \]

\[ w^6 \cdot z \]
\[ (1/2)x' - (\sqrt{3}/2)y' \]
\[ -z_2 \]
\[ 1 + z_2 \]

TABLE 3-4

<table>
<thead>
<tr>
<th>Elastic Constant</th>
<th>[ \frac{1}{6t} \sum_{\alpha=1}^{6} \left( \frac{\partial C_{\alpha}}{\partial \eta} \right)_{\eta=0} ]</th>
<th>Contribution to Elastic Constant in Units of [ \frac{2\sqrt{3}kT}{3a^2} ]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_{11} )</td>
<td>( 1/t )</td>
<td>( 1/t^2 )</td>
</tr>
<tr>
<td>( C_{22} )</td>
<td>( 1/t )</td>
<td>( 1/t^2 )</td>
</tr>
<tr>
<td>( C_{12} )</td>
<td>( 1/t ) for ( p=1 ), ( 1/t ) for ( p=2 )</td>
<td>( 1/t^2 )</td>
</tr>
<tr>
<td>( C_{66} )</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( C_{16} )</td>
<td>0 for ( p=6 ), ( 1/t ) for ( p=1 )</td>
<td>0</td>
</tr>
<tr>
<td>( C_{26} )</td>
<td>0 for ( p=6 ), ( 1/t ) for ( p=2 )</td>
<td>0</td>
</tr>
</tbody>
</table>
Figure 7: Undistorted hexagonal flat-sided free area appropriate for the high density limit. Unit vectors $\vec{w}_1 \cdots \vec{w}_6$ point toward lattice sites of nearest neighbors. The oblique coordinate system $z_1, z_2$ is used in evaluating the cluster integrals.
(3.50) \[ \frac{1}{6t} \sum_{a=1}^{6} \delta(\phi_a') \left( \frac{\partial C_a}{\partial \eta} \right)_{\eta=0}^d \prod_{d=1}^{6} H(\phi_d')dz_1dz_2 \]

where now \( w \cdot z \) is expressed in terms of oblique coordinates. See Table 3-3 for all possible values of \( \phi_a' \) in Cartesian and oblique coordinates and Fig. 7 for the \( \wedge \) vectors pointing to the six nearest neighbor disks.

The value of the integral in term (3.50) excluding \( 1/6t \) and \( \left( \frac{\partial C_a}{\partial \eta} \right)_{\eta=0} \) is always one (see Appendix I). Hence term (3.50) can easily be evaluated. These values are given in Table 3-4.

It now remains to evaluate the integrals in Eq. (3.33). In order to evaluate the integral involving \( \delta' \), we have to carry out an integration by parts.

Using
\[ \nabla_r \cdot C_a = 2(r - R_a)/\sigma^2 \]

we have
\[ \nabla_r \cdot \delta'(C_a) = \frac{\partial \delta(C_a)}{\partial r} + \frac{\partial \delta(C_a)}{\partial \eta} \]

and
\[ \nabla_r \cdot \delta(C_a) = \frac{\partial \delta(C_a)}{\partial r} + \frac{\partial \delta(C_a)}{\partial \eta} \]

Hence the integral involving \( \delta' \) in Eq. (3.33) becomes
\[ (3.55) \]
\[ -\int \sum_{a=1}^{6} \frac{2 (r-R_a) \nabla \delta (C_a)}{2 |r-R_a|^2} \left( \frac{\partial C_a}{\partial q} \right) \delta (\eta_q) \left( \frac{\partial C_a}{\partial \eta_p} \right) \delta (\eta_p) \prod_{d=1}^{6} H(C_d) \delta \nu \delta \omega \]

Upon reducing the arguments of the delta function and rearranging we get,
\[ (3.56) \]
\[ \frac{\alpha^2}{4} \int \sum_{a=1}^{6} \frac{R_a \cdot r}{|r-R_a|^2} \left( \frac{\partial C_a}{\partial \eta_q} \right) \delta (\eta_q) \left( \frac{\partial C_a}{\partial \eta_p} \right) \delta (\eta_p) \prod_{d=1}^{6} H(C_d) \frac{\nu \cdot r}{\sigma} - 1 \delta \nu \delta \omega \]

Let
\[ (3.57) \]
\[ G = \sum_{a=1}^{6} \frac{R_a \cdot r}{|r-R_a|^2} \left( \frac{\partial C_a}{\partial \eta_q} \right) \delta (\eta_q) \left( \frac{\partial C_a}{\partial \eta_p} \right) \delta (\eta_p) \prod_{d=1}^{6} H(C_d) \]

Making this substitution (3.56) becomes
\[ (3.58) \]
\[ \frac{\alpha^2}{4} \int \delta \nu \delta \omega \left[ \nu \cdot r \left( \delta \left( \frac{|r-R_a|}{\sigma} - 1 \right) G \right) - \nu \cdot G \right] \]

\[ = \frac{\alpha^2}{4} \int \delta \left( \frac{|r-R_a|}{\sigma} - 1 \right) G \cdot n \delta s - \frac{\alpha^2}{4} \int \delta \nu \delta \omega \delta \left( \frac{|r-R_a|}{\sigma} - 1 \right) \nu \cdot G \]

\[ = - \frac{\alpha^2}{4} \int \delta \nu \delta \omega \delta \left( \frac{|r-R_a|}{\sigma} - 1 \right) \nu \cdot G \cdot \]

Here we have used Green's theorem in the plane to write the integral over an area as a line integral about the boundary of that area. Since
this area completely encloses the area demarcated by the unit step functions in $G$, this line integral is equal to zero.

We now consider $\nabla \cdot G$. $G$ can be broken up into the product of three different functions, only one of which changes when we evaluate different integrals corresponding to different elastic constants.

$$
(3.59) \quad G = \sum_{a=1}^{6} \left[ \frac{(R - r)}{|r - R_a|^2} \right] \left[ \frac{\partial C_a}{\partial q} \right]_{\eta=0} \left[ \frac{\partial C_b}{\partial p} \right]_{\eta=0} \left[ \frac{6}{\Pi H(C_d)} \right] 
$$

Consideration will be given in Eq. (3.58) only to terms which give a $1/t^2$ contribution to the elastic constants. Quadratic functions of $z_1$ and $z_2$ describing the curved collision boundaries of the movable disk would have to be introduced into term (3.50) to obtain its $1/t$ contribution, but since this procedure will not be followed, we will consider only the $1/t^2$ contributions to the elastic constants. The only part of $\nabla \cdot G$ which will ultimately lead to a $1/t^2$ contribution in Eq. (3.58) will be that part which contains a delta function. This delta function will arise from the product of unit step functions as shown in Eq. (3.60).

$$
(3.60) \quad \nabla \cdot \sum_{d=1}^{6} \frac{6}{\Pi} H(C_d) = \sqrt{\frac{\sigma}{2}} \sum_{b=1}^{6} \delta(C_b) \left( R - r \right) \sum_{d=1}^{6} \frac{6}{\Pi} H(C_d)
$$

So that the corresponding part of $\nabla \cdot G$ makes the following contribution to the r.h.s. of Eq. (3.58)
(3.61)

$$\hat{a} = \int \sum_{a=1}^{6} \sum_{b=1}^{6} \frac{(r-R_a) \cdot (r-R_b)}{|r-R|} \left( \frac{\partial c}{\partial \eta q} \right) \left( \frac{\partial c}{\partial \eta p} \right) \delta \left( \frac{|r-R|}{\sigma} - 1 \right) \delta(C_b) \prod_{d=1}^{6} H(C_d) \delta \nu \delta w$$

Now proceeding as before to the high density limit, transforming to oblique coordinates and multiplying by \( \frac{NkT}{2\sqrt{3} \sigma t^2} = \frac{NkT}{Q} \), we get

(3.62)

$$\frac{NkT}{12t^2} \sum_{a=1}^{6} \sum_{b=1}^{6} \frac{x_a^2 + y_a^2}{x_b^2 + y_b^2} \left( \frac{\partial c}{\partial \eta q} \right) \left( \frac{\partial c}{\partial \eta p} \right) \int \delta(\phi_a') \delta(\phi_b') \prod_{d=1}^{6} H(\phi_d') \delta z_1 \delta z_2$$

If we label the integral in (3.62) by \( a, b \) corresponding to the values of \( a \) and \( b \), in the arguments of each particular delta function, we find that the values of this integral are as given in Table 3-5 (see Appendix II).

Using Table 3-5 we can now write down the total contribution of order \( 1/t^2 \) of Eq. (3.58) to the elastic constants which are given in Table 3-6.

The \( C_{66} \) contribution has been divided by four (see Appendix III).

Upon dividing by \( Q \), proceeding to the high density limit, and transforming to oblique coordinates as before the other integral on the r.h.s. of Eq. (3.33) can be written as
TABLE 3-5

The Value of \[ \int \int \delta(\phi_a') \delta(\phi_b') \prod_{d=1}^{6} H(\phi_d') \delta z_1 \delta z_2 \]
when \( d \neq a, b \)

<table>
<thead>
<tr>
<th>Integral Specified by ( a, b )</th>
<th>Value of Integral</th>
<th>Integral Specified by ( a, b )</th>
<th>Value of Integral</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2</td>
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### TABLE 3-6

<table>
<thead>
<tr>
<th>Elastic Constant</th>
<th>Contribution of Eq. (3.58) in Units of $\frac{2\sqrt{3}kT}{3a^2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{11}$</td>
<td>$3/4t^2$</td>
</tr>
<tr>
<td>$C_{22}$</td>
<td>$3/4t^2$</td>
</tr>
<tr>
<td>$C_{12}$ or $C_{21}$</td>
<td>$1/4t^2$</td>
</tr>
<tr>
<td>$C_{66}$</td>
<td>$1/4t^2$</td>
</tr>
<tr>
<td>$C_{16}$ or $C_{61}$</td>
<td>$0$</td>
</tr>
<tr>
<td>$C_{26}$ or $C_{62}$</td>
<td>$0$</td>
</tr>
</tbody>
</table>

### TABLE 3-7

<table>
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<tr>
<th>Elastic Constant</th>
<th>Contribution of Eq. (3.63) in Units of $\frac{2\sqrt{3}kT}{3a^2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{11}$</td>
<td>$-3/4t^2$</td>
</tr>
<tr>
<td>$C_{22}$</td>
<td>$-3/4t^2$</td>
</tr>
<tr>
<td>$C_{12}$, $C_{21}$</td>
<td>$-5/4t^2$</td>
</tr>
<tr>
<td>$C_{66}$</td>
<td>$1/4t^2$</td>
</tr>
<tr>
<td>$C_{61}$, $C_{16}$</td>
<td>$0$</td>
</tr>
<tr>
<td>$C_{62}$, $C_{26}$</td>
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</tr>
</tbody>
</table>
(3.63) \[
\frac{1}{12t^2} \int \sum_{a=1}^{6} \sum_{b=1}^{6} \delta(\phi'_a) \delta(\phi'_b) \left( \frac{\partial C_a}{\partial n_p} \right) \left( \frac{\partial C_b}{\partial n_q} \right) \prod_{\eta=0}^{6} H(\phi'_d)\delta z_1 \delta z_2 
\]

Again using Table 3-5 we can now write down the total contributions of Eq. (3.63) to the elastic constants which are given in Table 3-7. Here again we have divided the $C_{66}$ contribution by four (see Appendix III).

Finally upon summing the contributions given in the Tables 3-4, 3-6 and 3-7, we obtain the elastic constants to order $1/t^2$ given in Table 3-8 since the Jacobian does not make a $1/t^2$ contribution.

3. THE EFFECT OF VACANCIES ON THE ELASTIC CONSTANTS

If we introduce $m$ monovacancies into the lattice of $N$ rigid disks, the one particle cell cluster expression for the non-configurational free energy becomes:

(3.64) \[
F_N \propto kT \left[ Nln(\lambda^2 - \frac{N}{2}ln(\text{det}[2\eta_{ij} + \delta_{ij}]) - (N - 6m)lnQ - m \sum_{e=1}^{6} \frac{\eta Q_e}{v} \right]
\]

where

(3.65) \[
Q_e^v = \int_{d=1}^{6} \prod_{d \neq e} H(C_d) dx
\]
This expression assumes that no vacancy clusters are present. $Q_e^v$ represents the area in which the center of disk $e$ is free to move when it is surrounded by five fixed neighbors and a vacancy in the high density limit. This area can be obtained by omitting one side from the hexagon in Fig. 4 and extending the two adjacent sides until they intersect.

From geometry we can show that this area is equal to $(7/6)Q$. Although all the $Q_e^v$ are equal to $(7/6)Q$, it is necessary to write the last term in Eq. (3.64) as a summation over the six configuration integrals of the six disks surrounding a monovacancy because eventually the derivatives of these integrals are considered. These differ according to which disk is considered.

We can now write an expression for the elastic constants $C_{pq}^v$ associated with a lattice containing $m_1$ monovacancies. We again exclude terms arising from the Jacobian since again we are interested only in contributions of the order of $1/t^2$.

\[
\frac{\sqrt{3}}{2} N_{\mathrm{a}}^2 c_{pq}^v = \left( \frac{\partial^2 F}{\partial \eta_q \partial \eta_p} \right)_{\eta=0} = kT \left[ \frac{(N - 6m_1)}{Q^2} \left( \frac{\partial Q}{\partial \eta_p} \right) \left( \frac{\partial Q}{\partial \eta_q} \right) - \frac{(N - 6m_1)}{Q} \left( \frac{\partial^2 Q}{\partial \eta_q \partial \eta_p} \right) \right]
\]

\[
+ \sum_{e=1}^{6} \frac{m_1}{(Q_e^v)^2} \left( \frac{\partial Q_e^v}{\partial \eta_p} \right) \left( \frac{\partial Q_e^v}{\partial \eta_q} \right) - \sum_{e=1}^{6} \frac{m_1}{Q_e^v} \left( \frac{\partial^2 Q_e^v}{\partial \eta_q \partial \eta_p} \right)_{\eta=0}.
\]

Obviously the first two terms in Eq. (3.66) have already been considered in the perfect lattice case. Considering the first derivative of $Q_e^v$ we have
TABLE 3-8

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<tr>
<th>Elastic Constant</th>
<th>Value in Units of $\frac{2\sqrt{3}kT}{3a^2}$</th>
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<tr>
<td>$C_{22}$</td>
<td>$1/t^2$</td>
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<tr>
<td>$C_{66}$</td>
<td>$1/2t^2$</td>
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<td>$C_{16} = C_{61}$</td>
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<tr>
<td>$C_{26} = C_{62}$</td>
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TABLE 3-9

Value of Integral in Term (3.63) Excluding $\frac{1}{7t} \frac{\partial C}{\partial \eta} \bigg|_{\eta=0}$

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\[
\begin{align*}
\left( \frac{\partial Q_e}{\partial \eta_p} \right)_v &= \left[ \int \sum_{a=1}^{6} \delta(C_a) \left( \frac{\partial C_a}{\partial \eta_p} \right) \prod_{d=1}^{6} \eta_0 \right] H(C_d) \delta \nu \delta \omega \\
&= \left[ \int \sum_{a=1}^{6} \delta(C_a) \left( \frac{\partial C_a}{\partial \eta_p} \right) \prod_{d=1}^{6} \eta_{d=1} \delta z_1 \delta z_2 \right].
\end{align*}
\]

Upon making the appropriate transformations and simplifications and dividing through by \( Q_e v \), we obtain

\[
(3.68) \quad \frac{1}{7t} \int \sum_{a=1}^{6} \delta(\phi'_a) \left( \frac{\partial C_a}{\partial \eta_p} \right) \prod_{d=1}^{6} \eta_0 \right] H(\phi'_d) \delta z_1 \delta z_2.
\]

Omitting the derivative \( \left( \frac{\partial C_a}{\partial \eta_p} \right) \), which is just a constant in the high density limit and \( 1/7t \), this integral, for \( a \neq e \) is equal to one if \( a \) is not adjacent to \( e \) in the sequence 1, 2, 3, 4, 5, 6 where 1 and 6 are considered to be adjacent numbers, and is equal to two when \( a \) and \( e \) are adjacent numbers in this sequence (see Table 3-9 and Appendix IV).

We can now evaluate the contributions of the third term in Eq. (3.66) to the elastic constants which are given in Table 3-10. In Table 3-10 and the following tables, the vacancy concentration unit \( \theta = \frac{m_1}{N} \) is used.

We now consider the last term in Eq. (3.66)

\[
(3.69) \quad \sum_{e=1}^{6} \frac{m_1}{(Q_e v) \left( \frac{\partial Q_e}{\partial \eta_q \partial \eta_p} \right)} = \sum_{e=1}^{6} \frac{m_1}{(Q_e v) \left( \frac{\partial Q_e}{\partial \eta_q \partial \eta_p} \right)} \left[ \int \sum_{a=1}^{6} \delta'(C_a) \left( \frac{\partial C_a}{\partial \eta_q} \right) \left( \frac{\partial C_a}{\partial \eta_p} \right) \prod_{d=1}^{6} \eta_0 \right] H(C_d) \delta \nu \delta \omega \\
+ \left[ \int \sum_{a=1}^{6} \delta(C_a) \left( \frac{\partial C_a}{\partial \eta_p} \right) \sum_{b=1}^{6} \delta(C_b) \left( \frac{\partial C_b}{\partial \eta_q} \right) \prod_{d=1}^{6} \eta_0 \right] H(C_d) \delta \nu \delta \omega.
\]
TABLE 3-10

Elastic Constant

Contribution of \( \frac{2\sqrt{3}}{3a^2} \sum_{e=1}^{6} \frac{m_1}{(Q_e v)^2} \left( \frac{\partial Q}{\partial \eta_p} \right)_{\eta=0} \left( \frac{\partial Q}{\partial \eta_q} \right)_{\eta=0} ) \) kT

(in units of \( \frac{2\sqrt{3}}{3a^2} \frac{kT}{\theta} \))

\( c_{11} \) \hspace{1cm} 36/\tau^2

\( c_{22} \) \hspace{1cm} 36/\tau^2

\( c_{12}, c_{21} \) \hspace{1cm} 36/\tau^2

\( c_{66} \) \hspace{1cm} 0

\( c_{61}, c_{16} \) \hspace{1cm} 0

\( c_{62}, c_{26} \) \hspace{1cm} 0
The integral involving $\delta'$ is handled as before and an expression analogous to (3.62) is obtained.

\[(3.70)\]
\[
\frac{m_1}{14t^2} \sum_{e=1}^{6} \sum_{a=1}^{6} \sum_{b=1}^{6} \frac{x'^a_y + y'^y_b}{x'^a_x + y'^y_a} \left( \frac{\partial c}{\partial q} \right)_{\eta=0} \left( \frac{\partial c}{\partial p} \right)_{\eta=0} \int \int \delta'(\phi'_a) \delta'(\phi'_b) H(\phi'_d) \delta z_1 \delta z_2
\]

If the lines described by the arguments of the delta functions in the integral intersect within the area described by the unit step functions, the integral is equal to one; if not, or if the lines are parallel, the integral is equal to zero (see Appendix II). The values of all these integrals are given in Table 3-11. The contributions of term (3.70) to the elastic constants are given in Table 3-12.

Finally the last integral in Eq. (3.69) can be written in the high density limit as

\[(3.71)\]
\[
-\frac{m_1}{14t^2} \sum_{e=1}^{6} \sum_{a=1}^{6} \sum_{b=1}^{6} \left( \frac{\partial c}{\partial p} \right)_{\eta=0} \left( \frac{\partial c}{\partial q} \right)_{\eta=0} \int \int \delta'(\phi'_a) \delta'(\phi'_b) H(\phi'_d) \delta z_1 \delta z_2
\]

Here again we can use Table 3-11 to evaluate the integral. The contributions of term (3.71) to the elastic constants are given in Table 3-13.

Finally combining all the contributions from Tables 3-10, 3-12 and 3-13, and combining them with the results in Table 3-8, we can write out the elastic constants of the defect rigid disk system as given in Table 3-14.
TABLE 3-11

Evaluation of \[ \int \sum_{a=1}^{6} \sum_{b=1}^{6} \delta(\phi'_a)\delta(\phi'_b) \prod_{d=1}^{6} H(\phi'_d) \delta d \delta y \] 
\[ \text{with } a \neq e, b \neq a, e \quad d \neq a, b, e \]

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<td>4,5</td>
<td>1</td>
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<tr>
<td></td>
<td>4,6</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>5,2</td>
<td>0</td>
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<tr>
<td></td>
<td>5,3</td>
<td>0</td>
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<tr>
<td></td>
<td>5,4</td>
<td>1</td>
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<tr>
<td></td>
<td>5,6</td>
<td>1</td>
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<tr>
<td></td>
<td>6,2</td>
<td>1</td>
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<tr>
<td></td>
<td>6,3</td>
<td>0</td>
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<tr>
<td></td>
<td>6,4</td>
<td>0</td>
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<tr>
<td></td>
<td>6,5</td>
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</tr>
</tbody>
</table>
TABLE 3-12*

<table>
<thead>
<tr>
<th>Elastic Constant</th>
<th>Contribution of Eq.(3.70) in Units of $\frac{2\sqrt{3}}{3a^2} \theta kT$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_{11}^v$</td>
<td>27/14t²</td>
</tr>
<tr>
<td>$c_{22}^v$</td>
<td>27/14t²</td>
</tr>
<tr>
<td>$c_{12}^v$ and $c_{21}^v$</td>
<td>9/14t²</td>
</tr>
<tr>
<td>$c_{66}^v$</td>
<td>9/14t²</td>
</tr>
<tr>
<td>$c_{16}^v$ and $c_{61}^v$</td>
<td>0</td>
</tr>
<tr>
<td>$c_{26}^v$ and $c_{62}^v$</td>
<td>0</td>
</tr>
</tbody>
</table>

TABLE 3-13*

<table>
<thead>
<tr>
<th>Elastic Constant</th>
<th>Contribution of Eq.(3.71) in Units of $\frac{2\sqrt{3}}{3a^2} \theta kT$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_{11}^v$</td>
<td>- 45/14t²</td>
</tr>
<tr>
<td>$c_{22}^v$</td>
<td>- 45/14t²</td>
</tr>
<tr>
<td>$c_{12}^v$ and $c_{21}^v$</td>
<td>- 75/14t²</td>
</tr>
<tr>
<td>$c_{66}^v$</td>
<td>15/14t²</td>
</tr>
<tr>
<td>$c_{16}^v$ and $c_{61}^v$</td>
<td>0</td>
</tr>
<tr>
<td>$c_{26}^v$ and $c_{62}^v$</td>
<td>0</td>
</tr>
</tbody>
</table>

* Contributions to $c_{66}^v$ in Tables 3-12 and 3-13 have been divided by four as before (see Appendix III).
<table>
<thead>
<tr>
<th>Elastic Constant</th>
<th>Value in Units of $\frac{2\sqrt{3}}{3a^2} kT$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_{11}^v$, $c_{22}^v$</td>
<td>$\left[\left(1 - 6\theta_1\right) + \frac{243}{7} \theta_1\right] \frac{1}{t^2}$</td>
</tr>
<tr>
<td>$c_{21}^v$, $c_{12}^v$</td>
<td>$\frac{219}{7} \theta_1 \frac{1}{t^2}$</td>
</tr>
<tr>
<td>$c_{66}^v$</td>
<td>$\left[\left(\frac{1}{2} - 3\theta_1\right) + \frac{12}{7} \theta_1\right] \frac{1}{t^2}$</td>
</tr>
<tr>
<td>$c_{61}^v$, $c_{16}^v$</td>
<td>0</td>
</tr>
<tr>
<td>$c_{62}^v$, $c_{26}^v$</td>
<td>0</td>
</tr>
</tbody>
</table>
DISCUSSION

We see from our results that the elastic stiffness constants of a rigid disk crystal are proportional to the temperature. In contrast to this, the elastic constants of real crystals normally decrease as the temperature increases. In the rigid disk case, as temperature increases, the frequency at which we find a disk center within any area increment $\delta A$ of its free area increases making it more difficult to deform this area. This is the only consideration we need to make as the rigid disk potential we use only specifies that there can be no overlap of disks. Hence the elastic constants of a rigid disk solid are proportional to the temperature.

The elastic constants calculated for the two types of lattices we have considered obey the following relations.

\begin{align}
& (3.72) \quad c_{11} = c_{22} \\
& (3.73) \quad c_{66} = \frac{c_{11} - c_{12}}{2} = \frac{c_{22} - c_{12}}{2} \\
\end{align}

These relations found for a two-dimensional hexagonal lattice are the analogs of relations valid for three-dimensional hexagonal systems.\(^7\)

Using one-particle cell cluster theory, the elastic constant $c_{12}$ was calculated to be zero. Upon extending this calculation to include the correlated motion correction factor introduced through the consideration of two-particle clusters, $c_{12}$ is found to be nonzero and equal to about 0.13 (in units of $\frac{2\sqrt{3}}{3a^2} kT$). Hence, the result $c_{12} = 0$ appears to be an artifact of the one-particle approximation.

Poisson's ratio $\sigma$ is given by Eq. (3.74)
\[ \sigma = \frac{\eta_2}{\eta_1} = \frac{C_{12}}{C_{11} + C_{12}} \]

Hence if we apply a small positive strain \( \eta_1 \) to a perfect lattice of rigid disks near close packing, we expect a corresponding small, negative \( \eta_2 \) strain to arise. This is not due to any type of interdisk potential. The rigid disk potential of our system only specifies that there can be no overlap of disks. Hence, when strain \( \eta_1 \) is introduced into the system, there are no forces present to make it contract along the 2-direction resulting in a negative strain \( \eta_2 \); as in real solids, where potential interactions tend to deform the solid in such a way as to maintain its component atoms at their most stable separations. The fact that a small, negative strain \( \eta_2 \) actually arises in a rigid disk system in this situation is apparently due to the areas opening up between disks as they move apart in the l-direction which allows the \( \lambda \) components of the distances of separation of the disks to become slightly smaller on the average which is equivalent to a small, negative strain \( \eta_2 \).

The introduction of monovacancies into the lattice would be expected to enhance the effect mentioned in the previous paragraph since the areas opening up between disks if either of the strains \( \eta_1 \) or \( \eta_2 \) were introduced into a monovacancy-containing lattice would be on the average slightly larger, which would allow more relaxation into these areas to occur. Hence \( \sigma \) is predicted to be larger in a monovacancy-containing lattice, as indeed it turns out to be when we substitute our expressions for \( C_{12}^V \) and \( C_{11}^V \) into Eq. (3.74).

The equilibrium concentration of monovacancies in a rigid disk solid has been evaluated, and is given approximately by Eq. (3.75).
(3.75) \[ \theta_1 \approx \left( \frac{7}{6} \right)^6 \exp \left( -\frac{19}{18} \right) \exp \left( -\frac{1}{t} \right) \]

Only one-particle cell cluster theory has been used in the derivation of Eq.(3.59). As we approach the high density limit, \( t \) becomes small so \( \theta_1 \) becomes very small. When \( t = 0.10 \), we find \( \theta_1 \approx 4 \times 10^{-5} \) and when \( t = 0.05 \), we find \( \theta_1 \approx 2 \times 10^{-9} \). Hence, because the equilibrium concentration of monovacancies is so low near the high density limit, the effect of monovacancies on the calculated elastic constants near this limit is small. In Table 3-15 a comparison of the elastic constants in the perfect and vacancy-containing lattices is made for \( t = 0.10 \) and \( t = 0.05 \).

In this presentation we have been concerned only with rigid disk systems at a relatively high density where \( t \) is small. At such densities, curvature corrections, which we have neglected by approximating the circular cell boundaries by tangent lines, make at most a contribution of order \( 1/t \) to the elastic constants. Therefore, curvature corrections have been neglected.
TABLE 3-15*

<table>
<thead>
<tr>
<th>Elastic Constant $C_{pq}$</th>
<th>Value of $C_{pq}$</th>
<th>$C^V_{pq} - C_{pq}$</th>
<th>Value of $C_{pq}$</th>
<th>$C^V_{pq} - C_{pq}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{11}, C_{22}$</td>
<td>100</td>
<td>0.115</td>
<td>400</td>
<td>$2.30 \times 10^{-5}$</td>
</tr>
<tr>
<td>$C_{21}, C_{12}$</td>
<td>0</td>
<td>0.125</td>
<td>0</td>
<td>$2.50 \times 10^{-5}$</td>
</tr>
<tr>
<td>$C_{66}$</td>
<td>$\frac{100}{2}$</td>
<td>-0.005</td>
<td>$\frac{400}{2}$</td>
<td>$-1.03 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

* The values of the elastic constants used in this table are those obtained using only one-particle cell cluster theory, and they are expressed in units of $\frac{2\sqrt{3}}{3a^2}$ kT.
APPENDIX I

The integral we need to evaluate is

$$\int \sum_{a=1}^{6} \delta(\phi_a) \prod_{d=1, d \neq a}^{6} H(\phi_d) \delta z_1 \delta z_2$$  \hspace{1cm} (A-1)

where \( \phi_a = 1 - \omega_a \cdot z \).

Since the delta function is only satisfied along the line described by its argument, the limits of integration for this integral will be given by the two points of intersection of this line with the boundaries of the area described by the five unit step functions. Since we know that the complete set of six lines, five of which are the arguments of the unit step functions and one of which is the argument of the delta function, describe a hexagon, the limits of integration will be given by the points of intersection of one of these sides with its two adjacent sides. Let us consider the example shown in Fig. (A-1). Here the arguments of the unit step functions are denoted by solid lines and that of the delta function by a dotted line, also the oblique coordinates \( z_1, z_2 \) are plotted along the Cartesian coordinate axes.

The integral corresponding to this diagram written out fully is

$$\int \delta(1-z_1-z_2) H(1-z_1) H(1+z_1) H(1-z_2) H(1+z_2) H(1+z_1+z_2) \delta z_1 \delta z_2$$  \hspace{1cm} (A-2)

Using Fig. (A-1) to find the allowed region of integration, term (A-2) becomes

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\[ \int_0^1 \delta z_2 \int_0^1 \delta z_1 \delta \left[ z_1 - (1 - z_2) \right] = \int_0^1 \delta z_2 = 1 \quad . \] (A-3)

The integral containing \([1 + z_1 + z_2]\) is evaluated similarly.

In the cases where the argument of the delta function contains \(1 + z_2\), \(1 - z_2\), \(1 - z_1\) or \(1 + z_1\), an area of integration is no longer indicated since these arguments represent lines parallel to the coordinate axes.

For example, from Fig. (A-1) it is seen that if the argument of the delta function is \(1 + z_2\) the integral we need to evaluate is given by (A-4)

\[ \int_0^1 \delta z_1 \int_{-1}^{-1} \delta z_2 \delta (1 + z_2) = \int_0^1 \delta z_1 = 1 \quad . \] (A-4)

All of the other integrals in (A-1) fall into one or the other of the two above categories and can be evaluated accordingly.
Fig. (A-1): The lined region is the allowed region of integration for the integral (A-2).

Fig. (A-2): The lined region is the allowed region of integration for integral (A-8).
APPENDIX II

Integrals of the form

\[ \int d\delta(\phi_a')d\delta(\phi_b') \prod_{d=1}^{6} H(\phi_d)\delta z_1\delta z_2 \quad (A-5) \]

d#a,b

are especially easy to evaluate. Considering Fig. (A-1), if the two lines described by \( \phi_a' \) and \( \phi_b' \) intersect within the area demarcated by the unit step functions, the integral is equal to one; if not, the integral is equal to zero. If the lines described by \( \phi_a' \) and \( \phi_b' \) do not intersect, the integral is zero. More simply, if the two lines are adjacent sides of the hexagon described by the total set of lines, the integral is one; if not, the integral is zero.

If one of the four unit step functions is omitted from the product in (A-5), the argument above still applies except we must replace the word hexagon with five-sided figure.

APPENDIX III

In Table VI the total of the contributions to the elastic constant \( C_{66} \) has been divided by four because when the free energy is differentiated with respect to \( \eta_{ij} \) and \( \eta_{k\ell} \) where \( i\neq j \) and \( k\neq \ell \), four times the actual value of the elastic constant \( C_{ij\ell k} \) is obtained. This arises from the general form for the free energy of a deformed crystal as given in Eq. (A-6)
\[ F = A \sum_{ijkl} C_{ijkl} \delta n_{ij} \delta n_{kl} \]  \hspace{1cm} (A-6)

which is evident from Eq. (3.13). In the sum \( \sum_{ijkl} C_{ijkl} \delta n_{ij} \delta n_{kl} \) the term in the product differential involving \( \delta n_{ij} \) and \( \delta n_{kl} \) with \( i \neq j \) and \( k \neq l \) occurs four times. This is because each component of the symmetric strain tensor with \( i \neq j \) and \( k \neq l \) appears twice, hence their product terms appear four times. Thus it is necessary to divide through by four in such cases to obtain the correct elastic constant. In cases where \( i = j \) and \( k \neq l \), we must correspondingly divide through by two.

APPENDIX IV

The integrals included in the following summation, (A-7), can again be evaluated by finding the region of integration prescribed by the argument of the delta function.

\[ \sum_{e=1}^{6} \sum_{a=1}^{6} \delta (\phi'_a) \prod_{d=1}^{6} H(\phi'_d) \delta z_1 \delta z_2 \]  \hspace{1cm} (A-7)

From Appendix I we know that all the integrals whose region of integration is not affected by the summation over \( e \), will be equal to one. The region of integration is changed if the area described by the unit step functions is changed such that the length of the line described by the argument of the delta function inside this area is increased over what it would normally be in (A-1). This can occur only if \( e \) denotes one of the two boundary lines adjacent to the boundary line described by the argument of the delta function. If this is the case, the integral
is always equal to two. In these cases as in Appendix I we have two types of regions of integration, one in which both $z_1$ and $z_2$ vary over a range of values, and one in which only $z_1$ or $z_2$ vary over a range of values. The first case corresponds to having $1 - z_1 - z_2$ in the argument, that is argument number 2 of the delta function, and $e$ corresponding to argument 1 or 3.

Let us consider an example with $e = 3$. The region of integration will be the shaded region in Fig. (A-2). Hence the corresponding integral in (A-7) can be written and evaluated as follows

$$
\int \delta(1-z_1-z_2) \, H(1-z_1) \, H(1+z_1) \, H(1+z_2) \, H(1+z_1+z_2) \, \delta z_1 \, \delta z_2
$$

$$
= \int_{-1}^{1} \delta z_1 \int_{0}^{2} \delta \left[ z_2 - (1-z_1) \right] \, \delta z_2 = \int_{-1}^{1} \delta z_1 = 2. \quad \text{(A-8)}
$$

The second case corresponds to having one of the boundaries parallel to one of the coordinate axes in the argument of the delta function with the $e$ value corresponding to one of its adjacent boundaries. For example, consider $1-z_1$ as the argument of the delta function, argument number 1, with $e = 2$. Now we have

$$
\int \delta(1-z_1) \, H(1+z_1) \, H(1+z_2) \, H(1-z_2) \, H(1+z_1+z_2) \, \delta z_1 \, \delta z_2
$$

$$
= \int_{-1}^{1} \delta z_1 \int_{-1}^{1} \delta (1-z_1) \, \delta z_1 = \int_{-1}^{1} \delta z_2 = 2. \quad \text{(A-9)}
$$

All of the other integrals in (A-7) fall into one of these two cases and are evaluated accordingly.
REFERENCES


5. For the identity used here expressing the terms of a determinant which is the product of two other determinants see H. Margenau and G. M. Murphy, The Mathematics of Physics and Chemistry (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1964), p. 304.


8. J. C. Langeberg and G. V. Bettony, to be published.