An Application of Cell-Cluster Theory to a Rare Gas Crystal

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Thesis submitted in partial fulfillment of the requirements for the degree of Master of Science

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St. Catharines, Ontario.
May 1974
Abstract

The Lennard-Jones Devonshire\(^1\) (LJD) single particle theory for liquids is extended and applied to the anharmonic solid in a high temperature limit. The exact free energy for the crystal is expressed as a convergent series of terms involving larger and larger sets of contiguous particles called cell-clusters. The motions of all the particles within cell-clusters are correlated to each other and lead to non-trivial integrals of orders 3, 6, 9, ... \(3N\). For the first time the six dimensional integral has been calculated to high accuracy using a Lennard-Jones (6-12) pair interaction between nearest neighbours only for the f.c.c. lattice. The thermodynamic properties predicted by this model agree well with experimental results for solid Xenon.
ACKNOWLEDGEMENTS

I wish to thank the members of the Physics Department for their instruction and support over the years. I am especially grateful to Dr. E. R. Cowley for suggesting this problem and for his invaluable guidance during this study.

I would also like to thank my family and friends for their confidence and moral support.

Thanks are also extended to the Brock University Computing Centre whose service and assistance proved to be invaluable to me.

I would also like to thank Dr. M. L. Klein of N. R. C. for communicating his Monte Carlo numbers to us.

I am also deeply indebted to Mrs. Barbara Westera and Mrs. Karen Redmond for their fine typing of the earlier and final drafts respectively.

Finally, I wish to thank the National Research Council and the Ontario Graduate Awards Committee for their financial support of this project.
TO BARBARA, MY WIFE
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Introduction

Many methods have been employed in the past to describe the thermodynamic properties of rare gas crystals with limited success. The main methods: perturbation theory (PT), quasi-harmonic theory (QH), self consistent theory (SC), and improved self consistent theory (ISC) agree with experiment quite well for lower temperatures \( T < T_{\text{Melt}} \) but go astray for higher temperatures. Perturbation theory at higher temperatures gives unrealistically large anharmonic contributions to the free energy which Klein\(^{19}\) believes indicates the breakdown of the theory. Quasiharmonic theory predicts vibrational amplitudes which are too large leading to overly large volumes. This results in poor predictions for high temperature thermodynamic properties. On the other hand, the self consistent phonon theory under predicts the high temperature volume\(^{20}\). Although the improved self consistent theory gives properties closest to the more accurate Monte Carlo method, it does over estimate the volume and thus is not as good as one would wish. Monte Carlo calculations give exact results but the computing time required for good answers is very restrictive.

The theory of Lennard-Jones and Devonshire\(^{1}\) was an advance
over earlier work in that the molecule was assumed to move in the potential field generated by its neighbours rather than by a smeared or spherical potential. However, this theory does not take into account the communal entropy due to multiple occupancy (crystal disorder) or the correlated motions of molecules (which is necessary if quantum mechanical exchange effects between molecules are to be calculated). Pople suggests that the communal entropy does not become appreciable until the volume is five times the close packed volume, so that it can be entirely neglected for the solid and dense liquid states.

Correlated motions of atoms simply means that the potential experienced by an atom is determined by the instantaneous positions of the remaining atoms rather than their mean positions which are used in the theory of Lennard-Jones and Devonshire.

The majority of work on cell cluster theory published to date has been concerned with the liquid and gas states. Therefore great interest has been directed at the problem of communal entropy. Originally there were three groups which developed independent theories each giving identical results but calculated differently. De Boer and co-workers were the first actually to publish work on the cell-cluster theory. Initially a general technique was set up whereby the exact
partition function could be expressed simply as a product of the single particle (LJD) partition function $Z_{\text{LJD}}$ and a series involving cell-cluster terms with appropriate coefficients. The cell-cluster terms of DeBoer are integrals over the volumes of adjacent nearest neighbour cells. By integrating each particle over the entire cell-cluster volume one automatically includes a contribution to the entropy due to multiple occupancy of cells and exchanges of particles between cells. Hence, De Boer and co-workers have succeeded in accounting for the communal entropy and the correlation of motion of particles simply by introducing one new factor in the LJD classical partition function. It is in the evaluation of this cell-cluster expansion where De Boer and others differ in technique. De Boer selects from the entire series those terms with $Q_1$ (the six dimensional integral) raised to various powers. Other theories approximate the expansion by taking the first two terms exactly and replacing all higher order terms by ones involving powers of $Q_1$. De Boer, Cohen, Salsburg, and co-workers\textsuperscript{5-12} having defined their technique, then went on to apply their theory to one, two, and three dimensional systems of hard spheres and particles interacting with harmonic forces. They found that the expansion seems to converge\textsuperscript{*} and also that the convergence is better in three-dimensions than in one or two-dimensions\textsuperscript{12}.

In 1955, Barker\textsuperscript{14-17} also started to formulate his own cell-cluster theory. It differed from De Boer's in two ways. The

---

\textsuperscript{*} Matthew\textsuperscript{13} showed that for the linear chain the free energy is a convergent series of cluster integrals.
communal or disorder term was not intrinsically included in
the cell-cluster integrations and thus has to be included as
an extra term in the partition function. Also Barker took
the first few terms in the cell-cluster expansion exactly
and approximated the remaining terms as compared to De Boer's
method of approximating the entire series. Barker found that
disorder effects could be neglected for solids and for liquids
near the triple point. He also found that for harmonic forces
the correlation contributions (up to nine-dimensional or ternary
cell-cluster integrals) to the free energy were temperature
independent. This was inevitable since the Einstein model
already gives 3R for $C_v$. The correlation correction therefore
tends to increase the entropy but keeps the energy the same.
For the large part this would still hold true when anharmonic
terms are included. Having made harmonic calculations of
binary and ternary terms, Barker also found that the ternary
terms are "comparatively unimportant" as compared to the
binary ones. Hence he suggests that the inclusion of binary
terms in the cell-cluster theory "should give a satisfactory
description of the liquid and solid states".

Taylor, the third original worker in the field of cell-
cluster theory only presented his technique never following
this up with applications. His method of summing the correlation
series is similar to that used by Barker. In performing the
integrations he uses spherically averaged potential functions
in order to reduce the order of integrations. In 1957, Barker\textsuperscript{16}
found that smeared potentials led to quite unsatisfactory con-
vergence of the series.

In the past there has been a lack of completed calculations
on close packed three dimensional anharmonic solids. Presumably
this is due to the immense computational difficulties which are
involved. Assuming that these difficulties can be over-come,
cell-cluster theory does offer an exact classical description
provided that the series is summed to completion and thus would
be a viable alternative to the expensive Monte Carlo method. It
is to that end that this thesis has been written.
I The Partition Function

Consider a three dimensional crystal lattice of $N$ atoms each with mass $m$. The mean position of atom 1 is given by the vector $\hat{R}_1$ in a cartesian frame of reference. The instantaneous displacement of atom 1 from its mean position, $R_1$, is $\hat{u}_1 = u_x \hat{i} + u_y \hat{j} + u_z \hat{k}$. Here $\hat{i}$, $\hat{j}$, and $\hat{k}$ are the cartesian unit vectors corresponding to the $x$, $y$, and $z$ directions respectively.

Figure 1.1
M and N are the mean positions and $P$ and $Q$ are the instantaneous positions of atoms $i$ and $j$ respectively. Here $\hat{R}_{ij}$ means $\hat{R}_i - \hat{R}_j$ and similarly $\hat{u}_{ij}$ means $\hat{u}_i - \hat{u}_j$. $\hat{r}_{ij}$ is the vector separation of the two atoms.

If we assume two body interactions of the central force type then the potential, $\phi$, due to the interaction between atoms $i$ and $j$ is only a function of the distance between the two atoms. Now summing all pair interactions over the crystal, we can write the total potential energy, $\phi$, of the crystal as:

$$\phi = \frac{1}{2} \sum_{i,j} \phi(|\hat{R}_{ij} - \hat{R}_i + \hat{u}_i - \hat{u}_j|)$$  \hspace{1cm} 1.1

Here $i$ and $j$ are both to be varied from 1 until N with the prime signifying that $i \neq j$. Equation 1.1 can be decomposed as follows:

$$\phi = \frac{1}{2} \sum_{i,j} \phi(|\hat{R}_{ij}|) + \sum_{i,j} \{\phi(|\hat{R}_{ij} + \hat{u}_i|) - \phi(|\hat{R}_{ij}|)\}$$

$$+ \frac{1}{2} \sum_{i,j} \{\phi(|\hat{R}_{ij} + \hat{u}_i|) + \phi(|\hat{R}_{ij}|) - \phi(|\hat{R}_{ij} + \hat{u}_i|) - \phi(|\hat{R}_{ij} - \hat{u}_j|)\}$$  \hspace{1cm} 1.2
A quick examination verifies that equations 1.1 and 1.2 are equivalent. We can now write the total potential energy as a sum of three terms:

\[ \phi = N\phi_o + \sum_i \phi(\vec{u}_i) + \frac{1}{2} \sum_{i,j} \phi(\vec{u}_i, \vec{u}_j) \]  

where,

\[ \phi_o = \frac{1}{2} \sum_j \phi(|\vec{R}_{ij}|) \]  

\[ \phi_1 = \sum_j \{\phi(|\vec{R}_{ij} + \vec{u}_i|) - \phi(|\vec{R}_{ij}|)\} \]  

\[ \phi_2 = \phi(|\vec{R}_{ij}|) + \phi(|\vec{R}_{ij} + \vec{u}_i|) - \phi(|\vec{R}_{ij} + \vec{u}_j|) - \phi(|\vec{R}_{ij} - \vec{u}_j|) \]

Note that in the first term on the right hand side of equation 1.3, the summation over \( i \) has already been carried out. This term is the potential energy of the crystal when all atoms are at their mean positions. The next two terms are corrections to \( N\phi_o \), due to instantaneous displacements from the equilibrium positions of one and two atoms respectively. In the Lennard–Jones and Devonshire single particle theory, only the one particle term is used in \( \phi \). Hence correlations between atoms are neglected.

The classical partition function is;
\[ Z = \frac{\hbar^{-3N}}{N!} \int \cdots \int \exp \left\{ -\beta \left( \frac{1}{2m} \sum_{i=1}^{N} \mathbf{R}_{i} \cdot \mathbf{R}_{i} + \Phi \right) \right\} \, dp_{x1} \, dp_{y1} \cdots \]
\[ \, dp_{z1} \, d\tau_{1} \cdots d\tau_{N} \quad 1.7 \]

where \( \frac{1}{N!} \) arises due to the indistinguishability of the atoms.

By arranging the \( N \) atoms over the \( N \) cells the integral in Equation 1.7 becomes a sum of integrals with one, two, three, etc. atoms per cell. For solids, we can neglect multiple occupancy terms so that we are left only with those integrals with one atom per cell. Since there are \( N! \) ways of placing \( N \) atoms in \( N \) cells, the \( N! \) in Equation 1.7 is cancelled out and the integral reduces to the integral of \( N \) atoms over \( N \) cell volumes.

The integrations are to be performed over the \( 3N \) momentum coordinates and over the volumes of the \( N \) Wigner-Seitz cells.

The \( 3N \) momentum integrals are all independent and Gaussian in form so that the integrals over these coordinates can be carried out immediately. Using equation 1.3 to expand \( \Phi \), we are left with;

\[ Z = \frac{\hbar^{-3N}}{N!} \int \cdots \int \exp \left\{ -\beta \left[ N\phi_{0} + \Sigma \phi_{i} (\mathbf{\hat{u}_{i}}) + \frac{1}{2} \Sigma_{i,j} \phi_{2} (\mathbf{\hat{u}_{i}}, \mathbf{\hat{u}_{j}}) \right] \right\} d\tau_{1} \cdots d\tau_{N} \quad 1.8 \]
where,

\[ \lambda^2 = h^2 \beta / (2 \pi m) \]  

1.9

We will now introduce the factors \( F_{ij} \), where;

\[ F_{ij} = \exp \left\{ -\beta \phi_2 (\vec{u}_i, \vec{u}_j) \right\} - 1 \]  

1.10

Hence,

\[ \exp \left\{ -\frac{1}{2} \beta \sum_{i,j} \phi_2 (\vec{u}_i, \vec{u}_j) \right\} = \prod_{i > j} (1 + F_{ij}) \]

\[ = (1 + F_{21})(1 + F_{31}) \]

\[ \cdots (1 + F_{N,N-1}) \]

\[ = 1 + \frac{1}{2} \sum_{i,j} F_{ij} + \frac{1}{4} \sum_{i,j} \sum_{k,l} F_{ij} F_{kl} + \cdots \]

\[ (i,j) \neq (k,l) \]

\[ (j,i) \neq (k,l) \]  

1.11

Now 1.8 becomes:
\[ Z = \lambda^{-3N} \exp\{-\beta N \phi \} \mathcal{G}^N \left( 1 + \frac{1}{2} \sum_{i,j} \langle F_{ij} \rangle + \frac{1}{4} \sum_{i,j} \sum_{k,l} \langle F_{ijkl} \rangle + \cdots \right) \]  

where,

\[ G = \int_{\text{cell } i} \exp\{-\beta \phi_1 (\mathbf{r}_i)\} d\tau_i \]  

\[ \langle F_{ij} \rangle = G^{-2} \iint_{\text{cells } i,j} \exp\{-\beta [\phi_1 (\mathbf{r}_i) + \phi_1 (\mathbf{r}_j)]\} F_{ij} d\tau_i d\tau_j \]  

\[ \langle F_{ijkl} \rangle = G^{-4} \iiint_{\text{cells } i,j,k,l} \exp\{-\beta [\phi_1 (\mathbf{r}_i) + \phi_1 (\mathbf{r}_j) + \phi_1 (\mathbf{r}_k) + \phi_1 (\mathbf{r}_l)]\} F_{ijkl} d\tau_i d\tau_j d\tau_k d\tau_l \]  

It is interesting to note that if there are no correlations at all (which means that all terms \( \langle F_{ijkl} \rangle \) are zero) then equation 1.12 reduces to the familiar LJD partition function.

\[ \text{LJD} \quad Z = \lambda^{-3N} \exp\{-\beta N \phi \} \mathcal{G}^N \]
For convenience $Z$ can now be expressed in terms of $Z_{\text{LJD}}$:

$$Z = Z_{\text{LJD}}Z_{\text{cor}}$$ \hspace{1cm} 1.17

where,

$$Z_{\text{cor}} = \left\{ 1 + \frac{1}{2} \sum_{i,j} \langle F_{ij} \rangle + \ldots \right\}$$ \hspace{1cm} 1.18

The independent particle partition function, $Z_{\text{LJD}}$, which involves a three-dimensional integral has been evaluated to great accuracy in the past. However, as far as we have been able to determine, the correlation term, $Z_{\text{cor}}$, has not yet been solved in the anharmonic three-dimensional case. This is primarily due to two reasons:

a) $Z_{\text{cor}}$ is a sum of "cluster integrals"* each with non-trivial combinatorial factors. This makes the exact summing of $Z_{\text{cor}}$ an impossible task, at least in the anharmonic case.

b) $Z_{\text{cor}}$ also involves integrals of degree six and higher thus leading to complicated computer programs which require much computer time if reasonable accuracy is to be obtained.

* The meaning of cluster integrals will be clarified in the next section.
In sections 2 and 3, these problems are studied in greater detail enabling us to solve them and find $Z_{\text{cor}}$ to acceptable accuracy. The resulting thermodynamic properties for the F.C.C. lattice structure are then presented in section 4.
2 The Cluster Summation

Up until now virtually all of the work done on cell cluster theory has used $6 - 12$ potentials with nearest neighbour interactions only.

$$
\phi(r) = \varepsilon \left\{ (r_0/|\vec{r}|)^{12} - 2(r_0/|\vec{r}|)^6 \right\}
$$

The well depth, $\varepsilon$, and the zero point nearest neighbour distance, $r_0$, for various rare gas crystals are given in Horton's review article$^{24}$. Although the $6-12$ potential is a good model for the rare gas crystals$^{24}$, other potential functions can also be used. The theory developed in this thesis is limited to nearest neighbour interactions but is in no way limited to the $6 - 12$ potential. The addition of more distant neighbour effects further complicates the theoretical and computational problems without significantly improving the model. In fact, Guggenheim and McGlashan found that all neighbour models exaggerate the effect of non-nearest neighbours$^{23}$. Before we deal with the summing techniques for $Z_{cor}$, it is imperative that we have a good understanding of how cell clusters arise.
(a) Cell Clusters

Consider the cluster integral $<F_{ij}>$. For a given atom $i$ there are two possibilities for atom $j$. It either is or is not a nearest neighbour of $i$. If it is not a nearest neighbour of $i$, then the interaction $\phi$ between the two atoms is zero because our model is a nearest neighbour only model. From equation 1.6 we see that $\phi$ must also be zero which means that $F_{ij}$ and $<F_{ij}>$ are also zero. Hence for the cluster integrals, $<F_{ij} F_{kl} ... F_{mn}>$, to be non zero, all atom pairs $(i,j)$, $(k,l)$, ..., $(m,n)$ must be nearest neighbours of each other. In these cluster integrals $<F_{ij} ... F_{kl}>$ the correlated motions of atoms $i$ and $j$ can be indicated pictorially by a solid bar between the lattice sites "•" of the atoms $i$ and $j$ which are nearest neighbours.

![Figure 2.1](image)

This is the pictorial representation of $<F_{ij}>$ where atoms $i$ and $j$ are nearest neighbours of each other.
The final value of $<F_{ij}>$ cannot depend upon the orientation or position of the "ij bar" in the crystal. It can only depend on the form of the Wigner-Seitz cell, the distance between nearest neighbour lattice sites, the number and position of nearest neighbours, and on the temperature. Hence all cell clusters over the entire lattice, which are identical in form, give the same expectation values. This means that all $<F_{ij}>$'s are equivalent so it only remains for us to determine how many of these single ij bars are possible over the crystal lattice.

Assume the lattice in question has a coordination number $z$ ($z$ is the number of nearest neighbours). If atom $i$ is chosen in $N$ ways then atom $j$ can be chosen in $z$ ways. We could have chosen atom $j$ first so we have overcounted by a factor of two. Hence the combinational factor for is $\frac{N!}{2}$. It should be noted that for very large $N(\sim 10^{23})$ edge effects can be neglected.

The next term along in our expansion of $Z_{\text{cor}}$ consists of all two bar possibilities. The two bars either have or do not have one atom in common.

\begin{figure}[h]
\centering
\begin{subfigure}[b]{0.49\textwidth}
\includegraphics[width=\textwidth]{figure2a}
\caption{(a)}
\end{subfigure}\hfill
\begin{subfigure}[b]{0.49\textwidth}
\includegraphics[width=\textwidth]{figure2b}
\caption{(b)}
\end{subfigure}
\caption{Figure 2.2}
\end{figure}
Figures (a) and (b) respectively represent cluster integrals of the type $\langle F_{ij} F_{kl} \rangle$ with no atoms and with one atom in common between bars.

For a given lattice (two or three dimensional), atom $i$ in Figure 2.2 (b) can be chosen from $(z-1)$ neighbours of atom $j$. Since the value of $\langle F_{ij} F_{j1} \rangle$ depends on the relative orientation between bars $i$, $j$ and $j$, $1$, there will be in general more than one distinct cluster of the type in Figure 2.2 (b). For each cluster integral, the combinatorial factors must again be derived. These combinatorial factors rapidly grow more complicated as higher order clusters are considered. To illustrate these points further, we will go on to study the triangular two dimensional lattice.

(b) The Triangular Lattice

![Triangular Lattice Diagram](image)

Figure 2.3
Possible cell clusters for the triangular two-dimensional lattice up to \( l = 3 \) are indicated. A neighbour distance of \( r = r_0 \) is used. Appendix I illustrates how the cluster integrals are calculated. Values for most of the integrals were calculated by Salsburg\(^9\).
To simplify matters somewhat, we will in future identify each distinct cluster integral with a label $Q_{\ell,t}$. Here, $\ell$, gives the total number of pair correlations (bars) in the cell cluster and $t$ identifies the configuration.

We will illustrate the techniques used in compiling the multiplicities of Table 2.1 by considering two examples.

![Diagram](attachment:image.png)

(a) (b)

Figure 2.4

For the triangular two-dimensional lattice (a) and (b) are clusters $Q_{2,2}$ and $Q_{2,1}$ respectively.

$Q_{2,2}$:

1) Chose atom 1 in $N$ ways.

2) Chose atom 2 in $z$ ways.

3) Atom 2 could have been chosen first so divide $Nz$ by two.
<table>
<thead>
<tr>
<th>Cluster</th>
<th>Code</th>
<th>$g_{k,t}$</th>
<th>$&lt;F_{ij} \cdots F_{kl}&gt;$</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>$Q_{1,1}$</td>
<td>3N</td>
<td>0.60660174E (-1)</td>
</tr>
<tr>
<td></td>
<td>$Q_{2,1}$</td>
<td>$\frac{1}{2}$ 3N [3N -11]</td>
<td>0.36796567E (-2)</td>
</tr>
<tr>
<td></td>
<td>$Q_{2,2}$</td>
<td>3N</td>
<td>1.2573077E (-2)</td>
</tr>
<tr>
<td></td>
<td>$Q_{2,3}$</td>
<td>12N</td>
<td>0.5883381E (-2)</td>
</tr>
<tr>
<td></td>
<td>$Q_{3,1}$</td>
<td>$\frac{1}{3}$ 3N[3N-11][3N-22] + 23N</td>
<td>0.22320862E (-3)</td>
</tr>
<tr>
<td></td>
<td>$Q_{3,2}$</td>
<td>3N [3N - 16]</td>
<td>0.76268504E (-3)</td>
</tr>
<tr>
<td></td>
<td>$Q_{3,3}$</td>
<td>6N [3N - 16]</td>
<td>0.35688692E (-3)</td>
</tr>
<tr>
<td></td>
<td>$Q_{3,4}$</td>
<td>6N [3N - 15]</td>
<td>0.35688692E (-3)</td>
</tr>
<tr>
<td></td>
<td>$Q_{3,5}$</td>
<td>3N</td>
<td>2.7536259E (-3)</td>
</tr>
<tr>
<td></td>
<td>$Q_{3,6}$</td>
<td>24N</td>
<td>1.25252629E (-3)</td>
</tr>
<tr>
<td></td>
<td>$Q_{3,7}$</td>
<td>18N</td>
<td>0.57805329E (-3)</td>
</tr>
<tr>
<td></td>
<td>$Q_{3,8}$</td>
<td>24N</td>
<td>0.57805229E (-3)</td>
</tr>
<tr>
<td></td>
<td>$Q_{3,9}$</td>
<td>2N</td>
<td>-7.06106800E (-3)</td>
</tr>
<tr>
<td></td>
<td>$Q_{3,10}$</td>
<td>12N</td>
<td>1.76053839E (-3)</td>
</tr>
<tr>
<td></td>
<td>$Q_{3,11}$</td>
<td>18N</td>
<td>0.36934300E (-3)</td>
</tr>
</tbody>
</table>

Table 2.1
4) For a given "bar 1,2" atom 3 can only be picked in one way.

5) Multiply $\frac{\text{Nz}}{2}$ by one to get a combinatorial factor of $\frac{\text{Nz}}{2}$ for $Q_{2,2}$.

$Q_{2,1}$:

1) Chose "bar 1,2" in $\frac{\text{Nz}}{2}$ ways.

2)

![Diagram of a lattice with labeled bars 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14.]

Figure 2.5

Since bars 1,2 and 3,4 are not connected bar 3,4 can be chosen from all of the remaining bars in the lattice except for the ones shown in Figure 1.2. Since there are eleven of these, "bar 3,4" can be chosen in $(\frac{\text{Nz}}{2} - 11)$ ways. The combinatorial factor is then the product divided by 2 because bar 3,4 could have been chosen first. We therefore have $\frac{1}{2} \frac{\text{Nz}}{2} (\frac{\text{Nz}}{2} - 11)$.

The other combinatorial factors can be calculated in the same manner. The product in equation 1.11 leads, in general, to a total of $C(\text{Nz}/2, r) = \frac{1}{r!} \frac{\text{Nz}}{2} (\frac{\text{Nz}}{2} - 1) \cdots (\frac{\text{Nz}}{2} - r + 1)$ clusters containing r bars. This can be used as a check against the calculated combinatorial factors.

A detailed explanation of how the cluster integrals of Table 2.1 are evaluated is given in Appendix I.
Consider for a moment the expression \( (1 + \langle F_{ij} \rangle)^{\frac{Nz}{2}} \). If we expand this out in a Taylor's series, we get;

\[
(1 + \langle F_{ij} \rangle)^{\frac{Nz}{2}} = 1 + \frac{1}{1!} \frac{Nz}{2} \langle F_{ij} \rangle + \frac{1}{2!} \frac{Nz}{2} \left( \frac{Nz}{2} - 1 \right) \langle F_{ij} \rangle^2 + \ldots
\]

But;

\[
Z_{\text{cor}} = 1 + \frac{1}{1!} \frac{Nz}{2} \langle F_{ij} \rangle + \frac{1}{2!} \frac{Nz}{2} \left( \frac{Nz}{2} - 1 \right) \left\{ \langle F_{ij} F_{kl} \rangle \right\}_{\text{type terms}} + \ldots
\]

This means that if \( \langle F_{ij} F_{kl} \rangle = \langle F_{ij} \rangle^2 \) etc. is true, then

\[
Z_{\text{cor}} = (1 + \langle F_{ij} \rangle)^{\frac{Nz}{2}}. \quad \text{Although this is not exactly the case, it does seem to indicate that } Z_{\text{cor}} \text{ can be written in the form:}
\]

\[
Z_{\text{Cor}} = (1 + S_1 + S_2 + S_3 + \ldots)^{\frac{Nz}{2}}
\]
We will refer to the expression in curly brackets as $\Sigma$. By raising $\Sigma$ to a power linear in $N$ we are ensuring that the correct $N$ dependence arises for the thermodynamic limit. To satisfy this condition further we must also note that the $S_n$ terms must be independent of $N$. We find in Appendix III that this is indeed the case. Using equation 2.4 rather than an equation such as 2.3 should simplify things for us immensely. Since $\Sigma$ is independent of $N$ we expect it to converge more quickly than the expression for $\Sigma$ given in equation 2.3. If we were to evaluate only terms involving up to ninth order integrals say, then the higher order terms of equation 2.3 would be partly included by the expansion of lower order terms in equation 2.4.

Hoover$^{25}$ and Huckaby$^{26}$ using different methods have found that $\frac{Nz}{2} \ln[\Sigma_{\text{harm}}] = 0.27326N$. Hence for the triangular lattice:

$$\Sigma_{\text{harm}} = 1.0954$$  \hspace{1cm} 2.5

Various methods of approximating $\Sigma_{\text{harm}}$ using cell cluster theory have been used in the past. We now quickly review these:

Lennard-Jones and Devonshire - In LJD theory, the free energy due to correlations is zero. The sum $\Sigma_{\text{harm}}$ must then be identically
equal to one.

De Boer and Co-workers - De Boer retained only those diagrams consisting of a number of disconnected single bars, and used statistical arguments to approximate the remaining terms in the series. The expression for $Z_{\text{cor}}$ which he arrived at is given by:

$$Z_{\text{cor}} = \left[ \frac{(1 - \hat{\chi})^{z/2}}{(1 - z\hat{\chi})} \right]^N$$

where:

$$\hat{\chi} = \{2z\langle q_{1,1} \rangle + 1 - \sqrt{4(z - 1)\langle q_{1,1} \rangle + 1} \}/[2(z^2\langle q_{1,1} \rangle + 1]$$

Table 2.1 gives $\langle q_{1,1} \rangle$ and we know $z$ to be six for the triangular lattice. Therefore:

$$\sum_{\text{harm}}^{\text{De Boer}} = (1 - \hat{\chi})(1 - z\hat{\chi})^{-2/z} = 1.04822$$
Barker and Taylor - These workers assumed that \( \langle F_{ij}F_{kl} \rangle = \langle F_{ij} \rangle^2 \) etc. as mentioned earlier. \( \Sigma_{\text{harm}} \) then reduces exactly to

\[
\sum_{\text{harm}} (B + T) = (1 + \langle q_{1,1} \rangle) = 1.06066
\]

Salsburg and Co-workers - In the expression for \( Z_{\text{cor}} \), Salsburg excludes multiple cluster integrals of the type \( Q_{2,1}', Q_{3,1}', Q_{3,2} \) etc. and all clusters with uncorrelated nearest neighbours. His summing of \( Z_{\text{cor}} \) is still exact but the convergence of various order approximations to \( Z_{\text{cor}} \) changes. The results are given in Table 2.2.

Evaluation of \( \Sigma_{\text{harm}} \) - We perform the expansion of \( \frac{1}{N} \sum_{i>j} (1 + F_{ij}) \) exactly so that all of the integrals innumerated in Table 2.1 arise. The calculation of \( s_1, s_2, \) and \( s_3 \) is carried out in Appendix III.

<table>
<thead>
<tr>
<th>P Salsburg</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \sum_{\text{harm}} )</td>
<td>1.06066</td>
<td>1.07380</td>
<td>1.07739</td>
<td>1.08000</td>
</tr>
<tr>
<td>( \sum_{\text{harm}} )</td>
<td>1.06066</td>
<td>1.07837</td>
<td>1.07994</td>
<td>-------</td>
</tr>
</tbody>
</table>

Table 2.2
The order, \( p \), defines \( \Sigma_{\text{harm}} \) to be

\[
(1 + S_1 + \ldots + S_p)^{\frac{N_z}{2}} \cdot \Sigma_{\text{harm}}
\]

calculated using Salsburg's theory and ours is tabulated above.

Graph 2.1

Approximations to \( \Sigma_{\text{harm}} \) for the various techniques are illustrated above.
Reference to Graph 2.1 shows that our method and that of Salsburg give results in best agreement with the actual value of 1.0954. This is probably due to the fact that both methods try to sum the cell-cluster series exactly. The difference between the two methods is in the convergence of the summing technique. The convergence of our third order approximation is approximately that of Salsburg's fourth order approximation.

Suppose that only anharmonic integrals with \( \ell \) equal to one and two* at most, can be calculated accurately (this is most certainly the case with present computing facilities). The remaining possible integrals in the sum \( \Sigma_{\text{Exact}} \) can at least be included in a harmonic sense if \( \Sigma_{\text{harm}} \) is known as a function of lattice spacing**. \( \Sigma_{\text{harm}} \) can be calculated from the normal modes of the lattice:

\[
\Sigma_{\text{Exact}} = 1 + S_1^{\text{Exact}} + S_2^{\text{Exact}} + ... \tag{2.10}
\]

\[
\Sigma = 1 + S_1\text{Exact} + S_2\text{harm} + S_3\text{harm} + ... \tag{2.11}
\]

and,

\[
\Sigma_{\text{Exact}} = \{ \Sigma_{\text{harm}} - S_1\text{harm} \} + S_1^{\text{Exact}} \tag{2.12}
\]

* In two and three dimensions \( Q_{\ell, t} \) is a six degree integral for \( \ell \) equal to two and one respectively.

** \( \Sigma_{\text{harm}} \) is always independent of temperature. Refer to Appendix I.
Equation 2.11 is clearly superior to \( \Sigma_{\text{Exact}} = 1 + S_{l}^{\text{Exact}} \) which completely neglects all remaining terms. If the neglected anharmonic contributions are relatively small, as one might expect for \( l \gg 2 \), then equations 2.12 will be a very accurate expression for the exact result, Equations 1.17, 2.4, and 2.12 can now be combined to give:

\[
Z = Z_{LJD} \left( \Sigma_{\text{harm}} - S_{l}^{\text{harm}} + S_{l}^{\text{Exact}} \right)_{2}^{N_{z}}
\]

which will be used in our anharmonic calculations for the f.c.c. lattice.
3. The F.c.c. Lattice

(a) The Harmonic Model

A three-dimensional lattice of $N$ coupled harmonic oscillators has a total energy of:

$$E_{n_1, n_2, n_3, \ldots n_{3N}} = N\phi_0 + \sum_{m=1}^{3N} (n_m + \frac{1}{2})\hbar \omega_m$$

where the $3N$ normal modes ($m = 1, 2, \ldots 3N$) have frequencies $\omega_m$. Considering all possible states $n_1, n_2, \ldots, n_{3N}$ enables us to write the free energy, $F_H$ as:

$$F_H = -kT \ln(Z)$$

$$= N\phi_0 + kT \sum_{m=1}^{3N} \left\{ \frac{\hbar \omega_m}{2} + \ln(1 - e^{-\beta \hbar \omega_m}) \right\}$$  \hspace{1cm} (3.2)

In the high temperature limit $e^{-\beta \hbar \omega_m}$ can be expanded giving:

$$F_H = N\phi_0 + kT \sum_{m=1}^{3N} \ln(\beta \hbar \omega_m)$$  \hspace{1cm} (3.3)

We now define the "geometric mean frequency", $\omega_g$, as:

$$\omega_g = \exp \left\{ \frac{1}{3N} \sum_{m=1}^{3N} \ln(\omega_m) \right\}$$  \hspace{1cm} (3.4)
and also note that for our f.c.c. model equation 1.4 gives
\[ \phi = 6\phi(r). \] Hence:

\[ F_H = 6N\phi(r) + 3NkT \ln [\beta \omega_g] \] 3.5

The 3\(N\) equations of motion of the atoms can be uncoupled so that the vibrational frequencies, \(\omega_m (m = 1 \ldots 3N)\), can be found. The geometric mean frequency, which is a function only of the lattice spacing can therefore be calculated for large \(N\) at various lattice spacings (see Appendix IV). It turns out that \(\omega_g\) can then be written, with good accuracy, as:

\[ \omega_g = \left\{ a_1 + a_2 \gamma + a_3 \gamma^2 + a_4 \gamma^3 \right\} \left( \frac{\phi_II}{\phi_I} \right)^{m/4} \] 3.6

where:

\[ \gamma = \phi^I/(r\phi^II) \] 3.7

and where the constants \(a_1, a_2, a_3,\) and \(a_4\) can be determined by evaluating \(\omega_g\) using equation 3.4 at four well chosen nearest neighbour distances, \(r^*\). Now the harmonic free energy in the high temperature limit is essentially a known function of temperature and neighbour distance. From section 2, the cell cluster expression for \(F_{\text{harm}}\) is:

\[ F_{\text{harm}} = -kT \ln \left[ \frac{LJD}{\omega_{\text{harm}}} \right] \] 3.8

* From Appendix IV, we have \(a_1 = 1.84221, a_2 = 2.38253, a_3 = -2.35761,\) and \(a_4 = 3.46762.\)
If we make use of the fact that equations 3.5 and 3.8 are equivalent, we can solve for $\Sigma_{\text{harm}}$:

$$\Sigma_{\text{harm}} = \left[ \frac{2\pi}{\phi II \beta} \right]^{3/2} G_{\text{harm}} \left( a_1 + a_2 \gamma + a_3 \gamma^2 + a_4 \gamma^3 \right)^{3/2} \quad 3.9$$

Using Appendix II to find a harmonic expression for $\phi_1 (\hat{u})$, we get for $G_{\text{harm}}$:

$$G_{\text{harm}} = \int_{\text{cell}} \exp(-\beta A(u_x^2 + u_y^2 + u_z^2)) d\tau \quad 3.10$$

where:

$$A = 2(\phi II + 2\phi I/r) \quad 3.11$$

By extending the limits of integration over all space 3.10 reduces to a standard solvable integral giving equation 3.12. The error introduced by this approximation can be estimated using the error function. From erf(x) tables we find that the error introduced by integrating over all space is never worse than five parts in $10^9$ for the entire range of temperatures and lattice spacings under consideration.

$$G_{\text{harm}} = (\pi/\beta A)^{3/2} \quad 3.12$$
Now combining equations 3.9 and 3.12 we get;

\[ \Sigma_{\text{harm}} = \left( \frac{2A}{\phi^{II}} \right)^{\frac{1}{2}} (a_1 + a_2 \gamma + a_3 \gamma^2 + a_4 \gamma^3)^{\frac{1}{2}} \]  

<table>
<thead>
<tr>
<th>( \frac{R}{R_0} )</th>
<th>( \Sigma_{\text{harm}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.000</td>
<td>1.04195</td>
</tr>
<tr>
<td>1.0125</td>
<td>1.03990</td>
</tr>
<tr>
<td>1.0250</td>
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</tr>
<tr>
<td>1.0375</td>
<td>1.03480</td>
</tr>
<tr>
<td>1.050</td>
<td>1.03165</td>
</tr>
</tbody>
</table>

**Table 3.1**

The value of \( \Sigma_{\text{harm}} \) at \( R = 1.0 \) agrees well with Huckaby's accurate result\(^2\) of 1.042501. Huckaby's result at \( r = 1.0 \) also gives \( \omega = 1.8420 \left( \phi^{II}/m \right)^{\frac{1}{2}} \) which compares well with our result of \( a_1 \left( \phi^{II}/m \right)^{\frac{1}{2}} \).

\( S_{\text{harm}} \) was found in Appendix V to be the harmonic integral arising from the cluster \( Q_{1,1} \), as was the case for the triangular lattice. From Appendix II we find:

\[ S_{\text{harm}} = \frac{1}{G^2} \int \int_{\text{harm cells}} e^{-\beta \phi_1 (u_1)} e^{-\beta \phi_2 (u_2)} e^{-\beta \phi_{1,2} (u_1, u_2)} e^{-\beta \phi_{1,2} (u_1, u_2)} d\tau_1 d\tau_2 \]

where:

\[ \phi_1 (u_1) = 2(\phi^{II} + 2\phi^{I}/r) \sum_{a=1}^{3} u_a^2 \]  

3.15(a)
\[
\phi_2(\vec{u}_i, \vec{u}_j) = -\frac{1}{2}(\phi^{II} + \phi^{I}/r)(u_{x_i}u_{x_j} + u_{y_i}u_{y_j}) \\
- (\phi^{I}/r)u_{z_i}u_{z_j} - \frac{1}{2}(\phi^{II} - \phi^{I}/r)(u_{x_i}u_{y_j} + u_{y_j}u_{x_j}) \\
\]

By extending the limits of integration to infinity, \( S_1^{\text{harm}} \) becomes:

\[
S_1^{\text{harm}} = \{[(1 - b^2)(1 - b^2) \frac{b^2}{3} (1 - \frac{b^2}{b^2})] - 1\} \\
\]

where:

\[
b_0 = -\frac{1}{6}(\phi^{II} + \phi^{I}/r) / (\phi^{II} + 2\phi^{I}/r) \\
b_1 = -\frac{1}{12}(\phi^{I}/r) / (\phi^{II} + 2\phi^{I}/r) \\
b_2 = -\frac{1}{12}(\phi^{II} - \phi^{I}/r) / (\phi^{II} + 2\phi^{I}/r) \\
b_3 = 1 - b^2 / (1 - b^2) \\
b_4 = 1 + b^2 / (1 - b^2) \\
\]

\( G_{\text{harm}} \) is given in equation 3.12.

We now have expressions for \( \Sigma_1^{\text{harm}} \) and \( S_1^{\text{harm}} \) as functions of near neighbour distance \( r \) and absolute temperature \( T \). It now remains
for us to find $Z_{\text{LJD}}^1$ and $S_1$.

(b) The Anharmonic Model

Recall that:

$$Z_{\text{LJD}}^1 = \lambda^{-3N} \exp\{-\beta N \phi_0\} G^N$$

where:

$$\lambda^2 = \hbar^2 \beta / (2\pi m)$$

$$G = \int_{\text{cell}} \exp\{-\beta \phi_1 (\mathbf{u}_1)\} d\tau_1$$

When dealing with anharmonic three-dimensional integrals such as $G$, the conventional method used is to generate denser and denser uniform meshes over the cell until the summation approximation to $G$ has reached the required convergence. $G$ is approximated by:

$$G \approx dV \sum_{n_1, n_2, n_3 = -n_m}^{+n_m} \exp\{-\beta \phi_1 (\mathbf{U}_1 (u_{x, y, z, r}))\}$$
where,

\[ \Phi_i = \frac{1}{n_m} \langle n_1, n_2, n_3 \rangle \frac{r}{\sqrt{2}} \] 3.22

Here \( dV \) is the volume of a unit cell within the generated mesh and \( n_m \) refers to the maximum positive value of \( n \). From section 1, we recall that:

\[ \phi_i (\vec{u}_i) = \sum_{k=1}^{12} \{\phi(|\vec{R}_{ij} + \vec{u}_i|) - \phi(|\vec{R}_{ij}|)\} \] 3.23

If atom \( i \) is positioned at \((0,0,0)\) then its 12 nearest neighbours are at \((\pm 1, \pm 1, 0)\), \((\pm 1, 0, \pm 1)\), and \((0, \pm 1, \pm 1)\).

Graph 3.1

The nearest neighbours of atom \( i \).
These positions will be written as:

\[ \mathbf{R}_{ij} = \frac{r}{\sqrt{2}} \langle R_x, R_y, R_z \rangle \] 3.24

The deviation of atom i from its mean position \((0, 0, 0)\) is:

\[ \mathbf{u}_i = \frac{r}{\sqrt{2}} \langle \frac{n_1}{M}, \frac{n_2}{M}, \frac{n_3}{M} \rangle \] 3.25

finally giving:

\[ \phi(|\mathbf{R}_{ij} + \mathbf{u}_i|) = \varepsilon \left( \frac{r}{2r_o} \right)^{-12} \left[ (R_x + \frac{n_1}{M})^2 + (R_y + \frac{n_2}{M})^2 + (R_z + \frac{n_3}{M})^2 \right]^{-6} \]

\[ -2\left( \frac{r}{\sqrt{2}r_o} \right)^{-6} \left[ \varepsilon \{ \text{RNSQ} \} - 2\{ \text{RNSQ} \} \right] \] 3.26

also:

\[ \phi(|\mathbf{R}_{ij}|) = \varepsilon \{ R - 2R \} \] 3.27

where \( R = \frac{r}{r_o} \) and where RNSQ is the expression in square brackets.

\( G \) can now be approximated by generating a mesh over the Wigner-Seitz Cell and summing:
\[ G_{\text{mesh}} = \frac{r^3}{2V_{2n}^3} \sum_{n_1, n_2, n_3 = -n_M}^{n_M} e^{-T_Q \left( RNSQ -6 -2RNSQ + 2R -R \right)} \]

where \( T_Q = \frac{K_T}{\epsilon} \) is the reduced temperature.

Having generated various mesh densities, we found that using \( n_M = 30 \) resulted in a convergence of \( G_{\text{mesh}} \) to at least 9 digits for \( T_Q \)'s and \( R \)'s of interest.

<table>
<thead>
<tr>
<th>( T_Q )</th>
<th>1.0</th>
<th>1.0125</th>
<th>1.025</th>
<th>1.0375</th>
<th>1.05</th>
</tr>
</thead>
<tbody>
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<td>0</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
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</tr>
<tr>
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<td>185.394199</td>
<td>255.749546</td>
<td>352.771863</td>
</tr>
</tbody>
</table>

Table 3.2

This is a table of \( G_{\text{mesh}} \) in units of \( 10^{-5} \) \( r_0^3 \) for \( n_M = 30 \) with \( R = r/r_0 \) and \( T_Q = KT/\epsilon \).

The volume used was approximately one ninth that of the Wigner Seitz cell (i.e. \( t = 1/3 \)).

Refer to equation 3.32.

Using equation 3.28 with \( n_M = 30 \) as the expression for \( G \) in equation 3.18, \( Z_{\text{LJD}} \) becomes a known expression in \( r \) and \( T \).
We need now only find an expression for $S$ in equation 2.13 in order to know the anharmonic partition function of the f.c.c. lattice. This cannot be achieved by generating a dense 6-d mesh because the computer time required would be far too great. Instead we will attempt to achieve reasonable accuracy by generating low-density meshes.

The first step of course is to attain very accurate harmonic results using low-density meshes. Write $G$ as:

$$ G = \Delta^3 \sum_{n \leq n_1 \leq n_2 \leq n_3} e^{-\Delta^2(n_1^2 + n_2^2 + n_3^2)} $$

where,

$$ D = 2\beta (\phi \Pi^2 + 2\phi^2/r) = 24T_Q (11R - 5R) r_o $$

and:

$$ \Delta = t (\frac{R}{2n_M}) r_o $$

The parameter $t$, which varies from 0 to 1, indicates the volume
over which the mesh is to be generated. If \( t = 1 \), then the entire Wigner Seitz cell is used. If \( t = .5 \), then the mesh is only generated to half the linear distance of \( \frac{r}{2} \), etc.

Graph 3.2

The shaded areas of this 2-d illustration show the areas of integration corresponding to (a) \( t=1 \) and (b) \( t=.5 \).

From the previous work with dense meshes it was found that for low temperatures virtually all contribution to the integral came from the region with \( t < .5 \). Knowing also the exact result for \( G_{\text{Harm}} \) to be \( (\pi/D)^{3/2} \), we went ahead and calculated

\[
\frac{G_{\text{HarmMesh}}}{G_{\text{Harm}}} = \frac{G_{\text{MH}}}{G_{\text{Harm}}}
\]

for various values of \( t \) and \( n_M \) with \( R = 1.0 \) and \( T_Q = .05 \).
Notice that for $t/n_M=\text{constant (.1 and .5/6)}$ the ratio $G_{MH}/G_{\text{Harm}}$ stays constant. $t/n_M=\text{constant}$ simply states that the volume mesh density stays constant. Hence the mesh generated by $t/n_M=.4/4$ is identical to that generated by $t/n_M=.3/3$ except that additional vectors from outside the $t=.3$ volume are included in the sum. Since the ratio stays 3.49, we then know that the volume corresponding to $t=.3$ contains virtually all of the mesh contribution. In fact, using $t/n_M$ of $0.2/2$ and $0.1/1$ still gives 3.49. Hence for $R=1.0$ and $T_Q=0.05$, a $t/n_M$ of $0.1/1$ is sufficient to obtain a converged value for $G_{MH}$ (to 12 digits) at that mesh density. Table 3.4 shows the volumes at which $G_{MH}/G_{\text{Harm}}$ has converged for various mesh densities ($t/n_M$).

<table>
<thead>
<tr>
<th>$t/n_M$</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
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<tbody>
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<td>6.8</td>
<td>2.01</td>
<td>1.19</td>
<td>1.025</td>
</tr>
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<td>11.7</td>
<td>3.49</td>
<td>1.62</td>
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<td>3.49</td>
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<tr>
<td>.5</td>
<td>433</td>
<td>54.2</td>
<td>16.10</td>
<td>6.78</td>
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</tr>
<tr>
<td></td>
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<td></td>
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</tr>
<tr>
<td>$t/n_M$</td>
<td>6</td>
<td>7</td>
<td>8</td>
<td>9</td>
<td>10</td>
</tr>
<tr>
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<tr>
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</tr>
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<td>1.47</td>
<td>1.19</td>
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<td>1.03</td>
</tr>
</tbody>
</table>

Table 3.3
Table of $G_{MH}/G_{\text{Harm}}$ at $R=1.00$ and $T_Q=0.05$
Table 3.4

\( \frac{G_{MH}}{G_{Harm}} \) as varying with \( n_M \) for constant density at \( R = 1.0 \) and \( T_Q = .05 \).
From the results so far, it is obvious that there are no contributions from near the Wigner Sietz boundaries so that we can reduce the shape of the integration to a sphere for simplification. This follows from the spherical symmetry of the potential used. t then would be an indication of the sphere's radius.

If we wish to use an \( n_M \) of 4 or 5 (which is quite reasonable for 6-d integrals) then we must find the optimum t associated with those \( n_M \)'s. \( t_{\text{opt}}(n_M) \) is simply the value of t for a given \( n_M \) which results in \( G_{\text{MH}} \) matching \( G_{\text{Harm}} \) very accurately. Hence by varying t for different \( n_M \)'s, we were able to find \( t_{\text{opt}}(n_M, R, T) \) which matched \( G_{\text{MH}} \) to \( G_{\text{Harm}} \) to at least 11 digits. This was accomplished with the use of a Wang 700C programmable calculator.

<table>
<thead>
<tr>
<th>( n_M )</th>
<th>( t_{\text{opt}}(n_M, 1.0, .05) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>.05637532497</td>
</tr>
<tr>
<td>2</td>
<td>.08975505638</td>
</tr>
<tr>
<td>3</td>
<td>.1116433217</td>
</tr>
<tr>
<td>4</td>
<td>.131195282</td>
</tr>
<tr>
<td>5</td>
<td>.147286195</td>
</tr>
</tbody>
</table>

Table 3.5

This is a table of the values for \( t_{\text{opt}} \)
at \( R = 1.0 \) and \( T_Q = .05 \) for \( n_M = 1, 2, \ldots 5 \).

If for a given \( n_M \) we now keep \( \Delta \sqrt{D} \) (from the exponential in equation 3.30) constant we can force the sum to converge to 11 digit accuracy for any combination of \( R \) and \( T_Q \). \( \Delta \sqrt{D} \) is therefore equated to \( \Delta \sqrt{D} \) evaluated at a known \( t_{\text{opt}} (n_M, R_K, T_{QK}) = t_K(n_M) \), say. \( t_{\text{opt}} (n_M, R, T_Q) \) then becomes:

\[
t_{\text{opt}} (n_M, R, T_Q) = t_K(n_M) \left[ \frac{(11R_K^{-12} - 5R_K^{-6}) (T_Q)}{(11R^{-12} - 5R^{-6}) (T_{QK})} \right]^{-1/2}
\]

and:

\[
G_{MH} = g_K^3 \left[ T_Q / (11R^{-14} - 5R^{-8}) \right]^{3/2} \sum_{n_1 n_2 n_3} e^{-24g_K^2 (n_1^2 + n_2^2 + n_3^2)}
\]

where:

\[
g_K = \frac{t_K(n_M)}{2n_M} \left[ (11R_K^{-12} - 5R_K^{-6}) / T_{QK} \right]^{1/2}
\]

Low \( n_M \)'s of 1 or 2 give exact results for \( G_{\text{Harm}} \) because the poor convergence of the sum cancels the too small volume over which the series is summed. When \( n_M = 4 \), a change of 6.7%
in $t_{opt}$ (4) results in an error of less than .5% in $G_{Harm}$. Hence by $n_M = 4$, the sum has converged and the volume at $t_{opt}$ (4) includes most of the contributions to $G_{Harm}$. In our future calculations, we will use a $n_M = 5$ which gives an even more accurate result.

Using $n_M = 5$ and $t_{opt}$ (5), we went ahead and calculated $G_{Exact}$ for various values of $R$ and $T_q$ (a table similar to Table 3.2 was generated). All results agreed with the very accurate $G_{Mesh}$ values of Table 3.2 to at least 4 digits. In fact, 90% of the results agreed to at least 5 digits. We now know that good results are possible using non-dense meshes provided that great care is taken in choosing the volume of integration.

From previous studies, we have learned that even at higher temperatures atoms stay fairly close to their mean positions. Averaging its motion also puts it closer to its mean position. Hence in the 6 dimensional integral, one moving atom seems to the other moving atom, very much as if it is positioned at its mean position. This only means that the contribution to the 6 dimensional integral due to correlation of motions between the two atoms is small. If a separate $t_{opt}(n_M)$ for a 6-d integral was calculated, we certainly would not expect more than a 5% difference to be found in $t_{opt}$. This as we found earlier would change the sum very little.
As in the dense mesh which was used to calculate $G_{\text{mesh}}$, we again restricted the volume of integrations over the two zone volumes to spherical forms. This is possible because of the low value of $t_{\text{opt}} (n_M = 5)$. Symmetry further allowed us to reduce computing time by a factor of approximately three. If the atomic mean positions lie on the $x = y$ axis with $z = 0$, then the sum over the $z$ co-ordinates of the first atom, 

$$\sum_{n_3 = n_M}^{n_M} f(n_3),$$

can be replaced by \{\(f(0) + \sum_{n_3 = 1}^{n_M} f(n_3)\)\}. The $y$ component can also be kept smaller than the $x$ component. All together, this will reduce the volume over which the mesh is generated for atom $i$ by a factor of 4.

The actual formula used to generate $S_{\text{Exact}}^1$ is:

$$S_{\text{Exact}}^1 = \frac{dV^2}{G^2} \sum_{n_i_1 n_i_2 n_i_3 = -n_M}^{n_M} \sum_{n_j_1 n_j_2 n_j_3 = -n_M}^{n_M} \left\{ -\beta \phi_1 (\vec{u}_i) \right\}$$

$$\begin{bmatrix}
-\beta \phi_1 (\vec{u}_j) & -\beta \phi_2 (\vec{u}_i, \vec{u}_j) \\
-\beta \phi_2 (\vec{u}_i, \vec{u}_j) & \cdot & -1 \\
\end{bmatrix}$$

3.36
where:

\[ \tilde{u}_1 = \left\langle \frac{n_{11}}{n_M}, \frac{n_{12}}{n_M}, \frac{n_{13}}{n_M} \right\rangle \frac{r}{\sqrt{2}} \]

\[ \tilde{u}_j = \left\langle \frac{n_{11}}{n_M}, \frac{n_{12}}{n_M}, \frac{n_{13}}{n_M} \right\rangle \frac{r}{\sqrt{2}} \]

The term \( G \) was regenerated from equation 3.30 for \( t_{\text{opt}}(n_M=5) \).

The results for the complete range of \( R \) and \( T_Q \) are given in Table 3.6.

<table>
<thead>
<tr>
<th>( T_Q )</th>
<th>( R )</th>
<th>1.0</th>
<th>1.0125</th>
<th>1.025</th>
<th>1.0375</th>
<th>1.05</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.2796</td>
<td>3.0941</td>
<td>2.7872</td>
<td>2.6260</td>
<td>2.3309</td>
<td></td>
</tr>
<tr>
<td>.1</td>
<td>3.3080</td>
<td>3.1410</td>
<td>2.9545</td>
<td>2.7484</td>
<td>2.5249</td>
<td></td>
</tr>
<tr>
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<td>3.3311</td>
<td>3.1768</td>
<td>3.0080</td>
<td>2.8258</td>
<td>2.6325</td>
<td></td>
</tr>
<tr>
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<td>3.3517</td>
<td>3.2073</td>
<td>3.0518</td>
<td>2.8862</td>
<td>2.7127</td>
<td></td>
</tr>
<tr>
<td>.4</td>
<td>3.3708</td>
<td>3.2350</td>
<td>3.0905</td>
<td>2.9384</td>
<td>2.7803</td>
<td></td>
</tr>
<tr>
<td>.5</td>
<td>3.3892</td>
<td>3.2612</td>
<td>3.1263</td>
<td>2.9857</td>
<td>2.8446</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.6

\( S \) exact in units of \( 10^{-2} \) as generated with
n_M = 5 for temperatures and atomic spacings of interest. The zero temperature results are of course the temperature independent harmonic results. Each value on this table required the generation of 84,975 independent six dimensional vector configurations giving a total of 265,225 configurations.

Since we can now find S^{Exact}_1 to good accuracy, every unknown in equation 2.13 for the partition function, Z, is an obtainable quantity.

(c) Thermodynamic Properties

Now that Z is essentially a known function of temperature and lattice spacing we can now find the thermodynamic properties of the f.c.c. lattice from the Helmholtz Function. From standard thermodynamic texts, we have:

\[ F = -kT \ln (Z) \]  

The lattice spacing given by this model can be found by solving for R(T_Q) in the zero pressure equation. Thus solving:

\[ -P(r) = \left( \frac{\partial F}{\partial V} \right)_T \]
for r reduces to solving:

$$\left( \frac{\partial F}{\partial R} \right)_{TQ} = 0$$ \hspace{1cm} 3.40

for R in units of $r_0$. By solving equation 3.40 over the entire temperature range, we now essentially know the reduced lattice spacing, R, as a function of the reduced temperature. This enables us to determine $\alpha$, the coefficient of thermal expansion:

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$$ \hspace{1cm} 3.41

where:

$$V = NR^3r_0^3/\sqrt{2}$$ \hspace{1cm} 3.42

becomes:

$$\alpha = \frac{3}{R} \left( \frac{\partial R}{\partial T} \right)_P$$ \hspace{1cm} 3.43

in units of $K/\epsilon$. The isothermal compressibility, $K_T$:

$$K_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$$ \hspace{1cm} 3.44
can also be expressed in reduced units and becomes:

\[
K_T = -\frac{3}{\sqrt{2}} R^2 \alpha \left( \frac{\partial^2 F}{\partial R \partial T} \right)_P
\]

where \( F \) is in units of \( \varepsilon N \) and \( K_T \) is in units of \( r_0^3/\varepsilon \). The specific heats at constant volume and constant pressure can also be found in this manner and are expressed in units of \( Nk \):

\[
C_V = T \left( \frac{\partial^2 F}{\partial T^2} \right)_P
\]

\[
C_p = C_V - T \left( \frac{\partial R}{\partial T} \right)_P \left( \frac{\partial^2 F}{\partial R \partial T} \right)_P
\]

The last thermodynamic property which we are interested in is the Grüneisen parameter which is completely unitless and is given by:

\[
\gamma = -R \frac{\partial^2 F}{\partial R^2} / (3C_V)
\]

Each of the thermodynamic quantities will be numbers times the appropriate unit expressed as a combination of \( k \), \( N \), \( \varepsilon \) and \( r_0 \).
Thermodynamic Relation | Units
---|---
$F = -T_Q \ln \left( \frac{N \sqrt{2}}{r_0} \right)$ | N\epsilon
$R = R(T_Q)$ | $r_0$
$\alpha = -\frac{\sqrt{2}}{3R^2} K_T \left( \frac{\partial^2 F}{\partial \epsilon T_Q} \right)$ | K/\epsilon
$K_T = -\frac{2}{\sqrt{2}} R \left( \frac{\partial R}{\partial T_Q} / \left( \frac{\partial^2 F}{\partial \epsilon T_Q} \right) \right)$ | $r_0^3/\epsilon$
$C_V = -T_Q \left( \frac{\partial^2 F}{\partial T_Q^2} \right)$ | NK
$C_P = C_V - T_Q \left( \frac{\partial R}{\partial T_Q} \right) \left( \frac{\partial^2 F}{\partial \epsilon T_Q} \right)$ | NK
$\gamma = -R \frac{\partial^2 F}{\partial \epsilon T_Q} / (3C_V)$ | 1

Table 3.7

A summary of relations (and their units) used to obtain the thermodynamic properties of the f.c.c. lattice using cluster theory.

The advantage to calculating the above relations in a dimensionless form is that the results can be compared to any appropriate f.c.c. crystal by simply substituting suitable values for the parameters $\epsilon$ and $r_0$ from the 6-12 potential.
4 Theoretical Results

By combining equations 2.13 and 3.18, we can write an expression for the exact mesh generated free energy:

\[ F_{\text{Exact}} = - T \ln \left( \frac{N}{V^2} \right) \]

\[ = 3T \ln(\lambda) + 6 \frac{\phi(r)}{\varepsilon} - T \ln(G_{\text{Mesh}}) - 6T \ln(S_{\text{harm}}) + S_{\text{Exact}} \]

4.1

The harmonic free energy is a known function of \( R \) and \( T Q \).

It is:

\[ F_{\text{Harm}} = 3T \ln(\lambda) + 6 \frac{\phi(r)}{\varepsilon} - T \ln(G_{\text{harm}}) - 6T \ln(S_{\text{harm}}) \]

4.2

so that \( F_{\text{Exact}} \) can be written as:

\[ F_{\text{Exact}} = F_{\text{Harm}} + F_{\text{anharm}} \]

4.3

where:

\[ F_{\text{anharm}} = - T \ln \left( \frac{G_{\text{mesh}}}{G_{\text{harm}}} \right) + 6 \ln \left[ 1 - \left( \frac{S_{\text{harm}}}{S_{\text{harm}}} - \frac{S_{\text{Exact}}}{S_{\text{harm}}} \right) \right] \]

4.4
\( G_{\text{harm}} \), \( \Sigma_{\text{harm}} \), and \( S_{\text{harm}} \) are given by equations 3.12, 3.13, and 3.16 respectively.

Since \( F_{\text{harm}} \) is an explicitly known function of \( R \) and \( T_Q \), its derivatives can be obtained by direct differentiation. \( F_{\text{anharm}} \) will be relatively small as compared to \( F_{\text{harm}} \) and should be more well-behaved than \( F_{\text{exact}} \). Hence performing polynomial fits on \( F_{\text{anharm}} \) or its parts, or using numerical differentiations of \( F_{\text{anharm}} \), is more desirable than fitting the entire free energy.

It was first felt that polynomial fits to the data of Tables 3.2 and 3.6 would be the most straightforward way to derive the thermodynamic properties. Various fits were performed on \( G_{\text{mesh}} \), \( G_{\text{mesh}}/G_{\text{harm}} \) and \( \ln(G_{\text{mesh}}/G_{\text{harm}}) \) and on \( (\Sigma_{\text{harm}} - S_{\text{harm}} + S_{\text{Exact}}) \), \( (1-(S_{\text{harm}}-S_{\text{Exact}})/\Sigma_{\text{harm}}) \) and \( \ln[1-(S_{\text{harm}}-S_{\text{Exact}})/\Sigma_{\text{harm}}] \) and on various combinations of the two. Extra points for \( G_{\text{mesh}} \) and \( S_{\text{Exact}} \) had been generated in order that the reliability of the fits could be tested. No polynomial fit (in \( R \) and \( T_Q \)) could be found that predicted all values of Tables 3.2 and 3.6 to acceptable accuracy. However, it was found that if adjacent 3 x 3 blocks of data from Tables 3.2 and 3.6 were used to form quadratic fits to the forms above, extra points within the 3 x 3 block could be predicted with at least seven digit accuracy. Quadratic fits of the logarithms were found to give the best results. Of course a fit generated within one 3 x 3 block of data did not necessarily predict accurate results for points with \( R \) and \( T_Q \) outside that particular block. We therefore took the closest block of 3 x 3 to calculate \( R(T_Q) \).
and the remaining properties. T\textsubscript{Q} was varied from .005 to .5 in steps of .005 with R being found for each temperature. The original quadratic fits were created from the data at R = 1.00, 1.0125, and 1.025 and T\textsubscript{Q} = 0, .1, and .2, but were created from other blocks of 3 x 3 as R increased with increasing T\textsubscript{Q}. The R versus T\textsubscript{Q} graph became irregular whenever a shift occurred in data block used. This of course would destroy the accuracy of all properties near these points.

Since we did know where these discontinuities occurred, we could still make use of the information. By choosing values of T\textsubscript{Q} which yielded reliable results for R, we were able to generate a fine rectangular grid of nine points centred on the originally predicted zero pressure point (R\textsubscript{1}, T\textsubscript{Q1}), say. From previous work, it was found that respective differences of .001 and .01 in R and T\textsubscript{Q} resulted in a suitable mesh of points to form quadratic fits to the logarithms (as had been done before). The free energy around these points, (R\textsubscript{1}, T\textsubscript{Q1}), could now be found to seven digit accuracy.

By using a free energy accurate to seven digits we were able to find \( \frac{\partial^2 F}{\partial R \partial T\textsubscript{Q}} \) and \( \frac{\partial^2 F}{\partial T\textsubscript{Q}^2} \) to respective accuracies of four and five digits. To improve the accuracy of Cv which involves the second temperature derivative, we only calculated the deviation from the harmonic value of 3Nk. This deviation was approximately 10% of 3Nk so that Cv was found to five digit accuracy. The lattice spacing which the new mesh predicted was always in good agreement to the one
predicted earlier using Tables 3.2 and 3.6 (they agreed to at least five digits). The results are shown on Table 4.1 and Graphs 4.1 through 4.5. The zero temperature results for R, Cv and Cp are their harmonic values.

<table>
<thead>
<tr>
<th>$T_q$($\varepsilon/k$)</th>
<th>R ($r_o$)</th>
<th>$\alpha$ (K/$\varepsilon$)</th>
<th>$K_T$($r_o^3/\varepsilon$)</th>
<th>Cv (NK)</th>
<th>Cp(NK)</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
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<tr>
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<td>2.7806</td>
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</tr>
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<td>.04638</td>
<td>2.6265</td>
<td>4.268</td>
<td>2.883</td>
</tr>
</tbody>
</table>

Table 4.1

This table summarizes the computational results for the thermodynamic properties of an f.c.c. monatomic lattice with nearest neighbour only 6-12 interactions.

When considering these results, we should keep in mind that the cluster theory which has been introduced thus far is a classical model. The experimental results (of the specific heat in particular) seem to show that quantum mechanical effects only play an important part for reduced temperatures of below .2. Therefore the temperature region of .2 to .5 should be of most interest to us.
Graph 4.1

TEMPERATURE (E/k)

ATOMIC SEPARATION (\( r \))
Graph 4.2

Volume Expansion (V/V₀) vs. Temperature (ɛ/k)

Coefficient of Thermal Expansion
The curves of Graphs 4.1 to 4.5 were produced from the theoretical results of Table 4.1. The solid circles (and the triangles for $C_p$) are experimental results for solid Xenon as given by Trefny and Serin\textsuperscript{31}. In their paper, they used results for the thermal expansion (for temperatures higher than 90^\circ K) as given in a paper by Gavrilko and Manzhelii\textsuperscript{32} (1965). In a later paper Manzhelii, Gavrilko, and Kuchnev\textsuperscript{33} presented new values for the thermal expansion obtained from a purer (99.92% pure) solid Xenon sample. The older results were used by Trefny and Serin to calculate values for $C_v$ and the Grüneisen parameter. The hollow circles on the $C_v$, Grüneisen parameter, and a plot were plotted using the new results for the thermal expansion. Because of the higher sample purity, the hollow circles should be more accurate than the solid circles at given temperatures. The difference between these values is also somewhat indicative of the experimental accuracy that can presently be obtained when dealing with rare gas crystals. We might also add that for higher temperatures the uncertainty of the compressibility is quoted as nearly 20%. Since the compressibility is used to calculate $C_v$ and the Grüneisen parameter, uncertainties of about 8% and 28% respectively are introduced.

The cell cluster results agree quite well with the experimental results despite the uncertainties involved in the experimental data. This seems to indicate that the extension of cell cluster theory to the solid state model is justified and also seems to show that the Mie-Lennard-Jones potential is an appropriate potential for the rare gas crystals.
Since the Monte Carlo and cell cluster methods are both exact and can accommodate any type interaction, it would clearly be desirable to compare the two for the same crystal model. Results for the f.c.c. lattice with Lennard-Jones (6-12) interactions between nearest neighbours are given in Table 4.2. $\langle \Phi \rangle$ is the expectation value of the potential energy, including the static energy. The other symbols have been used earlier.
\[ T = 120^\circ K, \ r = 4.433 \, \text{Å} \]

\[ T = 160^\circ K, \ r = 4.493 \, \text{Å} \]

<table>
<thead>
<tr>
<th></th>
<th>Monte Carlo*</th>
<th>Cell-Cluster</th>
<th>Cell Theory</th>
<th>Monte Carlo*</th>
<th>Cell-Cluster</th>
<th>Cell Theory</th>
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<tr>
<td>(\phi)/NKT</td>
<td>-14.83±.01</td>
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<td>-14.834</td>
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<td>-10.607</td>
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<td>.349</td>
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<td>.655</td>
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<tr>
<td>(C_v)/Nk</td>
<td>2.82±.03</td>
<td>2.733</td>
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<td>2.78±.05</td>
<td>2.646</td>
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<tr>
<td>(\gamma)</td>
<td>2.99±.02</td>
<td>2.929</td>
<td>3.077</td>
<td>2.97±.05</td>
<td>2.876</td>
<td>3.001</td>
</tr>
</tbody>
</table>

Table 4.2

* These numbers were communicated to us by Dr. M. L. Klein.
The cluster correction to single cell theory contributes most significantly to the pressure, which of course leads to improved lattice spacing calculations. The cell theory values of all four quantities are altered in the direction of the Monte Carlo numbers by the cluster correction. This however does not account fully for the difference in the specific heat. The type of model studied may be responsible for the smallness of some of the corrections. This can be verified in the future by applying cluster theory to other crystal models. We hope to be able to carry out further cell-cluster and Monte Carlo comparisons when more Monte Carlo results become available.

At this point, we might mention that Weissmann and Mazo\textsuperscript{30} have carried out cell-cluster calculations for a model interacting with a 6-12 potential and at volumes larger than those of normal liquids. They used the cell-cluster theory as developed by DeBoer, Cohen, and Salzburg and were only concerned with the problem of evaluating the 6-dimensional cluster integral by use of Monte Carlo numerical integration. The integrals were only found to one digit accuracy and the results gave poorer agreement with experiment than single cell theory. A refinement of their technique would be necessary in order to obtain meaningful results.
5 Summary

We have developed the theory and described a practical method of evaluating the Helmholtz free energy of a crystal in the cell-cluster approximation. By considering the relatively simple two-dimensional harmonic triangular lattice, we were able to derive cluster sums to orders of up to three and consequently compare our convergence with other cluster summing techniques. We were able to attain approximately the same convergence for \( \sum_{\text{harm}} \) with a third order approximation as Salsburg was able to attain by including up to fourth order terms. This would seem to indicate that our method of grouping cluster terms in the summation of \( \sum \) leads to a more convergent series. Extending this summing technique over to the harmonic f.c.c. lattice, we were able to derive first and second order expressions for \( \sum_{\text{harm}} \) which accounted for 78% and 95% of the difference between the exact and Einstein results respectively. Our convergence for the f.c.c. model again proved to be superior in convergence to the other methods discussed.

We have evaluated the first order anharmonic cluster integral to a higher accuracy than had been done before. This was carried out on a relatively modest computer (Burroughs 5500) for less than 1/50th the estimated price which Monte Carlo
calculations would have cost. For temperatures near \( T_e = .5 \),
the inclusion of cluster corrections in the free energy led
to increases of approximately .3%, 20%, 14%, -.4%, 10%, and 9% in
\( r, \alpha, K_T, C_v, C_p, \) and \( \gamma \) respectively over the cell theory
results. Since the harmonic cluster terms were temperature
independent, it is easy to understand why the cluster
correction in the anharmonic case had little effect upon \( C_v \).
By considering the remaining quantities, one must conclude
that cell-clusters have a real effect upon the thermodynamic
properties of the crystal studied. It is unfortunate that
the effect of the correlation term was small for \( C_v \) (for the
Monte Carlo comparison as well) but Dr. E. R. Cowley has found
more encouraging results in a subsequent application of
cell-cluster theory to alkali halides.

Monte Carlo calculations are presently restricted to
low sample numbers and suffer from low statistical accuracy
so that cluster theory, which is also an exact theory, offers
a powerful alternative. Our calculations have been restricted
to the classical model but an extension to quantum theory for
lower temperatures is possible. Levelt and Hurst\(^{34}\) have
carried out accurate quantum mechanical calculations of the
internal energies, entropies, and specific heats for \( H_2 \) and
deuterium in the cell theory approximation. By solving the
Schroedinger equation for many energy levels, they were able to
find the partition functions and hence the thermodynamic properties. The simplicity of the rare gas wave functions lends itself to such an application. The correlation terms would introduce complexity into the problem but theoretically the problem is do-able.

The theory developed here can be applied to any crystal structure and to any interaction. Extension of the theory to include more than nearest neighbour interactions or higher order cluster integrals is a straightforward matter but would be quite time consuming.
APPENDIX I

Cluster Integrals

We will evaluate the cluster integral, \( \langle Q_{l,t} \rangle \), for \( Q_{1,1} \).

We have:

\[
\langle Q_{1,1} \rangle = G^{-2} \int \int \exp\{-\beta[\phi_1(\vec{u}_1) + \phi_1(\vec{u}_2)] + \exp\{-\beta[\phi_2(\vec{u}_1, \vec{u}_2)]\} - 1\} d\tau_1 d\tau_2 \tag{I.1}
\]

Using the definition of \( G^2 \), equation I.1 becomes:

\[
\langle Q_{1,1} \rangle = G^{-2} \int \int \exp\{-\beta[\phi_1(\vec{u}_1) + \phi_1(\vec{u}_2) + \phi_2(\vec{u}_1, \vec{u}_2)]\} du_1 du_2 du_1 du_2 - 1 \tag{I.2}
\]

From equations II.6 and II.7 from Appendix II, we can find the harmonic expression for \( \phi_1(\vec{u}_1) \).

\[
\phi_1(\vec{u}_1) = \sum_{j} \frac{n'b'rs}{2!} \left\{ \sum_{a=1}^{2} u_a^2 D_a \right\} \phi(r)
\]

\[
= \sum_{j} \frac{n'b'rs}{2} \frac{u_j^2 D_j^2}{x_j x_j} + \sum_{j} \frac{n'b'rs}{2} \frac{u_j^2 D_j^2}{y_j y_j} \tag{I.3}
\]
Figure I.1
The coordinates of nearest neighbour cells to a cell at (0,0) are shown above.

By making use of the neighbour coordinates given in Figure I.1 equation II.3 then gives:

\[ \frac{1}{2} \sum_{i=1}^{n'b'rs} D_x^2 \phi = \frac{1}{2} \sum_{j=1}^{n'b'rs} D_y^2 \phi = \frac{3}{2} (\phi^I + \phi^I/r) \quad I.4 \]

Therefore:

\[ \phi(y_i) = \frac{3}{2} (\phi^I + \phi^I/r) \left\{ u_x^2 + u_y^2 \right\} \quad I.5 \]
For the triangular lattice equation II.9 becomes:

\[ \phi (u_i, u_j) = - \{ \sum_{\alpha=1}^{2} u_{\alpha i} u_{\alpha j} \frac{D^2}{\alpha} + (u_{x1} u_{yj} + u_{xj} u_{yi}) \frac{D}{xy} \} \phi \]  

I.6

If atom \( i \) is at the origin in Figure I.1 then we can put atom \( j \) at \((1,0)r\) for simplicity. Equation II.3 now gives:

\[ D^2_{\phi} = (\phi II - \phi I/r) + \phi I/r \]  

I.7(a)

\[ D^2_{\phi} = \phi I/r \]  

I.7(b)

\[ D_{xy} \phi = 0 \]  

I.7(c)

At \( r=r_0 \) the first derivative of \( \phi \) is zero. Hence:

\[ \phi (u_i, u_j) = - u_{x1} u_{y1} \phi II \]  

I.8

Equation I.2 now reduces to:

\[ \langle Q_{1,1} \rangle = G^{-2} \left\{ \exp \left\{ - \left[ A(u^2_{x1} + u^2_{y1} + u^2_{x2} + u^2_{y2}) \right. \right. \right. \]

\[ \left. \left. \left. + Bu_{x1} u_{x2} \right] \right\} du_{x1} \ldots du_{y2} \]  

I.9

-1
where,

\[ A = \frac{3}{2} \Phi^{II\beta} \quad \text{(I.10a)} \]

\[ B = -\frac{1}{2} \Phi^{II\beta} \quad \text{(I.10b)} \]

If we now extend the integration in I.9 to all of space, we can solve for \( \langle Q, 1 \rangle \) by completing the squares in I.9 in order to reduce the integral to a standard Gaussian form. If we write the exponent in I.9 in matrix form, we can solve the integral simply by evaluating the determinant of \( D \):

\[
A(u_{x_1}^2 + u_{y_1}^2 + u_{x_2}^2 + u_{y_2}^2) + Bu_{x_1}u_{x_2} = [u_{x_1}, u_{y_1}, u_{x_2}, u_{y_2}]
\]

\[
\begin{bmatrix}
A & 0 & \frac{1}{2}B & 0 \\
0 & A & 0 & 0 \\
\frac{1}{2}B & 0 & A & 0 \\
0 & 0 & 0 & A
\end{bmatrix}
\begin{bmatrix}
U_{x_1} \\
U_{y_1} \\
U_{x_2} \\
U_{y_2}
\end{bmatrix}
\]

\[ = \overline{u}^\dagger D \overline{u} \quad \text{(I.11)} \]

where, \( \overline{u}^\dagger = [u_{x_1}, u_{y_1}, u_{x_2}, u_{y_2}] \)
The integral is then equivalent to \( \frac{\pi^{S/2}}{\sqrt{\det(D)}} \) where \( S \) is the order of the integration. \( G \) is given by \( \pi/\sqrt{\Lambda^2} \) so that for \( \langle Q_{1,1} \rangle \) we get:

\[
\langle Q_{1,1} \rangle = \left( \frac{\pi}{\sqrt{A^2}} \right)^{-2} \pi^2 (A^4 - \frac{1}{4} A^2 B^2)^{-1/2} = (1 - \frac{1}{4} (\frac{B}{A})^2)^{-1/2}
\]

\[
= \frac{3}{\sqrt{8}} - 1 \approx 0.06066
\]

where use has been made of equations I.10(a) and (b). All of the harmonic cluster integrals \( \langle Q_{l,t} \rangle \) are independent of the exact potential form and of temperature. However the condition \( \phi^l = 0 \) at \( r = r_o \) is used.

The reader will note that certain clusters such as \( \bullet \) and \( \bullet \) seem to be missing from Table 2.1. If an end bar is reflected through either of it's connected ends, then the cluster integral turns out to be the same. Hence we need only include one specific cluster and account for all of the other reflected forms by increasing the combinatorial factor by an appropriate amount. Therefore \( \bullet \) and \( \bullet \) are accounted for by the clusters \( \bullet \) and \( \bullet \) respectively.
APPENDIX II

The Harmonic Expressions For $\phi_1$ and $\phi_2$

Assume a potential function $\phi(|\hat{r}_{ij}|)$ where

$$\hat{r}_{ij} = \vec{R}_{ij} + \hat{u}_{ij}$$

is the distance between atoms $i$ and $j$.

In order to be able to expand $\phi$ in a series of terms involving powers of $u_x$, $u_y$ and $u_z$ where $\hat{u} = <u_x,u_y,u_z>$, we must know the various derivatives of $\phi$ with respect to $u_x$, $u_y$ and $u_z$. Repetitive differentiations of $\phi$ gives:

$$\phi = \phi$$

$$\frac{\partial \phi}{\partial u_\alpha} = \frac{r_\alpha}{r} \phi I$$

$$\frac{\partial^2 \phi}{\partial u_\alpha \partial u_\beta} = \frac{r_\alpha r_\beta}{r^2} (\phi^{II} - \phi I/r) + \delta_{\alpha\beta} \phi I/r$$

$$\frac{\partial^3 \phi}{\partial u_\alpha \partial u_\beta \partial u_\gamma} = \frac{r_\alpha r_\beta r_\gamma}{r^3} (\phi^{III} - 3\phi^{II}/r + 3\phi I/r)$$

$$+ (\delta_{\alpha\beta} \frac{r_\gamma}{r} + \delta_{\alpha\gamma} \frac{r_\beta}{r} + \delta_{\beta\gamma} \frac{r_\alpha}{r})(\phi^{II}/r - \phi I/r^2)$$
\[
\frac{\partial^4 \phi}{\partial \alpha \partial \beta \partial \gamma \partial \delta} = \frac{r_{\alpha \beta} r_{\gamma \delta}}{r^4} (\phi_{IV} - 6\phi_{III}/r + 15\phi_{II}/r^2 - 15\phi_{I}/r^3) \\
+ (\delta_{\alpha \beta} \frac{r_{\gamma \delta}}{r^2} + \delta_{\alpha \gamma} \frac{r_{\beta \delta}}{r^2} + \delta_{\alpha \delta} \frac{r_{\gamma \beta}}{r^2} + \delta_{\gamma \delta} \frac{r_{\alpha \beta}}{r^2}) \\
+ \delta_{\beta \delta} \frac{r_{\alpha \gamma}}{r^2} + \delta_{\gamma \delta} \frac{r_{\alpha \beta}}{r^2}) \\
x (\phi_{III}/r - 3\phi_{II}/r^2 + 3\phi_{I}/r^3) + (\delta_{\alpha \beta} \delta_{\gamma \delta} + \delta_{\alpha \gamma} \delta_{\beta \delta}) \\
+ \delta_{\alpha \delta} \delta_{\beta \gamma} \\
x(\phi_{III}/r^2 - \phi_{I}/r^3) \\
\]

where,

\[\phi_{I} = \frac{\partial \phi}{\partial r}\]

\[\phi_{II} = \frac{\partial^2 \phi}{\partial r^2}\]

The \(r_\alpha\)'s are the Cartesian components of \(\mathbf{r}\) which is the vector separation of two atoms.
Recall equation 1.5:

\[ \phi_i = \sum_j \left\{ \phi(|\vec{R}_{ij} + \vec{u}_i|) - \phi(|\vec{R}_{ij}|) \right\} = \sum_j \phi_i \]

\( \phi_i \) which is the term in curly brackets can be expanded in a Taylor's expansion about \( \vec{R}_{ij} \). Hence:

\[ \phi_i = \phi(R_{ij} + u_x, R_{ij}, y_i, R_{ij} + u_z) - \phi(R_{ij}, y_i, R_{ij}) \]

\[ = \left\{ \sum_{a=1}^{3} u_{a1}D_{a1} \right\} + \frac{1}{2} \left\{ \sum_{a=1}^{3} u_{a1}D_{a1}^2 + 2(u_{x1}u_{y1}D_{xy} + u_{y1}u_{z1}D_{yz} + u_{z1}u_{x1}D_{zx}) \right\}
\]

\[ + \frac{1}{3} \left\{ \sum_{a=1}^{3} u_{a1}D_{a1}^3 + 3 \sum_{a=1}^{3} u_{a1}D_{a1}^2 \right\} \]

\[ + \frac{1}{4} \left\{ \sum_{a=1}^{3} u_{a1}D_{a1}^4 + 4 \sum_{a=1}^{3} u_{a1}D_{a1}^3 \right\} \]

\[ + \frac{1}{6} \left\{ \sum_{a=1}^{3} u_{a1}D_{a1}^5 + 5 \sum_{a=1}^{3} u_{a1}D_{a1}^4 + 10 \sum_{a=1}^{3} u_{a1}D_{a1}^3 \right\} \]

\[ + \left\{ 6u_{x1}u_{y1}u_{z1}D_{xyz} + 12u_{x1}u_{y1}u_{z1}D_{x} + u_{x1}u_{y1}u_{z1}D_{y} + u_{z1}u_{x1}u_{y1}D_{z} \right\} \]

\[ + 6(u_{x1}u_{y1}D_{x} + u_{y1}u_{z1}D_{y} + u_{z1}u_{x1}D_{z}) \]

\[ + \ldots \right\} \phi_T = \vec{R}_{ij} \]

* For the f.c.c. lattice \( j \) is summed over atom \( i \)'s twelve nearest neighbours.
where:

\[ D_\alpha = \frac{\partial}{\partial u_\alpha} \]

\[ D_{\alpha\beta} = \frac{\partial^2}{\partial u_\alpha \partial u_\beta} \]

\[ D_{\alpha\beta\gamma} = \frac{\partial^3}{\partial u_\alpha \partial u_\beta \partial u_\gamma} \]

Subscripts 1, 2 and 3 mean \( x, y, \) and \( z \) respectively.

From equations II.2, II.4, ... we can see that if terms in \( \phi_i \) involving odd powers of \( u_\alpha \) are summed over the twelve nearest neighbours in the f.c.c. lattice, their total contribution in \( \phi_1 = \sum \phi_i \) is zero. Using equations II.3, II.5, ..., and equation II.7, and dropping higher than second order terms, II.6 becomes;

\[ \phi_1 = 2(\phi^{II} + 2\phi^I/r) \sum_{\alpha=1}^{3} u_\alpha^2 \]

By following the same procedure, a similar expression for \( \phi_2 \) can be obtained. In general the harmonic result is:
\[
\phi_2(\mathbf{\hat{u}_i}, \mathbf{\hat{u}_j}) = - \left\{ \frac{3}{a} u_i u_j D^2 + (u_{x_i} u_{y_j} + u_{x_j} u_{y_i})D_{xy} \right\} - (u_{y_i} u_{z_j} + u_{y_j} u_{z_i})D_{yz} + (u_{z_i} u_{x_j} + u_{z_j} u_{x_i})D_{xz} \}
\]

Let cell i be located at the origin and let cell j be at \( R_{ji} = \frac{r}{\sqrt{2}} \langle 1, 1, 0 \rangle \). The form of \( \phi_2 \) is then given by:

\[
\phi_2(\mathbf{\hat{u}_i}, \mathbf{\hat{u}_j}) = - \frac{1}{2} \left( \phi^{II} + \phi^{I/r} \right)(u_{x_i} u_{x_j} + u_{y_i} u_{y_j}) - (\phi^{I/r})u_{y_i} u_{z_j}
\]

\[
- \frac{1}{2} \left( \phi^{II} - \phi^{I/r} \right)(u_{x_i} u_{y_j} + u_{x_j} u_{y_i}) \quad \text{II.10}
\]

The exact form of \( \phi_2 \) will depend on the relative positions of cells i and j.
APPENDIX III

S, S, and S for The Triangular Lattice

Considering only cell-clusters of up to third order for the triangular lattice gives:

\[ Z_{\text{cor}} = 1 + \sum_{\ell=1}^{3} \sum_{t=1}^{t_m(\ell)} g_{\ell,t} <Q_{\ell,t}> + O(\text{terms with } \ell > 4) \]  

III.1

where \( t_m(\ell) \) is the maximum value of \( t \) for a given \( \ell \). Reference to Table 2.1 for the combinatorial factors enables us to write \( Z_{\text{cor}} \):

\[ Z_{\text{cor}} = 1 + 3N<Q_{1,1}> + \frac{1}{2!} 3N(3N - 11)<Q_{2,1}> + 3N<Q_{2,2}> + 12N<Q_{2,3}> + \left( \frac{1}{3!} 3N(3N - 11)(3N - 22) + 23N \right)<Q_{3,1}> + 3N(3N - 16)<Q_{3,2}> + 6N(3N - 16)<Q_{3,3}> + 6N(3N - 15)<Q_{3,4}> + 3N<Q_{3,5}> + 24N<Q_{3,6}> + 18N<Q_{3,7}> + 24N<Q_{3,8}> + 2N<Q_{3,9}> + 12N<Q_{3,10}> + 8N<Q_{3,11}> \]  

III.2
Making use of:

\[ <Q_{x,1}^1 > = <Q_{1,1}^1 > \]

\[ <Q_{3,2}^1 > = <Q_{1,1}^1 > <Q_{2,2}^1 > \]

\[ <Q_{3,3}^4 > = <Q_{3,4}^1 > <Q_{1,1}^1 > <Q_{2,3}^1 > \]

enables us to rewrite equation III.2.

\[ Z_{\text{cor}} = (1 + <Q_{1,1}^1 >) + 3N\{-5<Q_{1,1}^1 >^2 + <Q_{2,2}^1 > + 4<Q_{2,3}^1 >\} \]

\[ + 3N\{47\frac{2}{3} <Q_{1,1}^1 >^3 - 16<Q_{1,1}^1 >^2 <Q_{2,2}^1 > - 62<Q_{1,1}^1 >^2 <Q_{2,3}^1 > + <Q_{3,5}^1 > \}

\[ + 8<Q_{3,6}^1 > + 6<Q_{3,7}^1 > + 8<Q_{3,8}^1 > + \frac{2}{3} <Q_{3,9}^1 > + 4<Q_{3,10}^1 > + \frac{2}{3} <Q_{3,11}^1 > \}

\[ + 9N^2\{-5<Q_{1,1}^1 >^3 + <Q_{1,1}^1 >^2 <Q_{2,2}^1 > + 4<Q_{1,1}^1 > <Q_{2,3}^1 >\} \]

If we assume \( Z_{\text{cor}} \) to be of the form:

\[ Z_{\text{cor}} = (1 + S_{1} + S_{2} + S_{3} + \ldots)^{\frac{Nz}{2}} \]

III.5
and expand this in a Taylors series, we get:

\[
Z_{\text{cor}} = 1 + 3N(S_1 + S_2 + S_3) + \frac{1}{2!} 3N(3N - 1)(S_1 + S_2 + S_3)^2 \\
+ \frac{1}{3!} 3N(3N - 1)(3N - 2)(S_1 + S_2 + S_3)^3 + \ldots \quad \text{III.6}
\]

A rearrangement of equation III.6 gives:

\[
Z_{\text{cor}} = (1 + S_1)^{3N} + 3N\{S_2\} + 3N\{S_3 - S_1\} \\
+ 9N^2\{S_1S_2\} + O(\text{terms with } l>4) \quad \text{III.7}
\]

A comparison of equations III.4 and III.7 immediately gives:

\[
S_1 = \langle Q_{1,1} \rangle \quad \text{III.8(a)}
\]

\[
S_2 = 5\langle Q_{1,1} \rangle^2 + \langle Q_{2,2} \rangle + 4\langle Q_{2,3} \rangle \quad \text{III.8(b)}
\]

\[
S_3 = 4\frac{2}{3} \langle Q_{1,1} \rangle^3 - 15\langle Q_{1,1} \rangle \langle Q_{1,2} \rangle + \frac{2}{3} \langle Q_{2,3} \rangle + 4\langle Q_{3,3} \rangle + 2\langle Q_{3,6} \rangle + 6\langle Q_{3,7} \rangle + 8\langle Q_{3,8} \rangle + \frac{2}{3} \langle Q_{3,9} \rangle + \frac{2}{3} \langle Q_{3,11} \rangle \quad \text{III.8(c)}
\]
Now using Table 2.1, we find:

\[ S_1 = 0.060660174 \]

\[ S_2 = 0.017708317 \]

\[ S_3 = 0.001570115 \]
APPENDIX IV

Geometric Mean Frequency

By using the theory of lattice dynamics, it is possible to uncouple the motions of $N$ atoms in a lattice. The equations of motion reduce to:

\[ \omega^2 mU = MU \]  

Here $m$ is a diagonal matrix, $U(q)$ a column matrix and $M(q)$ is a square matrix. These equations are soluable if:

\[ \det(M - \omega^2 I) = 0 \]

The force matrix, $M$, for the F.c.c. lattice is:

\[
\begin{bmatrix}
-2(1-\gamma)(C_2 + C_3) & 2(1-\gamma)S_1 & 2(1-\gamma)S_3 \\
-4C_2 C_3 \gamma + 4 + 8\gamma & -2(1+\gamma)(C_2 + C_3) & 2(1-\gamma)S_1 \\
2(1-\gamma)S_1 & -2C_1 C_2 \gamma + 4 + 8\gamma & -2(1+\gamma)(C_1 + C_3) \\
2(1-\gamma)S_3 & 2(1-\gamma)S_3 & -2C_1 C_2 \gamma + 4 + 8\gamma
\end{bmatrix}
\]

* The complete theoretical arguments have been performed by many authors including W. Cochran, Born and Huang.
where:

\[ S_\alpha = \sin \left( q\alpha \sqrt{2} \right) \]
\[ C_\alpha = \cos \left( q\alpha \sqrt{2} \right) \]

\[ \gamma = \frac{\phi_1}{(\vec{r}\phi)_{II}} \]  
IV.4

and \( \vec{q} = (q_x, q_y, q_z) \) is a vector in reciprocal space. By considering a definite \( \vec{q} \) in momentum space and a definite \( \vec{r} \), we can solve IV.2 for the three normal mode frequencies (one transverse plus two longitudinal). A uniform mesh of \( N \) such wave vectors over the Brillouin zone will give us the 3N vibrational frequencies of a lattice of \( N \) atoms. Having generated 27, 151, and 915 such vectors* in 1/48th space, we found that \( \omega \) as given by equation 3.4 was already highly converged with a mesh of 915 distinct vectors, (this actually is equivalent to 32,000 vectors over the entire Brillouin zone).

Approximately a 5% increase in the nearest neighbour distance \( r \), over the temperature range of absolute zero to the melting point is experimentally found for the inert gas crystals. The range that \( \gamma \) is expected to fall within then is from 0 at absolute zero to .1 at the melting point.

* Various random meshes tried led to relatively poor convergence for \( \omega \).
The geometric mean frequency (times $\sqrt[\frac{3}{2}]{\frac{m}{\phi^{II}}}$) variation with $\gamma$ as found by generating a mesh of 915 independent momentum vectors in 1/48th space over the Brillouin zone.

Having generated numerous values of $\omega_{g\phi^{II}}(\frac{m}{\phi^{II}})^{\frac{3}{2}}$ over the range of $\gamma$, we then fit $\omega_{g\phi^{II}}(\frac{m}{\phi^{II}})^{\frac{3}{2}}$ and its inverse to quadratic and cubic expressions in $\gamma$. The fit:

$$\omega_{g} = \left\{ a_{1} \gamma + a_{2} \gamma^{2} + a_{3} \gamma^{3} \right\} \left( \frac{\phi^{II}}{m} \right)^{\frac{3}{2}}$$

where:
\[ a_1 = 1.84221 \]
\[ a_2 = 2.38253 \]
\[ a_3 = -2.35761 \]
\[ a_4 = 3.46762 \]

Equation IV.5, therefore, constitutes an accurate and continuous expression for the geometric mean frequency.
APPENDIX V

F.C.C. Cell Clusters

The f.c.c. lattice cell-clusters and their respective combinatorial factors can be found by using the same techniques which were used in compiling Table 2.1. Table V.1 results. The reader is reminded that $l$ represents the total number of pair correlations within a particular cluster and that $t$ identifies the configurations.

Again we consider only cell clusters of up to third order.

$$Z_{\text{cor}} = 1 + \sum_{l=1}^{3} \sum_{t=1}^{t_m(l)} g_{l,t} \cdot \langle Q_{l,t} \rangle + O(\text{with } l \geq 4)$$

V.1

where $t_m(l)$ is the maximum value of $t$ for a given $l$. With the aid of Table V.1 and the following definitions:

\[ \langle Q_{l,1} \rangle = \langle Q_{1,1} \rangle \]

V.2(a)

\[ \langle Q_{3,2} \rangle = \langle Q_{1,1} \rangle \langle Q_{2,2} \rangle \]

V.2(b)

\[ \langle Q_{3,3} \rangle = \langle Q_{1,1} \rangle \langle Q_{2,3} \rangle \]

V.2(c)

\[ \langle Q_{3,4} \rangle = \langle Q_{1,1} \rangle \langle Q_{2,4} \rangle \]

V.2(d)
equation V.1 (up to third order terms) can be rearranged to give:

\[ Z_{\text{cor}} = (1 + \langle Q_{1,1} \rangle + 6N\langle Q_{2,1} \rangle + 2\langle Q_{2,2} \rangle + 8\langle Q_{2,3} \rangle + 11\langle Q_{1,1} \rangle^2) + 6N\{215\langle Q_{1,1} \rangle^3 - 34\langle Q_{1,1} \rangle\langle Q_{2,2} \rangle - 64\langle Q_{1,1} \rangle\langle Q_{2,3} \rangle \}
- 68\langle Q_{1,1} \rangle\langle Q_{2,3} \rangle - 268\langle Q_{1,1} \rangle\langle Q_{2,4} \rangle + \frac{1}{6N} \sum_{t=0}^{20} \left( 2g_{3,t} \langle Q_{3,t} \rangle \right) + 36N^2\{2\langle Q_{2,2} \rangle\langle Q_{1,1} \rangle + 2\langle Q_{2,3} \rangle\langle Q_{1,1} \rangle + 8\langle Q_{2,4} \rangle\langle Q_{1,1} \rangle \}
- 11\langle Q_{1,1} \rangle^3 \]  

V.3

If we assume that \( Z_{\text{cor}} \) can be written as:

\[ Z_{\text{cor}} = (1 + S_1 + S_2 + S_3 + \ldots)^2 \]  

V.4

which can be expanded in a Taylor's series to third order, we have:

\[ Z_{\text{cor}} = 1 + 6N(S_1 + S_2 + S_3) + \frac{1}{2!} 6N(6N - 1)(S_1 + S_2 + S_3)^2 + \ldots \]  

V.5
Rearranging equation V.5 leads to:

\[ Z_{\text{cor}} = (1 + S) + 6N(S_1) + 6N(S_2 - S_3) + 9N^2(S_1S_2) + O(\text{with } l \geq 4) \]

V.6

A comparison of equations V.3 and V.6 gives:

\[ S = \langle Q_1 \rangle \]

V.7(a)

\[ S_2 = \langle Q_{2,2} \rangle + 2\langle Q_{2,3} \rangle + 8\langle Q_{2,4} \rangle - 11\langle Q_{1,1} \rangle^2 \]

V.7(b)

\[ S_3 = -204\langle Q_{1,1} \rangle^3 - 33\langle Q_{1,1} \rangle \langle Q_{2,2} \rangle - 66\langle Q_{1,1} \rangle \langle Q_{2,3} \rangle - 260\langle Q_{1,1} \rangle \langle Q_{2,4} \rangle + \frac{1}{6N} \sum_{t=6}^{20} g_{3,t} \langle Q_{3,t} \rangle \]

V.7(c)

At \( r = r_0 \) we thus have \( S_1 = 0.0327956 \), \( S_2 = 0.0071230 \), and \( S_3 = 0.0013148 \). These lead to second and third order approximations to \( \Sigma_{\text{harm}} \) which are closer to the accurate value of 1.0420126 than similar order approximations made using the summation techniques of Huckaby and Salsburg\(^{12}\). In the high temperature region where our theory applies \( S_3 \) becomes small and positive so that the convergence of \( \Sigma_{\text{harm}} \) to third order is well behaved at volumes of interest.
Graph V.1

Third order approximations to $\Sigma_{\text{harm}}$. 
<table>
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<tr>
<th>Cluster Code</th>
<th>g_{et}</th>
<th>r = r_o</th>
<th>r = 1.0125r_o</th>
<th>r = 1.025r_o</th>
<th>r = 1.0375r_o</th>
<th>r = 1.05r_o</th>
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<td>Q_1,1</td>
<td>6N</td>
<td>3.27956(-2)</td>
<td>3.09406(-2)</td>
<td>2.87824(-2)</td>
<td>2.62602(-2)</td>
<td>2.33085(-2)</td>
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<tr>
<td>Q_2,1</td>
<td>6N</td>
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<td>9.57321(-4)</td>
<td>8.28429(-4)</td>
<td>6.89596(-4)</td>
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<td>6.98797(-4)</td>
<td>5.62351(-4)</td>
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<tr>
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<td>2.38446(-5)</td>
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<tr>
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<td>2.75975(-5)</td>
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<td>Q_3,4</td>
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Table V.1

In the pictoral representations of clusters a dash between atoms implies that they are nearest neighbours with uncorrelated motions.
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<td>$\Sigma^{(3)}_{\text{harm}} = S_1 + S_2 + S_3$</td>
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Table V.2
References

17. J. A. Barker, Lattice Theories of the Liquid State
