On the Equation of State and Atomic Mean Square Displacement of Crystals.

by

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to Caroline
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Abstract

We have presented a Green's function method for the calculation of the atomic mean square displacement (MSD) for an anharmonic Hamiltonian. This method effectively sums a whole class of anharmonic contributions to MSD in the perturbation expansion in the high temperature limit.

Using this formalism we have calculated the MSD for a nearest neighbour fcc Lennard Jones solid. The results show an improvement over the lowest order perturbation theory results, the difference with Monte Carlo calculations at temperatures close to melting is reduced from 11% to 3%.

We also calculated the MSD for the Alkali metals Na, K, Cs where a sixth neighbour interaction potential derived from the pseudopotential theory was employed in the calculations. The MSD by this method increases by 2.5% to 3.5% over the respective perturbation theory results.

The MSD was calculated for Aluminum where different pseudopotential functions and a phenomenological Morse potential were used. The results show that the pseudopotentials provide better agreement with experimental data than the Morse potential. An excellent agreement with experiment over the whole temperature
range is achieved with the Harrison modified point-ion pseudo-potential with Hubbard-Sham screening function.

We have calculated the thermodynamic properties of solid Kr by minimizing the total energy consisting of static and vibrational components, employing different schemes: The quasiharmonic theory (QH), $\lambda^2$ and $\lambda^4$ perturbation theory, all terms up to $O(\lambda^4)$ of the improved self consistent phonon theory (ISC), the ring diagrams up to $O(\lambda^4)$ (RING), the iteration scheme (ITER) derived from the Greens's function method and a scheme consisting of ITER plus the remaining contributions of $O(\lambda^4)$ which are not included in ITER which we call $E(\text{FULL})$. We have calculated the lattice constant, the volume expansion, the isothermal and adiabatic bulk modulus, the specific heat at constant volume and at constant pressure, and the Grüneisen parameter from two different potential functions: Lennard-Jones and Aziz.

The Aziz potential gives generally a better agreement with experimental data than the LJ potential for the QH, $\lambda^2$, $\lambda^4$ and $E(\text{FULL})$ schemes. When only a partial sum of the $\lambda^4$ diagrams is used in the calculations (e.g. RING and ISC) the LJ results are in better agreement with experiment. The iteration scheme brings a definitive improvement over the $\lambda^2$ PT for both potentials.
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1. Introduction

At low temperatures the displacement of atoms from their equilibrium position in a crystal lattice is usually small (except for quantum crystals) and a truncation of the Taylor's expansion of the potential energy, ϕ, after the quadratic term, is sufficient for the description of the thermodynamic properties of the crystal. This approximation is known as the harmonic approximation. At higher temperatures the vibrational amplitudes are larger and the higher order (anharmonic) terms in the Taylor expansion of ϕ become important, so much so, that some properties are a direct consequence of the anharmonic part of the potential and cannot be explained without it. Among these anharmonic effects are thermal expansion, the deviation of the specific heat from the classical Dulong-Petit law at high temperatures and thermal conductivity. In some cases the inclusion of the anharmonic terms in the calculation provides a quantitative improvement of the results, for example if the calculated harmonic phonon dispersion curves are not in good agreement with experiment they can be brought into better agreement if the anharmonic corrections (or phonon frequency shifts) are added.

The anharmonic contributions to the thermodynamic properties of a crystal can be calculated by a number of methods. The most common is perturbation theory (PT), where the anharmonic contributions are evaluated from the harmonic eigenfunctions and eigen-
values and the derivatives of $\phi$. This method creates problems in cases where successive orders of PT do not converge fast enough. It is also inadequate for crystals where the harmonic Hamiltonian cannot be defined properly (i.e. He, Ne, H). In other computational methods such as the Monte Carlo (MC) and Molecular-dynamics (MD) simulation methods a Taylor expansion of the potential function is not needed and thus all harmonic and anharmonic contributions to a physical property are included in the results. A comparison of MC or MD results with experimental values then indicates, how well the real physical situation is represented by a particular potential function. Similarly, for a given potential the comparison of PT and simulation method results provides an estimate of the convergence of the PT method or the adequacy of different orders of PT.

In the evaluation of anharmonic contributions to quantities such as the Helmholtz free energy ($F$) or the atomic mean square displacement (MSD) by means of perturbation theory, two points have to be considered: On the one hand the PT leads to an infinite series of $F$ or MSD in terms of the perturbing potential, on the other hand this perturbing potential itself is an infinite series of terms in the Taylor expansion of $\phi$. Thus some kind of scheme is needed to group terms of the same order of magnitude in this infinite series expression of $F$ or MSD. One such scheme is given by the Van Hove (1961) ordering parameter $\lambda$. Contributions arising in PT are then ordered (or grouped together) according to powers of $\lambda$ where $\lambda$ is defined as the square root of the mean square dis-
placement divided by the nearest neighbour distance. Only even powers of $\lambda$ contribute to $F$ and MSD because all odd powers of $\lambda$ are zero by symmetry. In the lowest order of perturbation theory, which is of order $\lambda^2$, two terms (cubic and quartic) are obtained in the calculation of $F$ as well as MSD. The next order of PT is of order $\lambda^4$. These contributions arise from the various terms in the Taylor's expansion of $\phi$ involving up to the sixth derivative of $\phi$.

The knowledge of MSD or $<u^2>$ is essential in calculating the Debye-Waller factor which enters in the intensity of X-ray and neutron diffraction in crystals. It is important in the theory of melting through the Lindemann criterion. The MSD also determines the Van Hove ordering parameter $\lambda$.

The Helmholtz free energy and its dependence on temperature and volume is used to determine the equation of state and thermodynamic quantities such as the thermal expansion ($\beta$), the specific heat at constant volume ($C_v$) or constant pressure ($C_p$), the isothermal ($B_T$) and adiabatic ($B_S$) bulk modulus, and the Grüneisen parameter ($\gamma$).

In the past anharmonic contributions to $F$ and MSD have been calculated by several authors. Maradudin, Flinn, and Coldwell-Horsfall (1961) derived the $O(\lambda^2)$ contributions to $F$, $F(\lambda^2)$, and calculated them for a nearest neighbour central force (NNCF) crystal in the leading term approximation (LTA) and in the high
temperature limit (H.T. limit) \( T > \Theta_0 \) (where \( \Theta_0 \) is the Debye temperature). Both the \( \lambda^2 \) contributions are of \( O(T^2) \) in the H.T. limit. Shukla and Cowley (1971) have derived the contributions to \( F \) to \( O(\lambda^4) \), \( F(\lambda^6) \), by the diagrammatic method. They derived finite temperature free energy expressions for a crystal with inversion symmetry and evaluated their contributions for a NNCF solid with a Lennard-Jones (LJ) interaction potential in LTA and in the H.T. limit for a fixed volume. All the \( \lambda^4 \) contributions are of \( O(T^3) \) in this limit. In a subsequent paper Shukla and Wilk (1974) calculated the same terms without the LTA and showed that this approximation is quite useful for the study of the convergence of PT, however, it leads to significant errors in the total \( F(\lambda^2) \) and \( F(\lambda^4) \). They changed by 44% and 38% respectively. More recently Shukla and Cowley (1985) carried out the calculations of \( F \) to \( O(\lambda^2) \) and \( O(\lambda^6) \) without making any approximations like LTA for a range of volumes and temperatures for the NNCF model of a fcc crystal with the LJ potential and determined the equation of state. They compared their results with Monte Carlo calculations for the same crystal model because the MC method in principle gives exact numerical results to all orders of anharmonicity. For each of the thermodynamic properties the \( \lambda^2 \) and \( \lambda^4 \) results diverged in opposite directions from the MC results. The \( \lambda^2 \) results in many cases (such as \( C_p, B_T \), and \( \beta \)) showed a wrong curvature at high temperatures. The magnitude and shape of the curves was represented correctly by
the $\lambda^4$ results up to 40\% of $T_m$ but for $T > 40\% T_m$ the $\lambda^4$ contributions drastically over-corrected the $\lambda^2$ results.

In order to investigate how the chosen potential function influences the convergence of the perturbation expansion, Shukla and Shanes (1985) calculated the thermodynamic properties of the rare gas solids Kr and Xe using different potentials. They used a NNCF model with LJ, Morse, and Rydberg potential functions. Their calculations showed that the $\lambda^2$ results were poor at temperatures beyond 1/3 $T_m$ for the LJ potential and somewhat better for the other two potentials. The inclusion of $\lambda^4$ terms definitively improved the results for all potential functions but again Morse and Rydberg yielded better results than LJ. The best overall results were obtained from the Morse potential and the $\lambda^4$ PT; with this combination the results were close to the experimental values for temperatures up to $T_m$.

Even though the nearest neighbour Morse and Rydberg potential functions yielded results which are in good agreement with experimental values, they are not very realistic potentials and it would be of interest to perform these calculations for a more realistic potential. Such a potential function has been proposed by Aziz (1978) for Kr. The numerous parameters of this potential function have been adjusted to provide a simultaneous fit to dilute gas properties (virial coefficients, viscosity, and thermal conductivity) as well as spectroscopic data and theoretical Hartree-Fock calculations (for the repulsive well).
Besides PT theories of $O(\lambda^4)$ and $O(\lambda^2)$, which include all anharmonic terms up to a certain order of $\lambda$, there are other criteria which also yield good results. Shukla and Cowley (1985) observed for the LJ potential, that some perturbation schemes, which employ only subsets of all $\lambda^4$ diagrams, provide results which are in good agreement with MC calculations almost up to $T_m$. One of these schemes is the improved self-consistent phonon theory (ISC). Similar results were obtained by schemes which use only one of the eight diagrams of $O(\lambda^4)$ (ladder) or by including all $\lambda^4$ diagrams except ladder. Several problems arise with the use of these schemes, one of them is the heavy cancellation among the $\lambda^4$-diagrams, their sum total is smaller in magnitude than most of the individual terms. It therefore is not clear at all which diagrams are more important and should be selected. Another problem is the sensitivity of these PT schemes to the potential function. Unpublished calculations by R.C. Shukla indicate that the ISC scheme, which performed well for the LJ-solid, does not work at all for the Morse and Rydberg potentials, the results are worse than for $\lambda^2$ PT.

The atomic mean square displacement has been calculated by Heiser, Shukla and Cowley (1986) (HSC) for a NN-LJ solid using the $\lambda^2$ PT as well as MD and MC calculations. The agreement between the $\lambda^2$ PT and MC results was quite good at low temperatures, however, at higher temperatures, there was a significant disagreement of up
to 20% at temperatures close to $T_m$. They concluded that the $\lambda^2$ PT contribution to MSD was not sufficient at these temperatures and, to bring agreement of the results with MC, the next order of PT of $O(\lambda^4)$ would be required. It is, however, tedious to derive and in particular very time consuming to compute these higher order terms individually. Shukla and Heiser (1986) also calculated the MSD for the Alkali metals Na, K, and Cs using a sixth-neighbour-interaction model and $\lambda^2$ PT. They compared these results for the alkali metals with MD calculations for the same model and concluded that there was a very good agreement between MD and LD calculations, which indicates the adequacy of the $\lambda^2$ PT for the alkali metals. Only for Cs there was a noticeable difference at the highest temperatures.

It has been shown by Shukla, Plint, and Ditmars (1985) that for Al a phenomenological Morse potential yields results for the specific heat at 0K-volume ($C_{v0}$) which are in very good agreement with results obtained from more sophisticated pseudopotential functions. It would be worthwhile to see whether this agreement extends to MSD as well.

Since the MC and MD results are in principle exact, the corresponding differences from PT results in a given order arise from even higher order terms in anharmonicity. It therefore would be of interest to find a procedure which sums certain types of PT
contributions to all orders of anharmonicity for both the calculations (i.e. MSD and free energy).

In this thesis we want to present a method of calculating the Helmholtz free energy and the mean square displacement for a crystal, which involves the summation of certain types of terms in the perturbation expansion to all orders of anharmonicity ($\lambda$). Such a summation can be accomplished by the Green's function method. We will generate the Green's function ($G$) by the Zubarev equation of motion method. Although the Zubarev (1960) prescription of generating $G$ is straightforward, the complicating feature is in the reduction of higher order Green's functions into lower order ones needed in the solution. Also in the Zubarev method certain thermal averages arise in the derivation of $G$ which are evaluated with respect to the full Hamiltonian, but this calculation, in turn, requires the knowledge of $G$ itself. Therefore a self consistency criterion is already built-in in obtaining the Green's function. This criterion will be used in the implementation of an iterative procedure which generates a whole class of new types of contributions to all orders of anharmonicity and all orders of temperature. These contributions are then summed by the integration over the coupling constant method as described in Shukla and Muller (1970). In their paper they showed that this method gives exactly the same Free energy contributions as those obtained from the $\lambda^2$ PT.
The outline of this thesis is as follows. In chapter 2, we present Zubarev's Green's function method and show how $G$ is used to derive two particle correlation functions which are needed in the calculation of $<u^2>$ and $F$. In chapter 3, the details of our numerical calculations of MSD are presented. In particular, the results are obtained for a NN LJ solid and compared with the Monte Carlo calculations. In order to investigate how sensitive the results of $<u^2>$ are to the choice of potential function (long or short range) we calculate $<u^2>$ for the alkali metals and aluminum using long range pseudopotential functions as well as much simpler short range potential functions.

In chapter 4, we present calculational details of the Helmholtz free energy and evaluate the thermodynamic properties for the rare gas solid Kr using the LJ interaction potential as well as a more realistic long range potential function suggested by Aziz.

A summary of our results is presented in chapter 5.
2. The Green's function method

In this section we outline the theory which is required for the calculation of the atomic mean square displacement and the Helmholtz free energy. We will demonstrate how the Green's function method can be used to calculate these quantities.

The motion of atoms in a crystal lattice can be described as a superposition of vibrational normal modes of the crystal. The quantized states of these normal modes are called phonons. The phonon frequencies and associated eigenvectors are given by \( \omega(qj) \) and \( e(qj) \), respectively, where \( q \) is the wave vector and \( j \) is the branch index. For a monatomic lattice the displacement in the cartesian direction \( \alpha \) of an atom at lattice site \( l \) and time \( t \) can be expanded in plane waves:

\[
u^1_{qj}(t) = \left( \frac{\hbar}{2NM} \right)^{1/2} \sum_q \sum_{j=1}^3 \frac{e_{\alpha}(q,j)}{\omega_{qj}^{1/2}} e^{iqr_l} \ A_{qj}(t) \quad (2.1)
\]

\[A_{qj} = a_{qj} + a_{qj}^+ \]

The various symbols arising in this equation are: \( a_{qj}^+ \) and \( a_{qj} \) are the usual phonon creation and annihilation operators, \( e_{\alpha}(qj) \) is the \( \alpha \)-component of the eigenvector, \( \hbar \) is Planck's constant divided by \( 2\pi \), \( M \) is the atomic mass, and \( N \) is the number of unit cells in
the crystal. The summation over \( q \) is over the first Brillouin zone (BZ).

The quasiharmonic and interaction parts of the Hamiltonian of an anharmonic crystal are given by \( H = H_0 + gH' \), where \( g \) is a formal coupling parameter defined over the interval \([0,1]\) i.e. \( 0 \leq g \leq 1 \). The procedure of introducing \( g \) in the calculation of \( F \) was carried out by Shukla and Muller (1971) for the derivation of the lowest order anharmonic contributions to \( F \). These terms in \( F \) were derived by the integration of the interaction energy over \( g \). We will implement this procedure numerically in the calculation of \( F \), where anharmonic contributions are included to all orders of anharmonicity. The parameter \( g \) is not needed in the calculation of MSD, therefore for MSD calculations the value of \( g \) is set equal to unity.

\[
H_0 = \sum_{q,j} \hbar \omega_q q_j (a_q^+ a_q + 1/2) \tag{2.2}
\]

\[
H' = \lambda \sum_{q_1} \sum_{j_1} \sum_{q_2} \sum_{j_2} \sum_{q_3} \sum_{j_3} v^3(q_{1j_1}, q_{2j_2}, q_{3j_3}) a_{q_{1j_1}} a_{q_{2j_2}} a_{q_{3j_3}} +
\]

\[
+ \lambda^2 \sum_{q_1} \sum_{j_1} \sum_{q_2} \sum_{j_2} \sum_{q_3} \sum_{j_3} \sum_{q_4} \sum_{j_4} v^4(q_{1j_1}, q_{2j_2}, q_{3j_3}, q_{4j_4}) a_{q_{1j_1}} a_{q_{2j_2}} a_{q_{3j_3}} a_{q_{4j_4}} \tag{2.3}
\]

\[
H' = \lambda v^3 + \lambda^2 v^4 = H_3 + H_4
\]

The coefficients \( v^3 \) and \( v^4 \) are completely symmetric in their indices (\( q_j \)) and their relationship with the force tensors \( \Phi(q_{1j_1}, \ldots, q_{nj_n}) \) is given by
\[ V(\lambda_1, \ldots, \lambda_n) = \frac{N^{1-n/2}}{n!} \Delta(q_1^+ \ldots + q_n) \left[ \frac{\gamma^n}{2^n \omega_1 \ldots \omega_n} \right]^{1/2} \Phi(\lambda_1, \ldots, \lambda_n) \] (2.4)

\[ \Phi(\lambda_1, \ldots, \lambda_n) = \frac{1}{2M^n/2} \sum l \sum \phi_{\alpha \ldots \delta}(|r_1|) e_\alpha(\lambda_1) \ldots e_\delta(\lambda_n)x^{\mathbf{-iq_1r_1}}x^{\ldots}x^{\mathbf{-iq_nr_n}} (1 - e^{-i\mathbf{qr_1}})(1 - e^{-i\mathbf{qr_1}}) \] (2.5)

Here \( \lambda_i \) represents collectively the wave vector \( q_i \) and branch index \( j_i \). The \( \Delta \)-function in Eq (2.4) is unity if \( q_1^+ \ldots + q_n = 0 \) or \( r \) (reciprocal lattice vector) and zero otherwise, and \( \phi_{\alpha \ldots \delta} \) is the \( n \)th order atomic tensor force constant where each of the indices \( \alpha, \ldots, \delta \) takes the cartesian values \( x, y, z \).

For the calculation of \( <u^2> \) and \( F \) we have to evaluate one particle correlation functions of the general type

\[ J_{qq'}(t-t') = <A^+_q A_{q'}^*(t') A_q(t)> \] (2.6)

(Shukla and Muller (1980)) where the angular bracket denotes the thermal average and is defined by

\[ \langle O \rangle = \frac{\text{Tr} \left( O e^{-\beta H} \right)}{\text{Tr} e^{-\beta H}} \] (2.7)

\( \beta = 1/(k_B T) \), \( k_B \) being the Boltzmann constant and \( T \) is the temperature. \( \text{Tr} \) denotes the trace and means the summation of diagonal
matrix elements of the operator \( A_{qj} \). The time dependence of \( A_{qj} \) is in the Heisenberg representation

\[
A_{qj}(t) = e^{iHt/\hbar} A_{qj} e^{-iHt/\hbar}
\]

In order to evaluate the correlation function, we introduce the following one-phonon double time, temperature dependent Green's function

\[
G_{qq'}^{jj'}(t-t') = \langle \langle A_{qj}(t), \hat{A}_{q'j'}(t') \rangle \rangle \\
= -i\Theta(t-t') \langle [A_{qj}(t), \hat{A}_{q'j'}(t')] \rangle \tag{2.8}
\]

The square brackets denote the commutator \([A, B] = AB - BA\) and

\[
\Theta(t) = \begin{cases} 
1 & \text{for } t \geq 0 \\ 
0 & \text{for } t < 0
\end{cases}
\]

The Fourier transforms \( J_{qq'}(\omega) \) and \( G_{qq'}(\omega) \) of the correlation function and the one particle Green's function are defined as

\[
J_{qq'}^{jj'}(t-t') = \int_{-\infty}^{\infty} J_{qq'}^{jj'}(\omega) e^{-i\omega(t-t')} \, d\omega
\]

and

\[
G_{qq'}^{jj'}(t-t') = \int_{-\infty}^{\infty} G_{qq'}^{jj'}(\omega) e^{-i\omega(t-t')} \, d\omega \tag{2.9}
\]

The function \( G_{qq'}(\omega) \) can be continued analytically in the complex frequency plane and Zubarev (1960) has shown that it is related to the correlation function \( J_{qq'}(\omega) \) by the spectral theorem.
\[ J_{\mathbf{q}\mathbf{q}'}^{jj'}(\omega) = -\lim_{\epsilon \to 0} \frac{2}{e^{\beta\hbar\omega} - 1} \text{Im} \ G_{\mathbf{q}\mathbf{q}'}^{jj'}(\omega + i\epsilon) \] (2.10)

Once \( G_{\mathbf{q}\mathbf{q}'}(\omega) \) is known, various physical properties can be calculated using this relation.

The Green's function can be generated by Zubarev's equation of motion method, which involves the Heisenberg equation of motion for an operator \( \hat{O}(t) \) viz

\[ i\hbar \frac{d}{dt} \hat{O}(t) = [\hat{O}, \hat{H}] \]

In particular we have for the above Hamiltonian

\[ i \frac{d}{dt} A_{\mathbf{q}j}(t) = \omega_{\mathbf{q}j} B_{\mathbf{q}j}(t) \] (2.11)

where \( B_{\mathbf{q}j} \) is the difference of phonon creation and annihilation operators

\[ B_{\mathbf{q}j} = a_{\mathbf{q}j} - a_{\mathbf{q}j}^+ \]

and

\[ i \frac{d}{dt} B_{\mathbf{q}j}(t) = \omega_{\mathbf{q}j} A_{\mathbf{q}j}(t) + \sum_{\mu} \sum_{\lambda_1, \lambda_2} v^3(\lambda_1, \lambda_2, -\mathbf{q}j) A_{\lambda_1}(t) A_{\lambda_2}(t) \]

\[ + \sum_{\mu} \sum_{\lambda_1, \lambda_2, \lambda_3} v^4(\lambda_1, \lambda_2, \lambda_3, -\mathbf{q}j) A_{\lambda_1}(t) A_{\lambda_2}(t) A_{\lambda_3}(t) \] (2.12)

In obtaining this relation the symmetry properties of \( v^3 \) and \( v^4 \) have been employed. Using these relations, the equation of motion for \( G_{\mathbf{q}\mathbf{q}'}(t-t') \) is given by
\[
\frac{d}{dt} G_{qq'}^{jj'}(t-t') = \omega_{qj} \langle \langle B_{qj}(t); A^+_{q'j'}(t') \rangle \rangle \\
= \omega_{qj} H_{qq'}^{jj'}(t-t') 
\]

(2.13)

The time derivative for this new Green's function \( H_{qq'}(t-t') \) can be evaluated through Eq(2.12), it contains the original Green's function \( G_{qq'}(t-t') \) as well as Green's functions of higher order, i.e.

\[
\langle \langle A_{q_1j_1} A_{q_2j_2} A_{q_3j_3} ; A^+_{q'j'} \rangle \rangle \text{ and } \langle \langle A_{q_1j_1} A_{q_2j_2} ; A^+_{q'j'} \rangle \rangle 
\]

(2.14)

If this procedure of taking the time derivatives is carried on, a chain of successively higher order (i.e. more operators) Green's functions is generated. This chain terminates only for very simple Hamiltonians. For a more complex Hamiltonian the chain can be terminated by decoupling higher order Green's functions. For example the first term of Eq(2.14) can be decoupled in terms of a sum of products of two-operator correlation functions and two-operator Green's functions according to the scheme

\[
\langle \langle ABC; D \rangle \rangle = \langle AB \rangle \langle \langle C; D \rangle \rangle + \langle AC \rangle \langle \langle B; D \rangle \rangle + \langle BC \rangle \langle \langle A; D \rangle \rangle .
\]

The second term in Eq(2.14) requires the generation of another equation of motion in order to yield Green's functions which can be decoupled. The details of this derivation are presented in Shukla and Muller (1971).

Another ingredient in this procedure is the extensive use of the ordering parameter \( \lambda \), all contributions beyond a certain order
of $\lambda$ are neglected. If all terms of $O(\lambda^2)$ are retained in this
derivation the Fourier transform of the Green function has the
following form

\[
G_{qq'}^{jj'}(\omega) = \frac{\omega_{qj} \delta_{qq'} \delta_{jj'}}{\pi (\omega^2 - \omega_j^2 - 2\omega_{qj} \Pi_{qj}(\omega))}
\]

(2.15)

where $\Pi_{qj}(\omega)$ is the phonon self-energy term, defined by

\[
\Pi_{qj}(\omega) = \frac{1}{\Pi_{qj}(\omega)} \Pi_{qj}^3(\omega) + \Pi_{qj}^4
\]

(2.16)

\[
\Pi_{qj}^3(\omega) = \frac{18 \lambda^2 q^2}{h^2} \sum_{q_{1j_1}, q_{2j_2}} \left| V^3(-q_j, q_{1j_1}, q_{2j_2}) \right|^2 \times
\]

\[
\times \left[ (N_1 + N_2) \frac{\omega_1 + \omega_2}{\omega^2 - (\omega_1 + \omega_2)^2} + (N_2 - N_1) \frac{\omega_1 - \omega_2}{\omega^2 - (\omega_1 - \omega_2)^2} \right]
\]

\[
\Pi_{qj}^4 = \frac{12 \lambda^2 q}{h} \sum_{q_{1j_1}} V^4(q_{1j_1}, -q_{1j_1}, q_j, -q_j) N_1
\]

The real and imaginary parts of $\Pi_{qj}(\omega)$ give the phonon frequency
shift $\Lambda_{qj}(\omega)$ and the phonon width $\Gamma_{qj}(\omega)$. In these equations $\omega_i$
and $N_i$ are short forms for $\omega(q_i, j_i)$ and $N(q_i, j_i)$, with

\[
N_{qj} = \langle A_{qj}^+ A_{qj} \rangle = \int_{-\infty}^{\infty} J_{qq}^{jj'}(\omega) \ d\omega
\]

(2.17)

where Eqs (2.6) and (2.9) have been used together with $t=t'$.  

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At this point the self consistent behaviour of this formalism is displayed clearly in Eqs (2.15) and (2.17). The calculation of the functions $N_{qj}$ requires the knowledge of $J(\omega)$ and thus of $G(\omega)$ through Eq(2.10), but $G(\omega)$ can only be calculated if the $N_{qj}$ are known.

The integral in Eq(2.17) can be evaluated using the Breit-Wigner expansion as described in Sec. 3 of Shukla and Muller (1971). Here we want to proceed in a different way: since $\Pi^4$ is independent of $\omega$, we assume that the dependence of $\Pi^3(\omega)$ on $\omega$ is also weak, therefore we set $\omega=0$ in $\Pi^3(\omega)$ (static approximation). This would imply that $\Gamma_{qj}=0$. With this approximation $G(\omega)$ simplifies significantly:

$$G_{qq'}^{jj'}(\omega) = \frac{\omega q_j \delta_{qq'} \delta_{jj'}}{\pi (\omega^2 - \Omega_{qj}^2(\omega=0))}$$  \hspace{1cm} (2.18)

where

$$\Omega_{qj}^2(\omega=0) = \omega^2_{qj} - \frac{\hbar \lambda^2 q^2}{8N} \sum_{q_1j_1} \sum_{q_2j_2} \Delta(q_1+q_2-q) \left[ \frac{N_1+N_2}{\omega_1+\omega_2} + \frac{N_2-N_1}{\omega_1-\omega_2} \right] + \frac{\hbar \lambda^2 q}{4N} \sum_{q_1j_1} \phi^4(q_{1j_1},-q_{1j_1},q_j,-q_j) \frac{N_1}{\omega_1}$$  \hspace{1cm} (2.19)

$\Omega_{qj}$ is the renormalized frequency of the phonon $(q,j)$. The validity of this static approximation will be given when we present the derivation of $<u^2>$ and $F$ in the high temperature limit to
\( O(\lambda^2) \). We can now resolve \( G(\omega) \) into partial fractions and, using the spectral theorem Eq(2.10) and the identity \( 1/(x+i\varepsilon) = P(1/x) + i\pi\delta(x) \), we obtain the spectral density \( J(\omega) \)

\[
J_{q j}^{q j'}(\omega) = -\frac{\omega_{q j} \delta_{q j} \delta_{q j'}}{\Omega_{q j} (e^{\beta\omega} - 1)} \left[ \delta(\omega - \Omega_{q j}) - \delta(\omega + \Omega_{q j}) \right] \tag{2.20}
\]

and

\[
N_{q j} = \coth \frac{1}{2} \beta \omega_{q j} \Omega_{q j}. \tag{2.21}
\]

The self consistency argument can be implemented in numerical calculations by an iterative procedure, where the renormalized frequencies \( \Omega_{q j} \) are fed back into the calculation of frequency shifts, which produces new shifted frequencies. In our calculations we used the high temperature approximation where \( N_{q j} \) is approximated to \( N_{q j} \approx 2/(\beta \Omega_{q j}) \) and we get the self consistent equation

\[
\Omega_{q j}^2 = \frac{\omega_{q j}^2 - \frac{k_s T}{2N} \lambda^2 g^2}{\sum_{q_1 j_1} \sum_{q_2 j_2} \Lambda(q_1^+ g_2 - q) \frac{\phi^3(-q_j, q_1 j_1, q_2 j_2)}{\Omega_{q_1}^2 \Omega_{q_2}^2}} + \frac{k_s T}{2N} \lambda^2 g \sum_{q_1 j_1} \frac{\phi^4(q_1 j_1, -q_1 j_1, q_j, -q_j)}{\Omega_{q_1}^2} \tag{2.22}
\]

Using the expressions for \( \phi^3 \) and \( \phi^4 \) as given by Eq(2.5), \( \Omega_{q j}^2 \) can also be written in a matrix form similar to the eigenvalue equation for the quasiharmonic frequencies \( \omega(q_j)^2 \):

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\[ \Omega^2_{q j} = \sum_{\alpha, \beta} e_\alpha(qj) \ e^\beta(qj) \] \hspace{2cm} (2.23)

\[ E_{\alpha \beta}(q) = D_{\alpha \beta}(q) + CS_{\alpha \beta}(q) + QS_{\alpha \beta}(q) \] \hspace{2cm} (2.24)

Here \( D(q) \) is the dynamical matrix for the wave vector \( q \), \( QS(q) \) and \( CS(q) \) represent matrix shifts due to the quartic and cubic parts of the Hamiltonian respectively. The quartic matrix shift is given by

\[ QS_{\alpha \beta}(q) = \frac{k_B T}{N \mu^2} \sum_{l} (1-\cos qr_l) \sum_{\gamma, \delta} \phi_{\alpha \beta \gamma \delta}(l) \ [S_{\gamma \delta}(0) - S_{\gamma \delta}(1)] \] \hspace{2cm} (2.25)

In this equation the tensors \( S_{\alpha \beta}(l) \) are defined as (Shukla and Wilk (1974))

\[ S_{\alpha \beta}(l) = \sum_{q, j} \frac{e_\alpha(qj)e^\beta(qj)}{\omega^2_{qj}} \cos qr_l \] \hspace{2cm} (2.26)

They contain all the information about the quasiharmonic frequencies and eigenvectors.

The calculation for the cubic matrix shift is more involved, it contains a \( \Delta \)-function which indicates momentum conservation at each three-phonon vertex. This \( \Delta \)-function can be represented by plane waves

\[ \Delta(q) = \frac{1}{N} \sum_{l} e^{i qr_l} \] \hspace{2cm} (2.27)
the summation being over all sites of the real lattice. With this plane wave representation and Eq(2.5) for $\phi^3$ we obtain the following representation for the cubic matrix shift

$$
\text{CS}_{\alpha\beta}(q) = -\frac{k_B^3}{2N 4M^3} \sum_{l, l', l''} \sum_{\sigma, \gamma}^{\mu, \pi} \phi_{\alpha\sigma\gamma}(l_1) \phi_{\beta\mu\pi}(l_2) \times [1 - \exp(iq_1 r_1)] [1 - \exp(-iq_1 r_2)] \exp(-iq_1 r_1) 
$$

$$
\sum_{q_1 j_1} \frac{1}{\omega_1^2} e_\alpha(q_1 j_1) e_\mu(q_1 r_1) (1 - e^{-iq_1 r_1}) (1 - e^{iq_1 r_2}) e^{iq_1 r_1}
$$

$$
\sum_{q_2 j_2} \frac{1}{\omega_2^2} e_\gamma(q_2 j_2) e_\pi(q_2 r_2) (1 - e^{-iq_2 r_1}) (1 - e^{iq_2 r_2}) e^{iq_2 r_1}
$$

\[ (2.28) \]

In the BZ sums there is a $-q$ for every $q$, therefore these sums can be simplified to the following form

$$
\sum_{q, j} \frac{1}{\omega_q^2} e_\alpha(qj) e_\beta(qj) (1 - e^{-iq_1 r_1}) (1 - e^{iq_1 r_2}) e^{iq_1 r_1}
$$

\[ (2.29) \]

$F_{\alpha\beta}(l, l_1, l_2)$ is a combination of S-tensors defined earlier, i.e.

$$
F_{\alpha\beta}(l, l_1, l_2) = S_{\alpha\beta}(1) - S_{\alpha\beta}(l-l_1) - S_{\alpha\beta}(l+1_2) + S_{\alpha\beta}(1-l_1+1_2) \quad (2.30)
$$
and it has the property \( F(-1, -1, -1) = F(1, 1, 1) \). Using this property and \( \phi_{\alpha \beta \gamma}(1) = -\phi_{\alpha \beta \gamma}(-1) \) the exponential factors in the second line of Eq(2.28) can be replaced by cosine factors because for every combination of lattice vectors \((1, 1, 1)\) there is a corresponding combination \((-1, -1, -1)\) in a lattice with inversion symmetry. The final expression for \( CS(q) \) is

\[
CS_{\alpha \beta}(q) = -\frac{k_s^T}{8N^2\mu^3} \sum_{l} \sum'_{l_1, l_2} g(q; l, l_1, l_2) \left( \phi_{\gamma \mu}(1_1) \phi_{\mu \sigma \beta}(1_2) F_{\gamma \mu}(1, l_1, l_2) F_{\delta \sigma}(1, l_1, 1_2) \right) \tag{2.31}
\]

where \( g(q; l, l_1, l_2) \) is defined by

\[
g(q; l, l_1, l_2) = \cos qr \mathbf{r}_1 - \cos q(\mathbf{r}_1 - \mathbf{r}_1) - \cos q(\mathbf{r}_1 + \mathbf{r}_2) \\
+ \cos q(\mathbf{r} - \mathbf{r}_1 + \mathbf{r}_2) \tag{2.32}
\]

The tensor \( E(q) \) in Eq(2.24) can now be viewed as a new dynamical matrix from which new eigenvalues \( \Omega_{qj}^2 \) and eigenvectors \( \epsilon_{qj} \) can be obtained. This new set of eigenvalues and eigenvectors can then be used to calculate new \( S \)-tensors.

With this procedure we effectively sum a whole class of diagrams (i.e. ring diagrams) to a very high order. This procedure is repeated until the tensors \( E_{\alpha \beta}(q) \) are converged.
2.1. The Green's Function Method in the Calculation of MSD

We have now all the necessary ingredients for the calculation of the mean square displacement, by multiplying Eq (2.1) with its complex conjugate and summing over the cartesian indexes we get

\[
<u^2> = \frac{\mathcal{H}}{2NM} \sum_{\alpha,q,q',j,j'} \frac{e_\alpha(q,j)e_\alpha(q',j')}{(\omega_q \omega_{q'})^{1/2}} e^{i(q-q')r_1} <A^+_{q'j}, A_{qj}> \tag{2.33}
\]

The average \(<A^+_{q'j}, A_{qj}>\) can be calculated from Eqs (2.17) and (2.20). In the harmonic approximation it is given by

\[
<A^+_{q'j}, A_{qj}>_0 = (2n_{qj} + 1) \delta_{qq'} \delta_{jj'}, \quad n_{qj} = \frac{1}{e^{\beta \hbar \omega_{qj}} - 1} \tag{2.34}
\]

When this average is substituted into Eq(2.33), \(<u^2>\) is given by

\[
<u^2> = \frac{\mathcal{H}}{2NM} \sum_{q,j} \frac{(2n_{qj} + 1)}{\omega_{qj}} \tag{2.35}
\]

\[
= \frac{\mathcal{H}}{2NM} \sum_{q,j} \frac{\coth \frac{1}{2} \beta \hbar \omega_{qj}}{\omega_{qj}}
\]

In the high temperature limit the harmonic MSD is linear in T. However most experimental results (simulated or real) for \(<u^2>\) are not accounted for by this expression of MSD. The experimental MSD results show a quadratic or even higher order temperature dependence. The above expression for MSD has some implicit temperature dependence arising through the BZ sum because the \(\omega(qj)\)
depend on volume at temperature $T$, $V(T)$. Clearly then if $<u^2>$ as
given by Eq(2.35) is evaluated for different volumes appropriate
for that $T$, one might find better agreement with the experimental
values. Such a calculation, where $\omega(qj)$ is allowed to change with
volume is then known as the quasiharmonic approximation. However,
explicit $T^2$ dependence in $<u^2>$ can be included only by including
the anharmonic terms in $H$.

Substituting Eq(2.20) into Eq(2.17) for the correlation function
$<A^+_q A_q>$ yields

$$
<u^2> = \frac{h}{2NM} \sum_{q,j} \coth \frac{1}{2} B q j \Omega_{qj}
$$

and in the high temperate limit we have

$$
<u^2> = \frac{k_b T}{NM} \sum_{q,j} \frac{1}{\Omega_{qj}^2}
$$

(2.36)

This equation has exactly the same form as the quasiharmonic
contribution for $<u^2>$ in Shukla and Heiser (1986), the only
difference being that the quasiharmonic frequencies $\omega(qj)$ are
replaced by their renormalized counterparts $\Omega_{qj}$. If the fraction
$(\Omega_{qj})^{-2}$ is expanded in powers of the perturbation using Eq(2.22),
three terms arise up to $O(\lambda^2)$. They can be identified as quasi-
harmonic, quartic and cubic contributions to $<u^2>$, respectively:

$$
<u^2>_{QH} = \frac{k_b T}{NM} \sum_{q,j} \frac{1}{\omega_{qj}^2}
$$
\[ \langle u^2 \rangle_Q = -\frac{(k_B T)^2 \lambda^2}{2 N^2 M} \sum_{q_1 q_2} \frac{\phi^4(q_{1j_1}, -q_{1j_1}, q_{2j_2}, -q_{2j_2})}{\omega_{q_1j_1}^2 \omega_{q_2j_2}^4} \]

\[ \langle u^2 \rangle_C = \frac{(k_B T)^2 \lambda^2}{2 N^2 M} \sum_{q_{1j_1} q_{2j_2} q_{3j_3}} \Lambda(q_{1j_1} + q_{2j_2} + q_{3j_3}) \frac{\phi^3(q_{1j_1}, q_{2j_2}, q_{3j_3})^2}{\omega_{q_{1j_1}}^2 \omega_{q_{2j_2}}^2 \omega_{q_{3j_3}}^4} \]

which are the same results as in HSC. This implies that the static approximation introduced earlier in \( H_q(j) \) for the calculation of \( \Omega_{qj}^2 \) (Eq(2.19)) is exact in this order of \( \lambda \). The higher order terms in this expansion, constitute the summation of the \( \lambda^2 \) type contributions to all orders of \( \lambda \). It is clear that this summation procedure does not include certain terms in \( \lambda^4 \) PT simply because the Hamiltonian in the beginning was truncated to \( O(\lambda^2) \).
2.2. The Green's Function Method in the Calculation of the Helmholtz Free Energy

The Helmholtz free energy \( F \) can be calculated from the above Hamiltonian using the definition

\[
F = -k_B T \ln( \text{Tr}(\exp(-\beta H)))
\]  

(2.37)

Now we make use of the coupling parameter \( g \) which was introduced earlier. The differential equation for \( F(g) \) with respect to \( g \) is obtained

\[
\frac{dF}{dg} = -k_B T \frac{1}{Z(g)} \frac{dZ(g)}{dg}, \quad Z(g) = \text{Tr} e^{-\beta (H_0 + gH')}
\]

\[
= \frac{1}{Z(g)} \text{Tr} H' e^{-\beta (H_0 + gH')}
\]

\[
= \frac{1}{g} \langle gH' \rangle
\]

The thermal average \( \langle gH' \rangle \) is to be evaluated with the full Hamiltonian and therefore it contains the parameter \( g \) explicitly as well as implicitly. After integrating over the coupling parameter from zero (no interaction) to one (full interaction) we get

\[
F = F_0 + \int_0^1 dg \frac{\langle gH' \rangle}{g}
\]

(2.38)

\( F_0 \) is the quasiharmonic free energy:
\[ F_0 = k_b T \sum_{q,j} \ln \left( 2 \sinh \left( \frac{\beta}{2} \omega q_j \right) \right) \]  \hspace{1cm} (2.39)

and \(<gH'>\) is given in Shukla and Muller(1971):

\[ <gH'> = \frac{\hbar}{6} \sum_{q,q',j,j'} \frac{1}{\omega q_j} \int_{-\infty}^{\infty} d\omega \ j_{j'}(g,\omega) \left( \omega^2 - \omega^2 q_j \right) - \frac{1}{3} <gH_4(g)> \]  \hspace{1cm} (2.40)

After carrying out the integration in Eq(2.40) with the spectral function Eq(2.20) we find

\[ <gH'> = \frac{\hbar}{3N} \sum_{q,j} \frac{\Omega_{qj}^2(g) - \omega_{qj}^2}{2 \Omega_{qj}(g)} N_{qj}(g) - \frac{1}{3} <gH_4(g)> \]  \hspace{1cm} (2.41)

In our calculations we used the high temperature limit for \(N_{qj}\), with this approximation the final expression for \(<gH'>\) is

\[ <gH'> = \frac{k_b T}{3N} \sum_{q,j} \left[ 1 - \frac{\omega_{qj}}{\Omega_{qj}^2(g)} \right] - \frac{1}{3} <gH_4(g)> \]  \hspace{1cm} (2.42)

Here the renormalized frequencies \(\Omega_{qj}(g)\) are explicitly shown to depend on \(g\). \(H_4\) also depends on the \(\Omega_{qj}(g)\) and is given by

\[ H_4(g) = \frac{k_b T^2}{8N} \sum_{q_1,j_1} \sum_{q_2,j_2} \frac{\delta^4(q_1 j_1, -q_1 j_1, q_2 j_2, -q_2 j_2)}{\Omega_1^2(g) \ N_2^2(g)} \]  \hspace{1cm} (2.43)

If the \(\Omega_{qj}(g)\) in Eqs (2.42) and (2.43) are carefully expanded in powers of \(\lambda\), and the integration in Eq(2.40) is carried out, all the terms which are obtained are of the ring type and they have exactly the same coefficients which are obtained by the dia-
grammatic method for these contributions (diagrams 2b, 2d, 2f as given in Shukla and Cowley (1971)). With this method these terms are summed to all orders of anharmonicity. However, the other contributions of $O(\lambda^4)$ which are not of this type are diagrams 2a, 2c, 2e, 2g, 2h and these are completely left out in this scheme. We will later refer to this method as the iteration procedure.

In a separate calculation of the free energy we included the $\lambda^4$ diagrams which are left out in the iteration procedure by simply adding their contributions to the above expression for $F$. This way we include all the diagrams up to $O(\lambda^4)$ as well as the class of above ring diagrams to all orders of $\lambda$. 
3. Mean Square Displacement

In this chapter we present the results of MSD calculations using the Green's function method for various crystal models. The first model is a fcc solid with NN-LJ interaction. We will compare the $<u^2>$ results with results obtained by HSC using lowest order PT as well as MC and MD calculations. This comparison with the results of the simulation methods will shed some light on the merits of the Green's function method.

Secondly we perform the MSD calculations for the Alkali metals Na, K, and Cs using a sixth-neighbour Ashcroft pseudopotential. We will compare these results with those obtained by Shukla and Heiser (1986) for the same potential using molecular dynamics calculations and $\lambda^2$ PT.

Finally we calculate the MSD for Al using various pseudopotential functions involving long range interactions and a phenomenological NN Morse potential. Here we want to investigate whether the results for MSD are similar for different pseudopotentials as in the case of specific heat calculations of Shukla and Plint (1980).

In a recent publication Shukla, Plint, and Ditmars (1985) showed that the simple Morse potential gives $C_v$ results which are in very
good agreement with the results obtained from the more sophisticated pseudopotentials. We want to examine whether this is also true for MSD calculations. In addition we will compare our results with the experimental data from McDonald (1967) obtained from neutron scattering experiments.

3.1. MSD for a Nearest Neighbour Lennard-Jones Solid

The well known Lennard-Jones 6-12 potential function is used, defined as

$$\phi_{LJ}(r) = \epsilon \left[ \left( \frac{r_0}{r} \right)^{12} - 2 \left( \frac{r_0}{r} \right)^6 \right]$$

(3.1)

where $\epsilon$ is the well depth and $r_0$ is the separation at the minimum.

The Brillouin zone summations for $<u^2>$ (Eq(2.36)) as well as for $Q_{qj}^2$ (Eq(2.22)) were carried out over the irreducible $1/48^{th}$ of the first BZ, a cubic mesh of wave vectors $\mathbf{q} = 2\pi/(L\mathbf{a}_0)\mathbf{p}$ was used with

$$2(p_x + p_y + p_z) \leq 3L, \quad \text{and} \quad 0 \leq p_x \leq p_y \leq p_z \leq L$$

(3.2)

where $p_x$, $p_y$, $p_z$, and the step length $L$ are integers and $\mathbf{a}_0$ is the lattice constant. The weight factor for each wave vector was determined from the 48 symmetry operations of a cube, and the proper sharing factors were taken into account for vectors on the BZ boundary.
As observed before by HSC the results for \( <u^2> \) converge very slowly with increasing \( L \), however, they are found to vary almost linearly with \( 1/L \). We calculated \( <u^2> \) for step lengths from \( L=4 \) (256 wave vectors in the first BZ) to \( L=10 \) (4000 wave vectors) and plotted the results versus the inverse mesh size. A simple linear extrapolation then gives the results for infinite step length.

3.1.1. Results and Discussion

In Table 3.1. and Table 3.2. we present the values of \( <u^2> \) which are calculated by the methods outlined above for the six temperatures at which the MC calculations have been performed. In order to show the breakdown of the contributions to \( <u^2> \) in \( \lambda^2 \) PT from the QH, quartic (Q), and cubic (C) parts, we present in Table 3.1. these contributions separately in columns 2, 3, and 4, respectively. The results obtained by the Green's function method are presented in column six of Table 3.1. under the heading RE (renormalized frequency). The temperatures \( T^* \) are expressed in reduced units \( \epsilon/k_B \) and \( <u^2> \) is in units of \( \sigma^2/1000 \), where \( \sigma \) is zero position of the LJ-potential, it is related to \( r_0 \) by \( r_0 = 2^{1/6} \sigma \). The calculations were performed for the same lattice spacings as those used in the work of HSC. For converged answers all the values in Table 3.1. are extrapolated to infinite mesh size as described above. The results for the PT calculations presented here are different from that of HSC because their result for the cubic contribution to \( <u^2> \) was calculated for only \( L=10 \) and not
extrapolated to $L=\infty$. This step of converging the cubic term reduces the maximum disagreement with the MC results from 20% to 11% at $T^*=0.5$. We also present in column seven of Table 3.1. the results of MSD calculated by Hardy and Day (1988) by the method of correlated-particles expansion (CPE) carried through second order. Clearly the CPE-2 results are worse than PT for $T^* \leq 0.375$ and only slightly better for $T^*=0.5$. As noted earlier by Hardy and Day (1988) the long wave length contributions which are more important in the lower temperature range are not adequately represented by CPE.

The RE result is identical to the PT result at the lowest temperature; as the temperature increases, there is an increasing difference between the values. At $T^*=0.5$ the RE value is 7% higher than the respective PT value. Over the whole temperature range the RE results are always closer to the MC results than the PT results, the highest deviation being 6% at $T^*=0.45$.

For the sake of interest we show in Table 3.2. the equivalence of sample size in real space to mesh size in reciprocal space. In both cases the number of atoms or mesh points is 256. The results in Table 3.2. display the same behaviour as in Table 3.1.

We can conclude from these results that summing the $\lambda^2$ contributions to all orders of anharmonicity with the Green's function method yields a contribution to MSD which accounts for much of the terms beyond lowest order PT.
**Table 3.1.** Mean-square displacement for a NN-LJ solid at infinite sample size.

<table>
<thead>
<tr>
<th>$\epsilon/k_B$</th>
<th>QH</th>
<th>C</th>
<th>Q</th>
<th>$\lambda^2$</th>
<th>PT</th>
<th>RE</th>
<th>CPE-2</th>
<th>MC</th>
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<tbody>
<tr>
<td>0.125</td>
<td>3.21</td>
<td>0.35</td>
<td>-0.41</td>
<td>3.15</td>
<td>3.15</td>
<td>2.84</td>
<td>3.15</td>
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<tr>
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<td>1.53</td>
<td>-1.80</td>
<td>6.36</td>
<td>6.38</td>
<td>5.83</td>
<td>6.38</td>
<td></td>
</tr>
<tr>
<td>0.300</td>
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<td>3.54</td>
<td>-4.18</td>
<td>9.34</td>
<td>9.41</td>
<td>8.70</td>
<td>9.69</td>
<td></td>
</tr>
<tr>
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<td>12.4</td>
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<td></td>
</tr>
<tr>
<td>0.450</td>
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<td>18.1</td>
<td>17.3</td>
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</tr>
<tr>
<td>0.500</td>
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<td>26.3</td>
<td>-31.1</td>
<td>21.0</td>
<td>22.5</td>
<td>21.7</td>
<td>23.2</td>
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</table>
Table 3.2. Mean-square displacement for a NN-LJ solid for samples with 256 wave vectors or atoms respectively.

<table>
<thead>
<tr>
<th>$\epsilon/k_B$</th>
<th>QH</th>
<th>C</th>
<th>Q</th>
<th>$\lambda^2$</th>
<th>PT</th>
<th>RE</th>
<th>MC</th>
<th>MD</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.125</td>
<td>2.75</td>
<td>0.30</td>
<td>-0.36</td>
<td>2.69</td>
<td>2.69</td>
<td>2.67</td>
<td>2.67</td>
<td></td>
</tr>
<tr>
<td>0.225</td>
<td>5.69</td>
<td>1.28</td>
<td>-1.57</td>
<td>5.40</td>
<td>5.43</td>
<td>5.40</td>
<td>5.40</td>
<td></td>
</tr>
<tr>
<td>0.300</td>
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</tr>
<tr>
<td>0.375</td>
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<td>11.11</td>
<td>11.3</td>
<td>11.7</td>
<td></td>
</tr>
<tr>
<td>0.450</td>
<td>17.5</td>
<td>13.2</td>
<td>-16.3</td>
<td>14.4</td>
<td>15.1</td>
<td>15.7</td>
<td>17.1</td>
<td></td>
</tr>
<tr>
<td>0.500</td>
<td>22.2</td>
<td>22.1</td>
<td>-27.3</td>
<td>17.0</td>
<td>18.5</td>
<td>19.3</td>
<td>22.7</td>
<td></td>
</tr>
</tbody>
</table>
3.2. MSD for the Alkali Metals

3.2.1. Potentials for the Alkali Metals:

We used the same real-space model of a sixth-neighbour Ashcroft pair potential function that was used by Shukla and Heiser (1986). The various parameters were obtained from Price, Singwi, and Tosi (1970) and are the same as used by Shukla and Heiser. The dielectric screening function of the electron gas, $\epsilon(q)$, was obtained from Vashishta and Singwi (1972) (VS).

The potential function has the form (Shukla and Plint (1980)):

$$
\phi(r) = \frac{Z^2 \epsilon^2}{r} - \frac{2 Z^2 \epsilon^2}{\pi} \int_0^\infty G(q) \frac{\sin qr}{qr} dq
$$

(3.3)

where the first term represents the direct Coulomb interaction of ions with charge $Ze$, and the second term represents the ionic interaction as screened by the valence electrons. The overlap term in $\phi(r)$ is ignored because the ion cores are small.

The function $G(q)$ was first introduced by Cochran (1963). For the Ashcroft pseudopotential $G(q)$ is given by

$$
G(q) = \cos^2(qr_C) \left[ 1 - \frac{1}{\epsilon(q)} \right]
$$

(3.4)
where \( r_c \) is the core radius of the Ashcroft pseudopotential. The Vashishta and Singwi (1972) form of \( \epsilon(q) \) is given by

\[
\epsilon_{\text{vs}}(q) = 1 + \frac{Q_0(q)}{1 - f_{\text{vs}}(q) Q_0(q)}
\]  
\[(3.5)\]

where

\[
Q_0(q) = (k_{\text{ff}}/q)^2 F(q/k_f)
\]  
\[(3.6)\]

\[
F(x) = \frac{1}{2} + \frac{4 - x^2}{8x} \ln \left| \frac{2 + x}{2 - x} \right|
\]  
\[(3.7)\]

\( k_f \) is the Fermi radius and \( k_{\text{ff}} \) is the Thomas-Fermi screening constant

\[
k_{\text{ff}}^2 = \frac{m^*}{m} \frac{4 k_f}{\pi a_0}
\]  
\[(3.8)\]

\( a_0 \) is the Bohr radius and \( m^* \) is the effective electron mass which includes band structure effects.

The function \( f_{\text{vs}}(q) \) in Eq(3.5) is tabulated in VS, it can be fitted quite well with a function of the form

\[
f_{\text{vs}}(q) = A \left[ 1 - e^{-B(q/k_f)^2} \right]
\]  
\[(3.9)\]

The constants \( A \) and \( B \) have a weak volume dependence expressed through the parameter

\[
r_s^* = (m^*/m)r_s
\]  
\[(3.10)\]
where \( r_s \) represents the interelectronic distance defined by

\[
\frac{\Omega}{Z} = \frac{4}{3} \pi r_s^3 a_0^3,
\]

(3.11)

\( \Omega \) is the volume per ion. The parameters A and B are also listed in VS for \( r_s \) values ranging from 1 to 6. We obtained appropriate values for A and B by interpolation. The values for the core radius \( r_c \) and the effective electron mass \( m^* \) were obtained from Price, Singwi, and Tosi (1970) and are presented in Table 3.3.

In our calculations of MSD we evaluated \( \phi(r) \) and its first four radial derivatives numerically through Eq(3.3). The derivatives were obtained by differentiating this expression analytically with respect to \( r \) under the integral sign and then performing the integration over \( q \) numerically where a 5-point Newton-Cotes integration formula was used. Since \( G(q) \) has a volume dependence through Eq(3.11), these calculations were performed separately for the same lattice constants which were used by Shukla and Heiser (1986).

The alkali metals have a bcc lattice and therefore the sums over the irreducible 1/48th of the first BZ are over a cubic mesh of wave vectors \( \mathbf{q} = 2\pi/(L\mathbf{A}) \mathbf{p} \) defined by

\[
p_x + p_y \leq L, \quad p_x + p_z \leq L, \quad p_y + p_z \leq L, \quad \text{and} \quad 0 \leq p_x \leq p_y \leq p_z,
\]

(3.12)

where \( p_x, p_y, p_z \) and \( L \) are integers. The values of \( L \) ranged from \( L=6 \) (432 wave vectors in the first BZ) to \( L=11 \) (2662 wave vectors).
<table>
<thead>
<tr>
<th></th>
<th>Na</th>
<th>K</th>
<th>Cs</th>
</tr>
</thead>
<tbody>
<tr>
<td>M(amu)</td>
<td>22.99</td>
<td>39.1</td>
<td>132.91</td>
</tr>
<tr>
<td>r_c</td>
<td>1.69</td>
<td>2.226</td>
<td>2.62</td>
</tr>
<tr>
<td>m'/m</td>
<td>1.0</td>
<td>0.93</td>
<td>0.86</td>
</tr>
</tbody>
</table>
Converged results for $<u^2>$ were again obtained by extrapolation as described above.

3.2.2. MSD Results for Alkali Metals

The MSD results are presented in Table 3.4. The PT and RE results at the lowest temperatures are almost equal, whereas at the highest temperatures the RE results are about 3% higher than PT. This demonstrates, that the higher order PT contributions to $<u^2>$ are quite small for the Alkali metals. A comparison of RE and MD results shows that the MD results are 5% to 10% lower than the respective RE results at lower temperatures, which is not surprising because the MD method yields essentially all anharmonic contributions in the high temperature (or classical) limit. However, at the highest temperatures the MD result is almost equal to the RE result (Na and K) or it is even higher (Cs). This behaviour is consistent with the fact that the MD results were evaluated for a sample with 250 atoms whereas the RE numbers are fully converged. Judging from the experience with the LJ-solid we can assume that MD results for an infinite sample size would certainly be higher. This would eliminate much of the difference with the RE results at the lower temperatures, leaving a disagreement at the highest temperatures (in particular so for Cs).
Table 3.4. MSD results at zero pressure volume for Na, K, Cs from $\lambda^2$ PT, Green's function method (RE), and Molecular dynamics (MD). The results are in units $10^{-18}$ cm$^2$.

<table>
<thead>
<tr>
<th>Elem.</th>
<th>Lattice const(Å)</th>
<th>T(K)</th>
<th>PT</th>
<th>RE</th>
<th>MD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.234</td>
<td>93</td>
<td>8.83</td>
<td>8.84</td>
<td>8.30</td>
<td></td>
</tr>
<tr>
<td>4.251</td>
<td>163</td>
<td>16.39</td>
<td>16.47</td>
<td>16.11</td>
<td></td>
</tr>
<tr>
<td>4.288</td>
<td>294</td>
<td>33.39</td>
<td>34.05</td>
<td>32.82</td>
<td></td>
</tr>
<tr>
<td>4.309</td>
<td>365</td>
<td>44.32</td>
<td>45.92</td>
<td>45.42</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.261</td>
<td>101</td>
<td>14.58</td>
<td>14.61</td>
<td>13.22</td>
<td></td>
</tr>
<tr>
<td>5.277</td>
<td>163</td>
<td>24.68</td>
<td>24.84</td>
<td>22.94</td>
<td></td>
</tr>
<tr>
<td>5.305</td>
<td>215</td>
<td>34.72</td>
<td>35.13</td>
<td>31.29</td>
<td></td>
</tr>
<tr>
<td>5.343</td>
<td>291</td>
<td>51.29</td>
<td>52.58</td>
<td>51.24</td>
<td></td>
</tr>
<tr>
<td>Cs</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.069</td>
<td>103</td>
<td>20.81</td>
<td>20.87</td>
<td>19.69</td>
<td></td>
</tr>
<tr>
<td>6.092</td>
<td>160</td>
<td>34.14</td>
<td>34.38</td>
<td>31.70</td>
<td></td>
</tr>
<tr>
<td>6.119</td>
<td>218</td>
<td>49.54</td>
<td>50.27</td>
<td>46.08</td>
<td></td>
</tr>
<tr>
<td>6.163</td>
<td>293</td>
<td>72.93</td>
<td>75.16</td>
<td>82.51</td>
<td></td>
</tr>
</tbody>
</table>
3.3. MSD for Aluminum

3.3.1. Potentials for Aluminum

We calculated $<u^2>$ for Al using four different potential functions. These potentials were:

a) Ashcroft pseudopotential with the Vashishta-Singwi screening function (AVS) as described above for the alkali metals in Eqs (3.3)-(3.11); the parameters $r_c = 1.117a_0$ and $m^*/m = 0.94$ were obtained from Rao (1973).

b) Ashcroft pseudopotential with Hubbard screening function (AH), where $\epsilon_h(q)$ has the same form as $\epsilon_{vs}(q)$ in Eq(3.5) but now the function $f_h(q)$ is given by

$$f_h(q) = \frac{q^2}{2(q^2 - \xi k_f^2)} \quad (3.13)$$

The values for $r_c = 1.12 a_0$, $m^*/m = 1$, and $\xi = 1.699$ are obtained from Shukla and Plint (1980).

c) Harrison modified point-ion pseudopotential with Hubbard-Sham $\epsilon(q)$ (HHS):

$$G_{HHS}(q) = \left[ \frac{\Omega}{4\pi Z e^2} V_b(q) \right]^2 \frac{\epsilon(q) - 1}{1 + (\epsilon(q) - 1)(1 - q)} \quad (3.14)$$

40
\[ V_b(q) = \frac{1}{\Omega} \left[ -\frac{4\pi Ze^2}{q^2} + \frac{\beta}{(1 + q^2 \rho^2)^2} \right] \]  

(3.15)

\[ g_q = \frac{q^2}{[2(q^2 + \xi k_r^2)]} \]  

(3.16)

and \( \epsilon(q) \) is the Hartree dielectric function \( \epsilon(q) = 1 + Q_0(q) \)

The parameters \( \rho \), \( \beta \), and \( \xi \) were obtained from Shukla and Plint

\[ \rho = 0.24 \; a_0, \quad \beta = 47.5 \; a_0^3 \; (\text{Ry}), \quad \xi = 1.90 \; . \]

d) NN Morse potential

\[ \phi_{\text{Mo}}(r) = D \left[ e^{-2\alpha(r - r_0)} - 2 e^{-\alpha(r - r_0)} \right] \]  

(3.17)

the parameters \( D = 0.6369 \times 10^{-12} \) erg, \( \alpha = 1.1611 \; \text{Å}^{-1} \), \( r_0 = 2.8485 \; \text{Å} \)

were obtained from Shukla and McDonald (1980).

The MSD calculations were performed in the temperature range

\[ 300 K \leq T \leq 850 K \]

for zero pressure volumes appropriate in this temperature interval. The volumes were obtained from Shukla and Plint (1980). The step lengths for the BZ sums varied from \( L=4 \) to \( L=10 \); converged results were obtained by extrapolation.

3.3.2. The Range of the Pseudopotential Functions

In preliminary calculations we found that the \( \langle u^2 \rangle \) results were very sensitive to the number of shells used in setting up the
matrix $D_{\alpha\beta}(q)$ whose diagonalization gives $\omega(qj)$. The results changed by as much as 10% for different numbers of neighbours used in the calculation of $D_{\alpha\beta}(q)$ and hence $\omega(qj)$. We experimented this calculation by including as much as 23 shells of neighbours but finally decided to use a formalism that evaluates at least the quasiharmonic part of our MSD calculations exactly. Therefore $D_{\alpha\beta}(q)$ was not calculated from the real space potential Eq(3.3), instead converged results were obtained from the following expression (Price, Singwi, and Tosi(1970)):

$$D_{\alpha\beta}(q) = D^C_{\alpha\beta}(q) + D^E_{\alpha\beta}(q) \quad (3.18)$$

where $D^C(q)$ is the dynamical matrix arising from the direct Coulomb interaction between the ions. The matrix $D^E(q)$ represents the electron-ion interaction as screened by other electrons. It is related to the function $G(q)$ defined before:

$$D^E_{\alpha\beta}(q) = -\frac{Z^2e^2}{\pi \hbar \Omega} \sum_\tau \left[ \frac{(q_\alpha^+ \tau_\alpha)(q_\beta^+ \tau_\beta)}{|q + \tau|^2} G(|q + \tau|) - \frac{\tau_\alpha \tau_\beta}{\tau^2} G(\tau) \right] (3.19)$$

the sum is over all reciprocal lattice vectors.

The matrix $D^C(q)$ in Eq(3.18) has the form

$$D^C_{\alpha\beta}(q) = \frac{Z^2e^2}{M} \left[ \sum_{l'} \lambda_\alpha \lambda_\beta \frac{\cos(qr_{l})}{r_{l}^5} - \delta_{\alpha\beta} \sum_{l'} \frac{\cos(qr_{l})}{r_{l}^3} \right] \quad (3.20)$$
The sums in this equation converge very slowly because the number of neighbours at a distance \( r_i \) is proportional to \( r_i^2 \) and therefore each sum falls off of like \( \cos(qr)/r \) with increasing distance. However, this convergence problem of the lattice sums in Eq(3.20) can be solved by using the Ewald procedure (Shukla (1980a)) which splits the sums into sums over the real and the reciprocal lattice vectors, each of which can be made to converge rapidly.

In the treatment of anharmonic contributions to the various thermodynamic properties there is no general rule of how many neighbours should be included in the calculations. If the tensor derivatives \( \phi_{\alpha \beta \gamma} \) and \( \phi_{\alpha \beta \gamma \delta} \) are obtained from the effective interionic potential in Eq(3.3), the interaction is usually truncated after a certain number of neighbours. This number varies from as few as 2 (Copley (1973)) up to 28 shells (Shukla and Plint (1980)). The results, however, are very sensitive to the number of neighbours included in the calculation. Shukla (1980a), for example, showed that the quartic anharmonic contribution to the free energy was still far from converged after 23 shells by comparing the real space (shell by shell) contributions and the exact result obtained by the Ewald procedure. This is because of variations of the tensor derivatives as well as the S-tensors.

In the calculations of the quartic and cubic matrix shifts \( QS_{\alpha \beta}(q) \) and \( CS_{\alpha \beta}(q) \), respectively, we used a mixed approach. The S-tensors which arise in the calculation of \( QS(q) \) and \( CS(q) \) were
evaluated from the converged $D_{\alpha\beta}(q)$ as described above, however, the tensors derivatives in Eqs (2.25) and (2.28) were still derived from the real space potential in Eq(3.3) and were truncated after 8 and 4 shells of neighbours for the quartic and cubic parts, respectively.

3.3.3. MSD Results for Aluminum

The results for the MSD calculations are presented in Table 3.5. in terms of the quantity B(T) because the experimental data for the Debye-Waller factor is usually expressed in terms of this quantity:

$$B(T) = \frac{8\pi^2}{3} < u^2 >$$ (3.21)

The results for the Ashcroft pseudopotential seem to be independent of the screening function, both (Hubbard and Vashishta-Singwi) screening functions give almost identical results for the QH theory as well as for PT and the Green's function method (RE). At the highest temperature the RE values are 6% higher than the respective PT values. The Harrison modified point ion model potential with Hubbard-Sham screening yields QH results which are very similar to the Ashcroft pseudopotentials, however, the PT and RE corrections are larger for this potential and the RE value for 850K is 10% higher than for the Ashcroft potential. The Morse potential results are lower than the corresponding pseudopotential
Table 3.5. B(T) results for Al using Ashcroft pseudopotential with Vashishta-Singwi and Hubbard $\epsilon(q)$, Harrison modified point-ion potential with Hubbard-Sham $\epsilon(q)$ and a Morse potential. The results are in units Å$^2$.

<table>
<thead>
<tr>
<th>Temp(K)</th>
<th>QH</th>
<th>PT</th>
<th>RE</th>
</tr>
</thead>
<tbody>
<tr>
<td>AVS</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>300.0</td>
<td>0.8506</td>
<td>0.9413</td>
<td>0.9554</td>
</tr>
<tr>
<td>450.0</td>
<td>1.2759</td>
<td>1.4585</td>
<td>1.5007</td>
</tr>
<tr>
<td>600.0</td>
<td>1.7012</td>
<td>1.9855</td>
<td>2.0703</td>
</tr>
<tr>
<td>750.0</td>
<td>2.1265</td>
<td>2.5057</td>
<td>2.6399</td>
</tr>
<tr>
<td>850.0</td>
<td>2.4100</td>
<td>2.8388</td>
<td>3.0022</td>
</tr>
<tr>
<td>AH</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>300.0</td>
<td>0.8497</td>
<td>0.9423</td>
<td>0.9573</td>
</tr>
<tr>
<td>450.0</td>
<td>1.2745</td>
<td>1.4619</td>
<td>1.5074</td>
</tr>
<tr>
<td>600.0</td>
<td>1.6994</td>
<td>1.9930</td>
<td>2.0860</td>
</tr>
<tr>
<td>750.0</td>
<td>2.1242</td>
<td>2.5178</td>
<td>2.6668</td>
</tr>
<tr>
<td>850.0</td>
<td>2.4075</td>
<td>2.8574</td>
<td>3.0422</td>
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<td>HHS</td>
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<td>1.5816</td>
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<tr>
<td>750.0</td>
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<tr>
<td>850.0</td>
<td>2.4569</td>
<td>2.9976</td>
<td>3.3285</td>
</tr>
</tbody>
</table>

Morse

<table>
<thead>
<tr>
<th>Temp(K)</th>
<th>QH</th>
<th>PT</th>
<th>RE</th>
</tr>
</thead>
<tbody>
<tr>
<td>300.0</td>
<td>0.8267</td>
<td>0.8430</td>
<td>0.8434</td>
</tr>
<tr>
<td>450.0</td>
<td>1.2700</td>
<td>1.3073</td>
<td>1.3088</td>
</tr>
<tr>
<td>600.0</td>
<td>1.7395</td>
<td>1.8077</td>
<td>1.8114</td>
</tr>
<tr>
<td>750.0</td>
<td>2.2425</td>
<td>2.3521</td>
<td>2.3595</td>
</tr>
<tr>
<td>850.0</td>
<td>2.6009</td>
<td>2.7445</td>
<td>2.7558</td>
</tr>
</tbody>
</table>
results, in particular so for the PT and RE theories. This is a result of the much smaller anharmonic corrections for this potential as compared to the pseudopotentials (the QH and RE results differ by less than 6% whereas for HHS the difference is 35% at 850K).

The results obtained by the Green's function method are also plotted in Figure 3.1. together with the experimental data from McDonald (1965).

The best overall agreement with experiment is obtained for the Harrison modified point ion model potential with Hubbard-Sham screening. The deviation from experimental values is less than 10% throughout the range $300K \leq T \leq 900K$. This potential gives particulary good results at the highest temperature where the calculated value is only 6% smaller than the experimental one. At lower temperatures the HHS results are somewhat too low.

The agreement with experiment for both Ashcroft pseudopotentials at low temperatures ($T \leq 600K$) is better than with HHS, however, at high temperatures there is a considerable disagreement of up to 15%.

The Morse potential results are in poor agreement with experiment compared to the other potential functions. The results are close to the experimental values only for $T \leq 500K$, at higher temperatures the results are as much as 22% too low.
Figure 3.1. B(T) results for Al using Ashcroft pseudopotential with Vashishta-Singwi (AVS) and Hubbard (AH) ε(q), Harrison modified point-ion potential with Hubbard-Sham ε(q) (HHS) and the Morse potential. Crosses represent experimental data.
4. Calculation of the Thermodynamic Properties of Krypton

4.1. Potential Functions for Kr

For the calculation of the thermodynamic properties of Kr two different two body potential functions were used. One is the Lennard-Jones potential defined earlier in Eq(3.1), the two parameters $\epsilon$ and $r_0$ were obtained by Shukla and Shanes (1985). They derived them from the zero pressure volume at $T = 0K$ and the experimental value for the sublimation energy. In their calculations they included the harmonic zero-point energy. These parameters for Krypton are given in Table 4.1.

The other pair potential function is by Aziz (1979) and has the following form

$$\phi_{AZ}(r) = \epsilon \phi^*(r)$$  \hspace{1cm} (4.1)

$$\phi^*(r) = A X^\gamma e^{-aX} - \left[ \frac{C_6}{X^6} + \frac{C_8}{X^8} + \frac{C_{10}}{X^{10}} \right] F(X)$$

$$X = \frac{r}{r_m}$$

$$F(X) = \begin{cases} 
\exp\left[-\left(\frac{D}{X} - 1\right)^2\right] & \text{for } X \leq D \\
1 & \text{for } X > D
\end{cases}$$
The parameters of this potential function (a total of nine of them) have been adjusted to provide a simultaneous fit to dilute gas properties (virial coefficients, viscosity, collision cross sections and thermal conductivity) as well as spectroscopic data and theoretical Hartree-Fock calculations (for the repulsive well).

4.1.1. The Three Body Potential Function

The total interaction energy of a system of \( N \) rare gas atoms is generally assumed to be a sum of many body interactions (Bobetic and Barker (1970)):

\[
U = \sum_{n=2}^{N} \sum_{l_1, l_2, \ldots, l_n} U_n(l_1, l_2, \ldots, l_n)
\]  \hspace{1cm} (4.2)

It is assumed that the coefficients \( U_n \) vanish if one of the atoms is far away from the others.

If a pair potential is fitted to reproduce crystal properties as in the case of the above LJ potential, the many body contributions are already incorporated in that potential function. Since the parameters of the Aziz potential are fitted to two-body interactions, many-body forces are not included in this potential. If the equation of state is calculated for the Aziz potential without explicitly taking into account these many-body terms the results for the lattice constant are much too low over the whole
Table 4.1. Potential parameters for Kr.

For the Aziz potential:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\epsilon/k_B$</td>
<td>199.2 K</td>
</tr>
<tr>
<td>$r_m$</td>
<td>4.012 Å</td>
</tr>
<tr>
<td>D</td>
<td>1.28</td>
</tr>
<tr>
<td>A</td>
<td>0.1215312</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>16.496763</td>
</tr>
<tr>
<td>$C_6$</td>
<td>1.1561739</td>
</tr>
<tr>
<td>$C_8$</td>
<td>0.5414923</td>
</tr>
<tr>
<td>$C_{10}$</td>
<td>0.2839735</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>2.4</td>
</tr>
</tbody>
</table>

For the LJ-potential:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\epsilon$</td>
<td>$3.248 \times 10^{-14}$ erg</td>
</tr>
<tr>
<td>$r_0$</td>
<td>3.965 Å</td>
</tr>
</tbody>
</table>
temperature range. We therefore included a three-body interaction term \( U_3 \) in the form of the Axilrod-Teller triple-dipole potential as described in Bobetic and Barker (1970):

\[
U_3 = D_3 \sum_{i<j<k} \frac{(1 + 3 \cos \theta_{1i} \cos \theta_{2j} \cos \theta_{3k})}{R_i^3 R_j^3 R_k^3}
\]  

(4.3)

where the summation is over all lattice sites, the \( R_n \) (n=1,2,3) are the distances between pairs of the three atoms at positions i,j, and k and \( \theta_m \) (m=1,2,3) are the corresponding angles defined by the \( R_n \). The constant \( D_3 = 2.239 \times 10^{-82} \) \text{ erg cm}^{-9} is obtained from Bell and Kingston (1966). The lattice sum required in the calculation of \( U_3 \) was evaluated to four digits accuracy. The inclusion of this term produced a dramatic change in the calculated values of \( A_0 \) and the other thermodynamic properties. The contribution of \( U_3 \) to the total static energy is positive and accounts for 10% of this energy. However, the contributions from \( U_3 \) to \( \omega(q) \) are small and we ignore them in the calculation of \( F_0 \) and the other BZ sums.
4.2. Numerical Methods for the Calculation of the Thermodynamic Properties

The calculations of the various thermodynamic properties were carried out from the following expressions for the total free energy:

\[
E(\text{QH}) = U + F_0 \\
E(\lambda^2) = E(\text{QH}) + F(\lambda^2) \\
E(\lambda^4) = E(\lambda^2) + F(\lambda^4) \\
E(\text{ISC}) = E(\lambda^2) + \text{diagrams } F_{2a}, F_{2b}, F_{2c}, F_{2d} \\
E(\text{RING}) = E(\lambda^2) + \text{diagrams } F_{2b}, F_{2d}, F_{2f} \\
E(\text{ITER}) = F_0 + \text{sum of the iterated diagrams} \\
E(\text{FULL}) = E(\text{ITER}) + \text{diagrams } F_{2a}, F_{2c}, F_{2e}, F_{2g}, \text{ and } F_{2h}
\]

where \( U \) is the static energy. For the nearest neighbour LJ potential it is given by

\[
U_{\text{LJ}} = \frac{1}{2} \sum_{1}^{\text{\phi}_{\text{LJ}}(r_1)} = 6\phi_{\text{LJ}}(r_1) \tag{4.4}
\]

\( r_1 \) is the nearest neighbour distance.

For the Aziz potential the summation is extended over all neighbours and the three-body contribution is added:

\[
U_{\text{AZ}} = \frac{1}{2} \sum_{1}^{\phi_{\text{AZ}}(r_1)} + U_3(r) \tag{4.5}
\]
In the calculation of $F_0$ for both the LJ and the Aziz potential the finite temperature expression Eq(2.39) was used. The sum over $q$ was evaluated with a simple cubic mesh (Eq(3.2)) of step length 30 (which yields 108000 points in the first BZ). This sum was tabulated for 15 temperatures and 11 different lattice constants. The equation of state was calculated by minimizing the sum of the total static energy $U$ as a converged sum over all neighbours and $F_0$. In the minimization procedure intermediate values of $F_0$ were obtained by cubic spline interpolation of the tabulated values.

Next we calculated the explicit anharmonic contributions to $F$ of $O(\lambda^2)$ and $O(\lambda^4)$ in the high temperature limit. The contributions from diagrams $F_{1a}$ and $F_{1b}$ can be represented by

$$F(1a) = \frac{3N\hbar^2}{24MB} \left[ D \left( S_{2A} + \frac{2C}{r} S_{2B} + \frac{4B}{r^2} S_{2C} \right) \right]$$

$$+ \frac{3N(k_B T)^2}{192B^2} \left[ D \left( S_{4A} + \frac{2C}{r} S_{4B} + \frac{4B}{r^2} S_{4C} \right) \right]$$

$$F(1b) = -\frac{3N(k_B T)^2 C^2}{921B^3} \left[ D \left( S_{3A} + \frac{12B}{rC} S_{3B} + \frac{4B^2}{r^2 C^2} S_{3C} \right) \right]$$

(4.6)

(4.7)

where $B$, $C$, $D$ are defined in terms of the operator $G = (1/r)d/dr$ and $\phi(r)$:
\[ B(r) = r^2 G^2 \phi(r), \quad C(r) = r^3 G^3 \phi(r), \quad D(r) = r^4 G^4 \phi(r) \]

The functions \( S_{2a}, \ldots, S_{4c} \) are BZ sums which depend on the lattice constant via the parameter \( a_1 = \phi'(r)/[r\phi''(r)-\phi'(r)] \). These sums have been evaluated for \( a_1 \) in the range \(-0.1 \leq a_1 \leq 0.1\) by Shukla (1980b) and fitted to 6th degree exponential polynomials

\[ S_i(a_1) = \exp \left( \sum_{n=0}^{6} b_n^i (a_1)^n \right), \quad i = 2A, \ldots, 4C \]

by Shukla and MacDonald (1980) where the coefficients \( b_n^i \) are listed.

The multiple BZ sums for the \( \lambda^4 \) contributions (diagrams \( F_{2a}, \ldots, F_{2h} \)) are needed in the evaluation of \( E(\lambda^4), E(ISC), E(RING) \) and \( E(FULL) \). They are of \( O(r^3) \) and were supplied for both potential functions by R.C. Shukla (unpublished) for 9 different lattice spacings. From these numbers intermediate values were obtained by cubic spline interpolation.

The contribution from the iteration procedure was evaluated using Eqs (2.38), (2.42), and (2.43). The BZ summations were carried out over a cubic mesh of step length 10. The iteration process was continued until the elements of the dynamical matrix \( E_{q \delta}(q) \) were converged to 5 digits, which required 3 to 6 iteration steps depending on the values of \( g \) and the temperature \( T \). This
procedure was repeated for five equally spaced values of g in intervals of 0.2 and the integration over g was carried out numerically with a five point Newton-Cotes formula. This contribution was tabulated for six lattice spacings and 8 different temperatures, intermediate values were generated by cubic spline interpolation.

The zero pressure equation of state was obtained by minimizing the total Helmholtz free energy with respect to \( r \) at constant temperature using the Newton-Raphson method.

\[
\begin{align*}
    r_{i+1} &= r_i - \left[ \begin{array}{c} E'(r) \\ E''(r) \end{array} \right]_{r=r_i}^{-1} \\
\end{align*}
\]

where \( E' \) and \( E'' \) denote the first and second derivatives of \( E \) with respect to \( r \). These derivatives were obtained analytically for the parts of \( E \) which were represented by analytical functions (\( U, U_3, \) and \( F(\lambda^2) \)). For the other parts (\( F_0, \) the \( O(\lambda^4) \) diagrams, and the contributions obtained by integration over \( g \)) which were represented by cubic spline functions the derivatives were obtained by analytically differentiating the cubic spline expressions for these terms.

Once the zero pressure volume \( V(T) \) is known the other thermodynamic properties can be calculated by taking various derivatives of \( E \) with respect to \( V \) and \( T \). The derivatives with respect
to \( T \) were obtained numerically with a five point differentiation formula. We calculated the following quantities:

The specific heat at constant volume:

\[
C_V = -T \left[ \frac{\partial^2 E}{\partial T^2} \right]_V
\]  
(4.8)

The isothermal Bulk modulus:

\[
B_T = V(T) \left[ \frac{\partial^2 E}{\partial V^2} \right]_T
\]  
(4.9)

The adiabatic Bulk modulus:

\[
B_S = \frac{C_P}{C_V} B_T
\]  
(4.10)

The coefficient of volume expansion:

\[
\beta = -\frac{1}{B_T} \left[ \frac{\partial^2 E}{\partial V \partial T} \right]
\]  
(4.11)

The specific heat at constant pressure:

\[
C_P = C_V + V(T) B_T T \beta^2
\]  
(4.12)

The Grüneisen parameter:

\[
\gamma = \beta V B_T / C_V
\]  
(4.13)
4.3. Results and Discussion

4.3.1. Results for the Nearest Neighbour Lennard-Jones Solid

We present here the equation of state results of our calculations for Krypton using a NN-LJ potential from the different Helmholtz functions listed above. We will compare the computational results with the experimental data from Losee and Simmons (1968). The $E(QH)$, $E(\lambda^2)$, and $E(\lambda^4)$ equation of state results have been calculated before by Shukla and Shanes (1985) and are presented here to compare with the other PT schemes.

The curves obtained from $E(QH)$ have the same general shape as the experimental curves for $T \leq 1/2T_m$. At low temperatures ($T < 1/8 T_m$) the results are good (except for $B_v$), but at higher temperatures there is a considerable disagreement with experiment. This indicates that explicit anharmonic corrections (which are important at higher temperatures) are needed.

To bring better agreement, the first anharmonic contribution of $O(\lambda^2)$ is added to $E(QH)$. With this Helmholtz function the results show some improvement at lower temperatures (up to $1/3 T_m$) where the experimental values are in fairly good agreement with the calculated ones. However, at temperatures beyond $1/3 T_m$ the $\lambda^2$ curves are much lower than the experimental ones, the curves for $\beta$, $C_p$, $C_v$, $B_s$, and $B_v$ even have wrong curvatures. This is an
$\beta$, $C_p$, $C_v$, $B_s$, and $B_\tau$ even have wrong curvatures. This is an indication of a breakdown of the $\lambda^2$ PT.

When the $\lambda^4$ contributions are added to $E(\lambda^2)$ the shapes of the calculated curves are again similar to the $E(QH)$ curves. There is some improvement in the values of $C_p$ and $C_v$ in the temperature range $(1/3 \ T_m < T < 2/5 \ T_m)$ over the corresponding $E(\lambda^2)$ values. The results for $A_0$, $\beta$, $B_s$, $B_\tau$ and $\gamma$ are worse than for $E(\lambda^2)$ even at temperatures below $1/3 \ T_m$.

The next PT scheme, $E(\text{ITER})$, is the iteration procedure as described in Chapter 2. For $T \leq 1/2 \ T_m$ this scheme gives results which are almost identical to the $E(\lambda^2)$ results. At temperatures beyond that the $E(\text{ITER})$ values for most quantities are in between $E(\lambda^2)$ and experiment. In the case of the Grüneisen parameter the $\lambda^2$ PT gives better agreement with experiment than the ITER scheme.

Since the iteration procedure includes the ring type contributions to all orders of PT it will be of some interest to compare this procedure with a scheme that includes the ring type contributions up to $O(\lambda^4)$. We find that these two methods produce very similar curves for $T \leq 2/3 \ T_m$, beyond this temperature there is a noticeable divergence and the $E(\text{RING})$ results are much closer to experiment (except for $A_0$ and $\gamma$). This then shows that the most important ring type contributions come from the $\lambda^4$ PT for temperatures up to $2/3 \ T_m$. The small ring type contributions that arise from the high order ($\lambda^6$, $\lambda^8$, etc.) PT worsen the agreement with the experimental results for most thermodynamic properties.
Another PT scheme which has been used by Shukla and Cowley (1985) is the ISC. This scheme yields results for most quantities which are very similar to the RING scheme for temperatures almost up to $T_m$. These two schemes give the best agreement with the experimental data.

In the last procedure we used the contribution $E(\text{ITER})$ and added the contributions from the $O(\lambda^4)$ diagrams which are not included in the iteration procedure. This scheme produces results which are slightly better than the $O(\lambda^4)$ PT, the breakdown of this theory occurs about 5 degrees later than for $E(\lambda^4)$. 
Figure 4.1. Lattice Constant of Kr with a Lennard-Jones Potential. The Results are obtained from E(QH), E(λ^2), E(λ^4), E(RING), E(ITER), E(ISC), and E(FULL). The experimental values are represented by crosses.
Figure 4.2. Volume Expansion of Kr with a Lennard-Jones Potential. The legend is the same as in Figure 4.1.
Figure 4.3. Specific Heat at constant pressure of Kr with a Lennard-Jones Potential. The legend is the same as in Figure 4.1.
Figure 4.4. Specific Heat at constant volume of Kr with a Lennard-Jones Potential. The legend is the same as in Figure 4.1.
Figure 4.5. Adiabatic Bulk Modulus of Kr with a Lennard-Jones Potential. The legend is the same as in Figure 4.1.
Figure 4.6. Isothermal Bulk Modulus of Kr with a Lennard-Jones Potential. The legend is the same as in Figure 4.1.
Figure 4.7. Grüneisen Parameter of Kr with a Lennard-Jones Potential. The legend is the same as in Figure 4.1.
4.3.2. Results for the Aziz Potential

The QH results for the Aziz potential show the same general behaviour as we have seen for the LJ solid, the main difference is that the Aziz results are much closer to the experimental values than the respective LJ quantities. There is a good agreement with experiment for $T < 1/3 \ T_m'$, the best result is obtained for $B_s$ and $B_t$ where the agreement is good up to $3/4 \ T_m$.

When the $\lambda^2$ corrections are added to $E(QH)$ the results are over corrected and the calculated values for $A_0$, $B$, $C_p$ and $C_v$ which were too large in the quasiharmonic approximation are now too small and $B_t$, $B_s$, $B$ and $C_p$ even show wrong curvature for $T > 1/2 \ T_m$. The $\lambda^2$ PT provides only an improvement for $C_p$, $C_v$ and $\gamma$ over the QH theory for the Aziz potential.

The next scheme is $E(\lambda^4)$. This order of PT improves the results significantly. The calculated lattice constant is in excellent agreement up to $3/4 \ T_m$. Beyond this temperature $A_0$ as well as $B$ and $\gamma$ rise rapidly and the perturbation expansion breaks down (similar to the behaviour of the LJ solid). The values for $C_p$, $C_v$ and $B$ have a very good agreement with experiment up to 60% of $T_m$.

The results for $E(ITER)$ are almost identical to $E(\lambda^2)$ for $T \leq 2/3 \ T_m'$, beyond that temperature they are somewhat better than $E(\lambda^2)$, in particular there is no bending of curves in the wrong direction.
The E(RING) scheme which gives the best results for the LJ-solid does not work as well for the Aziz potential. The curves are slightly better than those for E(ITER).

For all quantities the E(ISC) scheme gives results which are very similar to the $\lambda^2$ PT over the whole temperature range.

The best overall results are obtained from E(FULL) which includes the sum of the ring diagrams to all orders of anharmonicity (i.e. the iterated scheme) and the remaining diagrams of $O(\lambda^4)$ left out from the iterated scheme. The curves are similar to $E(\lambda^4)$ but the range of close agreement with experiment is extended by 10 degrees which means that this scheme yields valid results for $T \leq 3/4 T_m$. 
Figure 4.8. Lattice Constant of Kr with the Aziz Potential. The Results are obtained from $E(QH)$, $E(\lambda^2)$, $E(\lambda^4)$, $E(RING)$, $E(ITER)$, and $E(FULL)$. The experimental values are represented by crosses.
Figure 4.9. Volume Expansion of Kr with the Aziz Potential. The legend is the same as in Figure 4.8.
Figure 4.10. Specific Heat at constant pressure of Kr with the Aziz Potential. The legend is the same as in Figure 4.8.
**Figure 4.11.** Specific Heat at constant volume of Kr with the Aziz Potential. The legend is the same as in Figure 4.8.
Figure 4.12. Adiabatic Bulk Modulus of Kr with the Aziz Potential. The legend is the same as in Figure 4.8.
Figure 4.13. Isothermal Bulk Modulus of Kr with the Aziz Potential. The legend is the same as in Figure 4.8.
Figure 4.14. Grüneisen Parameter of Kr with the Aziz Potential. The legend is the same as in Figure 4.8.
4.4. Comparison of Lennard-Jones and Aziz Results

In comparing these results two points are noteworthy. First, we observe the improvement of results obtained from the Aziz potential as compared to the LJ potential. This improvement is especially pronounced at lower temperatures \((T < 1/2 T_m)\) where the anharmonic effects are still small. There we see successively better values for QH, \(\lambda^2\), and \(\lambda^4\) theories as expected; all the \(\lambda^4\) results being off by less than 2% in this temperature range. This shows that the perturbation expansion converges very nicely in this temperature range. However, beyond \(3/4 T_m\) even the \(\lambda^4\) perturbation expansion breaks down. Extrapolating this behaviour to higher orders of PT one would expect that a complete \(\lambda^6\) PT extends the valid temperature range even further, though the computational effort would be prohibitive.

The LJ potential, in contrast, yields results for \(B_2\), \(B_1\), and \(\beta\) which are in rather poor agreement with experiment even at the lowest temperatures. The results for the other quantities at low temperatures are also not as close to the experimental data as with the Aziz potential which indicates that the NN-LJ potential is not a very good model for Kr.

As a second point we note that successive orders of the Van Hove ordering scheme \((\lambda^2, \lambda^4)\) show a similar qualitative behaviour. Schemes which involve only partial sums of \(\lambda^4\) diagrams tend to produce results which differ even qualitatively. For example the
E(ITER) results for LJ displays a pronounced bend at temperatures close to melting, whereas no such bending is observed for the Aziz potential. Likewise, the improved self consistent phonon theory which performs well for LJ (see Shukla and Cowley (1984)) does not work as well for the Aziz potential, the results are almost identical to \( \lambda^2 \) PT. This is a result of the strong cancellation among these diagrams, even a small change in their relative magnitude because of different choices of potential functions can produce quite different sums.
5. Summary

We have calculated the atomic mean square displacement for a NN LJ solid, Aluminum, and the alkali metals Na, K and Cs using a Green's function approach. This method effectively sums a whole class of contributions to all orders of anharmonicity. The results for a NN LJ solid show a definite improvement over the lowest order perturbation theory when compared to Monte Carlo calculations. For the alkali metals we used a sixth neighbour interaction potential derived from the pseudopotential theory. The MSD results change very little when the Green's function method is used instead of $\lambda^2$ PT. For the same sixth neighbour interaction potential employed in the MD and RE methods, the RE results for MSD are as much as 10% higher than the MD results in all cases except Cs at 293K. This is presumably an effect of the limited sample size used in the MD calculations.

In the case of Al we used three different pseudopotentials as well as a NN Morse potential. A comparison of the Green's function results with the experimental Debye-Waller factor data shows that the pseudopotential results are in better agreement than the Morse potential.
We calculated various thermodynamic properties of a Krypton solid using two different potential functions and different schemes of PT. For the LJ potential the E(RING) scheme yields the best results, while the more elaborate schemes E(ITER) and E(FULL) do not do as well. The more realistic Aziz potential gives overall better results than the LJ potential. The best results are obtained from E(FULL). This is even more remarkable in view of the fact that the parameters for this potential were derived from dilute gas properties and spectroscopic data.

The summation of the Ring type anharmonic contributions that is accomplished by the Green's function method brings improvements over the $O(\lambda^4)$ PT only when the $\lambda^4$-contributions, which are left out by this theory, are added separately.
References


