# ON THE PATH INTEGRAL FORMULATION AND THE EVALUATION OF QUANTUM STATISTICAL AVERAGES

by

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

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February 1979

To my parents, my cats and dogs

CONTENTS

## Abstract

Four problems of physical interest have been solved in this thesis using the path integral formalism.

Using the trigonometric expansion method of Burton and de Borde (1955), we found the kernel for two interacting one dimensional oscillators. The result is the same as one would obtain using a normal coordinate transformation.

We next introduced the method of Papadopolous (1969), which is a systematic perturbation type method specifically geared to finding the partition function Z, or equivalently, the Helmholtz free energy F, of a system of interacting oscillators. We applied this method to the next three problems considered.

First, by summing the perturbation expansion, we found F for a system of N interacting Einstein oscillators. The result obtained is the same as the usual result obtained by Shukla and Muller (1972).

Next, we found F to $O(\lambda^4)$, where $\lambda$ is the usual Van Hove ordering parameter. The results obtained are the same as those of Shukla and Cowley (1971), who have used a diagrammatic procedure, and did the necessary sums in Fourier space. We performed the work in temperature space.

Finally, slightly modifying the method of Papadopolous, we found the finite temperature expressions for the Debye-Waller factor in Bravais lattices, to $O(\lambda^2)$ and $O(|\vec{K}|^4)$,

where $\vec{K}$ is the scattering vector. The high temperature limit of the expressions obtained here, are in complete agreement with the classical results of Maradudin and Flinn (1963).

## Acknowledgements

The problems examined in this thesis were suggested and supervised by Dr. R. C. Shukla. I would like to express my gratitude to him for his constant encouragement and personal help.

I would like to express my gratitude to the Physics Department, students as well as faculty, for putting up with me.

I would also like to thank OGS for their financial support.

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# 1. Introduction to the Path Integral Formulation

In the more well known formulations of non-relativistic quantum mechanics, one is interested in studying the Hamiltonian of a system. This fact is evident when one writes down the time-dependent Schroedinger equation;

$$H\Psi = i\hbar \frac{\partial \Psi}{\partial t} \tag{1.1}$$

where $H$ is the Hamiltonian, $\Psi$ is the wave function, and $\hbar$ is Planck's constant divided by $2\pi$.

There are many reasons for the development of the Schroedinger formulation of quantum mechanics. The main one is that for most cases, one looks for a one-to-one correspondence between the operators of quantum mechanics and the classical quantities. For example, one can associate $H$ with the energy of the system.

However, one can formulate classical mechanics in terms of an action principle, or as more commonly known, Hamilton's principle, (Goldstein (1950)). When first formulated, one was interested in the Lagrangian of the system, and from the action principle, one obtained Lagrange's equations of motion. Later on, the Hamiltonian was related to the Lagrangian via a canonical transformation. In some ways the Lagrangian may be a more fundamental function describing a system.

One may then ask the following questions. Is it possible to formulate quantum mechanics in terms of the Lagrangian, and if so, how can this be done?

The answer to the first question is yes. The second question was partially answered by Dirac (1932) who laid down the foundations of the path integral formulation of quantum mechanics in his paper on the role of the Lagrangian in quantum theory. Feynman (1948) proposed a path integral formulation of quantum theory in terms of the Lagrangian as suggested by Dirac (1932).

As is shown in chapter 4 of the book by Feynman and Hibbs (1965), (from now on known as FH), the Schroedinger and path integral formulations are equivalent in the sense that the basic equations in either formulation can be derived from the other. What makes the path integral formulation worth studying separately is that it exhibits certain interesting features that are not evident in the Schroedinger formulation. We indicate some of these features presently.

In the Schroedinger formulation, there are basically two postulates. One of the postulates involves the equation of motion and the other involves the commutation relations among quantum mechanical operators, especially the canonically conjugate operators. This latter postulate is a consequence of the use of the Hamiltonian to describe a system, and hence the need for canonically conjugate operators. If instead, we use the Lagrangian to describe a system, then we avoid the necessity of introducing canonically conjugate variables, and hence we may be able to drop the postulate of the commutation relations. Hence we need only one postulate as Feynman used in his path integral formulation.

It is appropriate now to give a brief sketch of what arguments Feynman used in developing the path integral. Suppose the Lagrangian of a system under consideration is given by

$$L = \frac{1}{2} m \dot{q}^2 - V(q, \dot{q}, t) \tag{1.2}$$

Here $q$ is the position coordinate of the system, (not necessarily in one dimension), m is the mass, (not necessarily a constant and could be a vector), and $V(q, \dot{q}, t)$ is the potential. Given the system starts at $a \equiv (q_a, t_a)$, we want to find the probability that it will arrive near $b \equiv (q_b, t_b)$, $t_b > t_a$. Arguing that, in quantum mechanics, probability is like intensity, one must find the sum of the probability amplitudes of all possible paths from $a$ to $b$ that the system can take, and then take the square of its modulus to get the probability. Formally, one can write this as

$$K(b, a) = \sum_{\substack{\text{over all} \\ \text{paths from} \\ a \text{ to } b}} \Phi[q(t)] \tag{1.3}$$

where $\Phi[q(t)]$ $\equiv$ probability amplitude of a path described by $q(t)$ going from $a$ to $b$

Feynman postulated the following form for $\Phi[q(t)]$,

$$\Phi[q(t)] = \exp\left\{\frac{i}{\hbar} S[q(t)]\right\} \tag{1.4}$$

where $S[q(t)] = \int_{t_a}^{t_b} L(q,\dot{q},t)\,dt$ (1.5)

and the integral is evaluated along $q(t)$. S is called the action. In words, each path contributes equally in magnitude to $K(b,a)$ but differs in phase.

If we consider a one dimensional particle with a potential $V=V(q)$ that is well behaved, then the mathematical prescription for calculating the sum over paths (or also sometimes known as kernel) as given by Feynman (1948) is

$$K(b,a) = \lim_{N\to+\infty} \frac{1}{A}\int \frac{dq_1}{A} \cdots \int \frac{dq_{N-1}}{A} \exp\left\{\frac{i\varepsilon}{\hbar}\sum_{J=1}^{N}\left[\frac{m}{2}\frac{(q_J-q_{J-1})^2}{\varepsilon^2} - V(q_J)\right]\right\} \tag{1.6}$$

where $\varepsilon = \frac{t_b-t_a}{N}$, $A = \left(\frac{2\pi i\hbar\varepsilon}{m}\right)^{\frac{1}{2}}$, $q_0 \equiv q_a$, $q_N \equiv q_b$,

and the integration is done over all possible values of $q_J$. Feynman (1948) has also considered cases where the potential is of a different form in the sense that $V$ may depend on $t$ and $\dot{q}$. Then the expression in Eq. (1.6) becomes more complicated.

In defining the kernel, $K(b,a)$, in Eq. (1.3), one observes that the function $\Phi[q(t)]$ depends on the action $S[q(t)]$ which is a classical quantity. The $\hbar$ makes the argument of the exponential dimensionless, and brings in the quantum mechanical effects.

Intuitively, one can see that the path integral formulation has close ties with classical mechanics. This can be shown using the following arguments. If one formulates the classical laws of physics using Hamilton's principle, the path taken by the system, that is, the so-called classical path, will be the one that extremizes $S[q(t)]$. In the cases we consider, this extremum will be a minimum. Observe that as we move away from the classical path, the action will become larger, and because $\hbar$ is small, $\Phi[q(t)]$ will oscillate wildly. Hence all contributions to the kernel for paths that are not in the neighbourhood of the classical path will cancel out, (Gunther and Kalotas (1977)). Thus the classical path and the paths in the neighbourhood of it will contribute most to the kernel.

In the Schroedinger formulation, the wave function of a system associates a probability amplitude to the system at a particular position and time. The wave function gives a local description of the system. Furthermore, one must impose certain restrictions on the wave function which may be ad hoc or have a physically intuitive basis. While in the path integral formulation, the kernel associates a quantum mechanical amplitude to the motion of the system as a function of space and time. This is more of a global description. Also, the boundary conditions for the kernel can be chosen a priori.

One of the more appealing features of the path integral formulation is that the arbitrary phase factor of the wave function does not enter into the kernel because it is already fixed.

Looking at the expression for the kernel given in Eq. (1.6), one observes that one can perform the mathematical manipulations as is done in classical mechanics. This is also true for systems with other types of potentials, (Feynman (1948)). Hence one avoids the troublesome task of performing operator algebra. Since quantum mechanical operators are still of importance because they are related to physical quantities describing a system, one can use the path integral formalism to define "matrix" elements of an operator as was done by Feynman (1948), Davies (1963), Cohen (1970), and Mandelstam and Yourgrau (1968).

Although the path integral formulation is conceptually elegant, there is a major shortcoming which is expressed in Eq. (1.6). First, one has to determine whether or not Eq. (1.6) is well defined and second, one has to perform the integrations given in Eq. (1.6).

In fact, to obtain the kernel, one must perform a functional integral which is formally written as,

$$K(b,a) = \int_{q(t_a)=q_a}^{q(t_b)=q_b} \mathcal{D}[q(t)] \, \exp\left\{\frac{i}{\hbar} \int_{t_a}^{t_b} L\,dt\right\} \tag{1.7}$$

The expression given in Eq. (1.6) is similar in form to the Riemann sum definition of the Riemann integral.

Wiener (1923) developed, in connection with Brownian motion, what is now called the Wiener integral. The Wiener integral has a striking resemblance to the path integral given in Eq. (1.6). There has been much theoretical work done on the Wiener integral and how it is related to the path integral. This work is well covered in a review article by Koval'chik (1963). In fact, in developing an expression for the density matix, one can use the Wiener integral which is what will be done in section 3.

More recently, much theoretical work has been done on the study of Eq. (1.7). There are two points of concern. One is that the expression given in Eq. (1.6) used in defining the kernel given in Eq. (1.7) was developed on an intuitive basis and so should be put on a firm mathematical basis. Second, the convergence of the integrals in Eq. (1.6) must be handled carefully in a strict mathematical sense. Fundamental work discussing these points include Davison (1954), Itô (1961), Keller and McLaughlin (1975), De Witt (1972), Albeverio and Hoegh-Krohn (1976), and Mizrahi (1978). The latter three references give a definition of the path integral in Eq. (1.7) without recourse to the limiting procedure as given in Eq. (1.6).

From a more practical viewpoint, considerable effort has been put in to evaluate the path integral in Eq. (1.7). Unfortunately, there are not too many cases that can be done exactly, hence some effort is needed in finding good approximations to the path integral.

A class of path integrals that can be done exactly are the so-called Gaussian path integrals, that is, path integrals with quadratic Lagrangians. Notable examples of physical problems with quadratic Lagrangians include harmonic oscillators, free particles, particles in a constant magnetic field, and particles subject to a constant force. Papadopolous (1975) has evaluated the general Gaussian path integral, while examples of special cases can be found in FH (Ch. 3).

Some of the work that has been done in evaluating path integrals, either approximately or exactly, if possible, will be presently given.

The expression in Eq. (1.6) can be used, but is extremely tedious as is shown in FH (Ch. 3) for the free particle, and in Devreese and Papadopolous (1978), pg. 123, for the harmonic oscillator.

Davison (1954) developed the mathematics for evaluating the path integral by expanding the paths in a complete set of orthogonal functions. Davies (1957) and Glasser (1964) expand the paths in a trigonometric series to evaluate certain Gaussian path integrals. Burton and de Borde (1955) use a different expansion in trigonometric series and evaluate some Gaussian path integrals. This last method will be discussed in section 3.

The so-called semiclassical or WKB expansion has been explored. The method as described by Morette (1951) will be discussed in section 3 for non-relativistic quantum mechanics. More recent work along these lines is that of Gutzwiller (1967) and Levit and Smilansky (1977).

Much work has been done in expansion procedures also. This involves the expansion of the part of the exponential term of Eq. (1.7) that includes the potential or part of the potential, in a power series and term-by-term evaluation. Yaglom (1956) has followed this procedure in connection with the evaluation of the partition function. For further work on expansion formulae we refer to the work of Papadopolous (1969), Goovaerts and Devreese (1972 a,b), Siegel and Burke (1972), Goovaerts and Broeckx (1972), Goovaerts, Babenco, and Devreese (1973), and Maheshwari (1975).

In some cases it may not be possible to get a good approximation to the path integral. In those cases then, one may be able to get some bounds on what it should be. Specifically, these bounds are in terms of some physical quantity describing a system. Feynman, (FH (Ch. 11)), developed a generalized variational method in which he obtained an upper bound for the Helmholtz free energy of a system.

There are other methods for evaluating the path integral but they will not be indicated here.

The Feynman formulation, and hence the use of the path integral and Wiener integral, has been applied to solve or at least partially solve some important problems of physics. The areas of physics where the path integral has been applied include quantum, statistical, and solid state physics.

One of the most notable successes of the path integral formulation has been in the determination of certain properties of the polaron as described by Fröhlich (1954), such as the effective mass. Some of the work done on the polaron include Feynman (1955), Osaka (1959), Schultz (1960), Feynman, Hellwarth, Iddings, and Platzman (1962), and Thornber and Feynman (1970).

Feynman (1955) used the variational method, as noted above, in determining the effective mass of the polaron. This variational method has recently been applied by Celman and Spruch (1969) to problems in which the Hamiltonian of the system being studied has a term containing angular momentum.

Pechukas (1969) has used the path integral to derive the semiclassical theory of potential scattering.

Papadopolous (1971) has applied the path integral to the problem of a harmonically bound charge in a uniform magnetic field, from which he evaluated the partition function and density of states.

Lam (1966), Maheshwari and Sharma (1973), and Seshadri and Mathews (1975) have done some work on approximating the kernel of a one dimensional anharmonic oscillator with potential $V(x) = ax^2 + bx^4$.

Khandekar and Lawande (1972) and Goovaerts (1975) have applied the path integral formulation to a three body problem considered by Calogero (1969).

There are many more applications of the path integral formulation, some of which are of far greater importance than those mentioned. Many of these applications along with some of the theory of path integrals and Wiener integrals is given in the review articles of Gel'fand and Yaglom (1960), Brush (1961), Barbashov and Blokhintsev (1972), and Wiegel (1975). The standard text on path integrals is FH which gives the path integral formulation as developed by Feynman along with many applications including Feynman's work on quantum electrodynamics. More recently, the book edited by Devreese and Papadopolous (1978) gives some of the other developments of the path integral formulation and the present status of the path integral.

Before we end this introduction to the path integral, there are three points which should be noted.

First, Davies (1963) and Garrod (1966) have developed the path integral using the Hamiltonian. They showed that their path integral is the same as that using the Lagrangian.

Second, Mandelstam and Yourgrau (1968) have related Schwinger's variational principle to the Feynman path integral formulation.

Finally, work has been done in evaluating path integrals in general curvilinear coordinate systems other than the usual cartesian system. Most of the work has been done in polar or spherical coordinates; for example see (Edwards and Gulyaev (1964), Arthurs (1969), Peak and Inomata (1969), and Arthurs (1970)).

## 2. Outline of the Work done in the Thesis

Four problems of physical interest will be tackled using the path integral.

As can be found in many standard textbooks on solid state physics (Kittel, for example), a model that is frequently used in describing the dispersion forces of condensed matter is a system of coupled oscillators. In section 4, we use the expansion in trigonometric functions as discussed in section 3 to evaluate the path integral for two interacting one dimensional oscillators without using a normal coordinate transformation. This problem has already been solved using the normal coordinate transformation as is shown in FH (Ch. 8).

The partition function, or equivalently, the Helmholtz free energy, F, is an extremely useful quantity in describing systems which are in thermodynamic equilibrium. However, for a system of interacting oscillators, such as an anharmonic crystal, it is difficult to find an exact expression for F. Hence one must develop approximation methods to get F, one of which is a perturbation type expansion. In section 6, we derive the method of Papadopolous (1969). This is a perturbation method using the path integral and functional differentiation. Using this, we develop a systematic method of obtaining the usual perturbation expansion of the partition function for a system of interacting oscillators. This method is specifically geared for a system of interacting oscillators and will be applied to the next three problems discussed.

In section 7, we find the free energy of N interacting one dimensional Einstein oscillators. This problem has already been solved in the same vein by Shukla and Muller (1971) using a Green function method and again by Shukla and Muller (1972) using a diagrammatic procedure. In studying this problem, one is looking at the simplest problem which exhibits certain features that occur in more realistic models. To simplify greatly the calculations needed, one transforms the problem to wave vector space. In this space, one can use the symmetry of the system to apply periodic boundary conditions and develop the dispersion relationship. Also, when one is doing the perturbation expansion, the expansion cannot be cut off anywhere to give correct results because the interaction term is as strong as the harmonic part of the potential. Hence, one must sum the series to infinity.

The next two problems studied have to do with the anharmonic crystal. The interaction or anharmonic parts which are expanded out, are generally much smaller than the harmonic parts in their contribution to certain properties of a crystal, but are still necessary to describe the properties of a crystal such as thermal expansion, specific heat, etc. Perturbation theory is a standard method used in studying, theoretically, the properties of a crystal.

In section 8, we find the free energy of an anharmonic crystal, or system of anharmonic oscillators, as described in section 5, to $O(\lambda^4)$, where $\lambda$ is the usual Van Hove ordering parameter. This is the second lowest order of perturbation that gives a non-trivial contribution to the free energy. It has been found that the lowest order of perturbation, that is $O(\lambda^2)$, is inadequate in describing the temperature dependence of the heat capacity of certain materials at high temperatures, and hence, one must include the next order of perturbation to account for some of the discrepancy. Shukla and Cowley (1971) have done this calculation by using a diagrammatic procedure, and evaluating the necessary sums in Fourier space. We will perform the calculations in temperature space. These calculations have been done in temperature space to $O(\lambda^2)$, (Papadopolous (1969), and Barron and Klein (1974)), but to our knowledge have not been done to $O(\lambda^4)$. The results we obtain are equivalent to those of Shukla and Cowley. As a further sidelight, we will indicate how one can draw Feynman diagrams from the expressions we derive.

The decrease in intensity of x-rays scattered from a crystal occurs because of the thermal vibration of the atoms of the crystal about their lattice sites, and is accounted for, in theory, by using the Debye-Waller factor. In section 9, we determine the Debye-Waller factor for a monatomic Bravais lattice, which is a special case of the system described in section 5, to $O(\lambda^3)$ and $O(|\vec{K}|^4)$, where $\vec{K}$ is the scattering vector. We do the calculation to $O(\lambda^3)$ because this is the lowest order of perturbation that gives a non-trivial contribution to the Debye-Waller factor. The reason for doing the calculation to $O(|\vec{K}|^4)$ is that if one were to write out the full formal expression for the Debye-Waller factor, one would find that the lowest order term is proportional to $|\vec{K}|^2$ and the next lowest order term is proportional to $|\vec{K}|^4$, but both terms are of $O(\lambda^3)$ in anharmonicity. We then take the high temperature limit to show that our results coincide with those of Maradudin and Flinn (1963). Current numerical techniques make the calculation of the terms of the Debye-Waller factor extremely time consuming, even for the high temperature limit. However, the finite temperature results are of some interest in investigating the temperature dependence beyond the leading temperature terms derived in the classical procedure of Maradudin and Flinn (1963).

In section 10, we summarize our findings and make our conclusions.

## 3. Mathematical Preliminaries

In this section, we present a mathematical formulation of the path integral starting from the time dependent Schroedinger equation and its general solution. We then describe two methods for evaluating the path integral; (a) the semiclassical or WKB expansion of Morette (1951) for non-relativistic quantum mechanics, and (b) the expansion in trigonometric series as given by Burton and de Borde (1955). The trigonometric expansion method will be used in section 4 to solve the problem of two interacting one dimensional oscillators. The method of Morette will be used in section 6 in connection with the study of a system of N interacting Einstein oscillators (Sec. 7), and the anharmonic crystal (Sec. 8, 9). Finally, we show how the density matrix can be written in terms of a path (Wiener) integral. The density matrix, and hence the partition function, Z, or equivalently, the Helmholtz free energy, F, will be employed in sections 7 and 8.

### (A) The Path Integral

The time dependent Schroedinger equation is

$$H \Psi = i\hbar \frac{\partial \Psi}{\partial t} \tag{1.1}$$

where the symbols are defined in section 1. Suppose the Hamiltonian is given by

$$H = \frac{1}{2m} p^2 + V(q) \tag{3.1}$$

where $p, q$ are the usual momentum and position operators, respectively, (not necessarily one dimensional), m is the mass which is appropriate for the system considered, and $V(q)$ is the potential which depends on position only.

The general solution of Eq. (1.1) is then separable in the sense that it can be written as the product of two functions, one depending on time and the other on position. It then remains to find the energy eigenvalues and eigenstates of the associated time-independent Schroedinger equation. Let the stationary eigenstates be $\phi_E(q)$ and the associated energy levels be $E$ . As is well known, the set $\{\phi_E(q)\}$ forms a complete, orthonormal set.

Using the notation of section 1, and following the procedure of Schiff (1968), the wave function $\Psi(q_a, t_a)$ of the system under consideration can be expanded in terms of the energy eigenstates to give

$$\Psi(a) \equiv \Psi(q_a, t_a) = \sum_E a_E(t_a)\, \phi_E(q_a) \tag{3.2}$$

where $$a_E(t_a) = \int dq_a\, \phi_E^*(q_a)\, \Psi(q_a, t_a)$$

The wave function $\Psi(q_b, t_b)$ where $t_b > t_a$ is given by

$$\begin{aligned}
\Psi(b) \equiv \Psi(q_b, t_b) &= \sum_E a_E(t_b)\, \phi_E(q_b) \\
&= \sum_E a_E(t_a)\, \phi_E(q_b)\, e^{-\frac{i}{\hbar}E(t_b - t_a)} \\
&= \sum_E e^{-\frac{i}{\hbar}E(t_b - t_a)}\, \phi_E(q_b) \int dq_a\, \phi_E^*(q_a)\, \Psi(a) \\
&= \int \Big\{ \sum_E e^{-\frac{i}{\hbar}E(t_b - t_a)}\, \phi_E(q_b)\, \phi_E^*(q_a) \Big\}\, \Psi(a)\, dq_a
\end{aligned} \tag{3.3}$$

Let

$$K(b,a) = \begin{cases} \sum_E e^{-\frac{i}{\hbar}E(t_b-t_a)}\,\phi_E(q_b)\,\phi_E^*(q_a)\,, & t_b > t_a \\ 0 & , t_b < t_a \end{cases} \tag{3.4}$$

Then, Eq. (3.3) becomes

$$\Psi(b) = \int K(b,a)\,\Psi(a)\,dq_a \tag{3.5}$$

$K(b,a)$ is often called the kernel, propagator, or Green function.

Essentially, Eq. (3.5) is an integrated version of the Schroedinger equation, for given the wave function at some point in space and time, and the kernel, one can find the wave function at later times.

We note the following three important properties of the kernel.

First, $$K(b,a) = K(q_b, q_a\,; t_b - t_a) \tag{3.6}$$

The kernel is a function of the difference in time.

Second, $$\lim_{t_b\to t_a^+} K(b,a) = \sum_E \phi_E(q_b)\phi_E^*(q_a) = \delta(q_b - q_a) \tag{3.7}$$

where in taking the limit $t_b \to t_a^+$ , it is understood that one approaches $t_a$ from values greater than $t_a$ . The last equality is just the closure property, with $\delta(q_b-q_a)$ denoting the usual Dirac delta function.

Third, suppose that $c \equiv (q_c, t_c)$ is an intermediate point such that $t_a < t_c < t_b$ . Then, by Eq. (3.5),

$$\Psi(c) = \int K(c,a)\,\Psi(a)\,dq_a \qquad \text{, and}$$

$$\Psi(b) = \int K(b,c)\,\Psi(c)\,dq_c \qquad ,$$

whence $\quad \Psi(b) = \int dq_a \left\{ \int dq_c\, K(b,c)\, K(c,a) \right\} \Psi(a)$

Comparison of the above equation with Eq. (3.5) yields

$$K(b,a) = \int dq_c\, K(b,c)\, K(c,a) \tag{3.8}$$

One can proceed along the same lines as above to obtain the following;

$$K(b,a) = \int dq_{c_1} \cdots \int dq_{c_n}\, K(b,c_n) \cdots K(c_{j+1},c_j) \cdots K(c_1,a) \tag{3.9}$$

where $\quad t_b > t_{c_n} > \cdots > t_{c_1} > t_a$

In what is to follow, we shall restrict ourselves to one dimensional cases. The extension to higher dimensions is straightforward and follows along much the same lines as the extension of the Riemann integral to higher dimensions.

Now we will show, in a sketchy manner, how to express $K(b,a)$ in the form of the path integral.

It is well known that the energy eigenfunctions of a free particle of mass m are given by $\phi_E(q) = \exp(ikq)$, and the associated energy levels are $E = \frac{\hbar^2 k^2}{2m}$, where $k$ is the wave number. The energy levels are not discrete, but instead form a continuum, whence $\sum_E \longrightarrow \frac{1}{2\pi}\int_{-\infty}^{+\infty} dk$

For $t_b > t_a$, Eq. (3.4) becomes

$$K(b,a) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} dk \ \exp\left\{\frac{-i}{\hbar}\frac{\hbar^2 k^2}{2m}(t_b - t_a)\right\}\exp\left\{ikq_b\right\}\exp\left\{-ikq_a\right\}$$

$$= \left[\frac{m}{2\pi i\hbar(t_b-t_a)}\right]^{\frac{1}{2}}\exp\left\{\frac{i}{\hbar}\frac{m}{2}\frac{(q_b-q_a)^2}{(t_b-t_a)}\right\} \qquad (3.10)$$

The Lagrangian of the free particle is given by $L = \frac{1}{2}m\dot{q}^2$. Solving the corresponding Euler-Lagrange equation subject to $q(t_a) = q_a$, and $q(t_b) = q_b$, and substituting this into the action integral, we find that the action $S$, is given by

$$S \equiv S(b,a) = \int_{t_a}^{t_b} L\,dt = \frac{m}{2}\frac{(q_b-q_a)^2}{(t_b-t_a)} \qquad (3.11)$$

Noting Eq. (3.11), we observe that Eq. (3.10) is

$$K(b,a) = \left[\frac{m}{2\pi i\hbar(t_b-t_a)}\right]^{\frac{1}{2}}\exp\left\{\frac{i}{\hbar}S(b,a)\right\} \qquad (3.12)$$

We note that the form of $K(b,a)$ given in Eq. (3.12) is similar in form to the kernel given in Eq. (1.6).

Suppose now that instead of a free particle, we consider a particle whose Lagrangian is given by

$$L = \frac{1}{2}m\dot{q}^2 - V(q) \qquad (3.13)$$

where $V$ is the potential, depending only on the position of the particle.

Without getting into the mathematical details, we will derive an expression for the kernel of this particle which is similar to Eq. (3.12).

Suppose $t_b > t_a$ . Subdivide the interval $[t_a, t_b]$ into N subintervals, the $j^{th}$ such interval having length $\epsilon_j > 0$ . Put $t_j = t_a + \sum_{\ell=1}^{j} \epsilon_\ell$ , with $t_0 = t_a$ and $t_N = t_b$ . With each $t_j$ , we associate the position coordinate $q_j$ . Let $j \equiv (q_j, t_j)$.

Noting Eq. (3.9),

$$K(b,a) = \int dq_1 \cdots \int dq_{N-1}\, K(b,N-1) \cdots K(j+1,j) \cdots K(1,a) \tag{3.14}$$

If the $\epsilon_j$ are small and $V(q)$ is a fairly smooth function, $V(q) \approx V(q_j)$ for $t_j \le t < t_{j+1}$. The Lagrangian of the particle in the interval $t_j \le t < t_{j+1}$ is then approximately given by $L \approx \frac{1}{2} m \dot{q}^2 - V(q_j) \equiv L_j$ .

If one were to picture the approximate motion of the particle from $a$ to $b$ , one could conceive of the particle as moving like a free particle in the time intervals $t_j \le t < t_{j+1}$, while the points $(q_j, t_j)$ act as scattering centres of the particle that change its energy by $V(q_j) - V(q_{j-1})$, (see fig. 1).

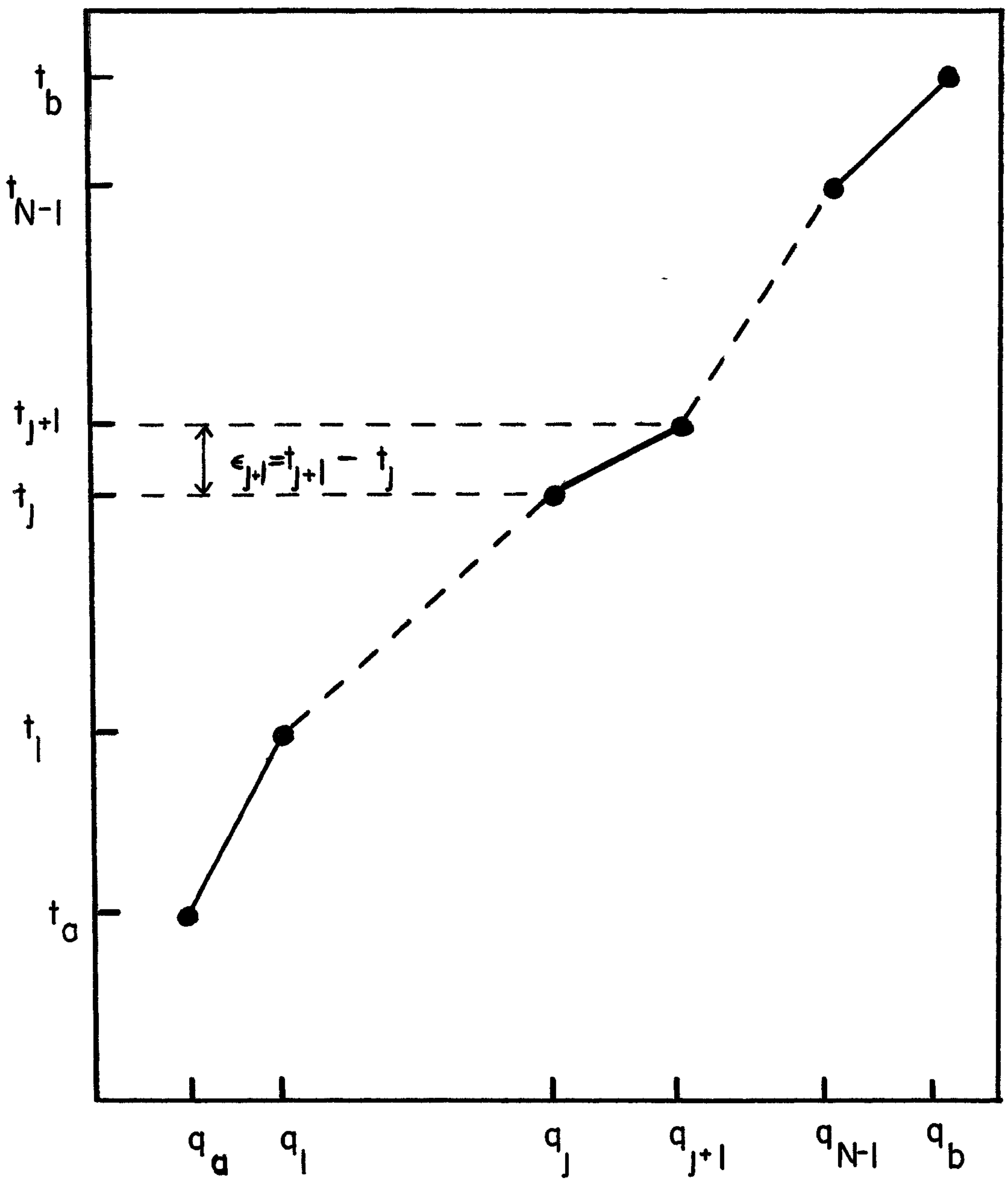
Hence,

$$\begin{aligned} K(j+1,j) &= \sum_E e^{-\frac{i}{\hbar} E \epsilon_{j+1}} \phi_E(q_{j+1})\, \phi_E^*(q_j) \\ &\approx A_{j+1}^{-1}\, e^{\frac{i}{\hbar} S(j+1,j)} \end{aligned} \tag{3.15}$$

where $A_{j+1} = \left[\frac{m}{2\pi i \hbar \epsilon_{j+1}}\right]^{-\frac{1}{2}}$, and $S(j+1,j) = \int_{t_j}^{t_{j+1}} L_j\, dt$ , with $q$ satisfying the corresponding Euler-Lagrange equation for $t_j \le t < t_{j+1}$ . Note that $\phi_E(q) = e^{i k_j q}$ , $\hbar^2 k_j^2 = 2m(E - V(q_j))$, and the eigenenergies form a continuum just as in the free particle case.

Figure 1: Hypothetical motion of a particle, with its Lagrangian given by Eq. (3.13), from $a = (q_a, t_a)$ to $b = (q_b, t_b)$. The scattering centres are the dots and the straight lines indicate the free particle motion between scattering centres.

FIG. 1



Further $\phi_E(q_{j+1})=e^{ik_jq_{j+1}}$ because $t_j \le t < t_{j+1}$. Substitution of Eq. (3.15) into Eq. (3.14) yields

$$K(b,a) \approx \int \frac{dq_1}{A_1} \cdots \int \frac{dq_{N-1}}{A_{N-1}} \frac{1}{A_N} \exp\left\{\frac{i}{\hbar}\sum_{j=0}^{N-1} S(j+1,j)\right\}$$

If we let $\max_j \epsilon_j \to 0^+$, or if all the $\epsilon_j$ are equal, we let $N \uparrow +\infty$, one observes that the approximation becomes better. Hence we expect

$$K(b,a) = \lim_{\max_j \epsilon_j \to 0^+} \int \frac{dq_1}{A_1} \cdots \int \frac{dq_{N-1}}{A_{N-1}} \frac{1}{A_N} \exp\left\{\frac{i}{\hbar}\sum_{j=0}^{N-1} S(j+1,j)\right\} \qquad (3.16)$$

This is the same as the expression given in Eq. (1.6)

(B) Methods of Evaluation

(a) Semiclassical or WKB Expansion Method.

Let us first consider the method of the semiclassical or WKB expansion as given by Morette (1951). We consider the case for non-relativistic quantum mechanics instead of for relativistic quantum mechanics as was done by Morette.

The action is given by $S[q] = \int_{t_a}^{t_b} L(q,\dot{q},t)$

Let $x_c(t)$ be the function which minimizes $S[q]$, that is, $x_c(t)$ is the classical path. Let $q(t) = x_c(t) + y(t)$. Hence, $y(t_a) = y(t_b) = 0$.

Expanding $S$ about $x_c(t)$ in a Taylor series, one has

$$S[q] = S[x_c] + \frac{1}{2!}\delta^2 S[x_c] + \frac{1}{3!}\delta^3 S[x_c] + \cdots \qquad (3.17)$$

where $\delta$ represents the variation of $S$ and $x_c \equiv x_c(t)$ is defined by $\delta S[x_c] = 0$.

As an approximation to $S$, we drop all terms higher than second order in the expansion of Eq. (3.17).

Put $$S_A = S[x_c] + \frac{1}{2!}\delta^2 S[x_c] \tag{3.18}$$

where $$\delta^2 S[x_c] = \int_{t_a}^{t_b} dt \sum_{\mu,\nu}\left\{ \left[\frac{\partial^2 L}{\partial q_\mu \partial q_\nu}\right]_{q=x_c} y_\mu y_\nu + \right.$$
$$\left. + 2\left[\frac{\partial^2 L}{\partial q_\mu \partial \dot{q}_\nu}\right]_{q=x_c} y_\mu \dot{y}_\nu + \left[\frac{\partial^2 L}{\partial \dot{q}_\mu \partial \dot{q}_\nu}\right]_{q=x_c} \dot{y}_\mu \dot{y}_\nu \right\}$$

and $\sum_{\mu,\nu}$ is the sum over the components of $q$.

The kernel for the action $S_A$, is then given by

$$K_A(b,a) = \int_{q_a}^{q_b} \mathcal{D}[q(t)]\, e^{\frac{i}{\hbar}S_A} = \int_{q_a}^{q_b} \mathcal{D}[q(t)] \exp\left[\frac{i}{\hbar}\left\{S[x_c] + \frac{1}{2!}\delta^2 S[x_c]\right\}\right] \tag{3.19}$$

We will give an intuitive argument for what follows next, but the following can be done rigorously, (Koval'chik (1963)).

We have written $q(t) = x_c(t) + y(t)$. Now, $x_c(t)$ is a fixed path and hence cannot be varied. It follows that $y(t)$ is the path to be varied with $y(t_a) = y(t_b) = 0$. Essentially what we have done is to perform a linear transformation. Further, since $S[x_c]$ is independent of $y(t)$, we can factor $\exp\left\{\frac{i}{\hbar}S[x_c]\right\}$ out of Eq. (3.19) as though it was a constant. It follows that

$$K_A(b,a) = e^{\frac{i}{\hbar}S[x_c]} \int_{y(t_a)=0}^{y(t_b)=0} \mathcal{D}[y(t)] \exp\left\{\frac{i}{\hbar}\frac{1}{2}\delta^2 S[x_c]\right\} \tag{3.20}$$

The above path integral is not necessarily zero, but just states that we must evaluate the path integral for all paths starting and ending at the same space coordinate, namely 0.

One can determine the path integral of Eq. (3.20) using the methods of Morette, and is given by

$$\int_{y(t_a)=0}^{y(t_b)=0} \mathcal{D}[y(t)] \exp\left\{\frac{i}{\hbar}\frac{1}{2}\delta^2 S[x_c]\right\} = \left[\det_{\mu\nu}\frac{1}{2\pi i\hbar}\frac{\partial^2 S[x_c]}{\partial q_{a\mu}\partial q_{b\nu}}\right]^{\frac{1}{2}} \quad (3.21)$$

The above method is exact for Gaussian path integrals because $\delta^n S[x_c]=0$ for n=3,4,... . In fact, the second factor on the right hand side of Eq. (3.20), for this case, is independent of $q_a$ and $q_b$, and depends only on $t_a$ and $t_b$.

(b) Trigonometric Expansion Method.

We now wish to discuss the method of expanding the paths in a trigonometric series as was done by Burton and de Borde (1955). We will again just discuss the one dimensional case, but these results can be extended if so desired. Instead of using the general time interval $[t_a, t_b]$, we will use $[0,T]$ . There is no loss of generality for the cases we consider, since the kernel depends only on the length of the time interval, as is observed in Eq. (3.6).

To evaluate the action integral, we expand the velocity term arising in L as follows;

$$\dot{q}(t) = \left(\frac{2\pi\hbar}{mT}\right)^{\frac{1}{2}} \sum_{n=0}^{+\infty} a_n \phi_n\left(\frac{t}{T}\right) \quad (3.22)$$

where $\phi_0(z)=1$ , $\phi_n(z)=\sqrt{2}\cos(n\pi z), n\geq 1$ , and the $a_n$ are independent of t. Plainly, $\{\phi_n(z)\}$ form a complete, orthonormal set of functions on $[0,T]$ as they are the functions used in Fourier cosine series expansions.

To find $q(t)$, we integrate the expression for $\dot{q}(t)$, noting that $q(0)=q_a$, and $q(T)=q_b$. Integration of Eq. (3.22) yields

$$q(t)-q_a = \int_0^t dt\ \dot{q}(t) = \left(\frac{2\pi\hbar}{mT}\right)^{\frac{1}{2}} \sum_{n=0}^{+\infty} a_n \int_0^t \phi_n\left(\frac{t}{T}\right) dt$$

$$= \left(\frac{2\pi\hbar}{mT}\right)^{\frac{1}{2}} \left\{ a_0 t + \frac{T\sqrt{2}}{\pi} \sum_{n=1}^{+\infty} \frac{a_n}{n} \sin\left(n\pi\frac{t}{T}\right)\right\} \quad (3.23)$$

Further, $$q(T) - q_a = q_b - q_a = \left(\frac{2\pi\hbar}{mT}\right)^{\frac{1}{2}} a_0 T$$

$$\text{i.e. } a_0^2 = \frac{m}{2\pi\hbar T}\left(q_b - q_a\right)^2 \quad (3.24)$$

The beauty of the method can be seen from the above expansions. One observes that the expansion coefficients $\{a_n\}$ characterize the path. Intuitively, at least, if one integrates over the $a_n$, one would be summing over all paths. The mathematical details involved are not trivial, and will not be given here. However, if we substitute Eq. (3.22), Eq. (3.23), and Eq. (3.24) in L, and then find the action integral in terms of the $a_n$, the kernel, $K(b,a)$, is then given by

$$K(b,a) = \left(\frac{m}{2\pi i\hbar T}\right)^{\frac{1}{2}} \int \frac{da_1}{\sqrt{i}} \cdots \int \frac{da_n}{\sqrt{i}} \exp\left\{\frac{i}{\hbar}\int_0^T L\, dt\right\} \quad (3.25)$$

The integrals are over all possible values of the $a_n$, $n \geq 1$, $a_0$ being fixed by Eq. (3.24). The factors $\sqrt{i}$ and $\left(\frac{m}{2\pi i\hbar T}\right)^{\frac{1}{2}}$ can be obtained by comparison with the result for a free particle which can be done by first principles, (FH (Ch. 3)). The other kernel needed in this thesis is that of an harmonic oscillator, the derivation of which will be given in section 4.

(C) Density Matrix

We now introduce the density matrix which is very useful in statistical physics. We then show how one can write the density matrix as a path (Wiener) integral following the method given in FH (Ch. 10).

We know, from statistical physics, that for a system in equilibrium and in thermal contact with a heat reservoir, the partition function Z, or equivalently, the Helmholtz free energy F, is all one needs to deduce the average properties of that system.

The partition function is defined as follows;

$$Z = \sum_r e^{-\beta E_r} \tag{3.26}$$

where $E_r$ energy of state r of the system,

$\beta = \frac{1}{k_B T}$ , $k_B \equiv$ Boltzmann's constant,

$T \equiv$ absolute temperature,

and $\sum_r$ is the sum over all possible states of the system.

The Helmholtz free energy is given by

$$F = -k_B T \ln Z \tag{3.27}$$

In what is to follow, the system can be described by the Hamiltonian given in Eq. (3.1). We can obtain the following results for other types of potentials, but the arguments needed must be changed.

If state r is defined by the normalized wave function $\phi_r(q)$, the probability of finding the system in state r "near" $q$, that is, in the region $[q, q+dq]$ is given by

$$P_r(q)\,dq = \frac{1}{Z} e^{-\beta E_r} \phi_r^*(q)\,\phi_r(q)\,dq \tag{3.28}$$

Here, we have also assumed that the system is in equilibrium, and is in contact with a heat reservoir at temperature $T$. Summing over all possible states, the probability of observing the system "near" $q$ is given by

$$P(q)\,dq = \sum_r P_r(q)\,dq = \frac{1}{Z}\sum_r e^{-\beta E_r} \phi_r^*(q)\,\phi_r(q)\,dq \tag{3.29}$$

If we are instead interested in a quantity $B$, say, where $B$ is some property of the system, then

$$\overline{B} = \frac{1}{Z}\sum_r \langle B \rangle_r e^{-\beta E_r} = \frac{1}{Z}\sum_r \int \phi_r^*(q)\,B(q)\,\phi_r(q)\,dq\; e^{-\beta E_r} \tag{3.30}$$

The bar denotes thermal average, and $\langle\ \rangle_r$ denotes quantum mechanical average with respect to state r.

If we know the quantity

$$\rho(q', q) = \sum_r \phi_r(q')\,\phi_r^*(q)\,e^{-\beta E_r} \tag{3.31}$$

we can evaluate $\overline{B}$, remembering that if $B = B(q')$, it acts on $\phi_r(q')$. $\rho$ is called the density matrix.

We note the following;

$$Z = \int \rho(q,q)\,dq \equiv Tr\,\rho \qquad ; \text{ (Tr = trace)} \tag{3.32}$$

$$P(q) = \frac{1}{Z} \rho(q, q) \tag{3.33}$$

$$\overline{B} = \frac{1}{Z} \mathrm{Tr}\,(B\rho) \tag{3.34}$$

Comparison of Eq. (3.31) with Eq. (3.4) yields, formally at least,

$$\begin{aligned}\rho(q', q) &= K(q', q; -i\beta\hbar) \\ &= \int_q^{q'} \mathcal{D}[u(\tau)] \exp\left\{-\frac{1}{\hbar}\int_0^{\beta\hbar}\left[\frac{m}{2}\dot{u}^2(\tau) + V(u)\right]d\tau\right\} \\ &= \int_q^{q'} \mathcal{D}[u(s)] \exp\left\{-\int_0^{\beta}\left\{\frac{m}{2\hbar^2}\dot{u}^2(s) + V[u(s)]\right\}\right\}\end{aligned} \tag{3.35}$$

The above integral is what is more commonly associated with the Wiener integral (Gel'fand and Yaglom (1960)). Yaglom (1956) demonstrates how one can derive Eq. (3.35) in a more rigorous fashion.

## 4. Two Interacting One Dimensional Oscillators

In this section, we use the method of expansion in a trigonometric series, as explained in section 3, to find the kernel of two interacting one dimensional oscillators.

Let the independent position coordinates of the oscillators be given by $x_1$ and $x_2$ . We use a subscript 1 to label the various quantities relevant to describe one oscillator, and a subscript 2 for the other oscillator.

Observe that two sets of coefficients will be needed for the trigonometric series, one for each independent coordinate. Thus, instead of integrating over one set of coefficients, we must now integrate over two sets.

The Lagrangian of the system can be written in the following form;

$$L = L_1 + L_2 - K_{12} x_1 x_2 \tag{4.1}$$

where $L_j = \frac{1}{2} m_j (\dot{x}_j^2 - \omega_j^2 x_j^2)$, $j = 1, 2$ . Let $K_{12} = \sqrt{m_1 m_2}\ \omega^2$.

Suppose the boundary conditions of the system are the following;

$$x_j(0) = a_j \ , \quad x_j(T) = b_j \quad ; \ j = 1, 2 \tag{4.2}$$

As given in Eq. (3.22), let

$$\dot{x}_j(t) = \left(\frac{2\pi\hbar}{m_j T}\right)^{\frac{1}{2}} \sum_{n=0}^{+\infty} c_{nj}\, \phi_n\left(\frac{t}{T}\right) \quad ; \ j = 1, 2 \tag{4.3}$$

where, now, the $c_{nj}$ are the expansion coefficients.

According to Eq. (3.24),

$$c_{0j}^2 = \frac{m_j}{2\pi\hbar T}\,(b_j - a_j)^2 \;;\; j=1,2 \tag{4.4}$$

and to Eq. (3.23),

$$x_j(t) = a_j + \left(\frac{2\pi\hbar}{m_j T}\right)^{\frac{1}{2}} \left\{ c_{0j}\,t + \frac{T\sqrt{2}}{\pi} \sum_{n=1}^{+\infty} \frac{c_{nj}}{n} \sin\left(n\pi\frac{t}{T}\right)\right\} ;\; j=1,2 \tag{4.5}$$

Substituting the above expressions into $L_1$ and $L_2$, and doing the appropriate integrations, we have, (Burton and de Borde (1955), Brush (1961)), for $j=1,2$,

$$\frac{i}{\hbar}\int_0^T L_j\,dt = \frac{i m_j T}{2\hbar}\left\{\frac{(b_j-a_j)^2}{T^2} - \frac{1}{3}\omega_j^2\left(b_j^2 + b_j a_j + a_j^2\right)\right.$$

$$\left. + i\sum_{n=1}^{+\infty}\left\{\pi\left(1-\frac{\omega_j^2T^2}{n^2\pi^2}\right)c_{nj}^2 - \left(\frac{\omega_j T}{n\pi}\right)^2\left(\frac{4\pi m_j}{\hbar T}\right)^{\frac{1}{2}}\left[a_j-(-1)^n b_j\right]c_{nj}\right\} \tag{4.6}$$

Finally, for $j=1,2$,

$$\begin{aligned}\frac{i}{\hbar}\int_0^T K_{12}x_1x_2\,dt = {} & \frac{i}{\hbar}K_{12}\frac{T}{6}\left(2b_1b_2 + b_1a_2 + b_2a_1 + 2a_1a_2\right)\\ & + i\left\{\left(\frac{4\pi m_2}{\hbar T}\right)^{\frac{1}{2}}\sum_{n=1}^{+\infty}\left[a_2-(-1)^n b_2\right]c_{n1}\left(\frac{\omega T}{n\pi}\right)^2\right.\\ & + \left(\frac{4\pi m_1}{\hbar T}\right)^{\frac{1}{2}}\sum_{n=1}^{+\infty}\left[a_1-(-1)^n b_1\right]c_{n2}\left(\frac{\omega T}{n\pi}\right)^2\\ & \left. + 2\pi\sum_{n=1}^{+\infty}c_{n1}c_{n2}\left(\frac{\omega T}{n\pi}\right)^2\right\}\end{aligned} \tag{4.7}$$

where, in obtaining Eq. (4.7), we have used

$$\left.\begin{aligned}\int_0^T t\sin\left(n\pi\frac{t}{T}\right)dt &= (-1)^{n+1}\frac{T^2}{n\pi} & \quad n=1,2,\ldots\\ \int_0^T \sin\left(n\pi\frac{t}{T}\right)\sin\left(k\pi\frac{t}{T}\right)dt &= \frac{T}{2}\,\delta_{n,k} & \quad n,k=1,2,\ldots\end{aligned}\right\}$$

$$\delta_{n,k} = \begin{cases}1, & \text{if } n=k\\ 0, & \text{otherwise}\end{cases}$$

Using Eqs. (4.6) and (4.7), the action is given by

$$
\begin{aligned}
\frac{i}{\hbar} S &= \frac{i}{\hbar} \int_0^T \left( L_1 + L_2 - K_{12} x_1 x_2 \right) dt \\
&= i \Big\{ \frac{m_1 T}{2} \Big[ \frac{(b_1 - a_1)^2}{T^2} - \frac{\omega_1^2}{3} \left( b_1^2 + a_1 b_1 + a_1^2 \right) \Big] \\
&\quad + \frac{m_2 T}{2} \Big[ \frac{(b_2^2 - a_2^2)}{T^2} - \frac{\omega_2^2}{3} \left( b_2^2 + a_2 b_2 + a_2^2 \right) \Big] \\
&\quad - \sqrt{m_1 m_2}\, \omega^2 \frac{T}{6} \left( 2 b_1 b_2 + a_1 b_2 + a_2 b_1 + 2 a_1 a_2 \right) \Big\} \\
&\quad + i \sum_{n=1}^{+\infty} \Big\{ \pi \Big( 1 - \frac{\omega_1^2 T^2}{n^2 \pi^2} \Big) c_{n1}^2 + \pi \Big( 1 - \frac{\omega_2^2 T^2}{n^2 \pi^2} \Big) c_{n2}^2 - 2\pi \Big( \frac{\omega T}{n\pi} \Big)^2 c_{n1} c_{n2} \\
&\qquad - \Big( \frac{\omega_1 T}{n\pi} \Big)^2 \Big( \frac{4\pi m_1}{\hbar T} \Big)^{\frac{1}{2}} \left[ a_1 - (-1)^n b_1 \right] c_{n1} \\
&\qquad - \Big( \frac{\omega_2 T}{n\pi} \Big)^2 \Big( \frac{4\pi m_2}{\hbar T} \Big)^{\frac{1}{2}} \left[ a_2 - (-1)^n b_2 \right] c_{n2} \\
&\qquad - \Big( \frac{\omega T}{n\pi} \Big)^2 \Big( \frac{4\pi m_1}{\hbar T} \Big)^{\frac{1}{2}} \left[ a_1 - (-1)^n b_1 \right] c_{n2} \\
&\qquad - \Big( \frac{\omega T}{n\pi} \Big)^2 \Big( \frac{4\pi m_2}{\hbar T} \Big)^{\frac{1}{2}} \left[ a_2 - (-1)^n b_2 \right] c_{n1} \Big\}
\end{aligned}
\tag{4.8}
$$

Substituting Eq. (4.8) into Eq. (3.25), the kernel is given by

$$
K(b_2, b_1, a_2, a_1; T) = \Big( \frac{m_1}{2\pi i \hbar T} \Big)^{\frac{1}{2}} \Big( \frac{m_2}{2\pi i \hbar T} \Big)^{\frac{1}{2}} \Big\{ \prod_{n=1}^{+\infty} \int_{-\infty}^{+\infty} \frac{dc_{n1}}{\sqrt{i}} \int_{-\infty}^{+\infty} \frac{dc_{n2}}{\sqrt{i}} \Big\} e^{\frac{i}{\hbar} S}
\tag{4.9}
$$

Since the coefficients $c_{n1}$ and $c_{n2}$ do not mix in each term of the expression in Eq. (4.8), we can separate Eq. (4.9) into a product of double integrals.

We introduce the following notation. Let

$$
\alpha_{nj} = \Big( \frac{\omega_j T}{n\pi} \Big)^2 , \quad \gamma_{nj} = \pi \left( 1 - \alpha_{nj} \right) , \quad \delta_j = \Big( \frac{4\pi m_j}{\hbar T} \Big)^{\frac{1}{2}}
$$

$$\varepsilon_{nj} = a_j - (-1)^n b_j \quad , \quad \alpha_n = \left(\frac{\omega T}{n\pi}\right)^2 \quad , \quad \gamma_n = 2\pi\alpha_n$$

Collecting all terms containing $c_{n1}$ in Eq. (4.8) yields

$$J_n = i\gamma_{n1}\left[c_{n1}^2 - \frac{\{\gamma_n c_{n2} + \alpha_{n1}\delta_1\varepsilon_{n1} + \alpha_n\delta_2\varepsilon_{n2}\}}{\gamma_{n1}} c_{n1}\right] \qquad (4.10)$$

Integrating over $c_{n1}$ , we find

$$\int_{-\infty}^{+\infty} \frac{dc_{n1}}{\sqrt{i}} e^{J_n} = \left(\frac{\pi}{\gamma_{n1}}\right)^{\frac{1}{2}} \exp\left[-i\frac{(\gamma_n c_{n2} + \alpha_{n1}\delta_1\varepsilon_{n1} + \alpha_n\delta_2\varepsilon_{n2})^2}{4\gamma_{n1}}\right] \qquad (4.11)$$

Collecting all terms in the exponent of the exponential containing $c_{n2}$ in Eq. (4.11), and Eq. (4.8) gives

$$I_n = i\left[-\frac{(\gamma_n c_{n2} + \alpha_{n1}\delta_1\varepsilon_{n1} + \alpha_n\delta_2\varepsilon_{n2})^2}{4\gamma_{n1}} + \gamma_{n2}c_{n2}^2 - (\alpha_{n2}\delta_2\varepsilon_{n2} + \alpha_n\delta_1\varepsilon_{n1})c_{n2}\right]$$

Integration over $c_{n2}$ yields

$$\int_{-\infty}^{+\infty} \frac{dc_{n2}}{\sqrt{i}} e^{I_n} = \sqrt{\pi}\left(\gamma_{n2} - \frac{\gamma_n^2}{4\gamma_{n1}}\right)^{-\frac{1}{2}} \exp\left\{\frac{-i(\alpha_{n1}\delta_1\varepsilon_{n1} + \alpha_n\delta_2\varepsilon_{n2})^2}{4\gamma_{n1}} + \right.$$

$$\left. + (-i)\frac{\left\{\alpha_{n2}\delta_2\varepsilon_{n2} + \alpha_n\delta_1\varepsilon_{n1} + \frac{\gamma_n}{2\gamma_{n1}}(\alpha_{n1}\delta_1\varepsilon_{n1} + \alpha_n\delta_2\varepsilon_{n2})\right\}^2}{4\left(\gamma_{n2} - \frac{1}{4\gamma_{n1}}\gamma_n^2\right)}\right\} \qquad (4.12)$$

Employing Eqs. (4.11), (4.12), and making use of the following identities;

(i) $\pi\left(\gamma_{n1}\gamma_{n2} - \frac{\gamma_n^2}{4}\right)^{-\frac{1}{2}} = \left(1 - \frac{\omega_+^2 T^2}{n^2\pi^2}\right)^{-\frac{1}{2}}\left(1 - \frac{\omega_-^2 T^2}{n^2\pi^2}\right)^{-\frac{1}{2}}$

where $\omega_\pm^2 = \frac{1}{2}\left\{(\omega_1^2 + \omega_2^2) \pm \sqrt{(\omega_1^2 - \omega_2^2)^2 + 4\omega^4}\right\}$ (4.13)

(ii) $\prod_{n=1}^{+\infty}\left(1 - \frac{z^2}{n^2}\right) = \frac{\sin(\pi z)}{\pi z}$

the kernel (Eq. (4.9)) can be expressed as

$$K(b_2, b_1, a_2, a_1; T) = \sqrt{m_1 m_2}\left(\frac{\omega_+}{2\pi i\hbar \sin(\omega_+ T)}\right)^{\frac{1}{2}}\left(\frac{\omega_-}{2\pi i\hbar \sin(\omega_- T)}\right)^{\frac{1}{2}}$$
$$\times \exp\left\{\frac{i}{\hbar}\left[\frac{m_1 T}{2}\left\{\frac{(b_1-a_1)^2}{T^2} - \frac{1}{3}\omega_1^2(b_1^2+a_1b_1+a_1^2)\right\}\right.\right.$$
$$+\frac{m_2 T}{2}\left\{\frac{(b_2-a_2)^2}{T^2} - \frac{1}{3}\omega_2^2(b_2^2+a_2b_2+a_2^2)\right\}$$
$$\left.\left.-\sqrt{m_1 m_2}\,\omega^2\frac{T}{6}(2b_1b_2+a_1b_2+a_2b_1+2a_1a_2)\right]+Q\right\} \tag{4.14}$$

where $Q = \frac{-i}{4}\sum_{n=1}^{+\infty} Q_n$

$$Q_n = \frac{(\alpha_{n1}\delta_1\varepsilon_{n1}+\alpha_n\delta_2\varepsilon_{n2})^2}{\gamma_{n1}} + \frac{\left\{\alpha_{n2}\delta_2\varepsilon_{n2}+\alpha_n\delta_1\varepsilon_{n1}+\frac{\gamma_n}{2\gamma_{n1}}(\alpha_{n1}\delta_1\varepsilon_{n1}+\alpha_n\delta_2\varepsilon_{n2})\right\}^2}{\left(\gamma_{n2}-\frac{1}{4\gamma_{n1}}\gamma_n^2\right)}$$

The above expression for $Q_n$ can be simplified to

$$Q_n = \frac{T^4}{2\pi^5}\left\{\left[A_n^2(\omega_1^4+\omega^4)+2A_nB_n\omega^2(\omega_1^2+\omega_2^2)+B_n^2(\omega^4+\omega_2^4)\right]D_n\right.$$
$$+\frac{C_n}{E}\left[A_n^2(\omega_1^6-\omega_2^2\omega_1^4+\omega_2^2\omega^4+3\omega_1^2\omega^4)\right.$$
$$+2A_nB_n\omega^2(\omega_1^4+2\omega^4+\omega_2^4)$$
$$\left.\left.+B_n^2(\omega^4\omega_1^2-\omega_1^2\omega_2^4+\omega_2^6+3\omega_2^2\omega^4)\right]\right\}$$

where

$$A_n^2 = \frac{4\pi m_1}{\hbar T}\left[a_1^2+b_1^2-2a_1b_1(-1)^n\right]$$

$$B_n^2 = \frac{4\pi m_2}{\hbar T}\left[a_2^2+b_2^2-2a_2b_2(-1)^n\right]$$

$$A_nB_n = \frac{4\pi\sqrt{m_1 m_2}}{\hbar T}\left[a_1a_2+b_1b_2-(-1)^n(a_1b_2+a_2b_1)\right]$$

$$C_n = \frac{1}{n^2\left(n^2 - \frac{\omega_+^2 T^2}{n^2\pi^2}\right)} - \frac{1}{n^2\left(n^2 - \frac{\omega_-^2 T^2}{n^2\pi^2}\right)}$$

$$D_n = \frac{1}{n^2\left(n^2 - \frac{\omega_+^2 T^2}{n^2\pi^2}\right)} + \frac{1}{n^2\left(n^2 - \frac{\omega_-^2 T^2}{n^2\pi^2}\right)}$$

$$E = \left[(\omega_1^2 - \omega_2^2)^2 + 4\omega^4\right]^{\frac{1}{2}}$$

Using the following identities,

$$\left.\begin{aligned} &\text{(iii)} \quad \sum_{n=1}^{+\infty} \frac{1}{n^2(n^2-z^2)} = \frac{1}{z^2}\left\{\frac{1}{2z^2} - \frac{\pi}{2z}\cot(\pi z) - \frac{\pi^2}{6}\right\} \\ &\text{(iv)} \quad \sum_{n=1}^{+\infty} \frac{(-1)^n}{n^2(n^2-z^2)} = \frac{1}{z^2}\left\{\frac{1}{2z^2} - \frac{\pi}{2z}\csc(\pi z) + \frac{\pi^2}{12}\right\} \end{aligned}\right\} \begin{array}{l} z^2 \text{ is not} \\ \text{a positive} \\ \text{integer} \end{array}$$

and the expression for $Q_n$, we find the following complicated form for $Q$,

$$Q = -\frac{i}{4}\sum_{n=1}^{+\infty} Q_n$$

$$= \frac{-iT^3}{2\hbar\pi^4}\Big\langle \Big[ m_1(a_1^2+b_1^2)\,\frac{(\omega_1^6 - \omega_2^2\omega_1^4 + \omega_2^2\omega^4 + 3\omega_1^2\omega^4)}{[(\omega_1^2-\omega_2^2)^2+4\omega^4]^{\frac{1}{2}}}$$

$$+ m_2(a_2^2+b_2^2)\,\frac{(\omega_2^6 - \omega_1^2\omega_2^4 + \omega_1^2\omega^4 + 3\omega_2^2\omega^4)}{[(\omega_1^2-\omega_2^2)^2+4\omega^4]^{\frac{1}{2}}}$$

$$+ 2\sqrt{m_1 m_2}\,(a_1a_2+b_1b_2)\,\frac{\omega^2(\omega_1^4+\omega_2^4+2\omega^4)}{[(\omega_1^2-\omega_2^2)^2+4\omega^4]^{\frac{1}{2}}}\Big] \times$$

$$\times\Big[\frac{\pi^2}{\omega_+^2T^2}\left\{\frac{\pi^2}{2\omega_+^2T^2} - \frac{\pi^2}{2\omega_+T}\cot(\omega_+T) - \frac{\pi^2}{6}\right\}$$

$$- \frac{\pi^2}{\omega_-^2 T^2} \left\{ \frac{\pi^2}{2\omega_-^2 T^2} - \frac{\pi^2}{2\omega_- T} \cot(\omega_- T) - \frac{\pi^2}{6} \right\} \Big]$$

$$- \frac{2}{[(\omega_1^2 - \omega_2^2)^2 + 4\omega^4]^{\frac{1}{2}}} \Big[ m_1 a_1 b_1 (\omega_1^6 - \omega_2^2 \omega_1^4 + \omega_2^2 \omega^4 + 3\omega_1^2 \omega^4)$$

$$+ m_2 a_2 b_2 (\omega_2^6 - \omega_1^2 \omega_2^4 + \omega_1^2 \omega^4 + 3\omega_2^2 \omega^4)$$

$$+ \sqrt{m_1 m_2}\, (a_1 b_2 + a_2 b_1) \omega^2 (\omega_1^4 + \omega_2^4 + 2\omega^4) \Big] \times$$

$$\times \Big[ \frac{\pi^2}{\omega_+^2 T^2} \left\{ \frac{\pi^2}{2\omega_+^2 T^2} - \frac{\pi^2}{2\omega_+ T} \csc(\omega_+ T) + \frac{\pi^2}{12} \right\}$$

$$- \frac{\pi^2}{\omega_-^2 T^2} \left\{ \frac{\pi^2}{2\omega_-^2 T^2} - \frac{\pi^2}{2\omega_- T} \csc(\omega_- T) + \frac{\pi^2}{12} \right\} \Big]$$

$$+ \Big[ m_1 (a_1^2 + b_1^2)(\omega_1^4 + \omega^4) + 2\sqrt{m_1 m_2}\, (a_1 a_2 + b_1 b_2) \omega^2 (\omega_1^2 + \omega_2^2)$$

$$+ m_2 (a_2^2 + b_2^2)(\omega^4 + \omega_2^4) \Big] \times$$

$$\times \Big[ \frac{\pi^2}{\omega_+^2 T^2} \left\{ \frac{\pi^2}{2\omega_+^2 T^2} - \frac{\pi^2}{2\omega_+ T} \cot(\omega_+ T) - \frac{\pi^2}{6} \right\}$$

$$+ \frac{\pi^2}{\omega_-^2 T^2} \left\{ \frac{\pi^2}{2\omega_-^2 T^2} - \frac{\pi^2}{2\omega_- T} \cot(\omega_- T) - \frac{\pi^2}{6} \right\} \Big]$$

$$- 2 \Big[ m_1 a_1 b_1 (\omega^4 + \omega_1^4) + m_2 a_2 b_2 (\omega^4 + \omega_2^4)$$

$$+ \sqrt{m_1 m_2}\, (\omega_1^2 + \omega_2^2) \omega^2 (a_1 b_2 + a_2 b_1) \Big] \times$$

$$\times \Big[ \frac{\pi^2}{\omega_+^2 T^2} \left\{ \frac{\pi^2}{2\omega_+^2 T^2} - \frac{\pi^2}{2\omega_+ T} \csc(\omega_+ T) + \frac{\pi^2}{12} \right\}$$

$$+ \frac{\pi^2}{\omega_-^2 T^2} \left\{ \frac{\pi^2}{2\omega_-^2 T^2} - \frac{\pi^2}{2\omega_- T} \csc(\omega_- T) + \frac{\pi^2}{12} \right\} \Big]$$

Finally, substituting the above expression for $Q$ into Eq. (4.14), and considerable manipulation, we find the kernel to be

$$K(b_2, b_1, a_2, a_1; T) = \sqrt{m_1 m_2}$$

$$\times \left(\frac{\omega_+}{2\pi i \hbar \sin(\omega_+ T)}\right)^{\frac{1}{2}} \exp\left\{\frac{i\omega_+}{2\hbar \sin(\omega_+ T)}\left[(u_0^2+u_1^2)\cos(\omega_+ T) - 2u_0 u_1\right]\right\}$$

$$\times \left(\frac{\omega_-}{2\pi i \hbar \sin(\omega_- T)}\right)^{\frac{1}{2}} \exp\left\{\frac{i\omega_-}{2\hbar \sin(\omega_- T)}\left[(y_0^2+y_1^2)\cos(\omega_- T) - 2y_0 y_1\right]\right\} \quad (4.15)$$

where

$$u_0 = a_1\sqrt{m_1}\left(\frac{\omega_1^2-\omega_-^2}{\omega_+^2-\omega_-^2}\right)^{\frac{1}{2}} + a_2\sqrt{m_2}\left(\frac{\omega_2^2-\omega_-^2}{\omega_+^2-\omega_-^2}\right)^{\frac{1}{2}}$$

$$u_1 = b_1\sqrt{m_1}\left(\frac{\omega_1^2-\omega_-^2}{\omega_+^2-\omega_-^2}\right)^{\frac{1}{2}} + b_2\sqrt{m_2}\left(\frac{\omega_2^2-\omega_-^2}{\omega_+^2-\omega_-^2}\right)^{\frac{1}{2}}$$

$$y_0 = a_1\sqrt{m_1}\left(\frac{\omega_+^2-\omega_1^2}{\omega_+^2-\omega_-^2}\right)^{\frac{1}{2}} - a_2\sqrt{m_2}\left(\frac{\omega_+^2-\omega_2^2}{\omega_+^2-\omega_-^2}\right)^{\frac{1}{2}}$$

$$y_1 = b_1\sqrt{m_1}\left(\frac{\omega_+^2-\omega_1^2}{\omega_+^2-\omega_-^2}\right)^{\frac{1}{2}} - b_2\sqrt{m_2}\left(\frac{\omega_+^2-\omega_2^2}{\omega_+^2-\omega_-^2}\right)^{\frac{1}{2}}$$

In fact, the expression in Eq. (4.15) is the product of kernels of the two harmonic oscillators with frequencies $\omega_+$ and $\omega_-$, respectively. These frequencies have been modified from the frequencies $\omega_1$ and $\omega_2$ because of the interaction.

The author has tried to extend this path integral method to the case of a linear chain of N interacting oscillators, but the expressions soon became excessively complicated, hence the work was discontinued.

If we let $K_{12} = 0$ , Eq. (4.1) reduces to the case of two non-interacting oscillators. If $\omega_1^2 \geq \omega_2^2$, then from Eq. (4.13), we have $\omega_+ = \omega_1$ , and $\omega_- = \omega_2$. In this case then, Eq. (4.15) reduces to

$$K(b_2, b_1, a_2, a_1; T)$$

$$= \left(\frac{m_1 \omega_1}{2\pi i\hbar \sin(\omega_1 T)}\right)^{\frac{1}{2}} \exp\left\{\frac{i m_1 \omega_1}{2\hbar \sin(\omega_1 T)}\left[(a_1^2 + b_1^2)\cos(\omega_1 T) - 2a_1 b_1\right]\right\}$$

$$\times \left(\frac{m_2 \omega_2}{2\pi i\hbar \sin(\omega_2 T)}\right)^{\frac{1}{2}} \exp\left\{\frac{i m_2 \omega_2}{2\hbar \sin(\omega_2 T)}\left[(a_2^2 + b_2^2)\cos(\omega_2 T) - 2a_2 b_2\right]\right\}$$

which is nothing but the product of the kernels of the individual oscillators of frequencies $\omega_1$ and $\omega_2$ , respectively.

For dispersion forces in condensed matter, as is given in Kittel (1976), pg. 78, we set

$$K_{12} = \frac{-2e^2}{R^3}$$

where e is the charge of each oscillator, and R is the interparticle separation. The zero point energy is then

$$U_0 = \frac{1}{2}\hbar(\omega_+ + \omega_-)$$

where $\omega_+$ and $\omega_-$ are given in Eq. (4.13). Expanding $\omega_+$ and $\omega_-$ for small interaction, we get the interaction energy, which varies inversely as the sixth power of R.

## 5. Lagrangian for an Anharmonic Crystal

In this section, we set up the Lagrangian for an anharmonic crystal, that is, a system of three dimensional interacting anharmonic oscillators. The basic procedure followed is that given by Born and Huang (1954). We assume that we are dealing with a perfect crystal that has N cells. We further assume that periodic boundary conditions hold, and that the usual adiabatic or Born-Oppenheimer approximation is valid.

The Hamiltonian for the crystal is given by

$$H = T + \Phi \tag{5.1}$$

where $T \equiv$ kinetic energy

$$= \sum_{\ell K \alpha} \frac{P_\alpha^2\binom{\ell}{K}}{2M_K}$$

Here $\ell \equiv$ cell index,

$K \equiv$ index for different atoms in each cell,

$\alpha \equiv$ x,y,z components,

$M_K \equiv$ mass of $K^{th}$ atom, and

$P_\alpha\binom{\ell}{K} \equiv \alpha^{th}$ component of the momentum of the $K^{th}$ atom in cell $\ell$.

$\Phi \equiv$ potential energy

$$\equiv \Phi\left(\ldots, \vec{x}\binom{\ell}{K} + \vec{u}\binom{\ell}{K}, \ldots, \vec{x}\binom{\ell'}{K'} + \vec{u}\binom{\ell'}{K'}, \ldots, \vec{x}\binom{\ell''}{K''} + \vec{u}\binom{\ell''}{K''}, \ldots\right)$$

where $\vec{x}\binom{\ell}{K} \equiv$ the equilibrium position of atom $K$ in cell $\ell$.

$$= \vec{x}(\ell) + \vec{x}(\vec{K})$$

Here, $\vec{x}(\ell)=\ell_1\vec{a}_1+\ell_2\vec{a}_2+\ell_3\vec{a}_3$, $\vec{x}(K)=K_1\vec{a}_1+K_2\vec{a}_2+K_3\vec{a}_3$, and $\{\vec{a}_1,\vec{a}_2,\vec{a}_3\}$ is the set of fundamental lattice translation vectors. $\{\ell_1,\ell_2,\ell_3\}$ is a set of integers, and $\{K_1,K_2,K_3\}$ is a set of non-integer numbers such that $0\le K_1,K_2,K_3\le 1$

$\vec{u}\binom{\ell}{K}\equiv$ the displacement of atom $K$ in cell $\ell$ from its equilibrium position.

Assuming that the $\vec{u}\binom{\ell}{K}$ are small, we can expand $\Phi$ in a Taylor series about its equilibrium position, whence

$$\Phi=\Phi_0+\sum_{\ell K\alpha}\phi_\alpha\binom{\ell}{K}u_\alpha\binom{\ell}{K}+\frac{1}{2!}\sum_{\substack{\ell K\alpha\\ \ell' K'\alpha'}}\phi_{\alpha\alpha'}\begin{pmatrix}\ell & \ell'\\ K & K'\end{pmatrix}u_\alpha\binom{\ell}{K}u_{\alpha'}\binom{\ell'}{K'}$$

$$+\frac{1}{3!}\sum_{\substack{\ell K\alpha,\,\ell'' K''\alpha''\\ \ell' K'\alpha'}}\phi_{\alpha\alpha'\alpha''}\begin{pmatrix}\ell & \ell' & \ell''\\ K & K' & K''\end{pmatrix}u_\alpha\binom{\ell}{K}u_{\alpha'}\binom{\ell'}{K'}u_{\alpha''}\binom{\ell''}{K''}+\cdots$$

where $\Phi_0=\Phi\Big|_{\vec{u}=0}=$ constant, and hence can be neglected in the following work,

$$\phi_\alpha\binom{\ell}{K}=\frac{\partial\Phi(\ldots,\vec{x}\binom{\ell}{K}+\vec{u}\binom{\ell}{K},\ldots)}{\partial u_\alpha\binom{\ell}{K}}\Bigg|_{\vec{u}=\vec{0}}=0,$$

since there is no net force on any atom, $\ell$ or $K$, in the like,

$$\phi_{\alpha\alpha'}\begin{pmatrix}\ell & \ell'\\ K & K'\end{pmatrix}=\frac{\partial^2\Phi(\ldots,\vec{x}\binom{\ell}{K}+\vec{u}\binom{\ell}{K},\ldots,\vec{x}\binom{\ell'}{K'}+\vec{u}\binom{\ell'}{K'},\ldots)}{\partial u_\alpha\binom{\ell}{K}\,\partial u_{\alpha'}\binom{\ell'}{K'}}\Bigg|_{\vec{u}=\vec{0}},\text{etc.}$$

Substitution of the above expressions for $T$ and $\Phi$ into Eq. (5.1) yields

$$H=H_0+H_A \tag{5.2}$$

where

$$H_0 = \sum_{\ell \kappa \alpha} \frac{P_\alpha^2\binom{\ell}{\kappa}}{2M_\kappa} + \frac{1}{2} \sum_{\substack{\ell \kappa \alpha \\ \ell' \kappa' \alpha'}} \phi_{\alpha\alpha'}\binom{\ell\,\ell'}{\kappa\,\kappa'} u_\alpha\binom{\ell}{\kappa} u_{\alpha'}\binom{\ell'}{\kappa'} \text{, and}$$

$$H_A = \sum_{n=3} \frac{1}{n!} \sum_{\ell_1 \kappa_1 \alpha_1} \cdots \sum_{\ell_n \kappa_n \alpha_n} \phi_{\alpha_1 \cdots \alpha_n}\begin{pmatrix} \ell_1 \cdots \ell_n \\ \kappa_1 \cdots \kappa_n \end{pmatrix} u_{\alpha_1}\binom{\ell_1}{\kappa_1} \cdots u_{\alpha_n}\binom{\ell_n}{\kappa_n}$$

By translation symmetry of the crystal,

$$\phi_{\alpha_1 \cdots \alpha_n}\begin{pmatrix} \ell_1 \cdots \ell_n \\ \kappa_1 \cdots \kappa_n \end{pmatrix} = \phi_{\alpha_1 \cdots \alpha_n}\begin{pmatrix} 0 & \ell_2 - \ell_1 & \cdots & \ell_n - \ell_1 \\ \kappa_1 & \kappa_2 & \cdots & \kappa_n \end{pmatrix} \quad ; n \geq 2$$

We define the dynamical matrix as follows;

$$D_{\alpha\gamma}\begin{pmatrix} \vec{q} \\ \kappa\;\kappa' \end{pmatrix} = \sum_{\ell} \frac{\phi_{\alpha\gamma}\begin{pmatrix} 0 & \ell \\ \kappa & \kappa' \end{pmatrix}}{\sqrt{M_\kappa M_{\kappa'}}} e^{-i\vec{q}\cdot\vec{x}(\ell)} \qquad (5.3)$$

where $\vec{q}$ ≡ a vector in reciprocal space.

It turns out that we need to find the eigenvectors and eigenvalues of the dynamical matrix, that is, we must solve the following set of equations;

$$\omega^2\binom{\vec{q}}{j} \varepsilon_\alpha\left(\kappa \, {\vec{q} \atop j}\right) = \sum_{\kappa'\alpha'} D_{\alpha\alpha'}\begin{pmatrix} \vec{q} \\ \kappa\;\kappa' \end{pmatrix} \varepsilon_{\alpha'}\left(\kappa' \, {\vec{q} \atop j}\right) \qquad (5.4)$$

Here $j$ ≡ the branch index,

$\omega^2\binom{\vec{q}}{j}$ ≡ the square of the eigenfrequency of vector $\vec{q}$ and branch index $j$ , and

$\varepsilon_\alpha\left(\kappa \, {\vec{q} \atop j}\right)$ ≡ the $\alpha^{th}$ component of the corresponding eigenvector.

Note that $\omega^2\binom{\vec{q}}{j} = \omega^2\binom{-\vec{q}}{j}$, $\omega\binom{\vec{q}}{j} \geq 0$ , and we use the convention $\varepsilon^*_\alpha\left(\kappa\ {\vec{q} \atop j}\right) = \varepsilon_\alpha\left(\kappa\ {-\vec{q} \atop j}\right)$

We now introduce the normal coordinate transformations. These are given by

$$\left.\begin{aligned} P_\alpha\left({\ell \atop K}\right) &= \frac{1}{\sqrt{N}} \sum_{\vec{q}J} \sqrt{M_K}\ \varepsilon_\alpha\left(K\ {\vec{q} \atop J}\right) e^{i\vec{q}\cdot\vec{x}(\ell)}\ P\left({\vec{q} \atop J}\right) \\ Q_\alpha\left({\ell \atop K}\right) &= \frac{1}{\sqrt{N}} \sum_{\vec{q}J} \frac{1}{\sqrt{M_K}}\ \varepsilon_\alpha\left(K\ {\vec{q} \atop J}\right) e^{i\vec{q}\cdot\vec{x}(\ell)}\ Q\left({\vec{q} \atop J}\right) \end{aligned}\right\} \tag{5.5}$$

Note that $P^*\left({\vec{q} \atop J}\right) = P\left({-\vec{q} \atop J}\right)$, and $Q^*\left({\vec{q} \atop J}\right) = Q\left({-\vec{q} \atop J}\right)$.

Then, substituting Eq. (5.5) into Eq. (5.2), and performing the usual operations, (Born and Huang (1954)), we get the following;

$$H_0 = \frac{1}{2} \sum_{\vec{q}J} \left\{ P\left({\vec{q} \atop J}\right) P\left({-\vec{q} \atop J}\right) + \omega^2\left({\vec{q} \atop J}\right) Q\left({\vec{q} \atop J}\right) Q\left({-\vec{q} \atop J}\right) \right\} \tag{5.6}$$

$$H_A = \sum_{n=3}^{+\infty} \sum_{\vec{q}_1 J_1} \cdots \sum_{\vec{q}_n J_n} V^n(\vec{q}_1 J_1, \ldots, \vec{q}_n J_n)\, Q\left({\vec{q}_1 \atop J_1}\right) \cdots Q\left({\vec{q}_n \atop J_n}\right) \tag{5.7}$$

where

$$V^n(\vec{q}_1 J_1, \ldots, \vec{q}_n J_n) = \frac{N}{N^{\frac{n}{2}}} \frac{1}{n!} \sum_{\ell_2 \cdots \ell_n} \sum_{K_1 \cdots K_n} \sum_{\alpha_1 \cdots \alpha_n} \frac{\Phi_{\alpha_1 \cdots \alpha_n}\left({0 \atop K_1}\ {\ell_2 \cdots \ell_n \atop K_2 \cdots K_n}\right)}{\sqrt{M_{K_1} \cdots M_{K_n}}}$$
$$\times \Delta(\vec{q}_1 + \cdots + \vec{q}_n)\, e^{i\vec{q}_2\cdot\vec{x}(\ell_2) + \cdots + i\vec{q}_n\cdot\vec{x}(\ell_n)}\ \varepsilon_{\alpha_1}\left(K_1\ {\vec{q}_1 \atop J_1}\right) \cdots \varepsilon_{\alpha_n}\left(K_n\ {\vec{q}_n \atop J_n}\right)$$

and

$$\Delta(\vec{q}) = \begin{cases} 1, & \text{if } \vec{q} = \vec{0} \text{ or is a vector of reciprocal lattice,} \\ 0, & \text{otherwise.} \end{cases}$$

To apply the path integral formulation to the problems to be considered, we will need the Lagrangian of the system.

Hamilton's equations yield $\dot{Q}(\vec{q}_J) = \dfrac{\partial H}{\partial P(\vec{q}_J)} = P(-\vec{q}_J)$ .

Here, we note that for every vector $\vec{q}$ in the sum over $\vec{q}$ , there is a corresponding vector $-\vec{q}$ .

The canonical relation between the Lagrangian and Hamiltonian yields

$$\begin{aligned} L &= \sum_{\vec{q}J} \dot{Q}(\vec{q}_J)\, P(\vec{q}_J) - H \\ &= L_0 - L_A \end{aligned} \tag{5.8}$$

where $L_0 = \frac{1}{2} \sum_{\vec{q}J} \left\{ \dot{Q}(\vec{q}_J)\dot{Q}(-\vec{q}_J) - \omega^2(\vec{q}_J) Q(\vec{q}_J) Q(-\vec{q}_J) \right\}$ ,

$$L_A = H_A$$

We introduce the symbol $\lambda_r \equiv \vec{q}_r J_r$ , noting that $-\lambda_r = -\vec{q}_r J_r$

Then, we write $Q(\vec{q}_{r}J_r) \equiv Q(\lambda_r) \equiv Q_{\lambda_r}$, $Q(-\vec{q}_r J_r) = Q_{-\lambda_r}$, and $\omega^2(\vec{q}_r J_r) \equiv \omega^2(\lambda_r) = \omega^2_{\lambda_r}$

An important property to note is that $V^n(\lambda_1, \ldots, \lambda_n)$ is completely symmetric in its arguments $\lambda_1, \ldots, \lambda_n$ .
Thus, $L_A$ is invariant under permutations of $\{\lambda_r\}$.

## 6. The Method of Papadopolous

We now introduce the method of Papadopolous (1969), which is used for evaluating the partition function Z, and hence the Helmholtz free energy F, of an anharmonic crystal. We have to change the derivation slightly from that of Papadopolous, but the basic ideas used are the same.

The Lagrangian of an anharmonic crystal is given by, Eq. (5.8),

$$\left.\begin{aligned} L &= \frac{1}{2}\sum_{\lambda_r}\left[\dot{Q}_{\lambda_r}\dot{Q}_{-\lambda_r}-\omega_{\lambda_r}^2 Q_{\lambda_r}Q_{-\lambda_r}\right]-L_A \\ L_A &= \sum_{n=3}^{+\infty}\sum_{\lambda_1\cdots\lambda_n} V^n(\lambda_1,\ldots,\lambda_n)\,Q_{\lambda_1}\cdots Q_{\lambda_n} \end{aligned}\right\} \tag{6.1}$$

For this Lagrangian, the density matrix of the system is given by, Eq. (3.35),

$$\rho(\underset{\sim}{\xi}_2,\underset{\sim}{\xi}_1)=\int_{\underset{\sim}{Q}(0)=\underset{\sim}{\xi}_1}^{\underset{\sim}{Q}(\beta)=\underset{\sim}{\xi}_2}\mathcal{D}[\underset{\sim}{Q}(s)]\exp\left\{-\frac{1}{2}\sum_{\lambda_r}\int_0^{\beta}ds\left[\frac{\dot{Q}_{\lambda_r}\dot{Q}_{-\lambda_r}}{\hbar^2}+\omega_{\lambda_r}^2 Q_{\lambda_r}Q_{-\lambda_r}\right]\right\}\exp\left\{-\int_0^{\beta}L_A\,ds\right\} \tag{6.2}$$

where $\mathcal{D}[\underset{\sim}{Q}(s)]=\prod_{\lambda_r}\mathcal{D}[Q_{\lambda_r}(s)]$ and $\underset{\sim}{\xi}_1$, and $\underset{\sim}{\xi}_2$ are the boundary coordinates. $\underset{\sim}{\xi}_\ell$ and hence, $\underset{\sim}{Q}$ is a vector with the same number of components as there are different values of $\lambda_r$.

From Eq. (3.32),

$$Z=\int d\underset{\sim}{\xi}_1\,\rho(\underset{\sim}{\xi}_1,\underset{\sim}{\xi}_1) \tag{6.3}$$

where $d\underset{\sim}{\xi}_1=\prod_{\lambda_r}d\xi_{1\lambda_r}$ and the integral extends over all possible values of $\underset{\sim}{\xi}_1$.

As it stands, the path integral in Eq. (6.2) is not known to have a neat closed form solution. Hence, to get some meaningful results, an expansion (perturbation) procedure is used on the term $\exp\left\{-\int_0^\beta L_A ds\right\}$

Formally expanding $\exp\left\{-\int_0^\beta L_A ds\right\}$, we obtain the following;

$$
\begin{aligned}
\exp\left\{-\int_0^\beta L_A ds\right\} &= \sum_{n=0}^{+\infty} \frac{(-1)^n}{n!}\left[\int_0^\beta L_A ds\right]^n \\
&= 1 - \Big\{\sum_{\lambda_1\lambda_2\lambda_3} V^3(\lambda_1,\lambda_2,\lambda_3)\int_0^\beta ds\, Q_{\lambda_1}(s)Q_{\lambda_2}(s)Q_{\lambda_3}(s) \\
&\quad + \sum_{\lambda_1\lambda_2\lambda_3\lambda_4} V^4(\lambda_1,\lambda_2,\lambda_3,\lambda_4)\int_0^\beta ds\, Q_{\lambda_1}(s)Q_{\lambda_2}(s)Q_{\lambda_3}(s)Q_{\lambda_4}(s) + \ldots\Big\} \\
&\quad + \frac{1}{2!}\Big\{\sum_{\lambda_1\lambda_2\lambda_3}\sum_{\lambda_4\lambda_5\lambda_6} V^3(\lambda_1,\lambda_2,\lambda_3)\,V^3(\lambda_4,\lambda_5,\lambda_6) \\
&\quad\quad \times \int_0^\beta ds_1 \int_0^\beta ds_2\, Q_{\lambda_1}(s_1)Q_{\lambda_2}(s_1)Q_{\lambda_3}(s_1)Q_{\lambda_4}(s_2)Q_{\lambda_5}(s_2)Q_{\lambda_6}(s_2) + \ldots\Big\} \\
&\quad - \ldots
\end{aligned}
\tag{6.4}
$$

Substituting Eq. (6.4) into Eq. (6.2), and then substituting this into Eq. (6.3) yields a linear combination of terms, a typical term of which that has to be evaluated, neglecting its coefficient, is of the form

$$
I^{(n)}_{\lambda_1^1\cdots\lambda_m^1;\lambda_1^2\cdots\lambda_p^n} = \int d\underset{\sim}{\xi_1}\int_{\underset{\sim}{\xi_1}}^{\underset{\sim}{\xi_1}} \mathcal{D}_0^\beta[\underset{\sim}{Q}(s)]\left\{\int_0^\beta ds_1\cdots\int_0^\beta ds_n\, Q_{\lambda_1^1}(s_1)\cdots Q_{\lambda_p^n}(s_n)\right\} \tag{6.5}
$$

where
$$
\mathcal{D}_0^\beta[\underset{\sim}{Q}(s)] = \mathcal{D}[\underset{\sim}{Q}(s)]\exp\left\{-\frac{1}{2}\sum_{\lambda_r}\int_0^\beta ds\left[\dot{Q}_{\lambda_r}\dot{Q}_{-\lambda_r}+\omega_{\lambda_r}^2 Q_{\lambda_r}Q_{-\lambda_r}\right]\right\} \tag{6.6}
$$

$\mathcal{D}_0^\beta[\underset{\sim}{Q}(s)]$ represents the measure used for the "averaging" process. Here, we note that it is of the same form as the Uhlenbeck-Ornstein measure, (Maheshwari (1975)). Further, we expect that the convergence behaviour of the above expansion will be the same as that of ordinary perturbation theory since we are developing the perturbation expansion via this method.

From the Caussian character of the measure, it follows that any symbol $I^{(n)}_{\lambda_1' \cdots \lambda_p^n}$ with an odd number of indices will contribute nothing to the expansion. That this is so will be sketched out in appendix 1. The way to evaluate the contributions from those terms with an even number of indices will become clear later on, and will be evaluated in later sections, (see secs. 7 and 8).

We note an important property of the $I^{(n)}_{\lambda_1' \cdots \lambda_p^n}$. As can be observed from Eq. (6.5), it follows that any permutation of the indices for a given variable $S_c$, say, will leave $I^{(n)}_{\lambda_1' \cdots \lambda_p^n}$ unchanged. This will be important in simplifying the various terms of the expansion for Z.

Combining the above results, we have

$$Z = Z_0 - \Big\{ \sum_{\lambda_1 \cdots \lambda_4} V^4(\lambda_1, \lambda_2, \lambda_3, \lambda_4)\, I^{(1)}_{\lambda_1 \lambda_2 \lambda_3 \lambda_4} + \sum_{\lambda_1 \cdots \lambda_6} V^6(\lambda_1, \ldots, \lambda_6)\, I^{(1)}_{\lambda_1 \cdots \lambda_6} + \cdots \Big\}$$
$$+ \frac{1}{2!} \Big\{ \sum_{\lambda_1 \cdots \lambda_6} V^3(\lambda_1, \lambda_2, \lambda_3) V^3(\lambda_4, \lambda_5, \lambda_6)\, I^{(2)}_{\lambda_1 \lambda_2 \lambda_3 ; \lambda_4 \lambda_5 \lambda_6} + \cdots \Big\} - \cdots \qquad (6.7)$$

where

$$Z_0 = \int d\underset{\sim}{\xi}_1 \int_{\underset{\sim}{\xi}_1}^{\underset{\sim}{\xi}_1} \mathcal{D}_0^\beta [\underset{\sim}{Q}(s)]$$

$$= \prod_{\lambda_r} \left[ 2 \sinh \left( \tfrac{1}{2} \beta \hbar \omega_\lambda \right) \right]^{-1} \tag{6.8}$$

$\equiv$ the partition function for a system of non-interacting harmonic oscillators.

Instead of evaluating the separate terms of Eq. (6.7) using Eq. (6.5), we can more easily generate these terms employing a "source term", $(J)$, (Tarski (1967)). Although we have followed Papadopolous (1969) and Tarski (1967) in the work presented in this thesis, the idea of introducing a "source term" in quantum statistical physics problems was introduced as early as 1951 by J. Schwinger.

We will show a little later in this section that obtaining Z is formally equivalent to the knowledge of some generating functional. The procedure then is to evaluate the integrals $I^{(n)}_{\lambda_1^1 \ldots \lambda_p^n}$ arising in Eq. (6.7), and explicitly given by Eq. (6.5), by functional differentiation of the following generating functional, viz.,

$$G = \int d\underset{\sim}{\xi} \int_{\underset{\sim}{\xi}}^{\underset{\sim}{\xi}} \mathcal{D}_0^\beta [\underset{\sim}{Q}(s)] \exp \left\{ \sum_{\lambda_r} \int_0^\beta ds \, J_{\lambda_r}(s) \, Q_{\lambda_r}(s) \right\} \tag{6.9}$$

Then Eq. (6.5) can be expressed in the form

$$I^{(n)}_{\lambda_1^1 \cdots \lambda_m^1 ; \lambda_1^2 \cdots \lambda_p^n} = \int d\underset{\sim}{\xi} \int_{\underset{\sim}{\xi}}^{\underset{\sim}{\xi}} \mathcal{D}_0^\beta [\underset{\sim}{Q}(s)] \int_0^\beta ds_1 \cdots \int_0^\beta ds_n$$

$$\times \left\{ \frac{\delta}{\delta J_{\lambda_1^1}(s_1)} \cdots \frac{\delta}{\delta J_{\lambda_m^1}(s_1)} \frac{\delta}{\delta J_{\lambda_1^2}(s_2)} \cdots \frac{\delta}{\delta J_{\lambda_p^n}(s_n)} \right\} \exp \left\{ \sum_{\lambda_r} \int_0^\beta ds \, J_{\lambda_r}(s) \, Q_{\lambda_r}(s) \right\} \Bigg|_{\underset{\sim}{J}=0} \tag{6.10}$$

with the help of $\frac{\delta}{\delta J(s)} e^{\int_0^\beta J(s)Q(s)ds} = Q(s) e^{\int_0^\beta J(s)Q(s)ds}, 0 \le s \le \beta.$

Since it is possible to perform the functional integrations over $\{Q_{\lambda_r}(s)\}$, then the various functional differentiations, and finally the integrals over $\{s_c\}$, (Papadopolous (1969)), Eq. (6.10) can be expressed in the following form;

$$I^{(n)}_{\lambda_1' \cdots \lambda_m'; \lambda_1^2 \cdots \lambda_p^n} = \int_0^\beta ds_1 \cdots \int_0^\beta ds_n \frac{\delta}{\delta J_{\lambda_1'}(s_1)} \cdots \frac{\delta}{\delta J_{\lambda_m'}(s_1)} \frac{\delta}{\delta J_{\lambda_1^2}(s_2)} \cdots \frac{\delta}{\delta J_{\lambda_p^n}(s_n)} G \Big|_{\underset{\sim}{J}=0} \tag{6.11}$$

What remains left is to evaluate Eq. (6.9) which first requires the evaluation of the following path integral;

$$Y = \int_{\underset{\sim}{\xi}}^{\xi} \mathcal{D}_0^\beta [\underset{\sim}{Q}(s)] \exp\left\{ \sum_{\lambda_r} \int_0^\beta ds\, J_{\lambda_r}(s) Q_{\lambda_r}(s) \right\}$$

$$= \int_{\underset{\sim}{\xi}}^{\xi} \mathcal{D}[\underset{\sim}{Q}(s)] \exp\left\{ -\sum_{\lambda_r} \int_0^\beta ds \left[ \frac{1}{2\hbar^2} \dot{Q}_{\lambda_r}(s) \dot{Q}_{-\lambda_r}(s) + \frac{\omega_\lambda^2}{2} Q_{\lambda_r} Q_{-\lambda_r} - J_{\lambda_r}(s) Q_{\lambda_r}(s) \right] \right\} \tag{6.12}$$

where in obtaining Eq. (6.12), we have used Eq. (6.6). We suppose the $\lambda_r^{th}$ component of $\underset{\sim}{\xi}$ can be written as $\xi_{\lambda_r} = x_{\lambda_r} + i y_{\lambda_r}$ ; $x_{\lambda_r}, y_{\lambda_r}$ are real. Since $Q^*_{\lambda_r}(s) = Q_{-\lambda_r}(s)$, then $\xi^*_{\lambda_r} = \xi_{-\lambda_r}$.

Since Eq. (6.12) is a Gaussian path integral, we use the semiclassical or WKB method outlined in section 3 to evaluate Eq. (6.12). Hence, we have the following;

$$Y = \left[ \prod_{\lambda_r} \frac{2\pi\hbar}{\omega_{\lambda_r}} \sinh(\beta\hbar\omega_{\lambda_r}) \right]^{-\frac{1}{2}} \exp\left\{ -A_0^\beta [\underset{\sim}{Q}(s)] \right\} \tag{6.13}$$

where,

$$A_0^\beta[\underset{\sim}{Q}(s)] = \sum_{\lambda_r} \int_0^\beta ds \left\{ \frac{1}{2\hbar^2} \dot{Q}_{\lambda_r} \dot{Q}_{-\lambda_r} + \frac{\omega_{\lambda_r}^2}{2} Q_{\lambda_r} Q_{-\lambda_r} - J_{\lambda_r} Q_{\lambda_r} \right\} \qquad (6.14)$$

This integral is to be evaluated along the path for which $Q_{\lambda_r}(s)$ is a solution of the following Euler-Lagrange equation;

$$\ddot{Q}_{\lambda_r}(s) - \hbar^2 \omega_{\lambda_r}^2 Q_{\lambda_r}(s) = -\hbar^2 J_{-\lambda_r}(s) \quad ; \quad Q_{\lambda_r}(0) = Q_{\lambda_r}(\beta) = \xi_{\lambda_r} \qquad (6.15)$$

Solving Eq. (6.15), we obtain

$$\begin{aligned} Q_{\lambda_r}(s) = {} & \left[\cosh(s\hbar\omega_{\lambda_r}) - \tanh(\tfrac{1}{2}\beta\hbar\omega_{\lambda_r}) \sinh(s\hbar\omega_{\lambda_r})\right] \xi_{\lambda_r} \\ & + \frac{\hbar}{\omega_{\lambda_r}} \int_0^\beta ds' \, J_{-\lambda_r}(s') \sinh[(\beta - s')\hbar\omega_{\lambda_r}] \frac{\sinh(s\hbar\omega_{\lambda_r})}{\sinh(\beta\hbar\omega_{\lambda_r})} \\ & - \frac{\hbar}{\omega_{\lambda_r}} \int_0^s ds' \, J_{-\lambda_r}(s') \sinh[(s-s')\hbar\omega_{\lambda_r}] \end{aligned}$$

Substituting this expression into Eq. (6.14), and performing an integration by parts on the first term in the integrand, we obtain

$$\begin{aligned} A_0^\beta[\underset{\sim}{Q}(s)] = {} & \frac{1}{2\hbar^2} \sum_{\lambda_r} \Big\{ [\dot{Q}_{-\lambda_r}(s) Q_{\lambda_r}(s)]_0^\beta - \hbar^2 \int_0^\beta J_{\lambda_r}(s) Q_{\lambda_r}(s) ds \\ & - \int_0^\beta Q_{\lambda_r}(s) [\ddot{Q}_{-\lambda_r}(s) - \omega_{\lambda_r}^2 \hbar^2 Q_{-\lambda_r}(s) + \hbar^2 J_{\lambda_r}(s)] ds \Big\} \\ = {} & \frac{1}{2\hbar^2} \sum_{\lambda_r} \Big\{ Q_{\lambda_r}(\beta) \dot{Q}_{-\lambda_r}(\beta) - Q_{\lambda_r}(0) \dot{Q}_{-\lambda_r}(0) - \hbar^2 \int_0^\beta J_{\lambda_r}(s) Q_{\lambda_r}(s) ds \Big\} \\ = {} & \frac{1}{\hbar} \sum_{\lambda_r} \omega_{\lambda_r} \xi_{\lambda_r} \xi_{-\lambda_r} \tanh(\tfrac{1}{2}\beta\hbar\omega_{\lambda_r}) - \end{aligned}$$

$$- \sum_{\lambda_r} \xi_{\lambda_r} \int_0^\beta ds\, J_{\lambda_r}(s) \left[ \cosh(s\hbar\omega_{\lambda_r}) - \tanh(\tfrac{1}{2}\beta\hbar\omega_{\lambda_r}) \sinh(s\hbar\omega_{\lambda_r}) \right]$$

$$- \frac{\hbar}{2} \sum_{\lambda_r} \frac{1}{\omega_{\lambda_r}} \int_0^\beta ds \int_0^\beta ds'\, J_{\lambda_r}(s)\, J_{-\lambda_r}(s') \left[ \frac{\sinh(s\hbar\omega_{\lambda_r})}{\sinh(\beta\hbar\omega_{\lambda_r})} \sinh\{(\beta-s')\hbar\omega_{\lambda_r}\} \right.$$

$$\left. - \Theta(s-s') \sinh\{(s-s')\hbar\omega_{\lambda_r}\} \right]$$

$$= \frac{1}{\hbar} \sum_{\lambda_r} \omega_{\lambda_r} \xi_{\lambda_r} \xi_{-\lambda_r} \tanh(\tfrac{1}{2}\beta\hbar\omega_{\lambda_r})$$

$$- \frac{1}{2} \sum_{\lambda_r} \xi_{\lambda_r} \int_0^\beta ds\, J_{\lambda_r}(s) \left[ \cosh(\omega_{\lambda_r} \hbar s) - \tanh(\tfrac{1}{2}\beta\hbar\omega_{\lambda_r}) \sinh(s\hbar\omega_{\lambda_r}) \right]$$

$$- \frac{1}{2} \sum_{\lambda_r} \xi_{-\lambda_r} \int_0^\beta ds\, J_{-\lambda_r}(s) \left[ \cosh(s\hbar\omega_{-\lambda_r}) - \tanh(\tfrac{1}{2}\beta\hbar\omega_{-\lambda_r}) \sinh(s\hbar\omega_{\lambda_r}) \right]$$

$$- \frac{\hbar}{2} \sum_{\lambda_r} \frac{1}{\omega_{\lambda_r}} \int_0^\beta ds \int_0^\beta ds'\, J_{\lambda_r}(s)\, J_{-\lambda_r}(s') \left[ \frac{\sinh(s\hbar\omega_{\lambda_r})}{\sinh(\beta\hbar\omega_{\lambda_r})} \sinh\{(\beta-s')\hbar\omega_{\lambda_r}\} \right.$$

$$\left. - \Theta(s-s') \sinh\{(s-s')\hbar\omega_{\lambda_r}\} \right]$$

$$= \frac{1}{\hbar} \sum_{\lambda_r} \omega_{\lambda_r} \tanh(\tfrac{1}{2}\beta\hbar\omega_{\lambda_r}) \left\{ x_{\lambda_r} - \frac{\hbar}{4\omega_{\lambda_r} \tanh(\tfrac{1}{2}\beta\hbar\omega_{\lambda_r})} \times \right.$$

$$\times \int_0^\beta ds \left[ \cosh(s\hbar\omega_{\lambda_r}) - \tanh(\tfrac{1}{2}\beta\hbar\omega_{\lambda_r}) \sinh(s\hbar\omega_{\lambda_r}) \right] \times$$

$$\left. \times \left[ J_{\lambda_r}(s) + J_{-\lambda_r}(s) \right] \right\}^2$$

$$+ \frac{1}{\hbar} \sum_{\lambda_r} \omega_{\lambda_r} \tanh(\tfrac{1}{2}\beta\hbar\omega_{\lambda_r}) \left\{ y_{\lambda_r} - \frac{i\hbar}{4\omega_{\lambda_r} \tanh(\tfrac{1}{2}\beta\hbar\omega_{\lambda_r})} \times \right.$$

$$\times \int_0^\beta ds \left[ \cosh(s\hbar\omega_{\lambda_r}) - \tanh(\tfrac{1}{2}\beta\hbar\omega_{\lambda_r}) \sinh(s\hbar\omega_{\lambda_r}) \right] \times$$

$$\times \left[ J_{\lambda_r}(s) \, J_{-\lambda_r}(s') \right] \Big\}^2$$

$$+\frac{\hbar}{4} \sum_{\lambda_r} \frac{1}{\omega_{\lambda_r}} \int_0^\beta ds \int_0^\beta ds' \; J_{\lambda_r}(s) \, J_{-\lambda_r}(s') \Big\{ \coth\left(\tfrac{1}{2}\beta\hbar\omega_{\lambda_r}\right) \cosh[(s-s')\hbar\omega_{\lambda_r}] - 2\theta(s-s') \sinh[(s-s')\hbar\omega_{\lambda_r}] \Big\}$$

where

$$\theta(x) = \begin{cases} 1 \, , & x > 0 \\ 0 \, , & x < 0 \end{cases}$$

From Eqs. (6.9), (6.12), (6.13), and the above result, we have

$$G = \int d\underset{\sim}{\xi} \, Y = \Big[ \prod_{\lambda_r} \int d\xi_{\lambda_r} \Big] Y$$

$$= \Big[ \prod_{\lambda_r} \frac{2\pi\hbar}{\omega_{\lambda_r}} \sinh(\beta\hbar\omega_{\lambda_r}) \Big]^{-\frac{1}{2}} \Big\{ \Big[ \prod_{(\lambda_r > 0)} \int d\xi_{\lambda_r} d\xi_{-\lambda_r} \Big] e^{-A_0^\beta [\underset{\sim}{Q}(s)]} \Big\}$$

$$= Z_0 \exp \Big\{ \sum_{\lambda_r \lambda_r'} \int_0^\beta ds \int_0^\beta ds' \; J_{\lambda_r}(s) \, J_{\lambda_r'}(s') \, K_{\lambda_r \lambda_r'}(s,s') \Big\} \tag{6.16}$$

where

$$K_{\lambda_r \lambda_r'}(s,s') = K_{\lambda_r \lambda_r'}(s-s')$$

$$= \frac{\hbar}{2\omega_{\lambda_r}} \Big\{ \tfrac{1}{2} \coth\left(\tfrac{1}{2}\beta\hbar\omega_{\lambda_r}\right) \cosh[(s-s')\hbar\omega_{\lambda_r}] - \theta(s-s') \sinh[(s-s')\hbar\omega_{\lambda_r}] \Big\} \delta_{\lambda_r, -\lambda_r'} \tag{6.17}$$

Note that $K_{\lambda_r \lambda_r'}(s,s') = K_{\lambda_r' \lambda_r}(s,s')$ .

To further simplify the notation, let

$$(JKJ) = \sum_{\lambda_r \lambda_r'} \int_0^\beta ds \int_0^\beta ds' \, J_{\lambda_r}(s) \, J_{\lambda_r'}(s') \, K_{\lambda_r \lambda_r'}(s, s')$$

Then,

$$G = Z_0 \, e^{(JKJ)} = Z_0 \sum_{n=0}^{+\infty} \frac{(JKJ)^n}{n!} \tag{6.18}$$

Observe that the above method is systematic in evaluating the partition function because the problem is reduced to tedious, but straightforward integration and functional differentiation. Other consequences of this method will be discussed in later sections, (see secs. 7, 8, and 9).

## 7. Interacting Einstein Oscillators

We will apply the method of Papadopolous to determine the free energy of the interacting Einstein oscillators, (Shukla and Muller (1971, 1972)). The system to be considered is a linear chain of N interacting oscillators, each of mass m, and frequency $\omega$ . Periodic boundary conditions will be assumed.

Let $u_\ell$ be the position coordinate of the $\ell^{th}$ oscillator. The Lagrangian of the system is then given by

$$L = \frac{m}{2}\sum_{\ell=1}^{N}\left[\dot{u}_\ell^2 - \omega^2 u_\ell^2\right] + \frac{m}{2}\omega^2\sum_{\ell=1}^{N} u_\ell u_{\ell+1} \quad ; \; u_j = u_{j+N} \qquad (7.1)$$

The normal coordinate transformation is given by

$$u_\ell = \frac{1}{\sqrt{Nm}}\sum_k \xi_k e^{ik\ell d} \quad ; \quad \xi_k^* = \xi_{-k} \qquad (7.2)$$

Here, $d$ is the equilibrium separation of two successive oscillators, and $k$ is the wave number. Note that

$$\sum_{\ell=1}^{N} e^{i(k+k')\ell d} = N\Delta(k+k') \qquad (7.3)$$

Substituting Eq. (7.2) into Eq. (7.1), and using Eq. (7.3), we get

$$L = L_0 - L_A \qquad (7.4)$$

where
$$L_0 = \frac{1}{2}\sum_k\left[\dot{\xi}_k\dot{\xi}_{-k} - \omega^2\xi_k\xi_{-k}\right] \qquad (7.5)$$

$$L_A = -\frac{1}{2}\sum_k\sum_{k'} v_{kk'}\xi_k\xi_{k'} \quad ; \; v_{kk'} = \omega^2\cos(kd)\delta_{k,-k'} \qquad (7.6)$$

Performing the expansion of the term containing $L_A$ in Eq. (6.2), which is given in Eq. (6.4), and using the notation of Eq. (6.7), we obtain

$$\begin{aligned} Z = Z_0 &+ \sum_{kk'} \frac{v_{kk'}}{2} I^{(1)}_{kk'} + \\ &+ \frac{1}{2!} \sum_{k_1k_1'} \sum_{k_2k_2'} \frac{v_{k_1k_1'}}{2} \frac{v_{k_2k_2'}}{2} I^{(2)}_{k_1k_1';k_2k_2'} + \cdots + \\ &+ \frac{1}{n!} \sum_{k_1k_1'} \cdots \sum_{k_nk_n'} \frac{v_{k_1k_1'}}{2} \cdots \frac{v_{k_nk_n'}}{2} I^{(n)}_{k_1k_1';\cdots;k_nk_n'} + \cdots \end{aligned} \tag{7.7}$$

where

$$I^{(n)}_{k_1k_1';\cdots;k_nk_n'} = Z_0 \int_0^\beta ds_1 \cdots \int_0^\beta ds_n \frac{\delta^2}{\delta J_{k_1}(s_1)\,\delta J_{k_1'}(s_1)} \cdots \frac{\delta^2}{\delta J_{k_n}(s_n)\,\delta J_{k_n'}(s_n)} e^{(JKJ)} \Big|_{\underset{\sim}{J}=0}$$

$$Z_0 = \left[\prod_k 2\sinh\left(\tfrac{1}{2}\beta\hbar\omega\right)\right]^{-1}$$

$$\begin{aligned} K_{kk'}(s,s') = \frac{\hbar}{2\omega} \Big\{ &\tfrac{1}{2}\coth\left(\tfrac{1}{2}\beta\hbar\omega\right)\cosh[(s-s')\hbar\omega] \\ &- \theta(s-s')\sinh[(s-s')\hbar\omega] \Big\}\, \delta_{k,-k'} \end{aligned}$$

Put $$C(s,s')\,\delta_{k,-k'} = K_{kk'}(s,s') + K_{k'k}(s',s) \tag{7.8}$$

From the definition of $I^{(n)}_{k_1\cdots k_n'}$, observe that it is necessary to only keep the $n^{th}$ term in the expansion of $\exp(JKJ)$ because all other terms will not contribute. Here, we use the fact that

$$\frac{\delta^2}{\delta J_k(s_1)\,\delta J_{k'}(s_2)} (JKJ) = K_{kk'}(s_1,s_2) + K_{k'k}(s_2,s_1)$$

The following definitions will be of use;

(i) $$C_n = \int_0^\beta ds_1 \cdots \int_0^\beta ds_n \; C(s_1, s_2) \cdots C(s_{n-1}, s_n)\; C(s_n, s_1)$$

(ii) $$a_n = \sum_k C_n \; \frac{[\omega^2 \cos(kd)]^n}{2^n} = \sum_k C_n \; \frac{v_{k,-k}^n}{2^n}$$

(iii) $$b_n = \frac{1}{n!} \sum_{\substack{k_1 \cdots k_n \\ k_1' \cdots k_n'}} \frac{v_{k_1 k_1'}}{2} \cdots \frac{v_{k_n k_n'}}{2} \; \frac{1}{Z_0} \; I^{(n)}_{k_1 k_1'; \cdots ; k_n k_n'}$$

Substituting the expression for $I^{(n)}_{k_1 \cdots k_n'}$, and Eq. (7.6) into Eq. (iii), we obtain

$$b_n = \frac{1}{n!} \sum_{k_1 \cdots k_n} \frac{v_{k_1,-k_1}}{2} \cdots \frac{v_{k_n,-k_n}}{2} \int_0^\beta ds_1 \cdots \int_0^\beta ds_n \frac{\delta^2}{\delta J_{k_1}(s_1)\, \delta J_{-k_1}(s_1)} \cdots \frac{\delta^2}{\delta J_{k_n}(s_n)\, \delta J_{-k_n}(s_n)} \frac{(JKJ)^n}{n!}$$

$$= \frac{1}{n!} \sum_{\substack{\sum_{\ell=1}^n \ell j_\ell = n \\ j_1, \ldots, j_n \geq 0}} \frac{n!}{[\prod_{r=1}^n j_r!]} \left\{ \prod_{r=1}^n \left[ \frac{(2r-2)!!}{r!} a_r \right]^{j_r} \right\}$$

$$= \sum_{\substack{\sum_{\ell=1}^n \ell j_\ell = n \\ j_1, \ldots, j_n \geq 0}} \left\{ \prod_{r=1}^n \frac{1}{j_r!} \left[ \frac{2^{r-1}}{r} a_r \right]^{j_r} \right\} \qquad (7.9)$$

Note that $$2^{r-1}(r-1)! = (2r-2)!! \; , \; r = 1, 2, \ldots .$$

We now give the following intuitive argument as to why Eq. (7.9) is true.

First note that the factor $n!$ of $\frac{(JKJ)^n}{n!}$ cancels out for each particular sequence of functional differentiation that is performed. For example, if in a given sequence, one performs the operation $\frac{\delta^2}{\delta J_{k_r}(s_r)\,\delta J_{k_p}(s_p)}$ then

$$\left\{\prod_{q=1}^{n}\frac{\delta}{\delta J_{k_q}(s_q)}\right\}\left\{\prod_{q=1}^{n}\frac{\delta}{\delta J_{-k_q}(s_q)}\right\}\frac{(JKJ)^n}{n!}=C(s_r,s_p)\delta_{k_r,-k_q}\left\{\prod_{\substack{q=1\\ q\neq r,p}}^{n}\frac{\delta}{\delta J_{k_q}(s_q)}\right\}\left\{\prod_{q=1}^{n}\frac{\delta}{\delta J_{-k_q}(s_q)}\right\}\frac{(JKJ)^{n-1}}{(n-1)!}$$

Second, observe that $b_n$ will be some combination of the $\{a_r\}_{r=1}^{n}$ . In the middle equality of Eq. (7.9), the $n!$ in the numerator accounts for all possible permutations of the operators $\left\{\frac{\delta^2}{\delta J_{k_r}(s_r)\,\delta J_{-k_r}(s_r)}\right\}_{r=1}^{n}$ . This accounts for the fact that all such operators contribute equally to $b_n$ under $\sum_{k_1\cdots k_n}$ . For a given sequence of functional differentiation, the condition $\sum_{\ell=1}^{n}\ell j_\ell=n$ must be satisfied. Here, $j_\ell$ denotes the number of closed cycles of $\ell$ variables, $\{s_r\}$ , formed. An example of a closed cycle of $\ell$ variables is $C(s_1,s_2)\cdots C(s_j,s_{j+1})\cdots C(s_{\ell-1},s_\ell)C(s_\ell,s_1)$. The variables $\{s_r\}_{r=1}^{\ell}$ form a closed cycle because one starts at $s_1$ , goes through $s_2,\ldots,s_\ell$ , and returns to $s_1$ . From the definition of $C_\ell$ , $a_\ell$ is independent of the particular labels of the closed cycle of $\ell$ variables. Suppose for a given sequence of functional differentiation, there are $j_r\,(\geq 0)$ of the $a_r$ . For each factor of $a_r$ , there are $(2r-2)!!$ ways of pairing the r variables in the closed cycle. Further, one must divide by $r!$ to account for the degeneracies in the $n!$ permutations of the operators mentioned above. Hence, from these $j_r$ $a_r$, one gets a contribution $\left[\frac{(2r-2)!!}{r!} a_r\right]^{j_r}$. This result must further be divided by $j_r!$ to account for the degeneracy in selecting the $j_r$ $a_r$. This contribution is multiplied by the other factors in the particular sequence of functional differentiation which leads to the expression given in Eq. (7.9).

Substituting Eq. (iii) into Eq. (7.9) yields

$$Z = Z_0 \left\{ 1 + \sum_{n=1}^{+\infty} b_n \right\}$$

Hence, the Helmholtz free energy F, is given by

$$\begin{aligned} F &= -k_B T \ln Z \\ &= -k_B T \ln Z_0 - k_B T \ln \left\{ 1 + \sum_{n=1}^{+\infty} b_n \right\} \end{aligned} \tag{7.11}$$

Using Eq. (7.9)

$$\begin{aligned} 1 + \sum_{n=1}^{+\infty} b_n &= 1 + \sum_{n=1}^{+\infty} \sum_{\substack{\sum_{l=1}^{n} l j_l = n \\ j_1, \cdots, j_n \geq 0}} \left\{ \prod_{r=1}^{n} \frac{1}{j_r!} \left( \frac{2^{r-1}}{r} a_r \right)^{j_r} \right\} \\ &= \prod_{r=1}^{+\infty} \sum_{n_r=0}^{+\infty} \frac{1}{n_r!} \left( \frac{2^{r-1}}{r} a_r \right)^{n_r} \\ &= \exp \left\{ \sum_{r=1}^{+\infty} \frac{2^{r-1}}{r} a_r \right\} \end{aligned}$$

The second equality can be verified by multiplication and rearrangement of the terms.

Using the above result, Eq. (7.11) becomes

$$F = -k_B T \ln Z_0 - k_B T \sum_{p=1}^{+\infty} \frac{2^{p-1}}{p} a_p \tag{7.12}$$

Our task is now to evaluate $a_p$. From the definition in Eq. (ii), it follows that to get $a_p$, $C_p$ must be evaluated. In evaluating $C_p$, the following integral must be evaluated;

$$A = \int_0^\beta du \; C(w,u)\, C(u,v) \tag{7.13}$$

where, by Eq. (7.8),

$$C(u,v) = \frac{\hbar}{2\omega}\left[\coth\left(\tfrac{1}{2}\beta\hbar\omega\right)\cosh\{(u-v)\hbar\omega\} + \{\Theta(v-u)-\Theta(u-v)\}\sinh\{(u-v)\hbar\omega\}\right]$$

Let $z = \hbar\omega$, $a = \beta z$, $x = vz$, and $y = wz$. Then,

$$\begin{aligned} A = \left(\frac{\hbar}{2\omega}\right)^2 \Big\{ & \left[\coth^2\left(\tfrac{a}{2}\right)-1\right]\frac{\beta}{2}\cosh(y-x) \\ & + \frac{1}{4z}\left[\coth^2\left(\tfrac{a}{2}\right)+1\right]\left[\sinh(2a-x-y)+\sinh(x+y)\right] \\ & + \coth\left(\tfrac{a}{2}\right)\Big[(v-w)\sinh(y-x) \\ & \qquad - \frac{1}{2z}\left\{\cosh(x+y-2a)+\cosh(x+y)\right\}\Big] \\ & + \left[\Theta(v-w)-\Theta(w-v)\right](v-w)\cosh(y-x)\Big\} \\ & + \frac{\hbar}{2\omega}\frac{1}{z}C(v,w) \end{aligned}$$

Let

$$\begin{aligned} D = {} & \coth\left(\tfrac{a}{2}\right)\left[(v-w)\sinh(y-x)\right] + \frac{2\coth\left(\frac{a}{2}\right)}{\sinh(a)}\frac{\beta}{2}\cosh(y-x) \\ & + \left[\Theta(v-w)-\Theta(w-v)\right](v-w)\cosh(y-x) \end{aligned}$$

Then,

$$A = \left(\frac{\hbar}{2\omega}\right)^2 D + \frac{\hbar}{2\omega}\frac{1}{z}C(v,w)$$

Note that $\frac{\partial}{\partial z} C(v, w) = -\frac{\hbar}{2\omega} D$

Hence, $$A = \frac{\hbar}{2\omega}\left(\frac{1}{z} - \frac{\partial}{\partial z}\right) C(v, w) \qquad (7.14)$$

In general, for $n \geq 2$ , we have

$$\begin{aligned} C_n &= \int_0^\beta ds_1 \cdots \int_0^\beta ds_n \; C(s_1, s_2) \cdots C(s_n, s_1) \\ &= \left(\frac{\hbar}{2\omega}\right) \int_0^\beta ds_1 \cdots \int_0^\beta ds_{n-1} \, C(s_1, s_2) \cdots C(s_{n-2}, s_{n-1}) \left(\frac{1}{z} - \frac{\partial}{\partial z}\right) C(s_{n-1}, s_1) \\ &= \left(\frac{\hbar}{2\omega}\right) \left[\frac{1}{z} - \frac{1}{n-1}\frac{\partial}{\partial z}\right] C_{n-1} \qquad (7.15) \end{aligned}$$

and in particular

$$C_1 = \int_0^\beta ds_1 \, C(s_1, s_1) = \beta \frac{\hbar}{2\omega} \coth\left(\frac{\beta z}{2}\right)$$

Repeating the procedure as in Eq. (7.15), we obtain

$$\begin{aligned} C_n &= \left(\frac{\hbar}{2\omega}\right)^{n-1} \prod_{\ell=1}^{n-1} \left[\frac{1}{z} - \frac{1}{n-\ell}\frac{\partial}{\partial z}\right] C_1 \\ &= \beta \left(\frac{\hbar}{2\omega}\right)^n \prod_{\ell=1}^{n-1} \left[\frac{1}{z} - \frac{1}{n-\ell}\frac{\partial}{\partial z}\right] \coth\left(\frac{\beta z}{2}\right) \qquad (7.16) \end{aligned}$$

Let $F_0 = -k_B T \ln Z_0$ , and $V_k = -\frac{\hbar\omega}{4}\cos(kd)$. Then Eq. (7.12)

becomes

$$\begin{aligned} F &= F_0 - k_B T \sum_{n=1}^{+\infty} \frac{2^{n-1}}{n} \sum_k C_n \frac{[\omega^2 \cos(kd)]^n}{2^n} \\ &= F_0 + \frac{1}{2} k_B T \sum_k \sum_{n=1}^{+\infty} \frac{(-1)^{n+1}}{n} 2^n \left(\frac{2\omega}{\hbar}\right)^n V_k^n C_n \\ &= F_0 + \frac{1}{2} \sum_k \sum_{n=1}^{+\infty} \frac{(-1)^{n+1}}{n} (2V_k)^n \left\{\prod_{\ell=1}^{n-1} \left[\frac{1}{z} - \frac{1}{n-\ell}\frac{\partial}{\partial z}\right]\right\} \coth\left(\frac{\beta z}{2}\right) \end{aligned}$$

(7.17)

For $0<|x|<\pi$, $\quad \coth(x) = \sum_{n=0}^{+\infty} \frac{2^{2n}}{(2n)!} B_{2n} x^{2n-1}$

Here, $\{B_n\}$ is the set of Bernoulli numbers, (Arfken (1970)). Substituting for $\coth(x)$ in terms of $\{B_n\}$ into Eq. (7.17), and assuming that the interchange of summation and differentiation is allowed, Eq. (7.17) becomes

$$F = F_0 + \frac{1}{2}\sum_k \sum_{n=1}^{+\infty} \sum_{r=0}^{+\infty} \frac{(-1)^{n+1}}{n} (2V_k)^n \frac{2^{2r}}{(2r)!} \times$$
$$\times B_{2r} \left(\frac{\beta}{2}\right)^{2r-1} \left[\prod_{\ell=1}^{n-1} \left(\frac{1}{z} - \frac{1}{n-\ell}\frac{\partial}{\partial z}\right)\right] z^{2r-1} \tag{7.18}$$

Put $J_{\alpha,n} = \prod_{\ell=1}^{n-1} \left(\frac{1}{z} - \frac{1}{n-\ell}\frac{\partial}{\partial z}\right) z^{\alpha}$. It can be shown in a straightforward manner, using induction, that for $n=1,2,\ldots,$

$$J_{-1,n} = \frac{2^{n-1}}{z^n} \quad ,$$

$$J_{\alpha,n} = \left[\prod_{\ell=1}^{n-1} (2\ell-1-\alpha)\right] \frac{z^{\alpha-n+1}}{(n-1)!} \quad ; \alpha = 1,2,\ldots .$$

Noting the above relations, Eq. (7.18) becomes

$$F = F_0 + \frac{1}{2}\sum_k \sum_{n=1}^{+\infty} \sum_{r=0}^{+\infty} \frac{(-1)^{n+1}}{n} (2V_k)^n \, 2 \, \frac{B_{2r}}{(2r)!} \beta^{2r-1} \times$$
$$\times \frac{z^{2r-n}}{(n-1)!} \left[\prod_{\ell=1}^{n-1} (2\ell-2r)\right]$$
$$= F_0 + \frac{1}{2\beta}\sum_k \sum_{n=1}^{+\infty} \frac{(-1)^{n+1}}{n} \left(\frac{4V_k}{z}\right)^n$$
$$+ \frac{1}{\beta}\sum_k \sum_{n=1}^{+\infty} \sum_{r=n}^{+\infty} \frac{1}{2r} \binom{r}{n} \frac{B_{2r}}{(2r)!} (\beta z)^{2r} \left(\frac{4V_k}{z}\right)^n$$

$$= F_0 + \frac{1}{\beta} \sum_k \ln \left[ \left(1 + \frac{4V_k}{z}\right)^{\frac{1}{2}} \right]$$

$$+ \frac{1}{\beta} \sum_k \sum_{r=1}^{+\infty} \frac{2^{2r} \left(\frac{\beta z}{2}\right)^{2r}}{2r[(2r)!]} B_{2r} \sum_{n=1}^{r} \left(\frac{4V_k}{z}\right)^n \binom{r}{n}$$

$$= F_0 + \frac{1}{\beta} \sum_k \ln \left[ \left(1 + \frac{4V_k}{z}\right)^{\frac{1}{2}} \right]$$

$$+ \frac{1}{\beta} \sum_k \sum_{r=1}^{+\infty} \frac{2^{2r} \left(\frac{\beta z}{2}\right)^{2r}}{2r[(2r)!]} B_{2r} \left[ \left(1 + \frac{4V_k}{z}\right)^r - 1 \right]$$

$$= \frac{1}{\beta} \sum_k \Big\{ \ln \left[ 2 \sinh \left(\frac{\beta z}{2}\right) \right] + \ln \left[ \frac{\beta z}{2} \left(1 + \frac{4V_k}{z}\right)^{\frac{1}{2}} \right]$$

$$- \ln \left(\frac{\beta z}{2}\right) + \sum_{r=1}^{+\infty} \left[ \frac{\beta z}{2} \left(1 + \frac{4V_k}{z}\right)^{\frac{1}{2}} \right]^r \frac{2^{2r}}{(2r)!\,2r} B_{2r}$$

$$- \sum_{r=1}^{+\infty} \left(\frac{\beta z}{2}\right)^{2r} \frac{2^{2r}}{(2r)!\,(2r)} B_{2r} \Big\}$$

$$= \frac{1}{\beta} \sum_k \left\{ \ln 2 + \ln \left[ \sinh \left(\frac{\beta z}{2}\right) \right] + \ln \left[ \sinh \left(\frac{\beta \hbar \omega_k}{2}\right) \right] - \ln \left[ \sinh \left(\frac{\beta z}{2}\right) \right] \right\}$$

$$= \frac{1}{\beta} \sum_k \ln \left[ 2 \sinh \left( \tfrac{1}{2} \beta \hbar \omega_k \right) \right] \qquad (7.19)$$

where in obtaining Eq. (7.19), we have substituted explicitly for $F_0$ , (the free energy of the individual Einstein oscillator), and the dispersion relation, $\omega_k^2 = \omega^2 [1 - \cos(kd)]$.

There are two points to be made about Eq. (7.19). First, this is the expression one expects for the free energy of the system under consideration, (Shukla and

Muller (1971, 1972)). Second, the expansion used in expanding $\coth\left(\frac{\beta z}{2}\right)$ is valid for only a limited range of $\frac{\beta z}{2}$. To extend this, one would have to find expansions for $\coth\left(\frac{\beta z}{2}\right)$ that are valid in other ranges, and then follow through with basically the same manipulations. The final result obtained would however be the same.

## 8. Helmholtz Free Energy of an Anharmonic Crystal to $O(\lambda^4)$

In this section, we use the method of Papadopolous to derive the Helmholtz free energy F, to $O(\lambda^4)$, for an anharmonic crystal, where $\lambda$ is the usual Van Hove ordering parameter. We will also point out the close relationship between the process of functional differentiation and the corresponding Feynman diagrams. However, we note that this procedure of evaluating F can be carried out without a priori knowledge of any Feynman diagrams. Another feature of this calculation is that the direct temperature space integration procedure is used, (Papadopolous (1969), Barron and Klein (1974)), as opposed to performing the calculations in Fourier space, (Shukla and Cowley (1971)).

It is useful to introduce the following notation.

Let

$$Z_0 X^{(n)}_{\lambda_1^1 \cdots \lambda_m^1 ; \lambda_1^2 \cdots \lambda_p^n} = I^{(n)}_{\lambda_1^1 \cdots \lambda_m^1 ; \lambda_1^2 \cdots \lambda_p^n} \tag{8.1}$$

where $I^{(n)}_{\lambda_1^1 \cdots \lambda_p^n}$ is defined in Eq. (6.5). The reason we do this is that the generator $G$, defined in Eq. (6.18), contains a factor $Z_0$.

Now we can enumerate "all" the contributions to $Z$ of $O(\lambda^4)$. They arise from the combination of $V_3, V_4, V_5$ terms in the Lagrangian, and a separate term from $V_6$. In increasing order of complexity, the various terms can be symbolically written down as; $V_6\ (1)$, $V_3 - V_5\ (2)$

$V_4 - V_4$ (3), $V_3 - V_3 - V_4$ (7) , and $V_3 - V_3 - V_3 - V_3$ (8), where the numbers in the parantheses give the number of terms in each combination. The evaluation of each of them requires the knowledge of $X^{(n)}_{\lambda_1' \cdots \lambda_p^n}$ . Following the procedure of section 7, $X^{(n)}_{\lambda_1' \cdots \lambda_p^n}$ can be obtained.

From Eq. (6.7), to $O(\lambda^4)$, the partition function is given by

$$
\begin{aligned}
Z = Z_0 \Big\{ 1 &- \sum_{\lambda_1 \cdots \lambda_4} V^4(\lambda_1, \ldots, \lambda_4)\, X^{(1)}_{\lambda_1 \cdots \lambda_4} \\
&+ \frac{1}{2!} \sum_{\lambda_1 \cdots \lambda_6} V^3(\lambda_1, \lambda_2, \lambda_3)\, V^3(\lambda_4, \lambda_5, \lambda_6)\, X^{(2)}_{\lambda_1 \cdots \lambda_3 ; \lambda_4 \cdots \lambda_6} \\
&- \sum_{\lambda_1 \cdots \lambda_6} V^6(\lambda_1, \ldots, \lambda_6)\, X^{(1)}_{\lambda_1 \cdots \lambda_6} \\
&+ \frac{2}{2!} \sum_{\lambda_1 \cdots \lambda_8} V^5(\lambda_1, \ldots, \lambda_5)\, V^3(\lambda_6, \lambda_7, \lambda_8)\, X^{(2)}_{\lambda_1 \cdots \lambda_5 ; \lambda_6 \cdots \lambda_8} \\
&+ \frac{1}{2!} \sum_{\lambda_1 \cdots \lambda_8} V^4(\lambda_1, \ldots, \lambda_4)\, V^4(\lambda_5, \ldots, \lambda_8)\, X^{(2)}_{\lambda_1 \cdots \lambda_4 ; \lambda_5 \cdots \lambda_8} \\
&- \frac{3}{3!} \sum_{\lambda_1 \cdots \lambda_{10}} V^3(\lambda_1, \lambda_2, \lambda_3)\, V^3(\lambda_4, \lambda_5, \lambda_6)\, V^4(\lambda_7, \ldots, \lambda_{10}) \times \\
&\qquad \times X^{(3)}_{\lambda_1 \lambda_2 \lambda_3 ; \lambda_4 \cdots \lambda_6 ; \lambda_7 \cdots \lambda_{10}} \\
&+ \frac{1}{4!} \sum_{\lambda_1 \cdots \lambda_{12}} V^3(\lambda_1, \lambda_2, \lambda_3)\, V^3(\lambda_4, \lambda_5, \lambda_6)\, V^3(\lambda_7, \lambda_8, \lambda_9)\, V^3(\lambda_{10}, \lambda_{11}, \lambda_{12}) \times \\
&\qquad \times X^{(4)}_{\lambda_1 \cdots \lambda_3 ; \lambda_4 \cdots \lambda_6 ; \lambda_7 \cdots \lambda_9 ; \lambda_{10} \cdots \lambda_{12}} \Big\}
\end{aligned} \tag{8.2}
$$

Note that the anharmonic coefficient $V^n(\lambda_1, \ldots, \lambda_n)$ is of $O(\lambda^{n-2})$. To avoid any confusion in the notation used here, we recall that $\lambda_r \equiv \vec{q}_r j_r$

The following definition will be of use.

$$K_{\lambda_r \lambda_r'}(s,s') + K_{\lambda_r' \lambda_r}(s',s) \equiv D_{\lambda_r}(s,s')\, \delta_{\lambda_r,-\lambda_r'}$$

$$= \frac{\hbar}{2\omega_{\lambda_r}}\, g(\lambda_r, s-s')\, \delta_{\lambda_r,-\lambda_r'} \qquad (8.3)$$

where, using the definition of $K_{\lambda_r \lambda_r'}(s,s')$ given in Eq. (6.17),

$$\begin{aligned} g(\lambda_r, s-s') &= \coth\left(\tfrac{1}{2}\beta\hbar\omega_{\lambda_r}\right)\cosh\left[(s-s')\hbar\omega_{\lambda_r}\right] \\ &\quad -\theta(s-s')\sinh\left[(s-s')\hbar\omega_{\lambda_r}\right] \\ &\quad -\theta(s'-s)\sinh\left[(s'-s)\hbar\omega_{\lambda_r}\right] \\ &= \sum_{\alpha=\pm 1} \alpha\, N_{\lambda_r}(\alpha)\exp\left[|s-s'|\,\alpha\,\hbar\omega_{\lambda_r}\right] \end{aligned}$$

where $\qquad N_{\lambda_r}(\alpha) = \left[\exp(\alpha\beta\hbar\omega_{\lambda_r}) - 1\right]^{-1}$

An important property of $g(\lambda_r, s-s')$ to note is that

$$g(\lambda_r, \tau+\beta) = g(\lambda_r, \tau) \quad , \ -\beta < \tau < 0$$

In the following calculations, one can use the properties of $V^n(\lambda_1, \dots, \lambda_n)$ mentioned in section 5, and the properties of $g(\lambda_r, s-s')$ mentioned above, to make some simplifications.

To simplify the notation, let

$$J \equiv \lambda_J \quad , \quad N_{\lambda_J}(\alpha_J) \equiv N_J \quad , \quad N_{\lambda_J}(1) = n(\lambda_J) \equiv n_J \, ,$$

$$N_{\lambda_J}(-1) = -(n_J+1) \quad , \ \omega(\lambda_J) \equiv \omega_J \ , \ a_J \equiv \alpha_J \omega_J \hbar \, .$$

The three terms of $O(\lambda^2)$ are quite simple to generate. They can be symbolically written down as; $V_4$ (1) ,and $V_3 - V_3$ (2) . We will write down their contributions to $Z$ first.

We will set up the evaluation of the various terms in the following manner. We put down a heading to indicate which symbolical terms are to be evaluated. Then, under each heading we write down the various terms to be evaluated, and the final result which is valid for all temperatures.

(I) Contributions from $V_4$ (1)

$$\beta W_1 = \sum_{\lambda_1 \cdots \lambda_4} V^4(\lambda_1, \ldots, \lambda_4)\; X^{(1)}_{\lambda_1 \cdots \lambda_4}$$

$$= 3 \sum_{\lambda_1 \cdots \lambda_4} V^4(\lambda_1, \ldots, \lambda_4)\; \delta_{1,-3}\, \delta_{2,-4} \int_0^\beta D_1(s,s)\, D_2(s,s)\, ds$$

$$= 3 \sum_{\lambda_1 \lambda_2} V^4(\lambda_1, \lambda_2, -\lambda_1, -\lambda_2) \left(\frac{\hbar}{2}\right)^2 \frac{1}{\omega_1 \omega_2} \int_0^\beta ds\; g(\lambda_1, 0)\, g(\lambda_2, 0)$$

$$= 3\beta \left(\frac{\hbar}{2}\right)^2 \sum_{\lambda_1 \lambda_2} V^4(\lambda_1, \lambda_2, -\lambda_1, -\lambda_2) \frac{1}{\omega_1 \omega_2} [2n_1 + 1][2n_2 + 1]$$

(II) Contributions from $V_3 - V_3$ (2)

$$\beta [W_2 + W_3] = \sum_{\lambda_1 \cdots \lambda_6} V^3(\lambda_1, \lambda_2, \lambda_3) V^3(\lambda_4, \lambda_5, \lambda_6)\, X^{(2)}_{\lambda_1 \lambda_2 \lambda_3 ; \lambda_4 \lambda_5 \lambda_6}$$

(a) $$\beta W_2 = \sum_{\lambda_1 \cdots \lambda_6} V^3(\lambda_1, \lambda_2, \lambda_3)\, V^3(\lambda_4, \lambda_5, \lambda_6)\; 6\, \delta_{1,-4}\, \delta_{2,-5}\, \delta_{3,-6}\, \times$$

$$\times \int_0^\beta ds_1 \int_0^\beta ds_2\; D_1(s_1, s_2)\, D_2(s_1, s_2)\, D_3(s_1, s_2)$$

$$= 6\beta \sum_{\lambda_1\lambda_2\lambda_3} V^3(\lambda_1,\lambda_2,\lambda_3)\, V^3(-\lambda_1,-\lambda_2,-\lambda_3) \left(\frac{\hbar}{2}\right)^3 \left(\frac{2}{\hbar}\right) \frac{1}{\omega_1\omega_2\omega_3} \times$$

$$\times \left\{ \frac{(n_1+1)(n_2+1)(n_3+1) - n_1 n_2 n_3}{\omega_1+\omega_2+\omega_3} + \right.$$

$$\left. + 3\left[\frac{n_1(n_2+1)(n_3+1) - (n_1+1)n_2 n_3}{\omega_2+\omega_3-\omega_1}\right]\right\}$$

(b) $$\beta W_3 = \sum_{\lambda_1\cdots\lambda_6} V^3(\lambda_1,\lambda_2,\lambda_3)\, V^3(\lambda_4,\lambda_5,\lambda_6)\; 9\; \delta_{1,-2}\,\delta_{3,-4}\,\delta_{5,-6} \times$$

$$\times \int_0^\beta ds_1 \int_0^\beta ds_2\; D_1(s_1,s_1)\, D_3(s_1,s_2)\, D_5(s_2,s_2)$$

$$= 9\beta \sum_{\lambda_1\lambda_3\lambda_5} V^3(\lambda_1,-\lambda_1,\lambda_3)\, V^3(-\lambda_3,\lambda_5,-\lambda_5) \left(\frac{\hbar}{2}\right)^3 \frac{1}{\omega_1\omega_3\omega_5} \times$$

$$\times \left(\frac{2}{\hbar\omega_3}\right)(2n_1+1)(2n_5+1)$$

(III) Contributions from $V_6$ (1)

$$\beta W_4 = \sum_{\lambda_1\cdots\lambda_6} V^6(\lambda_1,\ldots,\lambda_6)\; X^{(1)}_{\lambda_1\cdots\lambda_6}$$

$$= \sum_{\lambda_1\cdots\lambda_6} V^6(\lambda_1,\ldots,\lambda_6)\; 15\; \delta_{1,-4}\,\delta_{2,-5}\,\delta_{3,-6} \int_0^\beta ds\; D_1(s,s)\, D_2(s,s)\, D_3(s,s)$$

$$= 15\beta \sum_{\lambda_1\lambda_2\lambda_3} V^6(\lambda_1,\lambda_2,\lambda_3,-\lambda_1,-\lambda_2,-\lambda_3) \left(\frac{\hbar}{2}\right)^3 \frac{1}{\omega_1\omega_2\omega_3}(2n_1+1)(2n_2+1)(2n_3+1)$$

(IV) Contributions from $V_3 - V_5$ (2)

$$\beta[W_5 + W_6] = \sum_{\lambda_1\cdots\lambda_8} V^5(\lambda_1,\ldots,\lambda_5)\, V^3(\lambda_6,\lambda_7,\lambda_8)\; X^{(2)}_{\lambda_1\cdots\lambda_5 s \lambda_6\lambda_7\lambda_8}$$

(a) $$\beta W_5 = \sum_{\lambda_1\cdots\lambda_8} V^5(\lambda_1,\ldots,\lambda_5)\, V^3(\lambda_6,\lambda_7,\lambda_8)\; 45\; \delta_{1,-3}\,\delta_{2,-4}\,\delta_{5,-6}\,\delta_{7,-8}\,\times$$

$$\times \int_0^\beta ds_1 \int_0^\beta ds_2\; D_1(s_1,s_1)\, D_2(s_1,s_1)\, D_5(s_1,s_2)\, D_7(s_2,s_2)$$

$$= 45\beta \sum_{\lambda_1\lambda_2\lambda_5\lambda_7} V^5(\lambda_1,\lambda_2,-\lambda_1,-\lambda_2,\lambda_5)\, V^3(-\lambda_5,\lambda_7,-\lambda_7)\left(\frac{\hbar}{2}\right)^4 \times$$

$$\times \frac{1}{\omega_1\omega_2\omega_5\omega_7}\,(2n_1+1)(2n_2+1)(2n_7+1)\left(\frac{2}{\hbar\omega_5}\right)$$

(b) $$\beta W_6 = \sum_{\lambda_1\cdots\lambda_8} V^5(\lambda_1,\ldots,\lambda_5)\, V^3(\lambda_6,\lambda_7,\lambda_8)\; 60\; \delta_{1,-6}\,\delta_{2,-7}\,\delta_{3,-8}\,\delta_{4,-5}\,\times$$

$$\times \int_0^\beta ds_1 \int_0^\beta ds_2\; D_1(s_1,s_2)\, D_2(s_1,s_2)\, D_3(s_1,s_2)\, D_4(s_1,s_1)$$

$$= 60\beta \sum_{\lambda_1\lambda_2\lambda_3\lambda_4} V^5(\lambda_1,\lambda_2,\lambda_3,\lambda_4,-\lambda_4)\, V^3(-\lambda_1,-\lambda_2,-\lambda_3)\left(\frac{\hbar}{2}\right)^4 \times$$

$$\times \frac{1}{\omega_1\omega_2\omega_3\omega_4}\,(2n_4+1)\left(\frac{2}{\hbar}\right)\left\{ \frac{(n_1+1)(n_2+1)(n_3+1)-n_1n_2n_3}{\omega_1+\omega_2+\omega_3} + \right.$$

$$\left. +3\left[\frac{n_1(n_2+1)(n_3+1)-(n_1+1)n_2n_3}{\omega_2+\omega_3-\omega_1}\right]\right\}$$

(V) Contributions from $V_4 - V_4$ (3)

$$\beta[W_7 + W_8 + W_9] = \sum_{\lambda_1\cdots\lambda_8} V^4(\lambda_1,\ldots,\lambda_4)\, V^4(\lambda_5,\ldots,\lambda_8)\,\times$$

$$\times\; X^{(2)}_{\lambda_1\cdots\lambda_4;\,\lambda_5\cdots\lambda_8}$$

(a) $$\beta W_7 = \sum_{\lambda_1\cdots\lambda_8} V^4(\lambda_1,\ldots,\lambda_4)\, V^4(\lambda_5,\ldots,\lambda_8)\; 9\; \delta_{1,-3}\,\delta_{2,-4}\,\delta_{5,-7}\,\delta_{6,-8}\,\times$$

$$\times \int_0^\beta ds_1 \int_0^\beta ds_2\; D_1(s_1,s_1)\, D_2(s_1,s_1)\, D_5(s_2,s_2)\, D_6(s_2,s_2)$$

$$= 9\beta^2 \sum_{\lambda_1\lambda_2\lambda_5\lambda_6} V^4(\lambda_1,\lambda_2,-\lambda_1,-\lambda_2)\, V^4(\lambda_5,\lambda_6,-\lambda_5,-\lambda_6)\times$$

$$\times \left(\frac{\hbar}{2}\right)^4 \frac{1}{\omega_1\omega_2\omega_5\omega_6}\,(2n_1+1)(2n_2+1)(2n_5+1)(2n_6+1)$$

$$= (\beta W_1)^2$$

(b) $$\beta W_8 = \sum_{\lambda_1\cdots\lambda_8} V^4(\lambda_1,\ldots,\lambda_4)\, V^4(\lambda_5,\ldots,\lambda_8)\; 72\; \delta_{1,-5}\,\delta_{2,-6}\,\delta_{3,-4}\,\delta_{7,-8}\times$$

$$\times \int_0^\beta ds_1 \int_0^\beta ds_2\; D_1(s_1,s_2)\, D_2(s_1,s_2)\, D_3(s_1,s_1)\, D_7(s_2,s_2)$$

$$= 72\beta \sum_{\lambda_1\lambda_2\lambda_3\lambda_7} V^4(\lambda_1,\lambda_2,\lambda_3,-\lambda_3)\, V^4(-\lambda_1,-\lambda_2,\lambda_7,-\lambda_7)\left(\frac{\hbar}{2}\right)^4\times$$

$$\times \frac{1}{\omega_1\omega_2\omega_3\omega_7}\,(2n_3+1)(2n_7+1)\left(\frac{2}{\hbar}\right) T_{12}\;,$$

$$T_{1,2}^{(1)} = \begin{cases} \dfrac{(n_1+n_2+1)}{\omega_1+\omega_2} + \dfrac{n_1-n_2}{\omega_2-\omega_1}\;, & \omega_1 \neq \omega_2 \\[2ex] \dfrac{1}{\omega_1}(n_1+\frac{1}{2}) + \beta\hbar\, n_1(n_1+1)\;, & \omega_1 = \omega_2 \end{cases} \qquad (*)$$

(c) $$\beta W_9 = \sum_{\lambda_1\cdots\lambda_8} V^4(\lambda_1,\ldots,\lambda_4)\, V^4(\lambda_5,\ldots,\lambda_8)\; 24\; \delta_{1,-5}\,\delta_{2,-6}\,\delta_{3,-7}\,\delta_{4,-8}\times$$

$$\times \int_0^\beta ds_1 \int_0^\beta ds_2\; D_1(s_1,s_2)\, D_2(s_1,s_2)\, D_3(s_1,s_2)\, D_4(s_1,s_2)$$

$$= 24\beta \sum_{\lambda_1\lambda_2\lambda_3\lambda_4} V^4(\lambda_1,\lambda_2,\lambda_3,\lambda_4)\, V^4(-\lambda_1,-\lambda_2,-\lambda_3,-\lambda_4)\left(\frac{\hbar}{2}\right)^4\times$$

$$\times \frac{(-2)}{\omega_1\omega_2\omega_3\omega_4} \sum_{\alpha_1\alpha_2\alpha_3\alpha_4=\pm1} \frac{\alpha_1\alpha_2\alpha_3\alpha_4}{(a_1+a_2+a_3+a_4)}\, N_1 N_2 N_3 N_4$$

(VI) Contributions from $V_3 - V_3 - V_4$ (7)

$$\beta \left[ W_{10} + W_{11} + W_{12} + W_{13} + W_{14} + W_{15} + W_{16} \right]$$

$$= \sum_{\lambda_1 \cdots \lambda_{10}} V^3(\lambda_1,\lambda_2,\lambda_3)\, V^3(\lambda_4,\lambda_5,\lambda_6)\, V^4(\lambda_7,\dots,\lambda_{10})\, X^{(3)}_{\lambda_1\lambda_2\lambda_3;\lambda_4\lambda_5\lambda_6;\lambda_7\cdots\lambda_{10}}$$

(a) $$\beta W_{10} = \sum_{\lambda_1 \cdots \lambda_{10}} V^3(\lambda_1,\lambda_2,\lambda_3)\, V^3(\lambda_4,\lambda_5,\lambda_6)\, V^4(\lambda_7,\dots,\lambda_{10}) \times$$

$$\times\ 27\ \delta_{1,-2}\, \delta_{3,-4}\, \delta_{5,-6}\, \delta_{7,-9}\, \delta_{8,-10} \times$$

$$\times \int_0^\beta ds_1 \int_0^\beta ds_2 \int_0^\beta ds_3\ D_1(s_1,s_1)\, D_3(s_1,s_2)\, D_5(s_2,s_2)\, D_7(s_3,s_3)\, D_8(s_3,s_3)$$

$$= 27\beta^2 \sum_{\lambda_1\lambda_3\lambda_5\lambda_7\lambda_8} V^3(\lambda_1,-\lambda_1,\lambda_3)\, V^3(-\lambda_3,\lambda_5,-\lambda_5)\, V^4(\lambda_7,\lambda_8,-\lambda_7,-\lambda_8) \times$$

$$\times \left(\frac{\hbar}{2}\right)^5 \frac{1}{\omega_1\omega_3\omega_5\omega_7\omega_8} (2n_1+1)(2n_5+1)(2n_7+1)(2n_8+1)\left(\frac{2}{\hbar\omega_3}\right)$$

$$= (\beta W_1) \times (\beta W_3)$$

(b) $$\beta W_{11} = \sum_{\lambda_1 \cdots \lambda_{10}} V^3(\lambda_1,\lambda_2,\lambda_3)\, V^3(\lambda_4,\lambda_5,\lambda_6)\, V^4(\lambda_7,\dots,\lambda_{10}) \times$$

$$\times\ 216\ \delta_{1,-2}\, \delta_{3,-4}\, \delta_{5,-7}\, \delta_{6,-8}\, \delta_{9,-10} \times$$

$$\times \int_0^\beta ds_1 \int_0^\beta ds_2 \int_0^\beta ds_3\ D_1(s_1,s_1)\, D_3(s_1,s_2)\, D_5(s_2,s_3)\, D_6(s_2,s_3)\, D_9(s_3,s_3)$$

$$= 216\beta \sum_{\lambda_1\lambda_3\lambda_5\lambda_6\lambda_9} V^3(\lambda_1,-\lambda_1,\lambda_3)\, V^3(-\lambda_3,\lambda_5,\lambda_6)\, V^4(-\lambda_5,-\lambda_6,\lambda_9,-\lambda_9) \times$$

$$\times \left(\frac{\hbar}{2}\right)^5 \frac{1}{\omega_1\omega_3\omega_5\omega_6\omega_9} (2n_1+1)(2n_9+1)\left(\frac{2}{\hbar\omega_3}\right)\left(\frac{2}{\hbar}\right) T^{(1)}_{5,6}$$

(c) $$\beta W_{12} = \sum_{\lambda_1 \cdots \lambda_{10}} V^3(\lambda_1, \lambda_2, \lambda_3)\, V^3(\lambda_4, \lambda_5, \lambda_6)\, V^4(\lambda_7, \ldots, \lambda_{10}) \times$$
$$\times\, 108\; \delta_{1,-2}\, \delta_{3,-7}\, \delta_{4,-6}\, \delta_{5,-8}\, \delta_{9,-10} \times$$
$$\times \int_0^\beta ds_1 \int_0^\beta ds_2 \int_0^\beta ds_3\; D_1(s_1,s_1)\, D_3(s_1,s_3)\, D_4(s_2,s_2)\, D_5(s_2,s_3)\, D_9(s_3,s_3)$$
$$= 108\, \beta \sum_{\lambda_1 \lambda_3 \lambda_4 \lambda_5 \lambda_9} V^3(\lambda_1, -\lambda_1, +\lambda_3)\, V^3(+\lambda_4, \lambda_5, -\lambda_4)\, V^4(-\lambda_3, -\lambda_5, \lambda_9, -\lambda_9) \times$$
$$\times \left(\frac{\hbar}{2}\right)^5 \frac{1}{\omega_1 \omega_3 \omega_4 \omega_5 \omega_9}\; (2n_1+1) \left(\frac{2}{\hbar\omega_3}\right) (2n_4+1) \left(\frac{2}{\hbar\omega_5}\right) (2n_9+1)$$

(d) $$\beta W_{13} = \sum_{\lambda_1 \cdots \lambda_{10}} V^3(\lambda_1, \lambda_2, \lambda_3)\, V^3(\lambda_4, \lambda_5, \lambda_6)\, V^4(\lambda_7, \ldots, \lambda_{10}) \times$$
$$\times\, 144\; \delta_{1,-2}\, \delta_{3,-7}\, \delta_{4,-8}\, \delta_{5,-9}\, \delta_{6,-10} \times$$
$$\times \int_0^\beta ds_1 \int_0^\beta ds_2 \int_0^\beta ds_3\; D_1(s_1,s_1)\, D_3(s_1,s_3)\, D_4(s_2,s_3)\, D_5(s_2,s_3)\, D_6(s_2,s_3)$$
$$= 144\, \beta \sum_{\lambda_1 \lambda_3 \lambda_4 \lambda_5 \lambda_6} V^3(\lambda_1, -\lambda_1, \lambda_3)\, V^3(\lambda_4, \lambda_5, \lambda_6)\, V^4(-\lambda_3, -\lambda_4, -\lambda_5, -\lambda_6) \times$$
$$\times \left(\frac{\hbar}{2}\right)^5 \frac{1}{\omega_1 \omega_3 \omega_4 \omega_5 \omega_6}\; (2n_1+1) \left(\frac{2}{\hbar\omega_3}\right) \left(\frac{2}{\hbar}\right) \times$$
$$\times \left\{ \frac{(n_4+1)(n_5+1)(n_6+1) - n_4 n_5 n_6}{\omega_4 + \omega_5 + \omega_6} + 3\left[\frac{n_4(n_5+1)(n_6+1) - (n_4+1) n_5 n_6}{\omega_5 + \omega_6 - \omega_4}\right]\right\}$$

(e) $$\beta W_{14} = \sum_{\lambda_1 \cdots \lambda_{10}} V^3(\lambda_1, \lambda_2, \lambda_3)\, V^3(\lambda_4, \lambda_5, \lambda_6)\, V^4(\lambda_7, \ldots, \lambda_{10}) \times$$
$$\times\, 18\; \delta_{1,-4}\, \delta_{2,-5}\, \delta_{3,-6}\, \delta_{7,-9}\, \delta_{8,-10} \times$$
$$\times \int_0^\beta ds_1 \int_0^\beta ds_2 \int_0^\beta ds_3\; D_1(s_1,s_2)\, D_2(s_1,s_2)\, D_3(s_1,s_2)\, D_7(s_3,s_3)\, D_8(s_3,s_3)$$

$$= 18\beta^2 \sum_{\lambda_1\lambda_2\lambda_3\lambda_7\lambda_8} V^3(\lambda_1,\lambda_2,\lambda_3)\, V^3(-\lambda_1,-\lambda_2,-\lambda_3)\, V^4(\lambda_7,\lambda_8,-\lambda_7,-\lambda_8) \times$$

$$\times \left(\frac{\hbar}{2}\right)^5 \frac{1}{\omega_1\omega_2\omega_3\omega_7\omega_8} (2n_7+1)(2n_8+1) \left(\frac{2}{\hbar}\right) \times$$

$$\times \left\{ \frac{(n_1+1)(n_2+1)(n_3+1) - n_1n_2n_3}{\omega_1+\omega_2+\omega_3} + 3\left[\frac{n_1(n_2+1)(n_3+1) - (n_1+1)n_2n_3}{\omega_2+\omega_3-\omega_1}\right]\right\}$$

$$= (\beta W_1) \times (\beta W_2)$$

(f) $$\beta W_{15} = \sum_{\lambda_1\cdots\lambda_{10}} V^3(\lambda_1,\lambda_2,\lambda_3)\, V^3(\lambda_4,\lambda_5,\lambda_6)\, V^3(\lambda_7,\ldots,\lambda_{10}) \times$$

$$\times 216\, \delta_{1,-4}\, \delta_{2,-5}\, \delta_{3,-7}\, \delta_{6,-8}\, \delta_{9,-10} \times$$

$$\times \int_0^\beta ds_1 \int_0^\beta ds_2 \int_0^\beta ds_3\, D_1(s_1,s_2)\, D_2(s_1,s_2)\, D_3(s_1,s_3)\, D_6(s_2,s_3)\, D_9(s_3,s_3)$$

$$= 216\beta \sum_{\lambda_1\lambda_2\lambda_3\lambda_6\lambda_9} V^3(\lambda_1,\lambda_2,\lambda_3)\, V^3(-\lambda_1,-\lambda_2,\lambda_6)\, V^4(-\lambda_3,-\lambda_6,\lambda_9,-\lambda_9) \times$$

$$\times \left(\frac{\hbar}{2}\right)^5 \frac{1}{\omega_1\omega_2\omega_3\omega_6\omega_9} (2n_9+1) \times$$

$$\times \sum_{\alpha_1\alpha_2\alpha_3\alpha_6=\pm1} \frac{\alpha_1\alpha_2\alpha_3\alpha_6}{(a_1+a_2+a_3)} \left\{ T^{(2)}_{3,6}\,(N_1+N_2+1) + \frac{(N_1N_2 - N_1N_6 - N_2N_6 - N_6)}{(a_6-a_1-a_2)} \right\},$$

$$T^{(2)}_{3,6} = \left\{ \begin{array}{ll} \dfrac{(N_3-N_6)}{(a_6-a_3)}, & a_3 \neq a_6 \\ \beta N_3(N_3+1), & a_3 = a_6 \end{array} \right\} \qquad (**)$$

(g) $$\beta W_{16} = \sum_{\lambda_1 \cdots \lambda_{10}} V^3(\lambda_1,\lambda_2,\lambda_3)\, V^3(\lambda_4,\lambda_5,\lambda_6)\, V^4(\lambda_7,\ldots,\lambda_{10}) \times$$

$$\times\ 216\ \delta_{1,-4}\, \delta_{2,-7}\, \delta_{3,-8}\, \delta_{5,-9}\, \delta_{6,-10} \times$$

$$\times \int_0^\beta ds_1 \int_0^\beta ds_2 \int_0^\beta ds_3\ D_1(s_1,s_2)\, D_2(s_1,s_3)\, D_3(s_1,s_3)\, D_5(s_2,s_3)\, D_6(s_2,s_3)$$

$$= 216\,\beta \sum_{\lambda_1\lambda_2\lambda_3\lambda_5\lambda_6} V^3(\lambda_1,\lambda_2,\lambda_3)\, V^3(-\lambda_1,\lambda_5,\lambda_6)\, V^4(-\lambda_2,-\lambda_3,-\lambda_5,-\lambda_6) \times$$

$$\times \left(\frac{\hbar}{2}\right)^5 \frac{1}{\omega_1\omega_2\omega_3\omega_5\omega_6} \sum_{\alpha_1\alpha_2\alpha_3\alpha_5\alpha_6=\pm 1} \frac{\alpha_1\alpha_2\alpha_3\alpha_5\alpha_6}{(a_5+a_6-a_1)} \times$$

$$\times \left\{ \frac{(N_3+1)(N_2+1)(N_5+N_6+1) - (N_5+1)(N_6+1)(N_3+N_2+1)}{a_2+a_3-a_5-a_6} - \right.$$

$$\left. - \frac{(N_5+N_6+1)(N_2N_3 - N_2N_1 - N_3N_1 - N_1)}{a_3+a_2-a_1} \right\}$$

(VII) Contributions from $V_3 - V_3 - V_3 - V_3$ (8)

$$\beta\,[W_{17} + W_{18} + W_{19} + W_{20} + W_{21} + W_{22} + W_{23} + W_{24}]$$

$$= \sum_{\lambda_1\cdots\lambda_{12}} V^3(\lambda_1,\lambda_2,\lambda_3)\, V^3(\lambda_4,\lambda_5,\lambda_6)\, V^3(\lambda_7,\lambda_8,\lambda_9)\, V^3(\lambda_{10},\lambda_{11},\lambda_{12})\, X^{(4)}_{\lambda_1\lambda_2\lambda_3;\lambda_4\lambda_5\lambda_6;\lambda_7\lambda_8\lambda_9;\lambda_{10}\lambda_{11}\lambda_{12}}$$

(a) $$\beta W_{17} = \sum_{\lambda_1\cdots\lambda_{12}} V^3(\lambda_1,\lambda_2,\lambda_3)\, V^3(\lambda_4,\lambda_5,\lambda_6)\, V^3(\lambda_7,\lambda_8,\lambda_9)\, V^3(\lambda_{10},\lambda_{11},\lambda_{12}) \times$$

$$\times\ 243\ \delta_{1,-2}\, \delta_{3,-4}\, \delta_{5,-6}\, \delta_{7,-8}\, \delta_{9,-10}\, \delta_{11,-12} \times$$

$$\times \int_0^\beta ds_1 \int_0^\beta ds_2 \int_0^\beta ds_3 \int_0^\beta ds_4\ D_1(s_1,s_1)\, D_3(s_1,s_2)\, D_5(s_2,s_2)\, D_7(s_3,s_3)\, D_9(s_3,s_4)\, D_{11}(s_4,s_4)$$

$$= 243\ \beta^2 \sum_{\lambda_1\lambda_3\lambda_5\lambda_7\lambda_9\lambda_{11}} V^3(\lambda_1,-\lambda_1,\lambda_3)\, V^3(-\lambda_3,\lambda_5,-\lambda_5) \times$$

$$\times V^3(\lambda_7,-\lambda_7,\lambda_9)\, V^3(-\lambda_9,\lambda_{11},-\lambda_{11}) \left(\frac{\hbar}{2}\right)^6 \frac{1}{\omega_1\omega_3\omega_5\omega_7\omega_9\omega_{11}} \times$$

$$\times\ (2n_1+1)\left(\frac{2}{\hbar\omega_3}\right)(2n_5+1)(2n_7+1)\left(\frac{2}{\hbar\omega_9}\right)(2n_{11}+1)$$

$$= 3\,(\beta W_3)^2$$

(b) $$\beta W_{18} = \sum_{\lambda_1\cdots\lambda_{12}} V^3(\lambda_1,\lambda_2,\lambda_3)\, V^3(\lambda_4,\lambda_5,\lambda_6)\, V^3(\lambda_7,\lambda_8,\lambda_9)\, V^3(\lambda_{10},\lambda_{11},\lambda_{12}) \times$$

$$\times\ 324\ \delta_{1,-2}\,\delta_{3,-4}\,\delta_{5,-6}\,\delta_{7,-10}\,\delta_{8,-11}\,\delta_{9,-12} \times$$

$$\times \int_0^\beta ds_1 \int_0^\beta ds_2 \int_0^\beta ds_3 \int_0^\beta ds_4\ D_1(s_1,s_1) D_3(s_1,s_2)\, D_5(s_2,s_2) D_7(s_3,s_4) D_8(s_3,s_4) D_9(s_3,s_4)$$

$$= 324\,\beta^2 \sum_{\lambda_1\lambda_3\lambda_5\lambda_7\lambda_8\lambda_9} V^3(\lambda_1,-\lambda_1,\lambda_3)\, V^3(-\lambda_3,\lambda_5,-\lambda_5) \times$$

$$\times\ V^3(\lambda_7,\lambda_8,\lambda_9)\, V^3(-\lambda_7,-\lambda_8,-\lambda_9) \left(\frac{\hbar}{2}\right)^6 \frac{1}{\omega_1\omega_3\omega_5\omega_7\omega_8\omega_9} \times$$

$$\times (2n_1+1)\left(\frac{2}{\hbar\omega_3}\right)(2n_5+1)\left(\frac{2}{\hbar}\right)\left\{\frac{(n_7+1)(n_8+1)(n_9+1)-n_7n_8n_9}{\omega_7+\omega_8+\omega_9} + \right.$$

$$\left. + 3\left[\frac{n_7(n_8+1)(n_9+1)-(n_7+1)n_8n_9}{\omega_8+\omega_9-\omega_7}\right]\right\}$$

$$= 6\,(\beta W_2)\times(\beta W_3)$$

(c) $$\beta W_{19} = \sum_{\lambda_1 \cdots \lambda_{12}} V^3(\lambda_1,\lambda_2,\lambda_3)\, V^3(\lambda_4,\lambda_5,\lambda_6)\, V^3(\lambda_7,\lambda_8,\lambda_9)\, V^3(\lambda_{10},\lambda_{11},\lambda_{12}) \times$$

$$\times\, 108\, \delta_{1,-4}\, \delta_{2,-5}\, \delta_{3,-6}\, \delta_{7,-10}\, \delta_{8,-11}\, \delta_{9,-12} \times$$

$$\times \int_0^\beta ds_1 \int_0^\beta ds_2 \int_0^\beta ds_3 \int_0^\beta ds_4\, D_1(s_1,s_2)\, D_2(s_1,s_2)\, D_3(s_1,s_2)\, D_7(s_3,s_4)\, D_8(s_3,s_4)\, D_9(s_3,s_4)$$

$$= 108\beta^2 \sum_{\lambda_1\lambda_2\lambda_3\lambda_7\lambda_8\lambda_9} V^3(\lambda_1,\lambda_2,\lambda_3)\, V^3(-\lambda_1,-\lambda_2,-\lambda_3) \times$$

$$\times\, V^3(\lambda_7,\lambda_8,\lambda_9)\, V^3(-\lambda_7,-\lambda_8,-\lambda_9) \left(\frac{\hbar}{2}\right)^6 \frac{1}{\omega_1\omega_2\omega_3\omega_7\omega_8\omega_9} \times$$

$$\times \left(\frac{2}{\hbar}\right) \left\{ \frac{(n_1+1)(n_2+1)(n_3+1) - n_1 n_2 n_3}{\omega_1+\omega_2+\omega_3} + 3\left[\frac{n_1(n_2+1)(n_3+1)-(n_1+1)n_2 n_3}{\omega_2+\omega_3-\omega_1}\right]\right\} \times$$

$$\times \left(\frac{2}{\hbar}\right) \left\{ \frac{(n_7+1)(n_8+1)(n_9+1) - n_7 n_8 n_9}{\omega_7+\omega_8+\omega_9} + 3\left[\frac{n_7(n_8+1)(n_9+1)-(n_7+1)n_8 n_9}{\omega_8+\omega_9-\omega_7}\right]\right\}$$

$$= 3\,(\beta W_2)^2$$

(d) $$\beta W_{20} = \sum_{\lambda_1 \cdots \lambda_{12}} V^3(\lambda_1,\lambda_2,\lambda_3)\, V^3(\lambda_4,\lambda_5,\lambda_6)\, V^3(\lambda_7,\lambda_8,\lambda_9)\, V^3(\lambda_{10},\lambda_{11},\lambda_{12}) \times$$

$$\times\, 1944\, \delta_{1,-2}\, \delta_{3,-4}\, \delta_{5,-7}\, \delta_{6,-8}\, \delta_{9,-10}\, \delta_{11,-12} \times$$

$$\times \int_0^\beta ds_1 \int_0^\beta ds_2 \int_0^\beta ds_3 \int_0^\beta ds_4\, D_1(s_1,s_1)\, D_3(s_1,s_2)\, D_5(s_2,s_3)\, D_6(s_2,s_3)\, D_9(s_3,s_4)\, D_{11}(s_4,s_4)$$

$$= 1944\beta \sum_{\lambda_1\lambda_3\lambda_5\lambda_6\lambda_9\lambda_{11}} V^3(\lambda_1,-\lambda_1,\lambda_3)\, V^3(-\lambda_3,\lambda_5,\lambda_6) \times$$

$$\times\, V^3(-\lambda_5,-\lambda_6,\lambda_9)\, V^3(-\lambda_9,\lambda_{11},-\lambda_{11}) \left(\frac{\hbar}{2}\right)^6 \frac{1}{\omega_1\omega_3\omega_5\omega_6\omega_9\omega_{11}} \times$$

$$\times (2n_1+1)(2n_{11}+1)\left(\frac{2}{\hbar\omega_3}\right)\left(\frac{2}{\hbar\omega_9}\right)\left(\frac{2}{\hbar}\right) T^{(1)}_{5,6}$$

(e) $$\beta W_{21} = \sum_{\lambda_1\cdots\lambda_{12}} V^3(\lambda_1,\lambda_2,\lambda_3)\, V^3(\lambda_4,\lambda_5,\lambda_6)\, V^3(\lambda_7,\lambda_8,\lambda_9)\, V^3(\lambda_{10},\lambda_{11},\lambda_{12}) \times$$

$$\times\, 648\ \delta_{1,-2}\,\delta_{3,-4}\,\delta_{5,-7}\,\delta_{6,-10}\,\delta_{8,-9}\,\delta_{11,-12}\ \times$$

$$\times \int_0^\beta ds_1 \int_0^\beta ds_2 \int_0^\beta ds_3 \int_0^\beta ds_4\ D_1(s_1,s_1)\, D_3(s_1,s_2)\, D_5(s_2,s_3)\, D_6(s_2,s_4)\, D_8(s_3,s_3)\, D_{11}(s_4,s_4)$$

$$= 648\,\beta \sum_{\lambda_1\lambda_3\lambda_5\lambda_6\lambda_8\lambda_{11}} V^3(\lambda_1,-\lambda_1,\lambda_3)\, V^3(-\lambda_3,\lambda_5,\lambda_6)\ \times$$

$$\times\, V^3(-\lambda_5,\lambda_8,-\lambda_8)\, V^3(-\lambda_6,\lambda_{11},-\lambda_{11}) \left(\frac{\hbar}{2}\right)^6 \frac{1}{\omega_1\omega_3\omega_5\omega_6\omega_8\omega_{11}}\ \times$$

$$\times\ (2n_1+1)(2n_8+1)(2n_{11}+1)\left(\frac{2}{\hbar\omega_3}\right)\left(\frac{2}{\hbar\omega_5}\right)\left(\frac{2}{\hbar\omega_6}\right)$$

(f) $$\beta W_{22} = \sum_{\lambda_1\cdots\lambda_{12}} V^3(\lambda_1,\lambda_2,\lambda_3)\, V^3(\lambda_4,\lambda_5,\lambda_6)\, V^3(\lambda_7,\lambda_8,\lambda_9)\, V^3(\lambda_{10},\lambda_{11},\lambda_{12}) \times$$

$$\times\, 3888\ \delta_{1,-2}\,\delta_{3,-4}\,\delta_{5,-7}\,\delta_{6,-10}\,\delta_{8,-11}\,\delta_{9,-12}\ \times$$

$$\times \int_0^\beta ds_1 \int_0^\beta ds_2 \int_0^\beta ds_3 \int_0^\beta ds_4\ D_1(s_1,s_1)\, D_3(s_1,s_2)\, D_5(s_2,s_3)\, D_6(s_2,s_4)\, D_8(s_3,s_4)\, D_9(s_3,s_4)$$

$$= 3888\,\beta \sum_{\lambda_1\lambda_3\lambda_5\lambda_6\lambda_8\lambda_9} V^3(\lambda_1,-\lambda_1,\lambda_3)\, V^3(-\lambda_3,\lambda_5,\lambda_6)\ \times$$

$$\times\, V^3(-\lambda_5,\lambda_8,\lambda_9)\, V^3(-\lambda_6,-\lambda_8,-\lambda_9) \left(\frac{\hbar}{2}\right)^6 \frac{1}{\omega_1\omega_3\omega_5\omega_6\omega_8\omega_9}\ \times$$

$$\times\ (2n_1+1)\left(\frac{2}{\hbar\omega_3}\right) \times \left\{ \sum_{\alpha_5\alpha_6\alpha_8\alpha_9=\pm1} \frac{\alpha_5\alpha_6\alpha_8\alpha_9}{(a_5+a_8+a_9)}\ \times\right.$$

$$\times\left[ (N_8+N_9+1)\, T^{(2)}_{5,6} + \frac{(N_8 N_9 - N_6 N_8 - N_6 N_9 - N_6)}{(a_6 - a_8 - a_9)} \right]\Bigg\}$$

(g)
$$\beta W_{23} = \sum_{\lambda_1 \cdots \lambda_{12}} V^3(\lambda_1,\lambda_2,\lambda_3)\, V^3(\lambda_4,\lambda_5,\lambda_6)\, V^3(\lambda_7,\lambda_8,\lambda_9)\, V^3(\lambda_{10},\lambda_{11},\lambda_{12}) \times$$

$$\times\, 1944\, \delta_{1,-4}\, \delta_{2,-5}\, \delta_{3,-7}\, \delta_{6,-10}\, \delta_{8,-11}\, \delta_{9,-12} \times$$

$$\times \int_0^\beta ds_1 \int_0^\beta ds_2 \int_0^\beta ds_3 \int_0^\beta ds_4\, D_1(s_1,s_2)\, D_2(s_1,s_2)\, D_3(s_1,s_3)\, D_6(s_2,s_4)\, D_8(s_3,s_4)\, D_9(s_3,s_4)$$

$$= 1944\, \beta \sum_{\lambda_1\lambda_2\lambda_3\lambda_6\lambda_8\lambda_9} V^3(\lambda_1,\lambda_2,\lambda_3)\, V^3(-\lambda_1,-\lambda_2,\lambda_6) \times$$

$$\times V^3(-\lambda_3,\lambda_8,\lambda_9)\, V^3(-\lambda_6,-\lambda_8,-\lambda_9) \left(\frac{\hbar}{2}\right)^6 \frac{1}{\omega_1\omega_2\omega_3\omega_6\omega_8\omega_9} \times$$

$$\times \sum_{\alpha_1\alpha_2\alpha_3\alpha_6\alpha_8\alpha_9=\pm 1} \frac{\alpha_1\alpha_2\alpha_3\alpha_6\alpha_8\alpha_9}{(a_3-a_2-a_1)(a_6-a_8-a_9)} \times$$

$$\times \Bigg\{ \frac{(N_8+N_9+1)\left[(N_1+1)(N_2+1)N_6 - N_1N_2(N_6+1)\right]}{(a_6-a_1-a_2)} +$$

$$+ \frac{N_1N_2(N_8+1)(N_9+1) - (N_1+1)(N_2+1)N_8N_9}{(a_8+a_9-a_1-a_2)} +$$

$$+ \frac{(N_1+N_2+1)\left[N_3(N_8+1)(N_9+1) - (N_3+1)N_8N_9\right]}{(a_3-a_8-a_9)} +$$

$$+ (N_1+N_2+1)(N_8+N_9+1)\, T^{(2)}_{3,6} \Bigg\}$$

(h) $$\beta W_{24} = \sum_{\lambda_1 \cdots \lambda_{12}} V^3(\lambda_1,\lambda_2,\lambda_3)\, V^3(\lambda_4,\lambda_5,\lambda_6)\, V^3(\lambda_7,\lambda_8,\lambda_9)\, V^3(\lambda_{10},\lambda_{11},\lambda_{12}) \times$$

$$\times\ 1296\ \delta_{1,-4}\, \delta_{2,-7}\, \delta_{3,-10}\, \delta_{5,-8}\, \delta_{6,-11}\, \delta_{9,-12}$$

$$\times \int_0^\beta ds_1 \int_0^\beta ds_2 \int_0^\beta ds_3 \int_0^\beta ds_4\ D_1(s_1,s_2)\, D_2(s_1,s_3)\, D_3(s_1,s_4)\, D_5(s_2,s_3)\, D_6(s_2,s_4)\, D_9(s_3,s_4)$$

$$= 1296\,\beta \sum_{\lambda_1\lambda_2\lambda_3\lambda_5\lambda_6\lambda_9} V^3(\lambda_1,\lambda_2,\lambda_3)\, V^3(-\lambda_1,\lambda_5,\lambda_6) \times$$

$$\times\ V^3(-\lambda_2,-\lambda_5,\lambda_9)\, V^3(-\lambda_3,-\lambda_6,-\lambda_9) \left(\frac{\hbar}{2}\right)^6 \frac{1}{\omega_1\omega_2\omega_3\omega_5\omega_6\omega_9} \times$$

$$\times \sum_{\alpha_1\alpha_2\alpha_3\alpha_5\alpha_6\alpha_9 = \pm 1} \frac{\alpha_1\alpha_2\alpha_3\alpha_5\alpha_6\alpha_9}{(a_9+a_6-a_3)} \left[Y_1+Y_2+Y_3+Y_4+Y_5+Y_6\right],$$

$$Y_1 = \frac{(N_1+1)\, N_3 N_5 (N_9+1) - N_1 (N_3+1)(N_5+1) N_9}{(a_2+a_5-a_9)(a_1-a_3-a_5+a_9)}$$

$$Y_2 = \frac{(N_2-N_9)\left[(N_1+1) N_5 N_6 - N_1 (N_5+1)(N_6+1)\right]}{(a_2+a_5-a_9)(a_1-a_5-a_6)}$$

$$Y_3 = \frac{(N_9-N_5)\left[(N_1+1)(N_2+1) N_3 - N_1 N_2 (N_3+1)\right]}{(a_2+a_5-a_9)(a_1+a_2-a_3)}$$

$$Y_4 = \frac{N_1 N_2 (N_6+1)(N_9+1) - (N_1+1)(N_2+1) N_6 N_9}{(a_2+a_5-a_9)(a_1+a_2-a_6-a_9)}$$

$$Y_5 = \frac{(N_3-N_2)\left[(N_1+1) N_5 N_6 - N_1 (N_5+1)(N_6+1)\right]}{(a_1-a_5-a_6)(a_2-a_3+a_5+a_6)}$$

$$Y_6 = \frac{(N_5+N_6+1)\,[(N_1+1)(N_2+1)N_3 - N_1N_2(N_3+1)]}{(a_1+a_2-a_3)(a_2-a_3+a_5+a_6)}$$

The Helmholtz free energy F, is given by

$$F = -k_B T \ln Z$$

If in Eq. (8.2), we write $Z = Z_0(1+Z_1)$, where $Z_1$ is the contribution to $Z$ from the anharmonic terms, then

$$F = -k_B T \ln Z_0 - k_B T \ln(1+Z_1) \qquad (8.4)$$

For perturbation theory to be of any use, $|Z_1| < 1$ . Hence, we can expand $\ln(1+Z_1)$ in a Taylor series and keep all terms that contribute to F to $O(\lambda^4)$ . Substituting the above derived expressions for $X^{(n)}_{\lambda_1'\cdots\lambda_p^n}$ into Eq. (8.2), we obtain

$$-k_B T \ln(1+Z_1) = -k_B T \sum_{n=1}^{+\infty} \frac{(-1)^{n+1}}{n} Z_1^n$$

$$= -k_B T \left[ Z_1 - \tfrac{1}{2} Z_1^2 \right] \qquad (\text{to } O(\lambda^4))$$

$$= \Big\{ W_1 - \tfrac{1}{2!}[W_2+W_3] + W_4 - \tfrac{2}{2!}[W_5+W_6] -$$

$$- \tfrac{1}{2!}[W_7+W_8+W_9] +$$

$$+ \tfrac{3}{3!}[W_{10}+W_{11}+W_{12}+W_{13}+W_{14}+W_{15}+W_{16}] -$$

$$- \tfrac{1}{4!}[W_{17}+W_{18}+W_{19}+W_{20}+W_{21}+W_{22}+W_{23}+W_{24}]\Big\} +$$

$$+\frac{\beta}{2}\left\{W_1 - \frac{1}{2!}\left[W_2+W_3\right]\right\}^2 \qquad (\text{to } O(\lambda^4))$$

$$= W_1 - \frac{1}{2}\left[W_2+W_3\right] + W_4 - \left[W_5+W_6\right] - \frac{1}{2}\left[W_8+W_9\right] +$$

$$+\frac{1}{2}\left[W_{11}+W_{12}+W_{13}+W_{15}+W_{16}\right] -$$

$$-\frac{1}{24}\left[W_{20}+W_{21}+W_{22}+W_{23}+W_{24}\right] \qquad (8.5)$$

From Eq. (6.8), $-\frac{1}{\beta}\ln Z_0 = \frac{1}{\beta}\sum_{\lambda_r}\ln\left[2\sinh\left(\frac{1}{2}\beta\hbar\omega_{\lambda_r}\right)\right]$ (8.6)

The free energy is given by Eqs. (8.4), (8.5), and (8.6).

Observe that to $O(\lambda^4)$, there are no contributions from the terms $W_7$, $W_{10}$, $W_{14}$, $W_{17}$, $W_{18}$, and $W_{19}$ because of cancellation.

If every atom of the crystal is a centre of inversion symmetry, the contributions from $W_3, W_5, W_{11}, W_{12}, W_{13}, W_{20}, W_{21}$, and $W_{22}$ are zero. This follows from the symmetry properties of $V^n(\lambda_1,\ldots,\lambda_n)$, (Shukla and Muller (1970)).

Shukla and Cowley (1971) have evaluated the contributions to F to $O(\lambda^4)$ from $W_1$, $W_2$, $W_4$, $W_6$, $W_8$, $W_9$, $W_{15}$, $W_{16}$, $W_{23}$, and $W_{24}$ in Fourier space. To make a comparison of the results obtained here with their results, one has to try to match the various $\lambda_j$ symbols, and remember that the coefficient $V^n(\lambda_1,\cdots,\lambda_n)$ does not contain the factor $\left[\frac{\hbar^n}{2^n\omega_1\cdots\omega_n}\right]^{\frac{1}{2}}$. We have made the comparisons for most terms and they agree. It should also be noted that the results of Papadopolous (1969), to $O(\lambda^2)$, appear quite different from the results obtained here, but if one further simplifies his results they will reduce to the results obtained here.

The various sequences of functional differentiations arising in the evaluation of $W_1, \ldots, W_{24}$ can be described in the form of Feynman diagrams. Recall from Eqs. (6.11), (6.18), and (8.1),

$$X^{(n)}_{\lambda_1^1 \cdots \lambda_m^1 ; \lambda_1^2 \cdots \lambda_p^n} = \int_0^\beta ds_1 \cdots \int_0^\beta ds_n \frac{\delta}{\delta J_{\lambda_1^1}(s_1)} \cdots \frac{\delta}{\delta J_{\lambda_m^1}(s_1)} \frac{\delta}{\delta J_{\lambda_1^2}(s_2)} \cdots \frac{\delta}{\delta J_{\lambda_p^n}(s_n)} e^{(JKJ)} \Big|_{J=0}$$

As can be observed from the above equation, there must be an even number of $\lambda_j^k s$. Draw a dot for each of the different variables of integration. The number of dots equals the number of anharmonic coefficients. One must perform the functional differentiations in pairs, since

$$\frac{\delta^2}{\delta J_{\lambda_r^k}(s_k) \delta J_{\lambda_{r_1}^{k_1}}(s_{k_1})} (JKJ) = D_{\lambda_r^k}(s_k, s_{k_1}) \delta_{\lambda_r^k, -\lambda_{r_1}^{k_1}}$$

Draw a line joining $s_k$ to $s_{k_1}$. Continue in this manner till all differentiations are done. For the diagrams representing $W_1, \ldots, W_{24}$, see fig. 2.

As a final note, we present some general methods of evaluating certain types of integrals which arise in the evaluation of $W_1, \ldots, W_{24}$, in appendix 2. In appendix 3, we indicate some of the necessary steps to get the high and zero temperature results without having to perform a full calculation.

Figure 2: All diagrams relating to the functional differentiation in the derivation of the Helmholtz free energy to $O(\lambda^4)$

FIG. 2

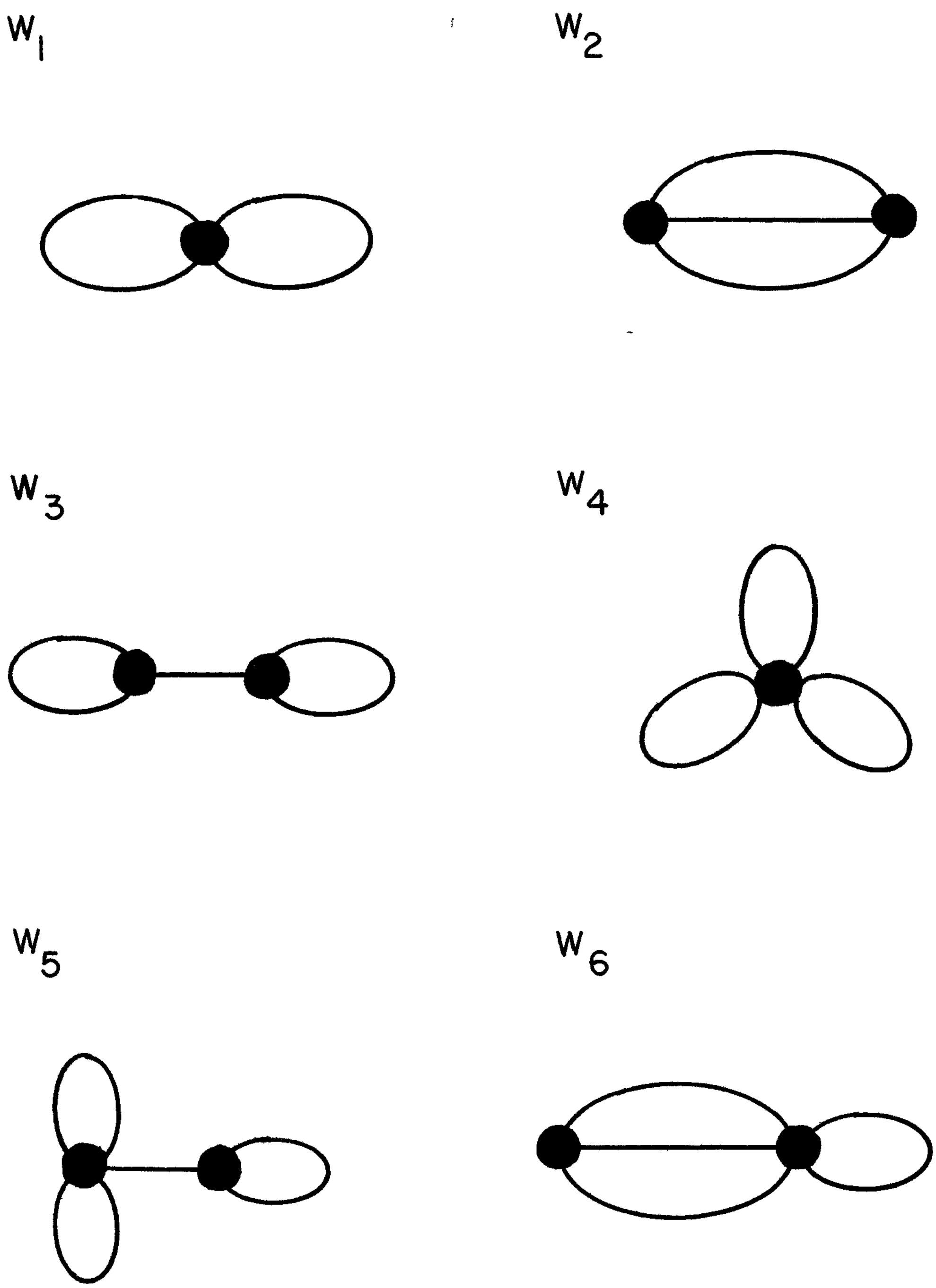


FIG. 2

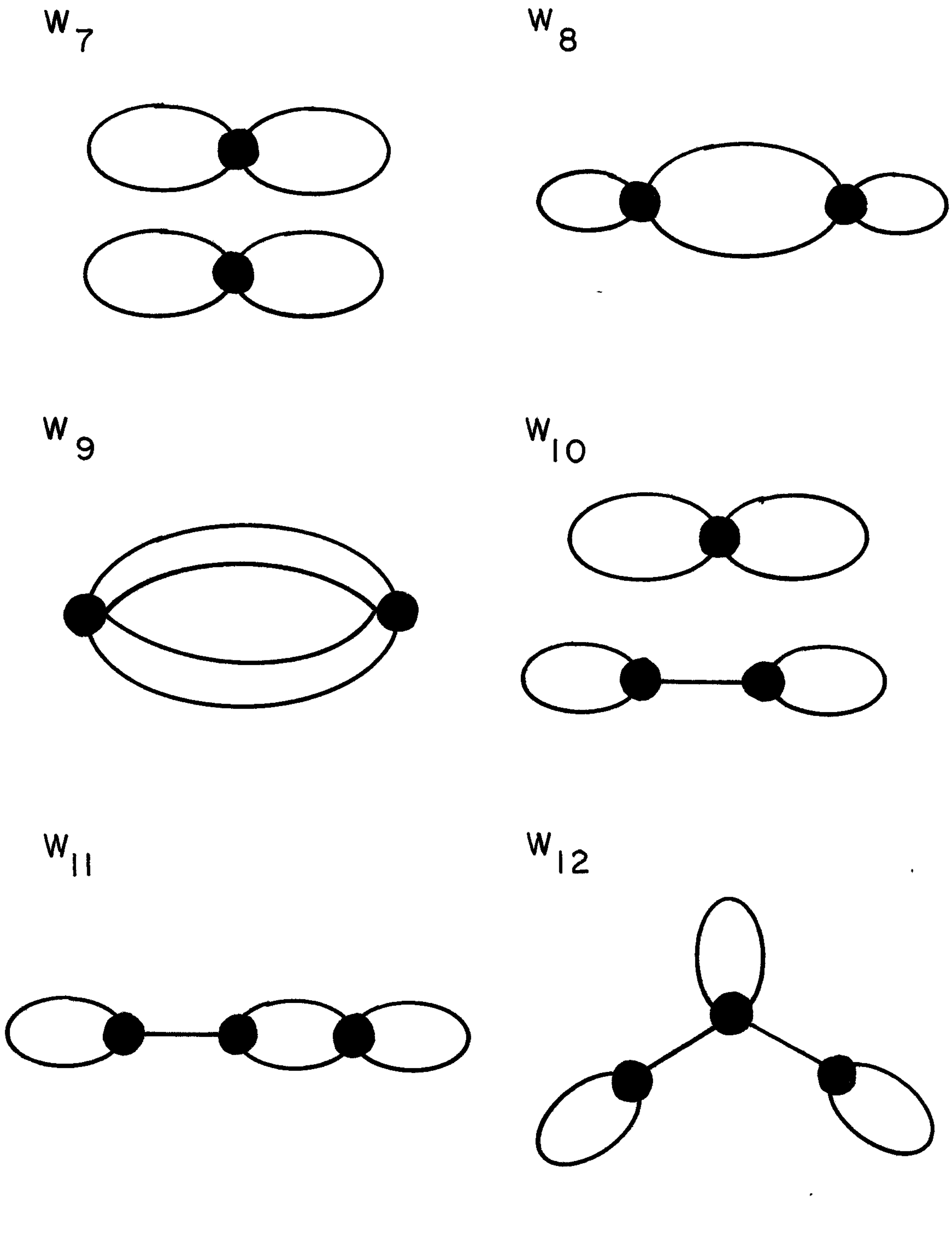
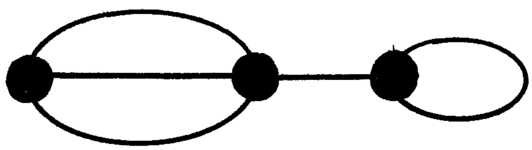
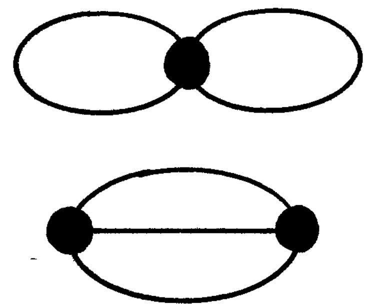


FIG. 2

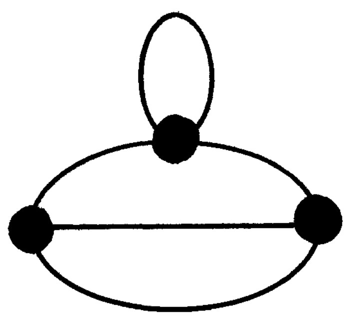
$W_{13}$



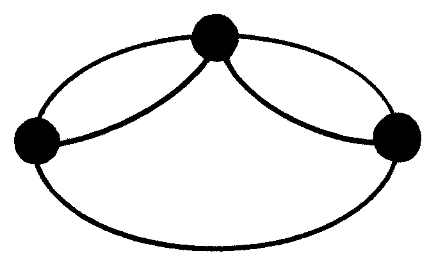
$W_{14}$



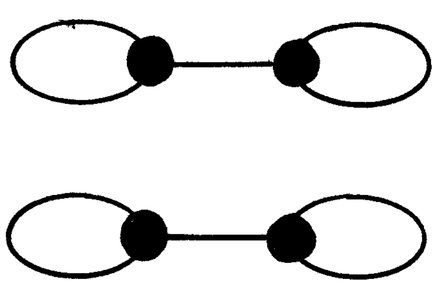
$W_{15}$



$W_{16}$



$W_{17}$



$W_{18}$

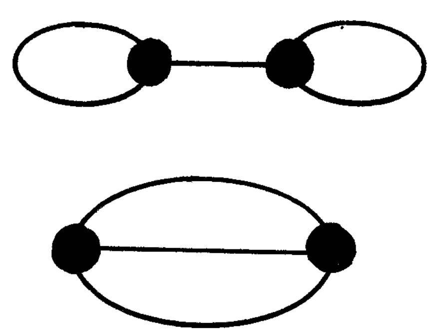
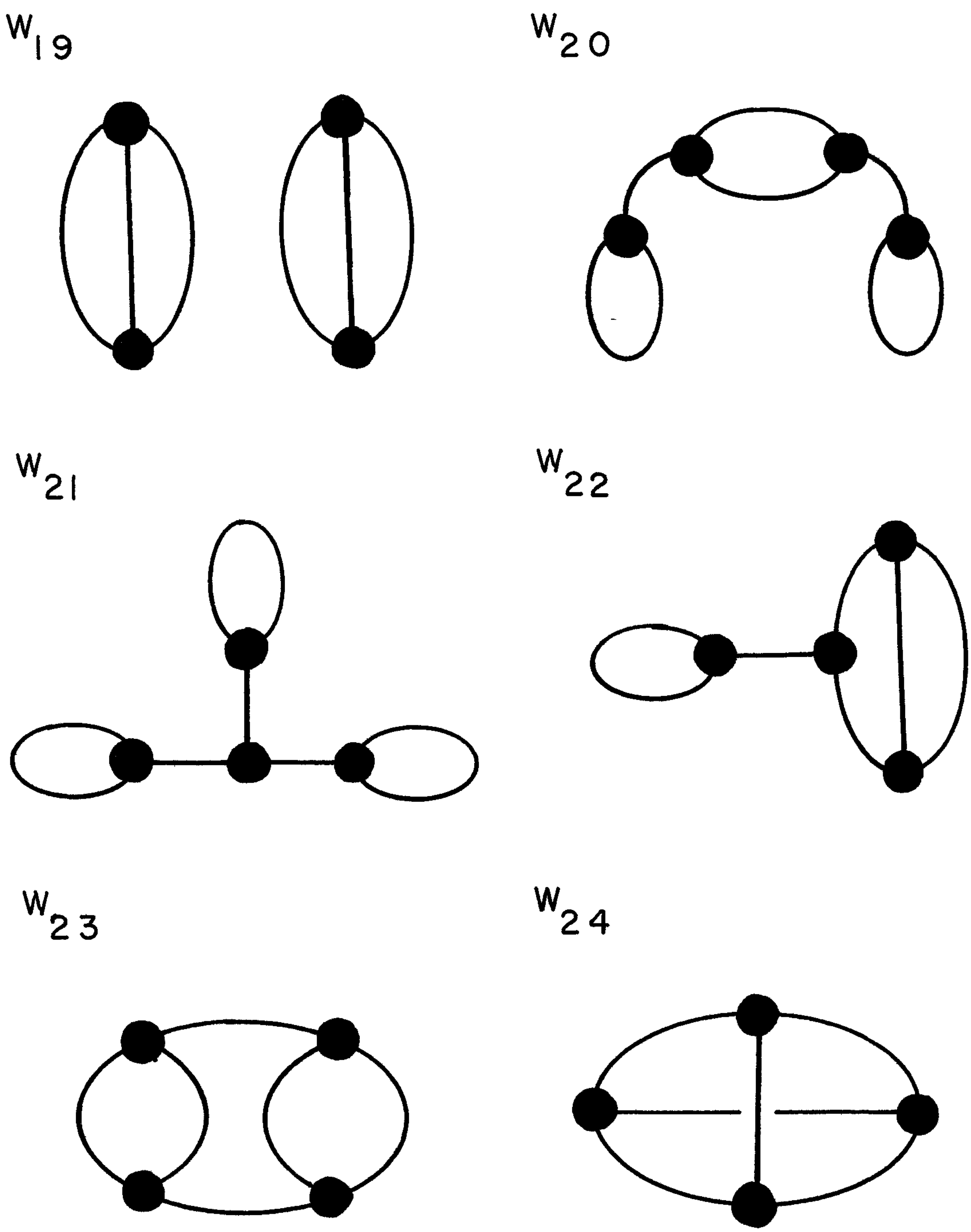


FIG. 2



## 9. The Debye-Waller Factor to $O(\lambda^2)$ and $O(|\vec{K}|^4)$

As a further example of the use of the method of Papadopolous, we evaluate the anharmonic contributions to the Debye-Waller factor to $O(\lambda^2)$ and $O(|\vec{K}|^4)$, (this will be defined later), for all temperatures.

For theoretical calculations of scattering intensities from x-ray or neutron scattering, etc., the averages needed differ from those of the free energy. When one calculates the intensities, the Debye-Waller factor enters. From the viewpoint of perturbation theory, one must determine what one wants to use as a perturbation parameter in the evaluation of the Debye-Waller factor. One can use the scattering vector $\vec{K}$ , or the Van Hove ordering parameter $\lambda$ , or both. In the work presented in this thesis, we do the expansions to $O(\lambda^2)$ because this gives the lowest non-zero anharmonic contributions to the Debye-Waller factor, and to $O(|\vec{K}|^4)$ because the terms of $O(|\vec{K}|^2)$ and $O(|\vec{K}|^4)$ are of $O(\lambda^2)$ . The terms of $O(|\vec{K}|^2)$ and $O(|\vec{K}|^4)$ provide the temperature dependences of $O(T^2)$ and $O(T^3)$, respectively, in the high temperature limit.

Maradudin and Flinn (1963) have evaluated these anharmonic contributions in the classical (high temperature) limit. We will use their notation and evaluate the contributions that they evaluated to the Debye-Waller factor. We then show that in the high temperature limit, our results reduce to their results.

In evaluating the expression for the observed intensity of x-rays scattered by the crystal, we must evaluate the following thermal average, (Maradudin and Flinn (1963)), $\left\langle e^{i\vec{K}\cdot[\vec{u}(\ell)-\vec{u}(\ell')]}\right\rangle$, where $\vec{K}$ is the scattering vector, and $\vec{u}(\ell)$, $\vec{u}(\ell')$ are the usual displacements of the atoms from their equilibrium positions in a monatomic lattice.

Introducing the eigenvector Fourier representation of $\vec{u}(\ell)$, and noting that $\vec{q}=2\pi\vec{k}$, where $\vec{k}$ is the same as in Maradudin and Flinn (1963), we have

$$u_\alpha(\ell) = \frac{1}{\sqrt{NM}} \sum_{\vec{q}_r j_r} \varepsilon_\alpha(\vec{q}_r j_r)\, Q(\vec{q}_r j_r)\, e^{i\vec{q}_r\cdot\vec{x}(\ell)}$$

The Lagrangian to $O(\lambda^2)$ is given by

$$L = L_0 - L_A \tag{9.1}$$

where

$$\begin{aligned} L_0 &= \frac{1}{2}\sum_{\vec{q}_r j_r}\left[\dot{Q}(\vec{q}_r j_r)\,\dot{Q}(-\vec{q}_r j_r) - \omega^2(\vec{q}_r j_r)\, Q(\vec{q}_r j_r)\, Q(-\vec{q}_r j_r)\right] \\ &= \frac{1}{2}\sum_{\lambda_r}\left[\dot{Q}_{\lambda_r}\dot{Q}_{-\lambda_r} - \omega^2_{\lambda_r} Q_{\lambda_r} Q_{\lambda_r}\right] \end{aligned} \tag{9.2}$$

$$\begin{aligned} L_A &= \sum_{\lambda_1\lambda_2\lambda_3} V^3(\lambda_1,\lambda_2,\lambda_3)\, Q_{\lambda_1}Q_{\lambda_2}Q_{\lambda_3} + \sum_{\lambda_1\cdots\lambda_4} V^4(\lambda_1,\dots,\lambda_4)\, Q_{\lambda_1}Q_{\lambda_2}Q_{\lambda_3}Q_{\lambda_4} \\ &= \frac{1}{6\sqrt{N}}\sum_{\lambda_1\lambda_2\lambda_3}\Delta(\vec{q}_1+\vec{q}_2+\vec{q}_3)\,\Phi^3(\lambda_1,\lambda_2,\lambda_3)\, Q_{\lambda_1}Q_{\lambda_2}Q_{\lambda_3} + \\ &\quad + \frac{1}{24N}\sum_{\lambda_1\cdots\lambda_4}\Delta(\vec{q}_1+\dots+\vec{q}_4)\,\Phi^4(\lambda_1,\dots,\lambda_4)\, Q_{\lambda_1}Q_{\lambda_2}Q_{\lambda_3}Q_{\lambda_4} \end{aligned} \tag{9.3}$$

Further, $\vec{K}\cdot[\vec{u}(\ell)-\vec{u}(\ell')] = \sum_{\lambda_r} C(\lambda_r)\, Q_{\lambda_r}$, (here $Q_{\lambda_r} \equiv Q_{\lambda_r}(0)$ ) (9.4) where $$C(\lambda_r) = \frac{[\vec{K}\cdot\vec{\varepsilon}(\lambda_r)]}{\sqrt{NM}}\left[e^{i\vec{q}_r\cdot\vec{x}(\ell)} - e^{i\vec{q}_r\cdot\vec{x}(\ell')}\right]$$

Then, by arguments given in section 3,

$$\left\langle e^{i\vec{K}\cdot[\vec{u}(\ell)-\vec{u}(\ell')]}\right\rangle = \left\langle e^{i\sum_{\lambda_r} C(\lambda_r)Q_{\lambda_r}}\right\rangle$$
$$= \frac{1}{Z}\int d\underset{\sim}{\xi}\, \rho(\underset{\sim}{\xi},\underset{\sim}{\xi})\, e^{i\sum_{\lambda_r} C(\lambda_r)Q_{\lambda_r}} \qquad (9.5)$$

where $\rho(\underset{\sim}{\xi},\underset{\sim}{\xi})$ is the density matrix and $Z$ is the partition function of the system.

In evaluating the partition function $Z$, we are essentially evaluating $\langle 1\rangle$, save for the normalizing factor, which happens to be $Z$. In the method of Papadopolous, we used a source term in evaluating $Z$. The source term was essentially an exponential function whose argument was linear in $Q_{\lambda_r}$. Now, we wish to calculate $\left\langle e^{i\sum_{\lambda_r} C(\lambda_r)Q_{\lambda_r}}\right\rangle$. The argument of the exponential function is again linear in $Q_{\lambda_r}$. We again will derive a generator for calculating $\left\langle e^{i\sum_{\lambda_r} C(\lambda_r)Q_{\lambda_r}}\right\rangle$, but with some manipulations, one can avoid extra work.

The generator we have found in this case is;

$$E = \int_{\underset{\sim}{Q}(0)=\underset{\sim}{\xi}}^{\underset{\sim}{Q}(\beta)=\underset{\sim}{\xi}} d\underset{\sim}{\xi}\; e^{i\sum_{\lambda_r} C(\lambda_r)\xi_{\lambda_r}}\, G_1 \qquad (9.6)$$

where

$$G_1 = \int_{\underset{\sim}{Q}(0)=\underset{\sim}{\xi}}^{\underset{\sim}{Q}(\beta)=\underset{\sim}{\xi}} \mathcal{D}[\underset{\sim}{Q}(s)]\exp\left\{-\sum_{\lambda_r}\int_0^\beta ds\left[\frac{1}{2\hbar^2}\dot{Q}_{\lambda_r}(s)\dot{Q}_{-\lambda_r}(s) + \frac{\omega_{\lambda_r}^2}{2}Q_{\lambda_r}(s)Q_{-\lambda_r}(s) - J_{\lambda_r}(s)\,Q_{\lambda_r}(s)\right]\right\}$$

The following operations performed will be purely formal. The only justification given will be that the final results make sense.

We make the following definition. Let

$$P_{\lambda_r}(s) = J_{\lambda_r}(s) + i\,\delta(s)\,C(\lambda_r)$$

where $\delta(s)$ is the Dirac delta function. We use the property that $\int_0^\beta \delta(s)\,ds = 1$. To be more mathematically precise, we should use $\delta(s-\alpha)$ for $\alpha \to 0^+$, $0<\alpha<\beta$.

Then,

$$E = \int d\underset{\sim}{\xi} \int_{\underset{\sim}{\xi}}^{\underset{\sim}{\xi}} \mathcal{D}[\underset{\sim}{Q}(s)]\, \exp\Big\{-\sum_{\lambda_r}\int_0^\beta ds\,\Big[\dot{Q}_{\lambda_r}(s)\,\dot{Q}_{-\lambda_r}(s) + \frac{\omega_{\lambda_r}^2}{2} Q_{\lambda_r}(s)\,Q_{-\lambda_r}(s) - P_{\lambda_r}(s)\,Q_{\lambda_r}(s)\Big]\Big\}$$

$$= Z_0 \exp\Big\{\sum_{\lambda_r\lambda_r'}\int_0^\beta ds\int_0^\beta ds'\,P_{\lambda_r}(s)\,P_{\lambda_r'}(s')\,K_{\lambda_r\lambda_r'}(s,s')\Big\}$$

(see Eq. (6.16))

$$= Z_0 \exp\Big\{\sum_{\lambda_r\lambda_r'}\int_0^\beta ds\int_0^\beta ds'\,[J_{\lambda_r}(s)+i\delta(s)C(\lambda_r)]\,[J_{\lambda_r'}(s')+i\delta(s')C(\lambda_r')]\times \times K_{\lambda_r\lambda_r'}(s,s')\Big\}$$

$$= Z_0 \exp\Big\{-\sum_{\lambda_r\lambda_r'} K_{\lambda_r\lambda_r'}(0,0)\,C(\lambda_r)\,C(\lambda_r')\Big\}\times$$

$$\times \exp\Big\{\sum_{\lambda_r\lambda_r'}\int_0^\beta ds\int_0^\beta ds'\,J_{\lambda_r}(s)\,J_{\lambda_r'}(s')\,K_{\lambda_r\lambda_r'}(s,s')\Big\}\times$$

$$\times \exp\Big\{i\sum_{\lambda_r\lambda_r'}\int_0^\beta ds\,\big[J_{\lambda_r}(s)\,C(\lambda_r')\,K_{\lambda_r\lambda_r'}(s,0) + J_{\lambda_r'}(s)\,C(\lambda_r)\,K_{\lambda_r\lambda_r'}(0,s)\big]\Big\} \tag{9.7}$$

Let

$$A = \exp\left\{-\sum_{\lambda_r\lambda_r'} K_{\lambda_r\lambda_r'}(0,0)\, C(\lambda_r)C(\lambda_r')\right\}$$

$$= \exp\left\{-\sum_{\lambda_r}\frac{\hbar}{4\omega_{\lambda_r}}\coth\left(\tfrac{1}{2}\beta\hbar\omega_{\lambda_r}\right) C(\lambda_r)C(-\lambda_r)\right\}$$

$$= \exp\left\{-\frac{\hbar}{2NM}\sum_{\lambda_r}\frac{1}{\omega_{\lambda_r}}\coth\left(\tfrac{1}{2}\beta\hbar\omega_{\lambda_r}\right)[\vec{K}\cdot\vec{\varepsilon}(\lambda_r)][\vec{K}\cdot\vec{\varepsilon}(-\lambda_r)]\times\right.$$

$$\left.\times\left(1-\cos[\vec{q}_r\cdot(\vec{x}(\ell)-\vec{x}(\ell'))]\right)\right\} \qquad (9.8)$$

$$\equiv \left\langle e^{i\sum_{\lambda_r} C(\lambda_r)Q_{\lambda_r}}\right\rangle_0$$ , (the harmonic average)

$$A(T\uparrow+\infty) = \exp\left\{-\frac{1}{\beta NM}\sum_{\lambda_r}\frac{[\vec{K}\cdot\vec{\varepsilon}(\lambda_r)][\vec{K}\cdot\vec{\varepsilon}(-\lambda_r)]}{\omega_{\lambda_r}^2}\times\right.$$

$$\left.\times\left[1-\cos(\vec{q}_r\cdot[\vec{x}(\ell)-\vec{x}(\ell')])\right]\right\}$$

which is the high temperature (classical) limit.

Further,

$$i\sum_{\lambda_r\lambda_r'}\int_0^\beta ds\,\left[J_{\lambda_r}(s)\,C(\lambda_r')\,K_{\lambda_r\lambda_r'}(s,0) + J_{\lambda_r'}(s)\,C(\lambda_r)\,K_{\lambda_r\lambda_r'}(0,s)\right]$$

$$= i\sum_{\lambda_r\lambda_r'} C(\lambda_r')\int_0^\beta ds\, J_{\lambda_r}(s)\left[K_{\lambda_r\lambda_r'}(s,0) + K_{\lambda_r'\lambda_r}(0,s)\right]$$

$$= i\sum_{\lambda_r\lambda_r'} C(\lambda_r')\,\delta_{\lambda_r,-\lambda_r'}\int_0^\beta ds\, J_{\lambda_r}(s)\, D_{\lambda_r}(s,0)$$ , (see Eq. (8.3))

$$= i\sum_{\lambda_r} C(-\lambda_r)\int_0^\beta ds\, J_{\lambda_r}(s)\, D_{\lambda_r}(s,0) \qquad (9.9)$$

$$\equiv \gamma\,(DJ)$$ , ( $\gamma$ is the ordering parameter for $\vec{K}$ )

$$\equiv \sum_{\lambda_r} i\,C(-\lambda_r)\,(DJ)_{\lambda_r}$$

Let $$(JKJ) = \sum_{\lambda_r \lambda_r'} \int_0^\beta ds \int_0^\beta ds'\, J_{\lambda_r}(s)\, J_{\lambda_r'}(s')\, K_{\lambda_r \lambda_r'}(s,s')$$

as in section 6.

Then, $$E = A\, Z_0 \exp\left[\gamma(DJ) + (JKJ)\right] \tag{9.10}$$

Observe that to generate the various terms in the perturbation expansion of the numerator and denominator of Eq. (9.5), we employ the method of functional differentiation of the source term for the functionals E and G , respectively, and then set it equal to zero as was done in section 6.

Hence, to $O(\lambda^2)$ ,

$$\left\langle e^{i\vec{K}\cdot[\vec{u}(\ell)-\vec{u}(\ell')]}\right\rangle = \frac{NUM}{DEN} \tag{9.11}$$

$$NUM = A Z_0 \Big\{ 1 - \sum_{\lambda_1\lambda_2\lambda_3} V^3(\lambda_1,\lambda_2,\lambda_3)\, R^{(1)}_{\lambda_1\lambda_2\lambda_3} - \sum_{\lambda_1\cdots\lambda_4} V^4(\lambda_1,\dots,\lambda_4)\, R^{(1)}_{\lambda_1\cdots\lambda_4} + \frac{1}{2!}\sum_{\lambda_1\cdots\lambda_6} V^3(\lambda_1,\lambda_2,\lambda_3)\, V^3(\lambda_4,\lambda_5,\lambda_6)\, R^{(2)}_{\lambda_1\lambda_2\lambda_3;\lambda_4\lambda_5\lambda_6} \Big\}$$

$$DEN = Z_0 \Big\{ 1 - \sum_{\lambda_1\cdots\lambda_4} V^4(\lambda_1,\dots,\lambda_4)\, X^{(1)}_{\lambda_1\cdots\lambda_4} + \frac{1}{2!}\sum_{\lambda_1\cdots\lambda_6} V^3(\lambda_1,\lambda_2,\lambda_3)\, V^3(\lambda_4,\lambda_5,\lambda_6)\, X^{(2)}_{\lambda_1\cdots\lambda_6} \Big\}$$

$$\equiv Z_0 \left\{ 1 - Y_1 + \frac{1}{2} Y_2 \right\}$$

where $X^{(n)}_{\lambda_1'\cdots\lambda_p^n}$ is defined by Eq. (8.1), and $R^{(n)}_{\lambda_1'\cdots\lambda_p^n}$ is obtained in the same manner as $X^{(n)}_{\lambda_1'\cdots\lambda_p^n}$ , but we use E as a generator instead of G.

In the following, we will indicate the various terms to be evaluated in Eq. (9.11), evaluate them for the finite temperature case, and then take the high temperature limit of the various terms. We use the notation of section 8.

First, we examine the two terms in the denominator, (see sec. 8), viz.,

(i) $$Y_1 = \sum_{\lambda_1 \cdots \lambda_4} V^4(\lambda_1, \ldots, \lambda_4)\, X^{(1)}_{\lambda_1 \cdots \lambda_4}$$

$$= \sum_{\lambda_1 \cdots \lambda_4} V^4(\lambda_1, \ldots, \lambda_4) \int_0^\beta ds \frac{\delta^4}{\delta J_{\lambda_1}(s)\, \delta J_{\lambda_2}(s)\, \delta J_{\lambda_3}(s)\, \delta J_{\lambda_4}(s)} \frac{(JKJ)^2}{2!}$$

(ii) $$Y_2 = \sum_{\lambda_1 \cdots \lambda_6} V^3(\lambda_1, \lambda_2, \lambda_3)\, V^3(\lambda_4, \lambda_5, \lambda_6)\, X^{(2)}_{\lambda_1 \lambda_2 \lambda_3 ; \lambda_4 \lambda_5 \lambda_6}$$

$$= \sum_{\lambda_1 \cdots \lambda_6} V^3(\lambda_1, \lambda_2, \lambda_3)\, V^3(\lambda_4, \lambda_5, \lambda_6) \times$$

$$\times \int_0^\beta ds_1 \int_0^\beta ds_2 \frac{\delta^3}{\delta J_{\lambda_1}(s_1)\, \delta J_{\lambda_2}(s_1)\, \delta J_{\lambda_3}(s_1)} \frac{\delta^3}{\delta J_{\lambda_4}(s_2)\, \delta J_{\lambda_5}(s_2)\, \delta J_{\lambda_6}(s_2)} \frac{(JKJ)^3}{3!}$$

Now, we examine the numerator where we note that, for example, $R^{(1)}_{\lambda_1 \lambda_2 \lambda_3}$ can be written in the following functional differentiation and integration form.

(I) $$R^{(1)}_{\lambda_1 \lambda_2 \lambda_3} = \int_0^\beta ds \frac{\delta^3}{\delta J_{\lambda_1}(s)\, \delta J_{\lambda_2}(s)\, \delta J_{\lambda_3}(s)}\, e^{[\gamma(DJ) + (JKJ)]} \Big|_{J=0}$$

Expanding the exponential in a Taylor series, we find that the terms that give a non-trivial contribution are

$$(JKJ)\,\gamma(DJ) + \frac{\gamma^3}{3!}(DJ)^3$$

Hence, $$R^{(1)}_{\lambda_1\lambda_2\lambda_3} = \int_0^\beta ds \, \frac{\delta^3}{\delta J_{\lambda_1}(s)\,\delta J_{\lambda_2}(s)\,\delta J_{\lambda_3}(s)} \left\{ \gamma(DJ)(JKJ) + \frac{\gamma^3}{3!}(DJ)^3 \right\}$$

(i) $$S_1 = \sum_{\lambda_1\lambda_2\lambda_3} V^3(\lambda_1,\lambda_2,\lambda_3) \int_0^\beta ds \, \frac{\delta^3}{\delta J_{\lambda_1}(s)\,\delta J_{\lambda_2}(s)\,\delta J_{\lambda_3}(s)} \gamma(DJ)(JKJ)$$

$$= \sum_{\lambda_1\lambda_2\lambda_3} V^3(\lambda_1,\lambda_2,\lambda_3) \; 3\,[iC(-\lambda_1)]\, \delta_{2,-3} \int_0^\beta ds \, D_2(s,s)\, D_1(s,0)$$

$$= 3i \sum_{\lambda_1\lambda_2} V^3(\lambda_1,\lambda_2,-\lambda_2)\, C(-\lambda_1)\, (2n_2+1) \left(\frac{2}{\hbar\omega_1}\right)$$

$$= \frac{i}{2N\sqrt{M}} \sum_{\lambda_2 j_1} \Phi^3(\vec{O}_{j_1},\lambda_2,-\lambda_2)\, [\vec{K}\cdot\vec{\varepsilon}(\vec{O}_{j_1})]\, (2n_2+1) \left(\frac{2}{\hbar\omega_1}\right) \times$$
$$\times \left[ e^{i\vec{O}\cdot\vec{x}(\ell)} - e^{i\vec{O}\cdot\vec{x}(\ell')} \right]$$

$$= 0$$

(ii) $$S_2 = \sum_{\lambda_1\lambda_2\lambda_3} V^3(\lambda_1,\lambda_2,\lambda_3) \int_0^\beta ds \, \frac{\delta^3}{\delta J_1(s)\,\delta J_2(s)\,\delta J_3(s)} \frac{\gamma^3}{3!}(DJ)^3$$

$$= \sum_{\lambda_1\lambda_2\lambda_3} V^3(\lambda_1,\lambda_2,\lambda_3)\, [iC(-\lambda_1)][iC(-\lambda_2)][iC(-\lambda_3)] \times$$
$$\times \int_0^\beta ds \, D_1(s,0)\, D_2(s,0)\, D_3(s,0)$$

$$= \frac{-i}{6M^{\frac{3}{2}}N^2} \sum_{\lambda_1\lambda_2\lambda_3} \Phi^3(\lambda_1,\lambda_2,\lambda_3)\, \Delta(\vec{q}_1+\vec{q}_2+\vec{q}_3)\, [\vec{K}\cdot\vec{\varepsilon}(-\lambda_1)]\, [\vec{K}\cdot\vec{\varepsilon}(-\lambda_2)] \times$$
$$\times [\vec{K}\cdot\vec{\varepsilon}(-\lambda_3)] \left[ e^{-i\vec{q}_1\cdot\vec{x}(\ell)} - e^{-i\vec{q}_1\cdot\vec{x}(\ell')} \right] \left[ e^{-i\vec{q}_2\cdot\vec{x}(\ell)} - e^{-i\vec{q}_2\cdot\vec{x}(\ell')} \right] \times$$
$$\times \left[ e^{-i\vec{q}_3\cdot\vec{x}(\ell)} - e^{-i\vec{q}_3\cdot\vec{x}(\ell')} \right] \left(\frac{\hbar}{2}\right)^3 \frac{1}{\omega_1\omega_2\omega_3} \times$$

$$\times\left(\frac{2}{\hbar}\right)\left\{\frac{(n_1+1)(n_2+1)(n_3+1)-n_1n_2n_3}{\omega_1+\omega_2+\omega_3}+3\left[\frac{n_1(n_2+1)(n_3+1)-(n_1+1)n_2n_3}{\omega_2+\omega_3-\omega_1}\right]\right\}$$

$$S_2(T\uparrow+\infty)=\frac{-i}{6M^{\frac{3}{2}}N^2\beta^2}\sum_{\lambda_1\lambda_2\lambda_3}\Phi^3(\lambda_1,\lambda_2,\lambda_3)\,\Delta(\vec{q}_1+\vec{q}_2+\vec{q}_3)\times$$

$$\times\frac{[\vec{K}\cdot\vec{\varepsilon}(-\lambda_1)][\vec{K}\cdot\vec{\varepsilon}(-\lambda_2)][\vec{K}\cdot\vec{\varepsilon}(-\lambda_3)]}{(\omega_1\omega_2\omega_3)^2}\times$$

$$\times\left[e^{-i\vec{q}_1\cdot\vec{x}(\ell)}-e^{-i\vec{q}_1\cdot\vec{x}(\ell')}\right]\left[e^{-i\vec{q}_2\cdot\vec{x}(\ell)}-e^{-i\vec{q}_2\cdot\vec{x}(\ell')}\right]\times$$

$$\times\left[e^{-i\vec{q}_3\cdot\vec{x}(\ell)}-e^{-i\vec{q}_3\cdot\vec{x}(\ell')}\right]$$

(II) $$R^{(1)}_{\lambda_1\cdots\lambda_4}=\int_0^\beta ds\,\frac{\delta^4}{\delta J_1(s)\delta J_2(s)\delta J_3(s)\delta J_4(s)}\,e^{[\gamma(DJ)+(JKJ)]}\Big|_{J=0}$$

Expanding the exponential in a Taylor series, we find that the terms that give a non-trivial contribution are

$$\frac{(JKJ)^2}{2!}+\frac{\gamma^2}{2!}(DJ)^2(JKJ)+\frac{\gamma^4}{4!}(DJ)^4$$

Hence,

$$R^{(1)}_{\lambda_1\cdots\lambda_4}=\int_0^\beta ds\,\frac{\delta^4}{\delta J_1(s)\,\delta J_2(s)\,\delta J_3(s)\,\delta J_4(s)}\left\{\frac{(JKJ)^2}{2!}+\frac{\gamma^2}{2!}(DJ)^2(JKJ)+\frac{\gamma^4}{4!}(DJ)^4\right\}$$

(i) $$S_3=\sum_{\lambda_1\cdots\lambda_4}V^4(\lambda_1,\ldots,\lambda_4)\int_0^\beta ds\,\frac{\delta^4}{\delta J_1(s)\delta J_2(s)\delta J_3(s)\delta J_4(s)}\,\frac{(JKJ)^2}{2!}=Y_1$$

(ii) $$S_4=\sum_{\lambda_1\cdots\lambda_4}V^4(\lambda_1,\ldots,\lambda_4)\int_0^\beta ds\,\frac{\delta^4}{\delta J_1(s)\delta J_2(s)\delta J_3(s)\delta J_4(s)}\,\frac{\gamma^2}{2!}(DJ)^2(JKJ)$$

$$=\sum_{\lambda_1\cdots\lambda_4}V^4(\lambda_1,\ldots,\lambda_4)\;6[iC(-\lambda_1)][iC(-\lambda_2)]\,\delta_{3,-4}\times$$

$$\times \int_0^\beta ds\, D_1(s,0)\, D_2(s,0)\, D_3(s,s)$$

$$= -6 \sum_{\lambda_1\lambda_2\lambda_3} V^4(\lambda_1,\lambda_2,\lambda_3,-\lambda_3)\, C(-\lambda_1) C(-\lambda_2) \left(\frac{\hbar}{2}\right)^3 \frac{1}{\omega_1\omega_2\omega_3} \times$$

$$\times (2n_3+1)\left(\frac{2}{\hbar}\right)\left\{ \frac{n_1+n_2+1}{\omega_1+\omega_2} + \frac{n_2-n_1}{\omega_1-\omega_2} \right\}$$

$$= \frac{-1}{2N^2M} \sum_{\vec{q}_1 j_1 j_2 \lambda_3} \Phi^4(\vec{q}_1 j_1, -\vec{q}_1 j_2, \lambda_3, -\lambda_3)\, [\vec{K}\cdot\vec{\varepsilon}(-\vec{q}_1 j_1)][\vec{K}\cdot\vec{\varepsilon}(\vec{q}_1 j_2)] \times$$

$$\times \left[1-\cos\{\vec{q}_1\cdot[\vec{x}(\ell)-\vec{x}(\ell')]\}\right] \left(\frac{\hbar}{2}\right)^3 \frac{1}{\omega(\vec{q}_1 j_1)\,\omega(\vec{q}_1 j_2)\,\omega_3} \times$$

$$\times (2n_3+1)\; T^{(1)}_{\vec{q}_1 j_2, \vec{q}_1 j_1} \times \left(\frac{2}{\hbar}\right)$$

$$T^{(1)}_{\lambda_r,\lambda_{r_1}} = \left\{ \begin{array}{ll} \dfrac{n_r - n_{r_1}}{\omega_{r_1}-\omega_r} + \dfrac{n_r+n_{r_1}+1}{\omega_r+\omega_{r_1}} , & \omega_r \neq \omega_{r_1} \\[2ex] \beta\hbar\, n_r(n_r+1) + \dfrac{1}{\omega_r}\left(n_r+\dfrac{1}{2}\right) , & \omega_r = \omega_{r_1} \end{array} \right\} \quad (*)$$

$$S_4(T\uparrow+\infty) = \frac{-1}{2N^2M\beta^2} \sum_{\vec{q}_1 j_1 j_2 \lambda_3} \Phi^4(\vec{q}_1 j_1, -\vec{q}_1 j_2, \lambda_3, -\lambda_3)\, [\vec{K}\cdot\vec{\varepsilon}(-\vec{q}_1 j_1)] \times$$

$$\times [\vec{K}\cdot\vec{\varepsilon}(\vec{q}_1 j_2)]\; \frac{\{1-\cos[\vec{q}_1\cdot\{\vec{x}(\ell)-\vec{x}(\ell')\}]\}}{[\omega(\vec{q}_1 j_1)\,\omega(\vec{q}_1 j_2)\,\omega_3]^2}$$

(iii) $$S_5 = \sum_{\lambda_1\cdots\lambda_4} V^4(\lambda_1,\ldots,\lambda_4) \int_0^\beta ds\, \frac{\delta^4}{\delta J_1(s)\,\delta J_2(s)\,\delta J_3(s)\,\delta J_4(s)}\, \frac{\gamma^4}{4!}(DJ)^4$$

$$= \sum_{\lambda_1 \cdots \lambda_4} V^4(\lambda_1, \ldots, \lambda_4) \; [iC(-\lambda_1)][iC(-\lambda_2)][iC(-\lambda_3)][iC(-\lambda_4)] \times$$

$$\times \int_0^\beta ds_1 \;\; D_1(s_1, 0)\, D_2(s_1, 0)\, D_3(s_1, 0)\, D_4(s_1, 0)$$

$$= \frac{1}{24N^3M^2} \sum_{\lambda_1 \cdots \lambda_4} \Delta(\vec{q}_1 + \cdots + \vec{q}_4)\, \Phi^4(\lambda_1, \ldots, \lambda_4) \; [\vec{K}\cdot\vec{\varepsilon}(-\lambda_1)][\vec{K}\cdot\vec{\varepsilon}(-\lambda_2)] \times$$

$$\times [\vec{K}\cdot\vec{\varepsilon}(-\lambda_3)][\vec{K}\cdot\vec{\varepsilon}(-\lambda_4)] \; [e^{-i\vec{q}_1\cdot\vec{x}(\ell)} - e^{-i\vec{q}_1\cdot\vec{x}(\ell')}] \times$$

$$\times [e^{-i\vec{q}_2\cdot\vec{x}(\ell)} - e^{-i\vec{q}_2\cdot\vec{x}(\ell')}]\, [e^{-i\vec{q}_3\cdot\vec{x}(\ell)} - e^{-i\vec{q}_3\cdot\vec{x}(\ell')}][e^{-i\vec{q}_4\cdot\vec{x}(\ell)} - e^{-i\vec{q}_4\cdot\vec{x}(\ell')}] \times$$

$$\times \left(\frac{\hbar}{2}\right)^4 \; \frac{(-2)}{\omega_1\omega_2\omega_3\omega_4} \sum_{\alpha_1\alpha_2\alpha_3\alpha_4 = \pm 1} \frac{\alpha_1\alpha_2\alpha_3\alpha_4}{(a_1+a_2+a_3+a_4)} \;\; N_1N_2N_3N_4$$

$$S_5(T\uparrow+\infty) = \frac{1}{24N^3M^2\beta^3} \sum_{\lambda_1 \cdots \lambda_4} \Delta(\vec{q}_1 + \cdots + \vec{q}_4)\, \Phi^4(\lambda_1, \ldots, \lambda_4) \times$$

$$\times \frac{[\vec{K}\cdot\vec{\varepsilon}(-\lambda_1)]}{\omega_1^2} \; \frac{[\vec{K}\cdot\vec{\varepsilon}(-\lambda_2)]}{\omega_2^2} \frac{[\vec{K}\cdot\vec{\varepsilon}(-\lambda_3)]}{\omega_3^2} \frac{[\vec{K}\cdot\vec{\varepsilon}(-\lambda_4)]}{\omega_4^2} \times$$

$$\times \; [e^{-i\vec{q}_1\cdot\vec{x}(\ell)} - e^{-i\vec{q}_1\cdot\vec{x}(\ell')}][e^{-i\vec{q}_2\cdot\vec{x}(\ell)} - e^{-i\vec{q}_2\cdot\vec{x}(\ell')}] \times$$

$$\times \; [e^{-i\vec{q}_3\cdot\vec{x}(\ell)} - e^{-i\vec{q}_3\cdot\vec{x}(\ell')}][e^{-i\vec{q}_4\cdot\vec{x}(\ell)} - e^{-i\vec{q}_4\cdot\vec{x}(\ell')}]$$

$$\text{(III)} \quad R^{(2)}_{\lambda_1\lambda_2\lambda_3;\lambda_4\lambda_5\lambda_6} = \int_0^\beta ds_1 \int_0^\beta ds_2 \; \frac{\delta^3}{\delta J_1(s_1)\delta J_2(s_1)\delta J_3(s_1)} \; \frac{\delta^3}{\delta J_4(s_2)\delta J_5(s_2)\delta J_6(s_2)} \times$$

$$\times \; e^{[\gamma(DJ) + (JKJ)]} \Big|_{J=0}$$

Expanding the exponential in a Taylor series, we find that the terms that give a non-trivial contribution, to $O(\gamma^4)$, are

$$\frac{(JKJ)^3}{3!} + \gamma^2\frac{(DJ)^2}{2!}\frac{(JKJ)^2}{2!} + \gamma^4\frac{(DJ)^4}{4!}(JKJ)$$

Hence,

$$R^{(2)}_{\lambda_1\lambda_2\lambda_3;\lambda_4\lambda_5\lambda_6} = \int_0^\beta ds_1 \int_0^\beta ds_2 \frac{\delta^3}{\delta J_1(s_1)\delta J_2(s_1)\delta J_3(s_1)} \frac{\delta^3}{\delta J_4(s_2)\delta J_5(s_2)\delta J_6(s_2)} \times$$
$$\times\left\{\frac{(JKJ)^3}{3!} + \gamma^2\frac{(DJ)^2}{2!}\frac{(JKJ)^2}{2!} + \gamma^4\frac{(DJ)^4}{4!}(JKJ)\right\}$$

(i) $$S_6 = \sum_{\lambda_1\cdots\lambda_6} V^3(\lambda_1,\lambda_2,\lambda_3)\, V^3(\lambda_4,\lambda_5,\lambda_6) \times$$
$$\times\int_0^\beta ds_1 \int_0^\beta ds_2 \frac{\delta^3}{\delta J_1(s_1)\delta J_2(s_1)\delta J_3(s_1)} \frac{\delta^3}{\delta J_4(s_2)\delta J_5(s_2)\delta J_6(s_2)} \frac{(JKJ)^3}{3!}$$
$$= Y_2$$

(ii) $$S_7 + S_8 + S_9 = \sum_{\lambda_1\cdots\lambda_6} V^3(\lambda_1,\lambda_2,\lambda_3)\, V^3(\lambda_4,\lambda_5,\lambda_6) \times$$
$$\times\int_0^\beta ds_1 \int_0^\beta ds_2 \frac{\delta^3}{\delta J_1(s_1)\delta J_2(s_1)\delta J_3(s_1)} \frac{\delta^3}{\delta J_4(s_2)\delta J_5(s_2)\delta J_6(s_2)} \left\{\gamma^2\frac{(DJ)^2}{2!}\frac{(JKJ)^2}{2!}\right\}$$

(a) $$S_7 = \sum_{\lambda_1\cdots\lambda_6} V^3(\lambda_1,\lambda_2,\lambda_3)\, V^3(\lambda_4,\lambda_5,\lambda_6)\; 18\,[iC(-\lambda_1)][iC(-\lambda_2)]\,\delta_{3,-4}\,\delta_{5,-6}$$
$$\times\int_0^\beta ds_1 \int_0^\beta ds_2\, D_1(s_1,0)\, D_2(s_1,0)\, D_3(s_1,s_2)\, D_5(s_2,s_2)$$

$$= -\frac{1}{N^2 M} \sum_{\vec{q}_1 j_1 j_2 j_3 \lambda_5} \Phi^3(\vec{q}_1 j_1, -\vec{q}_1 j_2, \vec{O} j_3)\, \Phi^3(\vec{O} j_3, \lambda_5, -\lambda_5) \times$$

$$\times [\vec{K}\cdot\vec{\varepsilon}(-\vec{q}_1 j_1)][\vec{K}\cdot\vec{\varepsilon}(\vec{q}_1 j_2)]\; [1 - \cos\{\vec{q}_1\cdot[\vec{x}(\ell)-\vec{x}(\ell')]\}] \times$$

$$\times \left(\frac{\hbar}{2}\right)^4 \frac{1}{\omega(\vec{q}_1 j_1)\,\omega(\vec{q}_1 j_2)\,\omega(\vec{O} j_3)\,\omega_5} (2n_5+1)\left(\frac{2}{\hbar\omega(\vec{O}_{j_3})}\right)\left(\frac{2}{\hbar}\right) T^{(1)}_{\vec{q}_1 j_2, \vec{q}_1 j_1}$$

$$= 0 \qquad \left[ \Phi^3(\vec{q}_1 j_1, -\vec{q}_1 j_2, \vec{O} j_3) = 0 \text{ since every atom is a centre of inversion symmetry.} \right]$$

(b) $$S_8 = \sum_{\lambda_1 \cdots \lambda_6} V^3(\lambda_1, \lambda_2, \lambda_3)\, V^3(\lambda_4, \lambda_5, \lambda_6)\; 18[iC(-\lambda_1)][iC(-\lambda_4)]\, \delta_{2,-5}\, \delta_{3,-6} \times$$

$$\times \int_0^\beta ds_1 \int_0^\beta ds_2\; D_1(s_1, 0)\, D_4(s_2, 0)\; D_2(s_1, s_2)\, D_3(s_1, s_2)$$

$$= -\frac{1}{N^2 M} \sum_{\vec{q}_1 j_1 j_4 \lambda_2 \lambda_3} \Delta(\vec{q}_1 + \vec{q}_2 + \vec{q}_3)\, \Phi^3(\vec{q}_1 j_1, \lambda_2, \lambda_3)\, \Phi^3(-\vec{q}_1 j_4, -\lambda_2, -\lambda_3) \times$$

$$\times [\vec{K}\cdot\vec{\varepsilon}(-\vec{q}_1 j_1)][\vec{K}\cdot\vec{\varepsilon}(\vec{q}_1 j_4)]\; [1 - \cos\{\vec{q}_1\cdot[\vec{x}(\ell)-\vec{x}(\ell')]\}] \times$$

$$\times \left(\frac{\hbar}{2}\right)^4 \frac{1}{\omega(\vec{q}_1 j_1)\,\omega(\vec{q}_1 j_4)\,\omega_2\,\omega_3} \times \sum_{\alpha_1\alpha_2\alpha_3\alpha_4 = \pm 1} \frac{\alpha_1\,\alpha_2\,\alpha_3\,\alpha_4}{\hbar^2[\alpha_1\omega_1 + \alpha_2\omega_2 + \alpha_3\omega_3]} \times$$

$$\times \Big\{ (N_2 + N_3 + 1)\, T^{(2)}_{\vec{q}_1 j_1, \vec{q}_1 j_4} +$$

$$+ \frac{[N_2 N_3 - N_2 N_{\vec{q}_1 j_4}(\alpha_4) - N_3 N_{\vec{q}_1 j_4}(\alpha_4) - N_{\vec{q}_1 j_4}(\alpha_4)]}{[\alpha_4\,\omega(\vec{q}_1 j_4) - \alpha_2\,\omega_2 - \alpha_3\,\omega_3]} \Big\}$$

$$T^{(2)}_{\lambda_r,\lambda_{r_1}} = \left\{ \begin{array}{ll} \dfrac{N_r(\alpha_r) - N_{r_1}(\alpha_{r_1})}{\alpha_{r_1}\omega_{r_1} - \alpha_r\omega_r} & , \alpha_{r_1}\omega_{r_1} \neq \alpha_r\omega_r \\ \\ \beta\hbar\, N_r(\alpha_r)\,[N_r(\alpha_r)+1] & , \alpha_{r_1}\omega_{r_1} = \alpha_r\omega_r \end{array} \right\} \qquad (**)$$

$$S_8(T\uparrow+\infty) = -\frac{1}{N^2M\beta^2} \sum_{\vec{q}_1 j_1 j_4 \lambda_2\lambda_3} \Delta(\vec{q}_1+\vec{q}_2+\vec{q}_3)\, \Phi^3(\vec{q}_1 j_1,\lambda_2,\lambda_3) \times$$

$$\times\, \Phi^3(-\vec{q}_1 j_4,-\lambda_2,-\lambda_3)\ [\vec{K}\cdot\vec{\varepsilon}(-\vec{q}_1 j_1)][\vec{K}\cdot\vec{\varepsilon}(\vec{q}_1 j_4)] \times$$

$$\times\, \frac{\{1 - \cos[\vec{q}_1\cdot\{\vec{x}(\ell)-\vec{x}(\ell')\}]\}}{[\omega_1\,\omega(\vec{q}_1 j_4)\,\omega_2\omega_3]^2}$$

(c) $$S_9 = \sum_{\lambda_1\cdots\lambda_6} V^3(\lambda_1,\lambda_2,\lambda_3)\, V^3(\lambda_4,\lambda_5,\lambda_6)\, 9[iC(-\lambda_1)][iC(-\lambda_4)]\,\delta_{2,-3}\,\delta_{5,-6} \times$$

$$\times \int_0^\beta ds_1 \int_0^\beta ds_2\ D_1(s_1,0)\, D_4(s_2,0)\, D_2(s_1,s_1)\, D_5(s_2,s_2)$$

$= 0$ (since $\vec{q}_1, \vec{q}_4$ are each zero or a vector of reciprocal lattice, whence $C(-\lambda_1)=C(-\lambda_4)=0$)

(iii) $$S_{10} + S_{11} = \sum_{\lambda_1\cdots\lambda_6} V^3(\lambda_1,\lambda_2,\lambda_3)\, V^3(\lambda_4,\lambda_5,\lambda_6) \times$$

$$\times \int_0^\beta ds_1 \int_0^\beta ds_2\ \frac{\delta^3}{\delta J_1(s_1)\delta J_2(s_1)\delta J_3(s_1)}\ \frac{\delta^3}{\delta J_4(s_2)\delta J_5(s_2)\delta J_6(s_2)} \left\{\gamma^4 \frac{(DJ)^4}{4!}(JKJ)\right\}$$

$$S_{10} = \sum_{\lambda_1\cdots\lambda_6} V^3(\lambda_1,\lambda_2,\lambda_3)\, V^3(\lambda_4,\lambda_5,\lambda_6)\ 6\,[iC(-\lambda_1)][iC(-\lambda_2)] \times$$

$$\times\, [iC(-\lambda_3)][iC(-\lambda_4)]\ \delta_{5,-6} \times$$

$$\times \int_0^\beta ds_1 \int_0^\beta ds_2 \, D_1(s_1,0)\, D_2(s_1,0)\, D_3(s_2,0)\, D_4(s_2,0)\, D_5(s_2,s_2)$$

$= 0$ (since $\vec{q}_4$ is zero or a vector of reciprocal lattice, whence $C(-\lambda_4)=0$)

(b) $$S_{11} = \sum_{\lambda_1 \cdots \lambda_6} V^3(\lambda_1,\lambda_2,\lambda_3)\, V^3(\lambda_4,\lambda_5,\lambda_6)\; 9\, [iC(-\lambda_1)][iC(-\lambda_2)] \times$$

$$\times [iC(-\lambda_4)]\,[iC(-\lambda_5)]\;\delta_{3,-6}\times$$

$$\times \int_0^\beta ds_1 \int_0^\beta ds_2 \, D_1(s_1,0)\, D_2(s_1,0)\, D_4(s_2,0)\, D_5(s_2,0)\, D_3(s_1,s_2)$$

$$= \frac{1}{4N^3M^2} \sum_{\lambda_1 \cdots \lambda_5} \Delta(\vec{q}_1+\vec{q}_2+\vec{q}_3)\,\Delta(\vec{q}_4+\vec{q}_5-\vec{q}_3)\; \Phi^3(\lambda_1,\lambda_2,\lambda_3)\times$$

$$\times \Phi(\lambda_4,\lambda_5,-\lambda_3)\,[\vec{K}\cdot\vec{\varepsilon}(-\lambda_1)][\vec{K}\cdot\vec{\varepsilon}(-\lambda_2)][\vec{K}\cdot\vec{\varepsilon}(-\lambda_4)][\vec{K}\cdot\vec{\varepsilon}(-\lambda_5)]\times$$

$$\times \left[e^{-i\vec{q}_1\cdot\vec{x}(\ell)} - e^{-i\vec{q}_1\cdot\vec{x}(\ell')}\right]\left[e^{-i\vec{q}_2\cdot\vec{x}(\ell)} - e^{-i\vec{q}_2\cdot\vec{x}(\ell')}\right]\times$$

$$\times \left[e^{-i\vec{q}_4\cdot\vec{x}(\ell)} - e^{-i\vec{q}_4\cdot\vec{x}(\ell')}\right]\left[e^{-i\vec{q}_5\cdot\vec{x}(\ell)} - e^{-i\vec{q}_5\cdot\vec{x}(\ell')}\right]\times$$

$$\times \left(\frac{\hbar}{2}\right)^5 \frac{1}{\omega_1\omega_2\omega_3\omega_4\omega_5} \sum_{\alpha_1\alpha_2\alpha_3\alpha_4\alpha_5=\pm1} \frac{\alpha_1\alpha_2\alpha_3\alpha_4\alpha_5}{(a_4+a_5-a_3)}\times$$

$$\times \left\{ \frac{(N_1+1)(N_2+1)(N_4+N_5+1) - (N_4+1)(N_5+1)(N_1+N_2+1)}{(a_1+a_2-a_4-a_5)} - \right.$$

$$\left. - \frac{(N_4+N_5+1)\,[N_1N_2 - N_1N_3 - N_2N_3 - N_3]}{(a_1+a_2-a_3)} \right\}$$

$$S_{11}(T\uparrow+\infty) = \frac{1}{4N^3M^2\beta^3} \sum_{\lambda_1\cdots\lambda_5} \Delta(\vec{q}_1+\vec{q}_2+\vec{q}_3)\Delta(\vec{q}_4+\vec{q}_5-\vec{q}_3)\times$$
$$\times\, \Phi^3(\lambda_1,\lambda_2,\lambda_3)\,\Phi^3(\lambda_4,\lambda_5,-\lambda_3)\,\left[e^{-i\vec{q}_1\cdot\vec{x}(\ell)} - e^{-i\vec{q}_1\cdot\vec{x}(\ell')}\right]\times$$
$$\times\left[e^{-i\vec{q}_2\cdot\vec{x}(\ell)} - e^{-i\vec{q}_2\cdot\vec{x}(\ell')}\right]\left[e^{-i\vec{q}_4\cdot\vec{x}(\ell)} - e^{-i\vec{q}_4\cdot\vec{x}(\ell')}\right]\times$$
$$\times\left[e^{-i\vec{q}_5\cdot\vec{x}(\ell)} - e^{-i\vec{q}_5\cdot\vec{x}(\ell')}\right]\times$$
$$\times\,\frac{[\vec{K}\cdot\vec{\varepsilon}(-\lambda_1)]\,[\vec{K}\cdot\vec{\varepsilon}(-\lambda_2)]\,[\vec{K}\cdot\vec{\varepsilon}(-\lambda_4)]\,[\vec{K}\cdot\vec{\varepsilon}(-\lambda_5)]}{(\omega_1\,\omega_2\,\omega_3\,\omega_4\,\omega_5)^2}$$

Substituting the above expressions for $S_1,\ldots,S_{12}$ into Eq. (9.11), we obtain

$$\left\langle e^{i\vec{K}\cdot[\vec{u}(\ell)-\vec{u}(\ell')]}\right\rangle = \frac{AZ_0\left\{1-[S_1+S_2+S_3+S_4+S_5]+\frac{1}{2!}[S_6+S_7+S_8+S_9+S_{10}+S_{11}]\right\}}{Z_0\left\{1-Y_1+\frac{1}{2!}Y_2\right\}}$$

$$= \frac{A\left\{1-S_2-Y_1-S_4-S_5+\frac{1}{2}[Y_2+S_8+S_{11}]\right\}}{1-Y_1+\frac{1}{2}Y_2} \qquad (9.12)$$

Since we assume the perturbation theory is valid, $|Y_1-\frac{1}{2}Y_2|<1$. Using $\frac{1}{1-x}=1+x+O(x^2)$ for $|x|<1$, we find that to $O(\lambda^2)$, Eq. (9.12) reduces to

$$\left\langle e^{i\vec{K}\cdot[\vec{u}(\ell)-\vec{u}(\ell')]}\right\rangle = A\left\{1-S_2-S_4-S_5+\frac{1}{2}[S_8+S_{11}]\right\}$$
$$\text{“}=\text{”}A\exp\left\{-S_2-S_4-S_5+\frac{1}{2}[S_8+S_{11}]\right\}$$
$$\equiv e^{-2M} \qquad (9.13)$$

where the second equality in the above is only true to the order of perturbation we are considering here. $2M$ is the Debye-Waller factor. To evaluate the Debye-Waller factor, we must find the part of Eq. (9.13) that is independent of $\ell$ and $\ell'$ because the Debye-Waller factor involves the zero phonon part of $\langle e^{i\vec{K}\cdot[\vec{u}(\ell)-\vec{u}(\ell')]}\rangle$.

Using the notation of Maradudin and Flinn,

$$2M = 2M_0 + 2M_1 + 2M_2 + 2M_3 + 2M_4 \qquad (9.14)$$

Since the term $S_2$ depends on $\ell$ and $\ell'$, that is, there is no part independent of $\ell$ and $\ell'$, it does not contribute to the Debye-Waller factor.

(1) $-2M_0$ comes from the harmonic average of the quantity defined in Eq. (9.5), that is, it equals the exponent of $A$.

$$2M_0 = \frac{\hbar}{2NM} \sum_{\lambda_r} \frac{1}{\omega_{\lambda_r}} \coth\left(\tfrac{1}{2}\beta\hbar\omega_{\lambda_r}\right) [\vec{K}\cdot\vec{\varepsilon}(\lambda_r)][\vec{K}\cdot\vec{\varepsilon}(-\lambda_r)]$$

$$2M_0(T\uparrow+\infty) = \frac{k_B T}{NM} \sum_{\lambda_r} \frac{[\vec{K}\cdot\vec{\varepsilon}(\lambda_r)][\vec{K}\cdot\vec{\varepsilon}(-\lambda_r)]}{\omega_{\lambda_r}^2}$$

(2) $2M_1$ comes from the zero phonon part of $+S_4$

$$2M_1 = -\frac{1}{2N^2M} \sum_{\vec{q}_1 j_1 j_2 \lambda_3} \Phi^4(\vec{q}_1 j_1, -\vec{q}_1 j_2, \lambda_3, -\lambda_3)\, [\vec{K}\cdot\vec{\varepsilon}(-\vec{q}_1 j_1)] \times$$
$$\times [\vec{K}\cdot\vec{\varepsilon}(\vec{q}_1 j_2)] \left(\frac{\hbar}{2}\right)^3 \frac{1}{\omega(\vec{q}_1 j_1)\omega(\vec{q}_1 j_2)\omega_3} (2n_3+1)\left(\frac{2}{\hbar}\right) T^{(1)}_{\vec{q}_1 j_2, \vec{q}_1 j_1}$$

$$2M_1(T\uparrow+\infty) = \frac{-(k_BT)^2}{2N^2M} \sum_{\vec{q}_1 j_1 j_2 \lambda_3} \Phi^4(\vec{q}_1 j_1, -\vec{q}_1 j_2, \lambda_3, -\lambda_3) \frac{[\vec{K}\cdot\varepsilon(-\vec{q}_1 j_1)][\vec{K}\cdot\vec{\varepsilon}(\vec{q}_1 j_2)]}{[\omega(\vec{q}_1 j_1)\,\omega(\vec{q}_1 j_2)\,\omega_3]^2}$$

(3) $2M_2$ comes from the zero phonon part of $\frac{-1}{2}S_8$

$$2M_2 = \frac{1}{2N^2M} \sum_{\vec{q}_1 j_1 j_4 \lambda_2 \lambda_3} \Delta(\vec{q}_1+\vec{q}_2+\vec{q}_3)\, \Phi^3(\vec{q}_1 j_1, \lambda_2, \lambda_3)\, \Phi^3(-\vec{q}_1 j_4, -\lambda_2, -\lambda_3) \times$$

$$\times \left(\frac{\hbar}{2}\right)^4 \frac{1}{\omega(\vec{q}_1 j_1)\,\omega(\vec{q}_1 j_4)\,\omega_2\,\omega_3} \quad [\vec{K}\cdot\vec{\varepsilon}(-\vec{q}_1 j_1)][\vec{K}\cdot\vec{\varepsilon}(\vec{q}_1 j_4)] \times$$

$$\times \sum_{\alpha_1\alpha_2\alpha_3\alpha_4=\pm 1} \frac{\alpha_1\alpha_2\alpha_3\alpha_4}{\hbar^2[\alpha_1\omega_1+\alpha_2\omega_2+\alpha_3\omega_3]} \left\{ (N_2+N_3+1)\, T^{(2)}_{\vec{q}_1 j_1, \vec{q}_1 j_4} + \right.$$

$$\left. + \frac{[N_2N_3 - N_2 N_{\vec{q}_1 j_4}(\alpha_4) - N_3 N_{\vec{q}_1 j_4}(\alpha_4) - N_{\vec{q}_1 j_4}(\alpha_4)]}{[\alpha_4\,\omega(\vec{q}_1 j_4) - \alpha_2\omega_2 - \alpha_3\omega_3]} \right\}$$

$$2M_2(T\uparrow+\infty) = \frac{(k_BT)^2}{2N^2M} \sum_{\vec{q}_1 j_1 j_4 \lambda_2 \lambda_3} \Delta(\vec{q}_1+\vec{q}_2+\vec{q}_3)\, \Phi^3(\vec{q}_1 j_1, \lambda_2, \lambda_3) \times$$

$$\times\, \Phi^3(-\vec{q}_1 j_4, -\lambda_2, -\lambda_3) \quad \frac{[\vec{K}\cdot\vec{\varepsilon}(-\vec{q}_1 j_1)][\vec{K}\cdot\vec{\varepsilon}(\vec{q}_1 j_4)]}{[\omega_1\,\omega(\vec{q}_1 j_4)\,\omega_2\,\omega_3]^2}$$

(4) $2M_3$ comes from the zero phonon part of $S_5$

$$2M_3 = \frac{1}{12N^3M^2} \sum_{\lambda_1\cdots\lambda_4} \Delta(\vec{q}_1+\cdots+\vec{q}_4)\, \Phi^4(\lambda_1,\ldots,\lambda_4) \times$$

$$\times [\vec{K}\cdot\vec{\varepsilon}(-\lambda_1)][\vec{K}\cdot\vec{\varepsilon}(-\lambda_2)][\vec{K}\cdot\vec{\varepsilon}(-\lambda_3)][\vec{K}\cdot\vec{\varepsilon}(-\lambda_4)] \times$$

$$\times \left(\frac{\hbar}{2}\right)^4 \frac{(-2)}{\omega_1\,\omega_2\,\omega_3\,\omega_4} \sum_{\alpha_1\alpha_2\alpha_3\alpha_4=\pm 1} \frac{\alpha_1\alpha_2\alpha_3\alpha_4\; N_1N_2N_3N_4}{(a_1+a_2+a_3+a_4)}$$

$$2M_3(T\uparrow+\infty) = \frac{(k_BT)^3}{12N^3M^2} \sum_{\lambda_1\cdots\lambda_4} \Delta(\vec{q}_1+\cdots+\vec{q}_4)\, \Phi^4(\lambda_1,\ldots,\lambda_4) \times$$

$$\times \frac{[\vec{K}\cdot\vec{\varepsilon}(-\lambda_1)]}{\omega_1^{\,2}} \frac{[\vec{K}\cdot\vec{\varepsilon}(-\lambda_2)]}{\omega_2^2} \frac{[\vec{K}\cdot\vec{\varepsilon}(-\lambda_3)]}{\omega_3^{\,2}} \frac{[\vec{K}\cdot\vec{\varepsilon}(-\lambda_4)]}{\omega_4^2}$$

(5) $2M_4$ comes from the zero phonon part of $-\frac{1}{2}S_{11}$

$$2M_4 = \frac{-1}{4N^3M^2} \sum_{\lambda_1\cdots\lambda_5} \Delta(\vec{q}_1+\vec{q}_2+\vec{q}_3)\,\Delta(\vec{q}_4+\vec{q}_5-\vec{q}_3) \times$$

$$\times \Phi^3(\lambda_1,\lambda_2,\lambda_3)\, \Phi^3(\lambda_4,\lambda_5,-\lambda_3)\, [\vec{K}\cdot\vec{\varepsilon}(-\lambda_1)]\,[\vec{K}\cdot\vec{\varepsilon}(-\lambda_2)] \times$$

$$\times [\vec{K}\cdot\vec{\varepsilon}(-\lambda_4)]\,[\vec{K}\cdot\vec{\varepsilon}(-\lambda_5)] \times \left(\frac{\hbar}{2}\right)^5 \frac{1}{\omega_1\omega_2\omega_3\omega_4\omega_5} \times$$

$$\times \sum_{\alpha_1\alpha_2\alpha_3\alpha_4\alpha_5=\pm 1} \frac{\alpha_1\,\alpha_2\,\alpha_3\,\alpha_4\,\alpha_5}{(a_4+a_5-a_3)} \times$$

$$\times \left\{ \frac{(N_1+1)(N_2+1)(N_4+N_5+1) - (N_4+1)(N_5+1)(N_1+N_2+1)}{(a_1+a_2-a_4-a_5)} - \right.$$

$$\left. - \frac{(N_4+N_5+1)\,[N_1N_2 - N_1N_3 - N_2N_3 - N_3]}{(a_1+a_2-a_3)} \right\}$$

$$2M_4(T\uparrow+\infty) = \frac{-(k_BT)^3}{4N^3M^2} \sum_{\lambda_1\cdots\lambda_5} \Delta(\vec{q}_1+\vec{q}_2+\vec{q}_3)\,\Delta(\vec{q}_4+\vec{q}_5-\vec{q}_3) \times$$

$$\times \Phi^3(\lambda_1,\lambda_2,\lambda_3)\, \Phi^3(\lambda_4,\lambda_5,-\lambda_3)\, [\vec{K}\cdot\vec{\varepsilon}(-\lambda_1)]\,[\vec{K}\cdot\vec{\varepsilon}(-\lambda_2)] \times$$

$$\times [\vec{K}\cdot\vec{\varepsilon}(-\lambda_4)]\,[\vec{K}\cdot\vec{\varepsilon}(-\lambda_5)] \frac{1}{[\omega_1\omega_2\omega_3\omega_4\omega_5]^2}$$

The high temperature expressions for the Debye-Waller factor obtained here are the same as obtained by Maradudin and Flinn.

Much work was saved in evaluating the necessary integrals for the various expressions because these integrals are similar to the ones evaluated in the derivation of the free energy expressions. We will use Feynman diagrams to indicate the similarities between the two.

We can draw the corresponding diagrams for the various terms of the Debye-Waller factor as was done for the free energy, but with one difference. For the free energy, we drew dots to represent the variables of the D functions, or interaction centres which multiply the integral involved. For the Debye-Waller factor, we see that sometimes there is a zero in the argument of D, for example, $D_{\lambda_r}(s,0)$ . We write down an extra dot ("x") for the zero argument and then draw the diagrams as in the free energy. The number of dots in each diagram for the Debye-Waller factor equals the number of anharmonic coefficients (interaction centres), and the "x" represents the scattering vertex.

The diagrams for the various terms of the Debye-Waller factor and free energy which have the same temperature space integrals are presented in Fig. 3.

Figure 3: Correspondence among the diagrams of the Debye-Waller factor and the Helmholtz free energy of $O(\lambda^4)$

FIG. 3

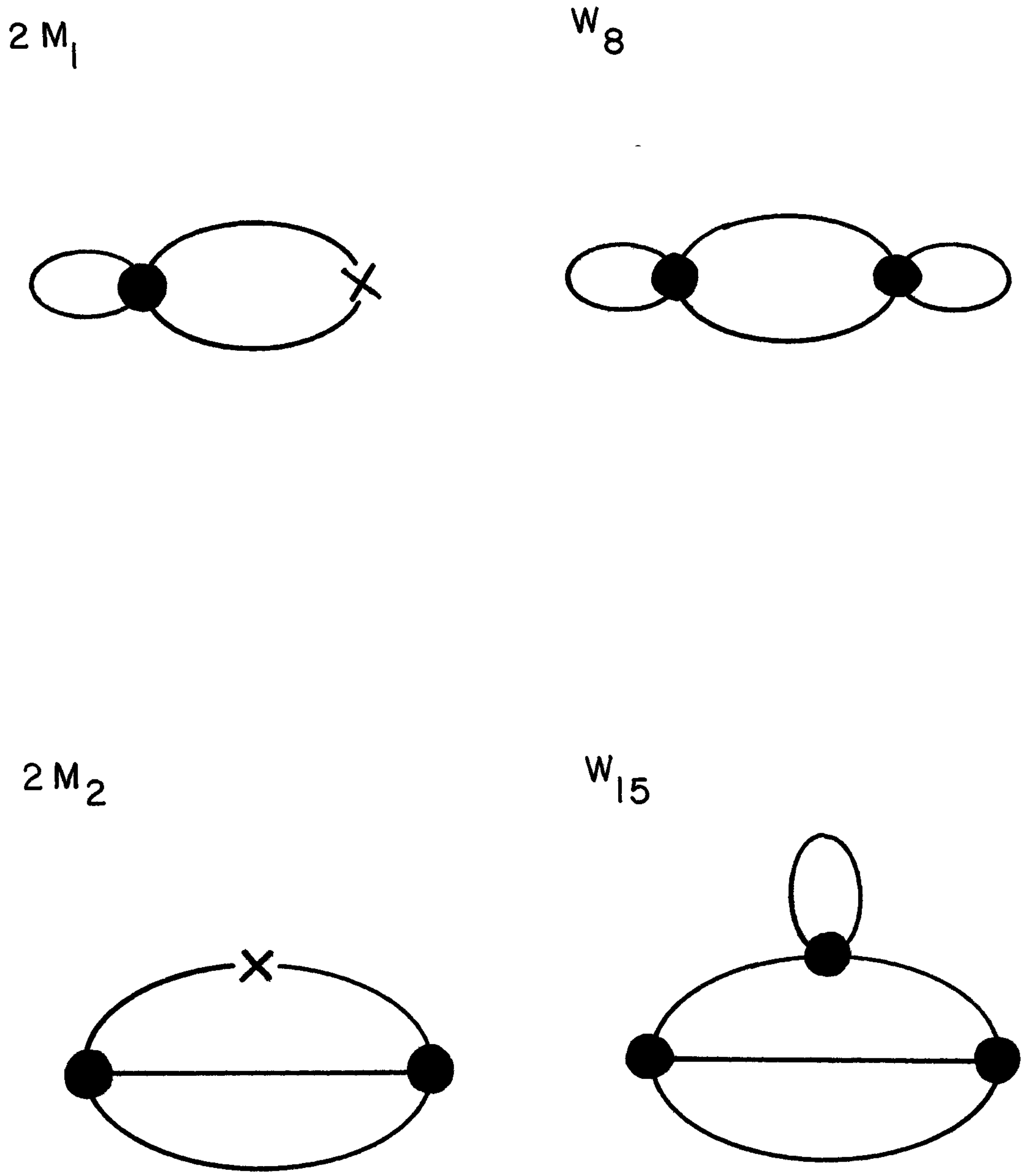
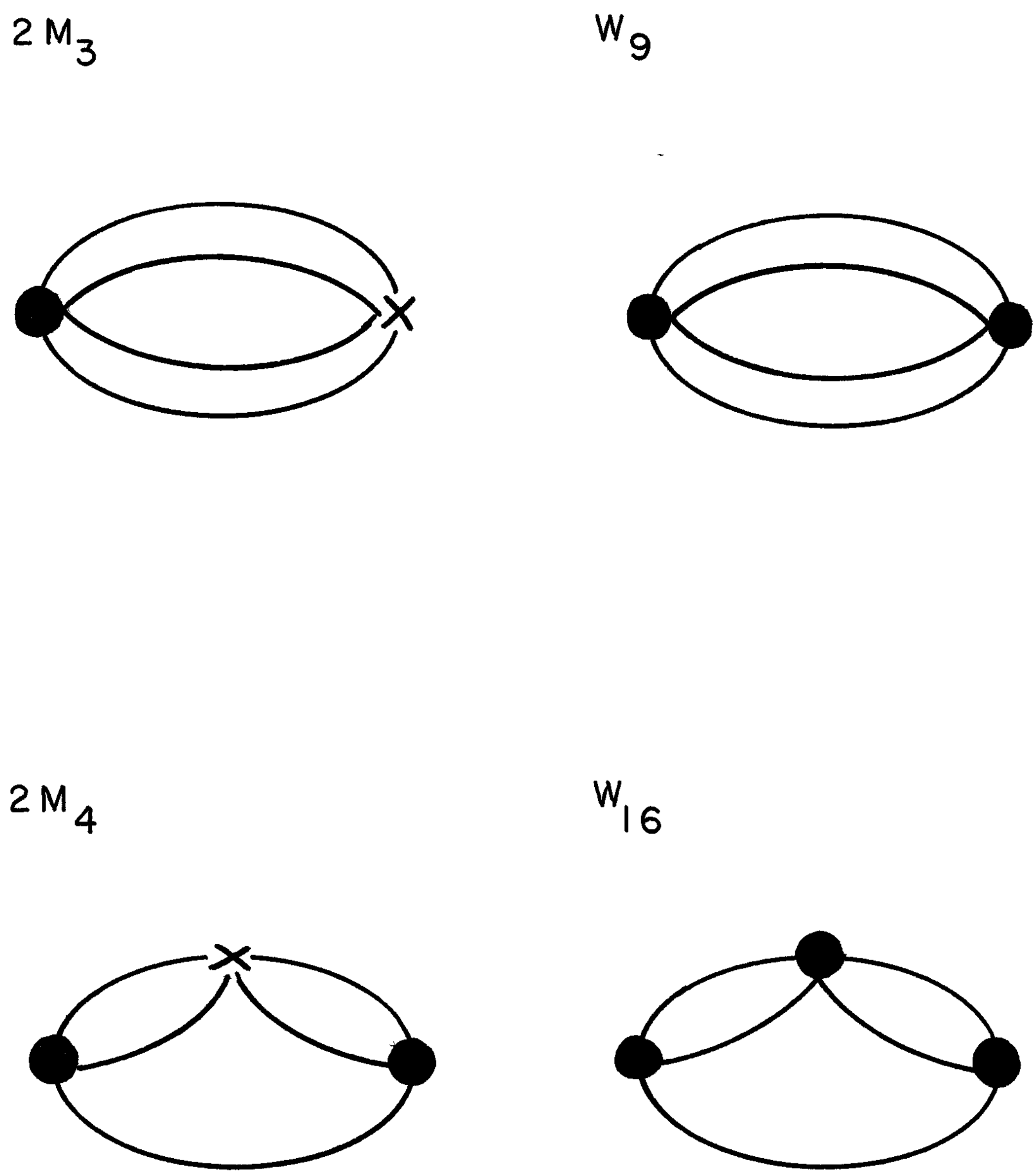


FIG. 3



## 10. Summary and Conclusions

We have critically examined the applicability of the path integral formalism in the study of four specific problems. These problems are: (a) two interacting one dimensional harmonic oscillators (sec. 4), (b) N interacting Einstein oscillators (sec. 7), (c) Helmholtz free energy of an anharmonic crystal to $O(\lambda^4)$ (sec. 8), and (d) Debye-Waller factor (sec. 9).

We have solved the problem of finding the kernel for two interacting one dimensional oscillators and found the algebra to be tedious and lengthy. An attempt was made to solve the problem of N interacting Einstein oscillators in real space, but the algebra became far too lengthy and cumbersome to continue. This work was not presented. Hence, the problem was investigated in k-space. The path integration in complex space was studied, and finally, the partition function and Helmholtz free energy F, was obtained following the procedure outlined in section 6.

We applied the method of Papadopolous, outlined in section 6, to the problem of N interacting Einstein oscillators. We evaluated the integrals involved, in temperature space instead of working with the sums in Fourier space, (Shukla and Muller (1972)).

Our next application of the method of Papadopolous was in finding the Helmholtz free energy, to $O(\lambda^4)$, of an anharmonic crystal. The evaluations of the various terms were again done in temperature space instead of Fourier space, (Shukla and Cowley (1971)). The calculations were greatly simplified by a form of the propagator (D function) suggested to the author by Dr. R. C. Shukla. We also demonstrated that the Feynman diagrams can be drawn quite naturally for various functional differentiation sequences. It was found that in evaluating all the terms of F to $O(\lambda^4)$ and the Debye-Waller factor, only two non-trivial types of integrals were central to the entire work.

We then modified the method of Papadopolous slightly, and evaluated the Debye-Waller factor, DWF, to $O(\lambda^2)$ and $O(|\vec{K}|^4)$ where $\vec{K}$ is the scattering vector. The high temperature limit was taken and the results obtained agreed with those of Maradudin and Flinn (1963). We also noted that the expressions needed in calculating the various contributions to DWF are similar to those needed in the evaluation of F.

Our strong feeling is that the Feynman path integral formulation should be studied on its own merit. In our opinion, this formulation is both conceptually and formally more elegant than the more well known formulations of quantum mechanics.

From the conceptual viewpoint, as is observed in the brief introduction, the arguments used in setting up the Feynman formulation are of a physically intuitive nature, the only ad hoc assumption being the introduction of $\hbar$. We would also stress that this formulation has a close connection with classical mechanics. The usual formulation of quantum mechanics cannot be simply connected with classical mechanics unless one goes through the Bohr's correspondence principle.

From a formal standpoint, we need only one operational hypothesis in the path integral formulation as opposed to the two (equation of motion, commutation relation) needed in the more well known formulations.

Also, the kernel, which is central in the path integral formulation, is a more useful quantity than the wave function if one is interested in transition probability calculations and the derivation of those physical quantities (F, DWF, etc.) which require the sum over all energy levels of a system.

Unfortunately, the application of the path integral formulation to any physical problem is quite laborious as can be seen from the work presented in this thesis. This is so even for such simple systems as two interacting one dimensional oscillators.

Hence, we cannot say in an absolute sense whether or not this formulation is superior in solving simple problems of quantum mechanics.

Appendix 1

As we indicated in section 6, the "average" of an odd number of normal coordinates, using a Gaussian measure, is zero. We sketch a brief demonstration of this fact.

It suffices to consider the following path integral;

$$I = \iiint\int_{Q_{\lambda_r}(0)=\xi_{\lambda_r}}^{Q_{\lambda_r}(\beta)=\xi_{\lambda_r}} \mathcal{D}[Q_{\lambda_r}(t)]\,\mathcal{D}[Q_{-\lambda_r}(t)]\; Q_{\lambda_r}(t_1)\cdots Q_{\lambda_r}(t_{2n+1}) \times$$

$$\times \exp\left\{-2\int_0^\beta dt\left[\frac{\dot{Q}_{\lambda_r}(t)\,\dot{Q}_{-\lambda_r}(t)}{2\hbar^2} + \frac{\omega_{\lambda_r}^2}{2} Q_{\lambda_r}(t) Q_{-\lambda_r}(t)\right]\right\} d\xi_{\lambda_r}\, d\xi_{-\lambda_r} \qquad \text{(A1.1)}$$

where n is a non-negative integer, and $0 \le t_1, \ldots, t_{2n+1} \le \beta$ We show that $I = 0$ .

The following argument is not a mathematically rigorous argument. In the process, however, we will indicate how the complex path integral in Eq. (A1.1) can be handled.

Observe that $Q_{\lambda_r}(t) = Q^*_{-\lambda_r}(t)$ and $Q_{\lambda_r}(0) = Q_{\lambda_r}(\beta) = \xi_{\lambda_r}$.

Suppose that $Q_{\lambda_r}(t) = x_{\lambda_r}(t) + i y_{\lambda_r}(t)$ ; $x_{\lambda_r}, y_{\lambda_r}$ are real.

The way in which we will demonstrate that $I = 0$ is to use the Riemann type definition of the path integral as given in Eq. (3.16).

Expanding the part of the exponential of Eq. (A1.1) that is independent of the derivatives, we obtain

$$I = \iint\int_{\xi_{\lambda_r}}^{\xi_{\lambda_r}} \mathcal{D}[Q_{\lambda_r}(t)]\,\mathcal{D}[Q_{-\lambda_r}(t)]\; Q_{\lambda_r}(t_1)\cdots Q_{\lambda_r}(t_{2n+1}) \times$$

$$\times \exp\left\{-\frac{1}{\hbar^2}\int_0^\beta dt\,\dot{Q}_{\lambda_r}(t)\dot{Q}_{-\lambda_r}(t)\right\}\sum_{\ell=0}^{+\infty}\frac{(-\omega_{\lambda_r}^2)^\ell}{\ell!}\left[\int_0^\beta dt\,Q_{\lambda_r}(t)Q_{-\lambda_r}(t)\right]^\ell d\xi_{\lambda_r}d\xi_{-\lambda_r}$$

$$= \sum_{\ell=0}^{+\infty}\frac{(-\omega_{\lambda_r}^2)^\ell}{\ell!}\int_0^\beta ds_1\cdots\int_0^\beta ds_\ell\iiint\int_{\xi_{\lambda_r}}^{\xi_{\lambda_r}}\mathcal{D}[Q_{\lambda_r}(t)]\,\mathcal{D}[Q_{-\lambda_r}(t)]\times$$

$$\times\ Q_{\lambda_r}(t_1)\cdots Q_{\lambda_r}(t_{2n+1})\ Q_{\lambda_r}(s_1)Q_{-\lambda_r}(s_1)\cdots Q_{\lambda_r}(s_\ell)\,Q_{-\lambda_r}(s_\ell)\times$$

$$\times\ \exp\left\{-\frac{1}{\hbar^2}\int_0^\beta dt\,\dot{Q}_{\lambda_r}(t)\dot{Q}_{-\lambda_r}(t)\right\}d\xi_{\lambda_r}d\xi_{-\lambda_r} \tag{A1.2}$$

where in deriving Eq. (A1.2), we have assumed that the Riemann and path integrations can be interchanged.

It suffices to show that $I_\ell = 0$ , where

$$I_\ell = \iiint\int_{\xi_{\lambda_r}}^{\xi_{\lambda_r}}\mathcal{D}[Q_{\lambda_r}(t)]\,\mathcal{D}[Q_{-\lambda_r}(t)]\ Q_{\lambda_r}(t_1)\cdots Q_{\lambda_r}(t_{2n+1})\times$$

$$\times\, Q_{\lambda_r}(s_1)\,Q_{-\lambda_r}(s_1)\cdots Q_{\lambda_r}(s_\ell)\,Q_{-\lambda_r}(s_\ell)\times$$

$$\times\ \exp\left\{-\frac{1}{\hbar^2}\int_0^\beta dt\,\dot{Q}_{\lambda_r}(t)\dot{Q}_{-\lambda_r}(t)\right\}d\xi_{\lambda_r}d\xi_{-\lambda_r} \tag{A1.3}$$

To this end, subdivide the interval $[0,\beta]$ into m subintervals with $2\ell+2n+1$ of the partition points given by $\{Q_{\lambda_r}(t_1),\ldots,Q_{\lambda_r}(t_{2n+1}),Q_{\lambda_r}(s_1),\ldots\ Q_{-\lambda_r}(s_\ell)\}$ . If some of the $t_j, s_k$ coincide, the above set may have fewer than $2\ell+2n+1$ elements. We will assume that all the $t_j$ , $j=1,2,\ldots,2n+1$, $s_j$ , $j=1,\ldots,\ell$ , are distinct. The arguments for the case when the $Q_{\lambda_r}(t_j), Q_{\lambda_r}(s_k)$ are not distinct is similar to the one we use. For each partition point $t_j'$, $j = 1, \ldots, m$, associate the special point $q_{\lambda_r}(t_j') = u_{\lambda_r}(t_j') + i v_{\lambda_r}(t_j')$ with the above restrictions. Suppose the $t_j'$ are distinct. Let $t_0' = 0$, $t_{m+1}' = \beta$, and $q_{\lambda_r}(t_0') = q_{\lambda_r}(t_{m+1}') = \xi_{\lambda_r}$. If we use the approximation given in Eq. (3.16), then

$$\exp\left\{ -\frac{1}{\hbar^2} \int_0^\beta dt\, \dot{Q}_{\lambda_r}(t)\, \dot{Q}_{-\lambda_r}(t) \right\}$$

$$\approx \exp\left\{ -\sum_{j=0}^{m} \left[ q_{\lambda_r}(t_{j+1}') - q_{\lambda_r}(t_j') \right] \left[ q_{-\lambda_r}(t_{j+1}') - q_{-\lambda_r}(t_j') \right] \frac{1}{\hbar^2 (t_{j+1}' - t_j')} \right\}$$

$$= \exp\left\{ -\frac{1}{\hbar^2} \sum_{j=0}^{m} \frac{1}{(t_{j+1}' - t_j')} \left[ \{ u_{\lambda_r}(t_{j+1}') - u_{\lambda_r}(t_j') \}^2 + \{ v_{\lambda_r}(t_{j+1}') - v_{\lambda_r}(t_j') \}^2 \right] \right\}$$

Hence

$$I_\ell = \lim_{\max |t_{j+1}' - t_j'|} \iint \int \left\{ \prod_{j=1}^{m} \frac{dq_{\lambda_r}(t_j')\, dq_{-\lambda_r}(t_j')}{[2\pi \hbar^2 (t_{j+1}' - t_j')]} \right\} \frac{Q_{\lambda_r}(t_1) \cdots Q_{\lambda_r}(t_{2n+1})\, Q_{\lambda_r}(s_1) \cdots Q_{-\lambda_r}(s_\ell)}{[2\pi \hbar^2 t_1']} \times$$

$$\times \exp\left\{ -\frac{1}{\hbar^2} \sum_{j=0}^{m} \frac{1}{(t_{j+1}' - t_j')} \left[ \{ u_{\lambda_r}(t_{j+1}') - u_{\lambda_r}(t_j') \}^2 + \{ v_{\lambda_r}(t_{j+1}') - v_{\lambda_r}(t_j') \}^2 \right] \right\} d\xi_{\lambda_r}\, d\xi_{-\lambda_r}$$

where the integration is over the whole complex plane. Transforming the integration variables to the real and imaginary parts of the $q_{\lambda_r}(t_j')$, just as is usually done, since the integrals are "ordinary" integrals, we obtain

$$I_\ell = \lim_{\max|t'_{j+1}-t'_j|\to 0} \iint \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \left[ \prod_{j=1}^{m} \left\{ \frac{2\,du_{\lambda_r}(t'_j)\,dv_{\lambda_r}(t'_j)}{2\pi\hbar^2 (t'_{j+1}-t'_j)} \right\} \right] \left( \frac{1}{2\pi\hbar^2 t'_1} \right)$$

$$\times \left[ x_{\lambda_r}(t_1) + i y_{\lambda_r}(t_1) \right] \cdots \left[ x_{\lambda_r}(t_{2n+1}) + i y_{\lambda_r}(t_{2n+1}) \right] \times$$

$$\times \left[ x^2_{\lambda_r}(s_1) + y^2_{\lambda_r}(s_1) \right] \cdots \left[ x^2_{\lambda_r}(s_\ell) + y^2_{\lambda_r}(s_\ell) \right] \times$$

$$\times \exp \left\{ -\frac{1}{\hbar^2} \sum_{j=0}^{m} \frac{1}{(t'_{j+1}-t'_j)} \left[ \left\{ u_{\lambda_r}(t'_{j+1}) - u_{\lambda_r}(t'_j) \right\}^2 + \right. \right.$$

$$\left. \left. + \left\{ v_{\lambda_r}(t'_{j+1}) - v_{\lambda_r}(t'_j) \right\}^2 \right] \right\} d\xi_{\lambda_r}\, d\xi_{-\lambda_r}$$

If we now multiply out $[x_{\lambda_r}(t_1)+iy_{\lambda_r}(t_1)] \cdots [x^2_{\lambda_r}(s_\ell)+y^2_{\lambda_r}(s_\ell)]$ and do each integral individually, we observe that each term will either contain an odd number of $x_{\lambda_r}(t_j)$ or $y_{\lambda_r}(t_j)$ Since the boundary points of the path integral are the same it follows that $I_\ell = 0$ , (Gel'fand and Yaglom (1960))*.

Observe further that this result is verified in Eq. (6.18), for if the generating functional is functionally differentiated an odd number of times and the "source term" set equal to zero, then the result will be zero.

*GEL'FAND, I.M., and YAGLOM, A.M., J. Math. Phys. 1, 48 (1960)

Appendix 2

While evaluating the various terms of the Helmholtz free energy to $O(\lambda^4)$, it is apparent that apart from a trivial integral connected with the loop at any vertex of the diagram, there are two basic types of integrals required. All special cases needed in the expressions of $W_1, \ldots, W_{24}$, and $S_1, \ldots, S_{11}$ for the Debye-Waller factor, can be obtained from the above two integrals.

Type 1: In this type, we have n dots, and suppose that the number of lines connecting $s_j$ to $s_{j+1}$ is $m_j$, where $s_j$ is the variable of integration and $m_j \geq 0$. We use the convention $s_1 \equiv s_{n+1}$. Then, the integral that is required is

$$I_n = \int_0^\beta ds_1 \cdots \int_0^\beta ds_n \prod_{j=1}^{n} \left[ \prod_{r_j=1}^{m_j} D_{\lambda_{r_j}}(s_j, s_{j+1}) \right]$$

$$= \int_0^\beta ds_1 \cdots \int_0^\beta ds_n \prod_{j=1}^{n} \prod_{r_j=1}^{m_j} \left(\frac{\hbar}{2\omega_{\lambda_{r_j}}}\right) \left\{ \sum_{\alpha_{r_j}=\pm 1} \alpha_{r_j} N_{\lambda_{r_j}}(\alpha_{r_j})\, e^{a_{r_j}|s_j - s_{j+1}|} \right\}$$

$$= A\left[\prod_{j=1}^{n}\left\{\prod_{r_j=1}^{m_j} \sum_{\alpha_{r_j}=\pm 1} \alpha_{r_j} N_{\lambda_{r_j}}(\alpha_{r_j})\right\}\right] \int_0^\beta ds_1 \cdots \int_0^\beta ds_n \exp\left\{\sum_{\ell=1}^{n} b_\ell |s_\ell - s_{\ell+1}|\right\} \tag{A2.1}$$

where $a_{r_j} = \alpha_{r_j} \hbar\omega_{\lambda_{r_j}}$, $N_{\lambda_{r_j}}(\alpha_{r_j}) = \left[e^{\alpha_{r_j}\beta\hbar\omega_{\lambda_{r_j}}} - 1\right]^{-1}$, $A = \prod_{j=1}^{n}\prod_{r_j=1}^{m_j}\left(\frac{\hbar}{2\omega_{\lambda_{r_j}}}\right)$

and

$$b_\ell = \sum_{r_\ell=1}^{m_\ell} a_{r_\ell} .$$

Note that if $m_\ell = 0$, put $\prod_{r_\ell=1}^{m_\ell} \left(\frac{\hbar}{2\omega_{\lambda_{r_\ell}}}\right) \sum_{\alpha_{r_\ell}=\pm 1} \alpha_{r_\ell} N_{\lambda_{r_\ell}}(\alpha_{r_\ell}) e^{a_{r_\ell}|s_\ell - s_{\ell+1}|} = 1.$

At once, it can be seen that the following integral must be evaluated.

$$J_n \equiv J_n(b_1,\dots,b_n) = \int_0^\beta ds_1 \cdots \int_0^\beta ds_n \exp\left\{\sum_{\ell=1}^{n} b_\ell |s_\ell - s_{\ell+1}|\right\} \tag{A2.2}$$

We perform the integral over $s_j$ remembering that we have to perform the integrals over the variables it is connected to later. Hence, the integral to be evaluated is

$$S(b_{j-1}, b_j) = \int_0^\beta ds_j \exp\left\{ b_{j-1}|s_{j-1} - s_j| + b_j |s_j - s_{j+1}|\right\}$$

$$= \Theta(s_{j+1} - s_{j-1})\, T_1(b_{j-1}, b_j) + \Theta(s_{j-1} - s_{j+1})\, T_2(b_{j-1}, b_j) \tag{A2.3}$$

where

$$\Theta(x) = \begin{Bmatrix} 0 & , x<0 \\ 1 & , x>0 \end{Bmatrix} \equiv \text{the Heaviside function}$$

and $T_1, T_2$ are ordinary integrals because later integrations are taken care of by the Heaviside function.

$$T_1(b_{j-1}, b_j) = \int_0^{s_{j-1}} ds_j\, e^{-b_{j-1}(s_j - s_{j-1}) - b_j(s_j - s_{j+1})} +$$

$$+ \int_{s_{j-1}}^{s_{j+1}} ds_j\, e^{b_{j-1}(s_j - s_{j-1}) - b_j(s_j - s_{j+1})} +$$

$$+ \int_{s_{j+1}}^{\beta} ds_j\, e^{b_{j-1}(s_j - s_{j-1}) + b_j(s_j - s_{j+1})}$$

$$= \frac{e^{b_{j-1} s_{j-1} + b_j s_{j+1}} - e^{b_j (s_{j+1} - s_{j-1})}}{b_j + b_{j-1}} +$$

$$+ \frac{e^{b_{j-1}(s_{j+1} - s_{j-1})} - e^{b_j (s_{j+1} - s_{j-1})}}{b_{j-1} - b_j} +$$

$$+ \frac{e^{b_{j-1}(\beta - s_{j-1}) + b_j(\beta - s_{j+1})} - e^{b_{j-1}(s_{j+1} - s_{j-1})}}{b_j + b_{j-1}}$$

$$T_2(b_{j-1}, b_j) = \int_0^{s_{j+1}} ds_j \; e^{-b_{j-1}(s_j - s_{j-1}) - b_j(s_j - s_{j+1})} +$$

$$+ \int_{s_{j+1}}^{s_{j-1}} ds_j \; e^{-b_{j-1}(s_j - s_{j-1}) + b_j(s_j - s_{j+1})} +$$

$$+ \int_{s_{j-1}}^{\beta} ds_j \; e^{b_{j-1}(s_j - s_{j-1}) + b_j(s_j - s_{j+1})}$$

$$= \frac{e^{b_{j-1} s_{j-1} + b_j s_{j+1}} - e^{b_{j-1}(s_{j-1} - s_{j+1})}}{b_j + b_{j-1}} +$$

$$+ \frac{e^{b_{j-1}(s_{j-1} - s_{j+1})} - e^{b_j (s_{j-1} - s_{j+1})}}{b_{j-1} - b_j} +$$

$$+ \frac{e^{b_{j-1}(\beta - s_{j-1}) + b_j(\beta - s_{j+1})} - e^{b_j (s_{j-1} - s_{j+1})}}{b_j + b_{j-1}}$$

Substituting these expressions into Eq. (A2.3) yields

$$S(b_{j-1}, b_j) = \frac{e^{b_{j-1}(\beta - s_{j-1}) + b_j(\beta - s_{j+1})} + e^{b_{j-1}s_{j-1} + b_j s_{j+1}}}{b_j + b_{j-1}} +$$

$$+ \frac{2}{b_j^2 - b_{j-1}^2} \left\{ b_{j-1} e^{b_j |s_{j-1} - s_{j+1}|} - b_j e^{b_{j-1}|s_{j-1} - s_{j+1}|} \right\} \quad \text{(A2.4)}$$

Finally, we consider the following integral, which arises in the first term of Eq. (A2.4) and Eq. (A2.2);

$$X(b_{j-1}, b_j') = \int_0^\beta ds_j \, e^{b_j' s_j + b_{j-1}|s_{j-1} - s_j|} \quad , (b_j' \neq b_{j-1})$$

$$= \int_0^{s_{j-1}} ds_j \, e^{b_{j-1}s_{j-1} + (b_j' - b_{j-1})s_j} +$$

$$+ \int_{s_{j-1}}^{\beta} ds_j \, e^{-b_{j-1}s_{j-1} + (b_j' + b_{j-1})s_j}$$

$$= \frac{e^{b_j' s_{j-1}} - e^{b_{j-1}s_{j-1}}}{(b_j' - b_{j-1})} + \frac{e^{\beta(b_j' + b_{j-1}) - b_{j-1}s_{j-1}} - e^{b_j' s_{j-1}}}{b_j' + b_{j+1}} \quad \text{(A2.5)}$$

The other kind of integral that arises from the first term of Eq. (A2.4) and Eq. (A2.2) is of a similar form as that given in Eq. (A2.5), and has the same property as that given in Eq. (A2.5), that we will use later on.

We want to simplify the expression for $S$ and hence,

$J_n$ further, but to do this, we must again consider the expression for $I_n$ .

First, note that the $D$ functions are periodic, that is,

$$D_{\lambda_r}(s+\beta) = D_{\lambda_r}(s) \quad , \quad -\beta < s < 0$$

We now make the following change of variables;

$$u_1 = s_1 \quad , \quad u_j = s_1 - s_j \quad , \quad j = 2, 3, \ldots, n$$

Then, $s_r - s_p = u_p - u_r \; , r, p = 2, \ldots, n$ , and the Jacobian for the transformation is $J = \dfrac{\partial(s_1, \ldots, s_n)}{\partial(u_1, \ldots, u_n)} = 1$ . Employing the periodicity of the $D$ functions so that the range of integration does not change, we find that

$$J_n = \int_0^\beta du_1 \cdots \int_0^\beta du_n \exp\left\{ b_1|u_2| + b_n|u_n| + \sum_{r=2}^{n-1} b_r|u_r - u_{r+1}| \right\} \qquad \text{(A2.6)}$$

We immediately observe that the integrand of Eq. (A2.6) is independent of $u_1$ , and hence the integral over $u_1$ gives us a factor of $\beta$ . Since Eq. (A2.6) = Eq. (A2.2), observe that the only way to get this factor of $\beta$ in Eq. (A2.2) is if the last integral performed is a trivial integral. We can see from the expression for $X(b_{j-1}, b_j')$, that this will never be the case for the integrand considered there. Hence, we can drop the first term in expression for $S(b_{j-1}, b_j)$ of Eq. (A2.4). When these integrals are explicitly evaluated and then substituted in the corresponding expressions of free energy and the summations over $\alpha_j$ are carried out and the symmetry of the $V^n(\lambda_1,\dots,\lambda_n)$ coefficients is taken into account, a total of zero contribution is obtained.

Hence,

$$S(b_{j-1},b_j) \text{ "=" } \frac{2}{b_j^2-b_{j-1}^2}\left\{b_{j-1}e^{b_j|s_{j-1}-s_{j+1}|} - b_j e^{b_{j-1}|s_{j-1}-s_{j+1}|}\right\} \tag{A2.7}$$

Performing the integration over $s_n$ first, and then using Eq. (A2.7) in Eq. (A2.2), we have

$$\begin{aligned} J_n(b_1,\dots,b_n) &= \frac{2}{b_n^2-b_{n-1}^2}\{b_{n-1}J_{n-1}(b_1,\dots,b_{n-2},b_n) - \\ &\quad - b_n J_{n-1}(b_1,\dots,b_{n-1})\} \ ; \ n \geq 2 \end{aligned} \tag{A2.8}$$

and $J_1(b_1) = \beta$

This can be substituted in the expression for $I_n$ to get the final result.

The first four expressions for $J_n$ are given below.

(i) $J_1(b_1) = \beta$

(ii) $J_2(b_1,b_2) = (-2)\beta \dfrac{1}{b_1+b_2}$

(iii) $J_3(b_1,b_2,b_3) = (-2)^2\beta \dfrac{(b_1+b_2+b_3)}{(b_1+b_2)(b_1+b_3)(b_2+b_3)}$

(iv) $J_4(b_1,b_2,b_3,b_4) = (-2)^3\beta \dfrac{NUM}{DEN}$,

$$NUM = (b_1+b_2+b_3+b_4)(b_1+b_2)(b_3+b_4) + b_1 b_2(b_1+b_2) + b_3 b_4(b_3+b_4)$$

$$DEN = (b_1+b_2)(b_1+b_3)(b_1+b_4)(b_2+b_3)(b_2+b_4)(b_3+b_4)$$

Loops are easily handled because they produce a factor of $\coth(\frac{1}{2}\beta\hbar\omega_{\lambda_r})$ for each loop, where $\lambda_r$ is chosen appropriately for the vertex in the diagram under consideration.

With the above considerations for loops and the expressions given in Eqs. (i)-(iv), one can evaluate all the contributions to the free energy to $O(\lambda^4)$, except for the terms $W_{21}, W_{22}, W_{24}$. To evaluate these terms, we require the following type 2 integral.

Type 2: It is apparent from the expressions of $W_{21}, W_{22}, W_{24}$ that the following integral must be evaluated;

$$L_n \equiv L_n(b_1, \ldots, b_n) = \int_0^\beta ds \, \exp\left\{\sum_{r=1}^{n} b_r |s - s_r|\right\} \tag{A2.9}$$

One must remember that the integration with respect to $\{s_1, \ldots, s_n\}$ over the interval $[0, \beta]$ is done later. The $b_r$ are constants which are linear combinations of the $a_{r_j}$ .

The evaluation of $L_n$ is extremely tedious for large n. We propose to do the integral of Eq. (A2.9) for a fixed sequence of the $\{s_r\}$ , and from this, one can evaluate the integral in general, using the Heaviside functions as a bookkeeping technique to account for the various terms. We note that the case for $n=2$ is the type 1 integral, and to obtain $W_{21}, W_{22}, W_{24}$ , it is necessary to find $L_3$ .

Suppose the ordering of the variables in Eq. (A2.9) is as follows;

$$s_{r_j} \le s_{r_{j+1}} \; , \; j = 0, 1, \ldots, n \; ; \; s_{r_0} = 0 , \; s_{r_{n+1}} = \beta$$

Then, if Eq. (A2.9) is handled as an integral without taking into consideration the other integrals, we obtain

$$Y_n = \int_0^\beta ds \; \exp \left\{ \sum_{j=1}^n b_{r_j} |s - s_{r_j}| \right\}$$

$$= \left\{ \int_0^{s_{r_1}} ds + \int_{s_{r_1}}^{s_{r_2}} ds + \ldots + \int_{s_{r_n}}^{\beta} ds \right\} \exp \left\{ \sum_{j=1}^n b_{r_j} |s - s_{r_j}| \right\}$$

$$= \int_0^{s_{r_1}} ds \; \exp \left\{ - \sum_{j=1}^n b_{r_j} (s - s_{r_j}) \right\} \quad +$$

$$+ \int_{s_{r_1}}^{s_{r_2}} ds \; \exp \left\{ b_{r_1} (s - s_{r_1}) + \sum_{j=2}^n b_{r_j} (s_{r_j} - s) \right\} \quad +$$

$$+ \quad \cdots \quad +$$

$$+ \int_{s_{r_\ell}}^{s_{r_{\ell+1}}} ds \; \exp \left\{ \sum_{j=1}^{\ell} b_{r_j} (s - s_{r_j}) + \sum_{j=\ell+1}^{n} b_{r_j} (s_{r_j} - s) \right\} +$$

$$+ \quad \cdots \quad +$$

$$+ \int_{s_{r_n}}^{\beta} ds \; \exp \left\{ \sum_{j=1}^n b_{r_j} (s - s_{r_j}) \right\}$$

$$= \frac{\exp\left\{\sum_{j=1}^{n} b_{r_j}(s_{r_j}-s_{r_1})\right\} - \exp\left\{\sum_{j=1}^{n} b_{r_j}(s_{r_j}-s_{r_0})\right\}}{-\sum_{j=1}^{n} b_{r_j}} + \cdots +$$

$$+ \frac{1}{\left[\sum_{j=1}^{\ell} b_{r_j} - \sum_{j=\ell+1}^{n} b_{r_j}\right]}\left\{\exp\left[\sum_{j=1}^{\ell} b_{r_j}(s_{r_{\ell+1}}-s_{r_j}) + \sum_{j=\ell+1}^{n} b_{r_j}(s_{r_j}-s_{r_{\ell+1}})\right] - \right.$$

$$\left. - \exp\left[\sum_{j=1}^{\ell} b_{r_j}(s_{r_\ell}-s_{r_j}) + \sum_{j=\ell+1}^{n} b_{r_j}(s_{r_j}-s_{r_\ell})\right]\right\}$$

$$+ \cdots +$$

$$+ \frac{\exp\left\{\sum_{j=1}^{n} b_{r_j}(s_{r_{n+1}}-s_{r_j})\right\} - \exp\left\{\sum_{j=1}^{n} b_{r_j}(s_{r_n}-s_{r_j})\right\}}{\sum_{j=1}^{n} b_{r_j}}$$

$$= \sum_{\ell=0}^{n} \frac{1}{\left[\sum_{j=1}^{\ell} b_{r_j} - \sum_{j=\ell+1}^{n} b_{r_j}\right]}\left\{\exp\left[\sum_{j=1}^{\ell} b_{r_j}(s_{r_{\ell+1}}-s_{r_j}) + \sum_{j=\ell+1}^{n} b_{r_j}(s_{r_j}-s_{r_{\ell+1}})\right] - \right.$$

$$\left. - \exp\left[\sum_{j=1}^{\ell} b_{r_j}(s_{r_\ell}-s_{r_j}) + \sum_{j=\ell+1}^{n} b_{r_j}(s_{r_j}-s_{r_\ell})\right]\right\} \tag{A2.10}$$

To get the result for Eq. (A2.9), we use Heaviside functions to account for all possible ordering schemes of the $s_r$ . There are $n!$ different orderings.

We now write down the result for $n = 3$.

$$L_3(b_1,b_2,b_3) = \int_0^\beta ds \ \exp\left\{ b_1|s-s_1| + b_2|s-s_2| + b_3|s-s_3| \right\}$$

$$= \Theta(s_1-s_2)\Theta(s_1-s_3)\Theta(s_2-s_3)Y_{31} + \Theta(s_1-s_2)\Theta(s_1-s_3)\Theta(s_3-s_2)Y_{32} +$$

$$+ \Theta(s_2-s_1)\Theta(s_2-s_3)\Theta(s_1-s_3)Y_{33} + \Theta(s_2-s_1)\Theta(s_2-s_3)\Theta(s_3-s_1)Y_{34} +$$

$$+ \Theta(s_3-s_1)\Theta(s_3-s_2)\Theta(s_1-s_2)Y_{35} + \Theta(s_3-s_1)\Theta(s_3-s_2)\Theta(s_2-s_1)Y_{36}$$

where $Y_{3J}$ is the same as in Eq. (A2.10), with the Heaviside functions determining the order of $\{s_1, s_2, s_3\}$.

Hence,

$$L_3 = \frac{e^{b_1(\beta-s_1)+b_2(\beta-s_2)+b_3(\beta-s_3)} + e^{b_1 s_1 + b_2 s_2 + b_3 s_3}}{b_1+b_2+b_3} +$$

$$+ \frac{2b_1 e^{b_2|s_1-s_2|+b_3|s_1-s_3|}}{(b_1+b_2+b_3)(b_2+b_3-b_1)} + \frac{2b_2 e^{b_1|s_1-s_2|+b_3|s_2-s_3|}}{(b_1+b_2+b_3)(b_3+b_1-b_2)} +$$

$$+ \frac{2b_3 e^{b_1|s_1-s_3|+b_2|s_2-s_3|}}{(b_1+b_2+b_3)(b_1+b_2-b_3)} - \frac{8 b_1 b_2 b_3}{(b_1+b_2+b_3)(b_2+b_3-b_1)(b_3+b_1-b_2)(b_1+b_2-b_3)} \times$$

$$\Big\{ \Theta(s_1-s_2)\Theta(s_3-s_1)e^{b_2(s_1-s_2)+b_3(s_3-s_1)} + \Theta(s_2-s_1)\Theta(s_1-s_3)e^{b_2(s_2-s_1)+b_3(s_1-s_3)} +$$

$$+ \Theta(s_1-s_2)\Theta(s_2-s_3)e^{b_1(s_1-s_2)+b_3(s_2-s_3)} + \Theta(s_2-s_1)\Theta(s_3-s_2)e^{b_1(s_2-s_1)+b_3(s_3-s_2)} +$$

$$+ \Theta(s_1-s_3)\Theta(s_3-s_2)e^{b_1(s_1-s_3)+b_2(s_3-s_2)} + \Theta(s_3-s_1)\Theta(s_2-s_3)e^{b_1(s_3-s_1)+b_2(s_2-s_3)} \Big\}$$

Appendix 3

If one is interested in the high temperature expansion of the Helmholtz function F, or the Debye-Waller factor DWF, where the first term of the expansion gives the classical limit, then the evaluation of the integrals described in appendix 2 is not necessary. We give some of the necessities for obtaining such expansions.

The two parts in the expressions for the various terms in F and DWF that contain temperature dependence are

$$N_{\lambda_r}(\alpha_r) = \left[e^{\alpha_r \beta \hbar \omega_{\lambda_r}} - 1\right] \quad , \alpha_r = \pm 1$$

and the exponentials in the integrals, one of which would have the following form $\exp[\alpha_r \hbar\, \omega_{\lambda_r} |s_j - s_\ell|]$.

To get the above expansion in F and DWF, one can expand $N_{\lambda_r}(\alpha_r)$ and $\exp[\alpha_r \hbar \omega_{\lambda_r} |s_j - s_\ell|]$ in terms of a Taylor series and keep the necessary terms. For example, in the classical limit, $(\beta \downarrow +0)$, $N_{\lambda_r}(\alpha_r) \approx [\alpha_r \beta \hbar \omega_{\lambda_r}]^{-1}$, and $\exp[\alpha_r \hbar \omega_{\lambda_r} |s_j - s_\ell|] \approx 1$, (this is a good approximation since the interval of integration is $[0, \beta]$ ). The integrals, in this case, become trivial, and in fact, the manipulations involving the temperature factors simplifies.

For high temperature results, the useful expansions are

$$N_{\lambda_r}(\alpha_r) = \left[e^{\alpha_r \beta \hbar \omega_{\lambda_r}} - 1\right]^{-1} = \sum_{n=0}^{+\infty} \frac{B_n}{n!} \left[\alpha_r \beta \hbar \omega_{\lambda_r}\right]^{n-1}$$

where the $B_n$ are the Bernoulli numbers, and

$$\exp\left[\alpha_r \hbar \omega_{\lambda_r} |s_j - s_\ell|\right] = \sum_{n=0}^{+\infty} \frac{1}{n!}\left[\alpha_r \hbar \omega_{\lambda_r} |s_j - s_\ell|\right]^n$$

To get the results for low (zero) temperatures, that is, $\beta \uparrow +\infty$, one has to perform the integrations of the exponential functions, and then use the low temperature expansions of $N_{\lambda_r}(\alpha_r)$. The appropriate expansions are

$$N_{\lambda_r}(1) = \left[e^{\beta\hbar\omega_{\lambda_r}} - 1\right]^{-1} = \sum_{n=0}^{+\infty} e^{-(n+1)\beta\hbar\omega_{\lambda_r}} \,,$$

$$N_{\lambda_r}(-1) = \left[e^{-\beta\hbar\omega_{\lambda_r}} - 1\right]^{-1} = -\sum_{n=0}^{+\infty} e^{-n\beta\hbar\omega_{\lambda_r}} = -\left[N_{\lambda_r}(1) + 1\right]$$

If one wants the zero temperature limit, one must set $D_{\lambda_r}(s,s') = \frac{\hbar}{2\omega_{\lambda_r}} e^{-\hbar\omega_{\lambda_r}|s-s'|}$, and then perform the necessary integrations.

There is no advantage in performing the zero temperature calculation because the integrals are as complicated as for the finite temperature case. Perhaps the only simplification over the finite temperature case lies in performing a fewer sums over $\alpha_j$.

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