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Function space integration for the evaluation of the statistical sum of coupled anharmonic oscillators

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Abstract. The functional integral representation of the Green function of Bloch's equation is employed for the derivation of a generating functional, used to obtain an expansion of the statistical sum of coupled anharmonic oscillators. The analysis basically involves averaging of functional polynomials against an appropriate Gaussian measure. Specific applications of the final results are not treated.

1. Introduction

The potential energy encountered in lattice vibrations for a system of N particles (usually nearest neighbours) consists of an harmonic part and anharmonic terms. Simultaneous diagonalization of the kinetic energy of the system and the harmonic part of the potential energy, via an appropriate congruent transformation (see e.g. Goldstein 1953), leads to the following Lagrangian for the system:

$$L = \tfrac{1}{2}\sum_{1}^{3N}(\dot{\xi}_i^2 - \Lambda_i^2\xi_i^2) - v_1(\boldsymbol{\xi}) \tag{1.1}$$

where

$$v_1(\boldsymbol{\xi}) = \sum_{1}^{3N}(V_{ijk}^{(3)}\xi_i\xi_j\xi_k + V_{ijkl}^{(4)}\xi_i\xi_j\xi_k\xi_l + \ldots) \tag{1.1a}$$

$\boldsymbol{\xi}$ is a $3N$-dimensional vector with components ξ_i. $v_1(\boldsymbol{\xi})$ is the anharmonic part of the potential energy. We shall restrict the discussion to the case when all Λ_j^2 are positive. This implies that in the absence of anharmonicities the motion is strictly vibrational.

For the statistical study of the thermodynamic properties of an assembly of independent systems, each with Hamiltonian H, it is of great importance to know the statistical sum (Boltzmann quantum partition function),

$$Z(\beta) = \sum_{\{n\}}\exp(-\beta E_n); \qquad \beta = \frac{1}{\kappa T} \tag{1.2}$$

of the system. The summation in (1.2) is taken over all states of the system. E_n are the quantum eigenvalues of the Hamiltonian operator of the system.

From (1.1) we obtain for the Hamiltonian operator

$$\mathscr{H} = -\tfrac{1}{2}\sum_{1}^{3N}\left(\hbar^2\frac{\partial^2}{\partial\xi_i^2} - \Lambda_i^2\xi_i^2\right) + v_1(\boldsymbol{\xi}). \tag{1.3}$$

It is well known that one may obtain the partition function Z of the system from the Green function

$$G(\boldsymbol{\xi}'\beta|\boldsymbol{\xi}''0) = \sum_{\{n\}}\Phi_n(\boldsymbol{\xi}')\Phi_n^*(\boldsymbol{\xi}'')\exp(-\beta E_n) \tag{1.4}$$

of the Bloch equation

$$\frac{\partial\Psi(\boldsymbol{\xi},\beta)}{\partial\beta} = -\mathscr{H}\Psi(\boldsymbol{\xi},\beta) \tag{1.5}$$

by setting $\boldsymbol{\xi}'' = \boldsymbol{\xi}'$ and subsequently integrating with respect to $\boldsymbol{\xi}'$ over all $\boldsymbol{\xi}'$ space.

The Green function of Bloch's equation takes the form of a conditional path integral (see e.g. Yaglom 1956). In the case of our Hamiltonian given in (1.3), we have

$$G(\boldsymbol{\xi}'\beta|\boldsymbol{\xi}''0) = \Big(\prod_{0\leqslant s<\beta} 2\pi\hbar^2\, ds\Big)^{-3N/2} \int_{\substack{\boldsymbol{\xi}(0)=\boldsymbol{\xi}'\\ \boldsymbol{\xi}(\beta)=\boldsymbol{\xi}'}} \exp\Big[-\int_0^\beta \Big\{\frac{1}{2\hbar^2}\dot{\tilde{\boldsymbol{\xi}}}(s)\dot{\boldsymbol{\xi}}(s)+\tfrac{1}{2}\tilde{\boldsymbol{\xi}}(s)\Lambda^2\boldsymbol{\xi}(s)\Big\}\, ds\Big]$$

$$\times \exp\Big\{-\int_0^\beta v_1(\boldsymbol{\xi}(s))\, ds\Big\} \prod_{0<s<\beta} d\boldsymbol{\xi}(s). \tag{1.6}$$

$\tilde{\boldsymbol{\xi}}$ stands for the transpose of $\boldsymbol{\xi}$, $d\boldsymbol{\xi}(s)$ for $d\boldsymbol{\xi}_1(s)\, d\boldsymbol{\xi}_2(s) \ldots d\boldsymbol{\xi}_{3N}(s)$ and $\dot{\boldsymbol{\xi}}(s)$ for $d\boldsymbol{\xi}(s)/ds$.

Since we are not interested in the Green function as such, but in the form $G(\boldsymbol{\xi}'\beta|\boldsymbol{\xi}'0)$, the end-point condition in the functional integral will be taken from now on as

$$\boldsymbol{\xi}(0) = \boldsymbol{\xi}(\beta) = \boldsymbol{\xi}'. \tag{1.7}$$

Thus, we shall be considering paths $\boldsymbol{\xi}(s)$ starting from $\boldsymbol{\xi}'$ at infinite temperature ($s = 0$) and terminating at the same point $\boldsymbol{\xi}'$ at temperature $T = 1/\kappa\beta$. More explicitly the partition function is expressed as

$$Z(\beta) = \int G(\boldsymbol{\xi}'\beta|\boldsymbol{\xi}'0)\, d\boldsymbol{\xi}'. \tag{1.8}$$

In § 2 we develop an expansion of Z with the harmonic as leading term. The subsequent terms are built up from the anharmonicity coefficients and averages of functional polynomials taken against a measure entirely dependent on the harmonic part of the Hamiltonian. Section 3 is devoted to the evaluation of a generating functional via which the functional averaging is effected. Lastly § 4 deals with an explicit evaluation of the first few correction terms, satisfactory for small anharmonicities.

The expansion method is independent of the size of the anharmonic coefficients, but the practical usefulness will depend greatly on them.

2. Expansion procedure

We begin by expanding the expontial functional involving v_1, in (1.6) as follows:

$$\exp\Big\{-\int_0^\beta v_1(\boldsymbol{\xi}(s))\, ds\Big\} = 1 - \Big\{\sum V^{(3)}_{ijk}\int_0^\beta \xi_i(s_1)\xi_j(s_1)\xi_k(s_1)\, ds_1$$

$$+\sum V^{(4)}_{ijkl}\int_0^\beta \xi_i(s_1)\xi_j(s_1)\xi_k(s_1)\xi_l(s_1)\, ds_1 + \ldots\Big\}$$

$$+\frac{1}{2!}\Big\{\sum V^{(3)}_{i_1j_1k_1}V^{(3)}_{i_2j_2k_2}\int_0^\beta\int_0^\beta \xi_{i_1}(s_1)\xi_{j_1}(s_1)\xi_{k_1}(s_1)$$

$$\times \xi_{i_2}(s_2)\xi_{j_2}(s_2)\xi_{k_2}(s_2)\, ds_1\, ds_2$$

$$+\sum V^{(3)}_{i_1j_1k_1}V^{(4)}_{i_2j_2k_2l_2}\int_0^\beta\int_0^\beta \xi_{i_1}(s_1)\xi_{j_1}(s_1)\xi_{k_1}(s_1)$$

$$\times \xi_{i_2}(s_2)\xi_{j_2}(s_2)\xi_{k_2}(s_2)\xi_{l_2}(s_2)\, ds_1\, ds_2 + \ldots\Big\} + \ldots. \tag{2.1}$$

The series (2.1) is convergent irrespectively of the sizes of the coefficients of anharmonicity $V^{(n)}$. However for small $V^{(n)}$ it will be sufficient to restrict the expansion to their lower powers.

Inserting (1.6) for the Green function into the expression (1.8) for the partition function and utilizing the expansion (2.1), we find that the partition function $Z(\beta)$ is expressed as a linear combination of functional polynomial averages of the following typical form:

$$I^{(n)}_{i_1\ldots p_1;\,i_2\ldots l_n} = \int d\boldsymbol{\xi}' \int_{\boldsymbol{\xi}(0)=\boldsymbol{\xi}(\beta)=\boldsymbol{\xi}'} \mathscr{D}_0{}^{\beta}[\boldsymbol{\xi}(s)]\left\{\int_0^{\beta}\cdots\int_0^{\beta}\xi_{i_1}(s_1)\ldots\xi_{p_1}(s_1)\right.$$

$$\left.\times\,\xi_{i_2}(s_2)\ldots\xi_{l_n}(s_n)\,ds_1\,ds_2\ldots ds_n\right\} \tag{2.2}$$

where we have adopted the notation:

$$\mathscr{D}_0{}^{\beta}[\boldsymbol{\xi}(s)] = \left(\prod_{0\leqslant s<\beta} 2\pi\hbar^2\,ds\right)^{-3N/2}$$

$$\times\exp\left\{-\int_0^{\beta}\left\{\frac{1}{2\hbar^2}\dot{\tilde{\boldsymbol{\xi}}}(s)\dot{\boldsymbol{\xi}}(s)+\tfrac{1}{2}\tilde{\boldsymbol{\xi}}(s)\Lambda^2\boldsymbol{\xi}(s)\right]ds\right\}\prod_{0<s<\beta}d\boldsymbol{\xi}(s) \tag{2.3}$$

which represents the basic measure for our averaging processes. This measure, besides the usual 'kinetic energy term' in the exponent, also involves the harmonic part of the potential energy. In the language of matrix element perturbation theory, this would mean that the complete set of functions is the set of all functions corresponding to the harmonic part of the Hamiltonian (1.3). Thus, the convergence behaviour of the present method is expected to be that of the above matrix element perturbation approach.

An important property of the symbols $I^{(n)}_{\ldots}$ defined in (2.2) is that any permutation of a set of indices of the same sublabel α (indicating a particular variable s_α of integration from 0 to β) leaves the symbol invariant. More explicitly if P_α denotes a permutation operator on the set of indices with label α, we have

$$P_\alpha I^{(n)}_{i_1\ldots p_1;\ldots;i_\alpha\ldots k_\alpha;\ldots l_n} = I^{(n)}_{i_1\ldots p_1;\ldots;i_\alpha\ldots k_\alpha;\ldots l_n}. \tag{2.4}$$

This is easily established from (2.2).

Furthermore, from the Gaussian character of the measure it follows that any symbol $I^{(n)}_{\ldots}$ with an odd number of indices is zero. Also, among the $I^{(n)}_{\ldots}$ with an even number of indices, there are zero elements. The rules for picking out the non-zero $I^{(n)}_{\ldots}$ with an even number of indices will become clear when we arrive at the evaluation of these symbols via a generating functional.

Combining (1.6), (1.8), (2.1) and (2.2) we express the partition function in terms of symbols $I^{(n)}_{\ldots}$ as follows:

$$Z(\beta) = Z_0(\beta)-\left(\sum V^{(4)}_{ijkl}I^{(1)}_{ijkl}+\sum V^{(6)}_{ijklmn}I^{(1)}_{ijklmn}+\ldots\right)$$

$$+\frac{1}{2!}\left(\sum V^{(3)}_{i_1j_1k_1}V^{(3)}_{i_2j_2k_2}I^{(2)}_{i_1j_1k_1;\,i_2j_2k_2}+\ldots\right.$$

$$\left.+\sum V^{(4)}_{i_1j_1k_1l_1}V^{(4)}_{i_2j_2k_2l_2}I^{(2)}_{i_1j_1k_1l_1;\,i_2j_2k_2l_2}+\ldots\right)+\ldots \tag{2.5}$$

where

$$Z_0(\beta) = \int d\boldsymbol{\xi}'\int_{\boldsymbol{\xi}(0)=\boldsymbol{\xi}(\beta)=\boldsymbol{\xi}'}\mathscr{D}_0{}^{\beta}[\boldsymbol{\xi}(s)] \tag{2.5a}$$

and Z_0 is the partition function of the system in the absence of anharmonicities. For the derivation of (2.5) we have taken into account that the $I^{(n)}_{\ldots}$ with an odd number of indices are zero.

The functional averages (2.2) are most easily obtained via integro-differential operations on the following generating functional:

$$\mathscr{Z}_0{}^{\beta}[J(s)] = \int d\boldsymbol{\xi}'\int_{\boldsymbol{\xi}(0)=\boldsymbol{\xi}(\beta)=\boldsymbol{\xi}'}\mathscr{D}_0{}^{\beta}[\boldsymbol{\xi}(s)]\exp\left\{\int_0^{\beta}\tilde{J}(s)\boldsymbol{\xi}(s)\,ds\right\}. \tag{2.6}$$

$J(s)$ is a $3N$-dimensional vector function. In fact (2.2) can be written as

$$I^{(n)}_{i_1 \ldots p_1; i_2 \ldots l_n} = \int \mathrm{d}\boldsymbol{\xi}' \int_{\boldsymbol{\xi}(0)=\boldsymbol{\xi}(\beta)=\boldsymbol{\xi}'} \mathscr{D}_0{}^{\beta}[\boldsymbol{\xi}(s)] \int_0^{\beta} \ldots \int_0^{\beta} \mathrm{d}s_1\, \mathrm{d}s_2 \ldots \mathrm{d}s_n$$
$$\times \frac{\delta}{\delta J_{i_1}(s_1)} \cdots \frac{\delta}{\delta J_{p_1}(s_1)} \frac{\delta}{\delta J_{i_2}(s_2)} \cdots \frac{\delta}{\delta J_{l_n}(s_n)} \exp\left\{\int_0^{\beta} \tilde{J}(s)\boldsymbol{\xi}(s)\, \mathrm{d}s\right\}\Bigg|_{J=0}. \tag{2.7}$$

It is possible to perform the functional integrations over all $\boldsymbol{\xi}(s)$ first and subsequently the various functional differentiations, followed by the corresponding integrations over s_j. The details for a similar case may be found in Tarski (1967). Therefore (2.7) can be written in terms of the generating functional (2.6) as

$$I^{(n)}_{i_1 \ldots p_1; i_2 \ldots l_n} = \int_0^{\beta} \ldots \int_0^{\beta} \mathrm{d}s_1\, \mathrm{d}s_2 \ldots \mathrm{d}s_n \frac{\delta}{\delta J_{i_1}(s_1)} \cdots \frac{\delta}{\delta J_{p_1}(s_1)}$$
$$\times \frac{\delta}{\delta J_{i_2}(s_2)} \cdots \frac{\delta}{\delta J_{l_n}(s_n)} \mathscr{Z}_0{}^{\beta}[J(s)]\Bigg|_{J=0}. \tag{2.8}$$

The vector function $J(s)$ is a temperature prescribed acceleration. It may be imagined to be responsible for the various phonon–phonon interactions. However, its role in the present work is to facilitate the averaging processes.

3. The generating functional

To evaluate the generating functional, let us first find the functional integral on the right of the operator $\int \mathrm{d}\boldsymbol{\xi}'$, in (2.6). Using (2.3) for the measure $\mathscr{D}_0{}^{\beta}[\boldsymbol{\xi}(s)]$, this integral can be written

$$G(\boldsymbol{\xi}'\beta|\boldsymbol{\xi}'0;{}_0{}^{\beta}[J(s)]) = \left(\prod_{0 \leqslant s < \beta} 2\pi\hbar^2\, \mathrm{d}s\right)^{-3N/2}$$
$$\times \int_{\boldsymbol{\xi}(0)=\boldsymbol{\xi}(\beta)=\boldsymbol{\xi}'} \exp\left\{-\int_0^{\beta}\left[\frac{1}{2\hbar^2}\dot{\tilde{\boldsymbol{\xi}}}(s)\dot{\boldsymbol{\xi}}(s) + \tfrac{1}{2}\tilde{\boldsymbol{\xi}}(s)\Lambda^2\boldsymbol{\xi}(s) - \tilde{J}(s)\boldsymbol{\xi}(s)\right]\mathrm{d}s\right\}$$
$$\times \prod_{0<s<\beta} \mathrm{d}\boldsymbol{\xi}(s). \tag{3.1}$$

To evaluate the path integral (3.1), it is convenient to employ the transformation (Feynman and Hibbs 1965)

$$\boldsymbol{\xi}(s) = \boldsymbol{X}(s) + \boldsymbol{y}(s) \tag{3.2}$$

where $\boldsymbol{X}(s)$ is the path which minimizes the integral in the exponential argument of (3.1):

$$A_0{}^{\beta}[\boldsymbol{\xi}(s)] = \int_0^{\beta}\left\{\frac{1}{2\hbar^2}\dot{\tilde{\boldsymbol{\xi}}}(s)\dot{\boldsymbol{\xi}}(s) + \tfrac{1}{2}\tilde{\boldsymbol{\xi}}(s)\Lambda^2\boldsymbol{\xi}(s) - \tilde{J}(s)\boldsymbol{\xi}(s)\right\}\mathrm{d}s \tag{3.3}$$

and satisfies the conditions

$$\boldsymbol{X}(0) = \boldsymbol{X}(\beta) = \boldsymbol{\xi}'. \tag{3.4}$$

The minimizing path satisfies the variational equation

$$\delta A_0{}^{\beta}[\boldsymbol{\xi}(s)] = 0 \tag{3.5}$$

with fixed $\boldsymbol{\xi}(s)$ at $s = 0$ and $s = \beta$. The Euler–Lagrange equations, derived from (3.5) are

$$\ddot{\boldsymbol{\xi}}(s) - \hbar^2\Lambda^2\boldsymbol{\xi}(s) = -\hbar^2 J(s). \tag{3.6}$$

The solution of (3.6), which satisfies the conditions (3.4) can be easily verified to be

$$
\begin{aligned}
X(s) = {} & \{\cosh(\Lambda\hbar s) - \tanh(\tfrac{1}{2}\Lambda\hbar\beta)\sinh(\Lambda\hbar s)\}\boldsymbol{\xi}' \\
& + \hbar\Lambda^{-1}\{\sinh(\Lambda\hbar\beta)\}^{-1}\int_0^\beta \sinh\{\Lambda\hbar(\beta - s')\}\sinh(\Lambda\hbar s)J(s')\,\mathrm{d}s' \\
& - \hbar\Lambda^{-1}\int_0^s \sinh\{\Lambda\hbar(s-s')\}J(s')\,\mathrm{d}s'.
\end{aligned} \tag{3.7}
$$

Introducing the transformation (3.2) into (3.3) we have

$$
A_0{}^\beta[\boldsymbol{\xi}(s)] = A_0{}^\beta[X(s)] + \int_0^\beta \left\{\frac{1}{2\hbar^2}\tilde{\dot{y}}(s)\dot{y}(s) + \tfrac{1}{2}\tilde{y}(s)\Lambda^2 y(s)\right\}\mathrm{d}s. \tag{3.8}
$$

In (3.8), the first-order term in $y(s)$ vanishes, since this is the first variation of the functional A, which has been taken to be zero in (3.5). Straightforward evaluation of $A_0{}^\beta[X(s)]$ is very laborious. However, integration by parts of the kinetic energy term, and utilization of the equation (3.6) for the minimizing path yields

$$
A_0{}^\beta[X(s)] = \frac{1}{2\hbar^2}[\tilde{X}(\beta)\dot{X}(\beta) - \tilde{X}(0)\dot{X}(0)] - \tfrac{1}{2}\int_0^\beta \tilde{X}(s)J(s)\,\mathrm{d}s. \tag{3.9}
$$

Using (3.7) for the minimizing path and recalling (3.4), we write (3.9) as

$$
\begin{aligned}
A_0{}^\beta[X(s)] = {} & \frac{1}{\hbar}\tilde{\boldsymbol{\xi}}'\Lambda\tanh(\tfrac{1}{2}\Lambda\hbar\beta)\boldsymbol{\xi}' \\
& - \tilde{\boldsymbol{\xi}}'\int_0^\beta \{\cosh(\Lambda\hbar s') - \tanh(\tfrac{1}{2}\Lambda\hbar\beta)\sinh(\Lambda\hbar s')\}J(s')\,\mathrm{d}s' \\
& - \frac{\hbar}{2}\int_0^\beta\int_0^\beta \tilde{J}(s)\Lambda^{-1}[\{\sinh(\Lambda\hbar\beta)\}^{-1}\sinh\{\Lambda\hbar(\beta-s')\}\sinh(\Lambda\hbar s) \\
& + \Theta(s-s')\sinh\{\Lambda\hbar(s-s')\}]J(s')\,\mathrm{d}s\,\mathrm{d}s'
\end{aligned} \tag{3.10}
$$

where in (3.10) we have introduced the step function Θ to extend the range of integration from 0 to β, in the last integral of (3.7). With the aid of transformation (3.2), relation (3.8) and the measure (2.3), (3.1) is written as

$$
G(\boldsymbol{\xi}'\beta|\boldsymbol{\xi}'0;\, {}_0{}^\beta[J(s)]) = \exp\{-A_0{}^\beta[X(s)]\}\int_{y(0)=y(\beta)=0} \mathscr{D}_0{}^\beta[y(s)]. \tag{3.11}
$$

The evaluation of the functional integral on the right-hand side of (3.11) is:

$$
\int_{y(0)=y(\beta)=0} \mathscr{D}_0{}^\beta[y(s)] = [\det\{2\pi\hbar\Lambda^{-1}\sinh(\Lambda\hbar\beta)\}]^{1/2}. \tag{3.11a}
$$

The details for the evaluation of (3.11a), appear, for example, in the treatment of a more general case of this type (Papadopoulos 1968). For the evaluation of the generating functional, we also need the result

$$
\begin{aligned}
\int_0^\beta \exp\{-A_0{}^\beta[X(s)]\}\,\mathrm{d}\boldsymbol{\xi}' = {} & [\det\{\pi\hbar\Lambda^{-1}\coth(\tfrac{1}{2}\Lambda\hbar\beta)\}]^{1/2} \\
& \times\exp\left\{\frac{\hbar}{4}\int_0^\beta\int_0^\beta \tilde{J}(s)\Lambda^{-1}[\coth(\tfrac{1}{2}\Lambda\hbar\beta)\cosh\{\Lambda\hbar(s-s')\}\right. \\
& \left. - 2\Theta(s-s')\sinh\{\Lambda\hbar(s-s')\}]J(s')\,\mathrm{d}s\,\mathrm{d}s'\right\}.
\end{aligned} \tag{3.12}
$$

For the derivation of (3.12) we have used (3.10) and taken into account the positive definiteness of the matrix Λ.

Combining (2.6), (3.1), (3.11) and (3.12), the following result for the generating functional is obtained:

$$\mathscr{Z}_0{}^\beta[J(s)] = [\det\{2\sinh(\tfrac{1}{2}\Lambda\hbar\beta)\}]^{-1}\exp\left\{\int_0^\beta\int_0^\beta \tilde{J}(s)K(s,s')J(s')\,\mathrm{d}s\,\mathrm{d}s'\right\} \quad (3.13a)$$

where K is a $3N\times 3N$ diagonal matrix given by

$$K(s,s') = \hbar\Lambda^{-1}[\tfrac{1}{4}\coth(\tfrac{1}{2}\Lambda\hbar\beta)\cosh\{\Lambda\hbar(s-s')\} - \tfrac{1}{2}\Theta(s-s')\sinh\{\Lambda\hbar(s-s')\}]. \quad (3.13b)$$

Putting $\boldsymbol{J} = \boldsymbol{0}$ in (3.13*a*), it is easily verified, using (2.5*a*), that the factor in front of the exponential functional of $J(s)$, is the partition function Z_0 corresponding to the harmonic part of the potential energy. Thus

$$Z_0 = \left[\prod_{j=1}^{3N}\{2\sinh(\tfrac{1}{2}\Lambda_j\hbar\beta)\}\right]^{-3N} \quad (3.13c)$$

(see e.g. Feynman and Hibbs (1965)).

4. Evaluation via the generating functional

We are now in a position, employing the generating functional, to obtain the quantities $I^{(n)}_{\cdots}$, required to evaluate the expansion (2.5) of the statistical sum. It is convenient to use an expanded form for the generating functional (3.13):

$$\mathscr{Z}_0{}^\beta[J(s)] = Z_0\left\{1+\frac{1}{1!}(\tilde{J}KJ)+\frac{1}{2!}(\tilde{J}KJ)^2+\dots\right\} \quad (4.1a)$$

where we have let

$$(\tilde{J}KJ) = \int_0^\beta\int_0^\beta \tilde{J}(s)K(s,s')J(s')\,\mathrm{d}s\,\mathrm{d}s'. \quad (4.1b)$$

To evaluate the various $I^{(n)}_{\cdots}$, we shall employ (2.8) and (4.1). It is easy to re-establish that every $I^{(n)}_{\cdots}$ with an odd number of indices is zero. To find the expression for an $I^{(n)}_{\cdots}$ with an even number of indices, say $2m$, one need not operate on the entire generating functional as indicated in (2.8), but just on the mth expansion term:

$$\frac{1}{m!}Z_0(\tilde{J}KJ)^m$$

of (4.1). This is so, since terms of order less than m contain less than $2m$ $\boldsymbol{J}$ components and, therefore, when acted upon by $2m$ $\boldsymbol{J}$ functional differentiations will yield zero. Also, the result for terms of order higher than m will become zero, upon evaluation at $\boldsymbol{J} = \boldsymbol{0}$.

We turn now to the explicit evaluation of the averages $I^{(1)}_{ijkl}$ and $I^{(2)}_{i_1j_1k_1;i_2j_2k_2}$. The first is associated with the first-order correction due to an anharmonic term of the form $V^{(4)}\xi\xi\xi$, whereas the second relates to the second-order correction due to a term of the form $V^{(3)}\xi\xi\xi$.

Employing (2.8) in the case of $I^{(4)}_{ijkl}$ together with (4.1*b*), we have

$$\begin{aligned} I^{(1)}_{ijkl} &= \int_0^\beta \mathrm{d}s\frac{\delta^4}{\delta J_i(s)\delta J_j(s)\delta J_k(s)\delta J_l(s)}\frac{1}{2!}Z_0(\tilde{J}KJ)^2 \\ &= Z_0\int_0^\beta \mathrm{d}s[\{K_{ij}(s,s)+K_{ji}(s,s)\}\{K_{kl}(s,s)+K_{lk}(s,s)\} \\ &\quad +\{K_{ik}(s,s)+K_{ki}(s,s)\}\{K_{jl}(s,s)+K_{lj}(s,s)\} \\ &\quad +\{K_{il}(s,s)+K_{li}(s,s)\}\{K_{jk}(s,s)+K_{kj}(s,s)\}]. \end{aligned} \quad (4.2)$$

If we introduce $C_i(s_1, s_2)$ via

$$K_{ij}(s_1, s_2)+K_{ji}(s_2, s_1) = \delta_{ij}C_i(s_1, s_2) \tag{4.3a}$$

C_i is symmetric with respect to s_1, s_2. Utilizing (3.13*b*) for the diagonal matrix K we find

$$C_i(s_1, s_2) = \tfrac{1}{2}\hbar\Lambda_i^{-1}[\coth(\tfrac{1}{2}\Lambda_i\hbar\beta)\cosh\{\Lambda_i\hbar(s_1-s_2)\} + \{\Theta(s_2-s_1)-\Theta(s_1-s_2)\}\sinh\{\Lambda_i\hbar(s_1-s_2)\}]. \tag{4.3b}$$

Inserting (4.3*a*) into (4.2) we have

$$I^{(1)}_{ijkl} = Z_0\left\{\delta_{ij}\delta_{kl}\int_0^\beta \mathrm{d}sC_i(s, s)C_k(s, s)+(\delta_{ik}\delta_{jl}+\delta_{il}\delta_{jk})\int_0^\beta \mathrm{d}sC_i(s, s)C_j(s, s)\right\}. \tag{4.4a}$$

The integrations in (4.4*a*) are very simple, since $C_i(s, s)$ is constant. We have

$$\int_0^\beta \mathrm{d}sC_i(s, s)C_j(s, s) = \beta\{\tfrac{1}{2}\hbar\Lambda_i^{-1}\coth(\tfrac{1}{2}\Lambda_i\hbar\beta)\}\{\tfrac{1}{2}\hbar\Lambda_j^{-1}\coth(\tfrac{1}{2}\Lambda_j\hbar\beta)\}. \tag{4.4b}$$

The form of (4.4*a*), shows that $I^{(1)}_{ijkl}$ is zero unless the indices *ijkl* can be grouped into pairs of equal indices. Thus, the non-zero components are

$$I^{(1)}_{iiii} = 3Z_0\beta\{\tfrac{1}{2}\hbar\Lambda_i^{-1}\coth(\tfrac{1}{2}\Lambda_i\hbar\beta)\}$$

$$I^{(1)}_{iikk} = I^{(1)}_{ikik} = I^{(1)}_{ikki} = Z_0\beta\{\tfrac{1}{2}\hbar\Lambda_i^{-1}\coth(\tfrac{1}{2}\Lambda_i\hbar\beta)\}\{\tfrac{1}{2}\hbar\Lambda_k^{-1}\coth(\tfrac{1}{2}\Lambda_k\hbar\beta)\} \tag{4.4c}$$

for $i \neq k$.

Next, we have, from (2.8) and (4.1*b*),

$$I^{(2)}_{i_1j_1k_1;\,i_2j_2k_2} = \frac{1}{3!}Z_0\int_0^\beta\int_0^\beta \mathrm{d}s_1\,\mathrm{d}s_2\frac{\delta^3}{\delta J_{i_1}(s_1)\delta J_{j_1}(s_1)\delta J_{k_1}(s_1)} \times\frac{\delta^3}{\delta J_{i_2}(s_2)\delta J_{j_2}(s_2)\delta J_{k_2}(s_2)}(\tilde{J}KJ)^3. \tag{4.5a}$$

The functional differentiations in (4.5*a*), though somewhat laborious, are but a matter of routine exercise. The various terms resulting from the functional differentiations may be obtained from the term

$$\{K_{i_1i_2}(s_1, s_2)+K_{i_2i_1}(s_2, s_1)\}\{K_{j_1j_2}(s_1, s_2)+K_{j_2j_1}(s_2, s_1)\}\{K_{k_1k_2}(s_1, s_2)+K_{k_2k_1}(s_2, s_1)\} \tag{4.5b}$$

by allocating the indices $i_1, j_1, k_1, i_2, k_2, j_2$, in all possible ways into the three curly brackets (putting two indices per curly bracket) and at the same time rearranging the continuous variables s_1, s_2, so that in each K their labels follow the order of the labels of the discrete indices. A diagrammatic technique for obtaining these terms in the form of ladders can be easily developed. The result for (4.5*a*) in terms of integrals of the quantities $C_i(s_1, s_2)$ defined in (4.3*b*) is

$$\begin{aligned}I^{(2)}_{i_1j_1k_1;\,i_2j_2k_2} = Z_0[&\delta_{k_1j_1}\delta_{i_1k_2}\delta_{i_2j_2}C^{(1)}_{k_1i_1i_2}\\ &+\delta_{k_1j_1}(\delta_{i_1i_2}\delta_{j_2k_2}+\delta_{i_1j_2}\delta_{i_2k_2})C^{(1)}_{k_1i_1k_2}+\delta_{k_1i_1}(\delta_{j_1i_2}\delta_{j_2k_2}+\delta_{j_1j_2}\delta_{i_2k_2})C^{(1)}_{k_1j_1k_2}\\ &+\delta_{j_1i_1}(\delta_{k_1i_2}\delta_{j_2k_2}+\delta_{k_1j_2}\delta_{i_2j_2})C^{(1)}_{i_1k_1j_2}+(\delta_{k_1i_1}\delta_{j_1k_2}+\delta_{j_1i_1}\delta_{k_1k_2})\delta_{i_2j_2}C^{(1)}_{i_1k_2j_2}\\ &+\{\delta_{i_2k_1}(\delta_{j_1j_2}\delta_{i_1k_2}+\delta_{i_1j_2}\delta_{j_1k_2})+\delta_{k_1j_2}(\delta_{i_2j_1}\delta_{i_1k_2}+\delta_{i_2i_1}\delta_{j_1k_2})\\ &+\delta_{k_1k_2}(\delta_{i_2j_1}\delta_{i_1j_2}+\delta_{i_2i_1}\delta_{j_1j_2})\}C^{(2)}_{i_1j_1k_1}]\end{aligned} \tag{4.5c}$$

where we have let

$$C^{(1)}_{ijk} = \int_0^\beta \int_0^\beta ds_1\, ds_2 C_i(s_1, s_1) C_j(s_1, s_2) C_k(s_2, s_2)$$

$$C^{(2)}_{ijk} = \int_0^\beta \int_0^\beta ds_1\, ds_2 C_i(s_1, s_2) C_j(s_1, s_2) C_k(s_1, s_2). \tag{4.5d}$$

The first integral of (4.5*d*), using (4.3*b*), is easily evaluated if we take into account that $C_i(s, s)$ is constant. We have:

$$C^{(1)}_{ijk} = \{\tfrac{1}{2}\Lambda_i^{-1}\hbar \coth(\tfrac{1}{2}\Lambda_i\hbar\beta)\}\{\Lambda_j^{-2}\beta + 2\Lambda_j^{-3}\hbar^{-1}\coth(\tfrac{1}{2}\Lambda_j\hbar\beta)\} \times \{\tfrac{1}{2}\Lambda_k^{-1}\hbar\coth(\tfrac{1}{2}\Lambda_k\hbar\beta)\}. \tag{4.5e}$$

The evaluation of the second integral is more laborious. If we define:

$$\begin{aligned} A_{ijk} &= \{(\Lambda_i + \Lambda_j + \Lambda_k)\hbar\}^{-2}\sinh^2\{\tfrac{1}{2}(\Lambda_i + \Lambda_j + \Lambda_k)\hbar\beta\} = A(\Lambda_i, \Lambda_j, \Lambda_k) \\ A_{i-jk} &= A(\Lambda_i, -\Lambda_j, \Lambda_k) \text{ etc.} \\ B_{ijk} &= \tfrac{1}{2}\{(\Lambda_i + \Lambda_j + \Lambda_k)\hbar\}^{-1}\beta - \tfrac{1}{2}\{(\Lambda_i + \Lambda_j + \Lambda_k)\hbar\}^{-2}\sinh\{(\Lambda_i + \Lambda_j + \Lambda_k)\hbar\beta\} \\ &= B(\Lambda_i, \Lambda_j, \Lambda_k) \\ B_{-ijk} &= B(-\Lambda_i, \Lambda_j, \Lambda_k) \text{ etc.} \end{aligned} \tag{4.5f}$$

then the second integral of (4.5*d*) can be expressed as

$$\begin{aligned} C^{(2)}_{ijk} = \left(\frac{\hbar}{2}\right)^3 (\Lambda_i\Lambda_j\Lambda_k)^{-1} \\ &\times \{\coth(\tfrac{1}{2}\Lambda_i\hbar\beta)\coth(\tfrac{1}{2}\Lambda_j\hbar\beta)\coth(\tfrac{1}{2}\Lambda_k\hbar\beta)(A_{ijk} + A_{-ijk} + A_{i-jk} + A_{ij-k}) \\ &+ \coth(\tfrac{1}{2}\Lambda_i\hbar\beta)\coth(\tfrac{1}{2}\Lambda_j\hbar\beta)(B_{ijk} + B_{-ijk} + B_{i-jk} - B_{ij-k}) \\ &+ (\text{two cyclic terms for } i \text{ and } j) \\ &+ \coth(\tfrac{1}{2}\Lambda_i\hbar\beta)(A_{ijk} + A_{-ijk} - A_{i-jk} - A_{ij-k}) \\ &+ (\text{two cyclic terms for } j \text{ and } k) \\ &+ (B_{ijk} + B_{-ijk} + B_{i-jk} + B_{ij-k})\}. \end{aligned} \tag{4.5g}$$

Thus, the six-indexed twofold integration symbol $I_{i_1j_1k_1;i_2j_2k_2}$ is decomposed into exterior products of Kronecker δ's and the three-indexed quantities $C^{(1)}_{ijk}$, $C^{(2)}_{ijk}$ given in (4·5*e*, *g*). The analysis for the higher-indexed $I^{(n)}_{\dots}$, involving higher multiplicity of s integrations is similar, but more involved. We may remark again that the six-indexed average in (4.5*c*) is zero unless the six indices i_1, j_1, k_1, i_2, j_2 and k_2 can be grouped into three pairs with equal indices in each pair.

As a simple application of the two averages that we have just found, let us write down the result for the partition function to first-order correction in $V^{(4)}$ and second-order correction in $V^{(3)}$, in the case of the following potential energy:

$$v' = \tfrac{1}{2}\sum \Lambda_i^2\xi_i^2 + \sum V^{(3)}_{ijk}\xi_i\xi_j\xi_k + \sum V^{(4)}_{ijkl}\xi_i\xi_j\xi_k\xi_l. \tag{4.6}$$

When the anharmonic coefficients $V^{(3)}$ and $V^{(4)}$ are small, the following result is sufficient for the required partition function:

$$Z' = Z_0 - \sum V^{(4)}_{ijkl} I^{(1)}_{ijkl} + \tfrac{1}{2}\sum V^{(3)}_{i_1j_1k_1} V^{(3)}_{i_2j_2k_2} I^{(2)}_{i_1j_1k_1;i_2j_2k_2}. \tag{4.6a}$$

As is well known, the two corrections in (4.6*a*) are of the same order, in temperature, as $\hbar \to 0$.

By enlarging the store of the averages $I^{(n)}_{\dots}$, one may investigate the phonon–phonon interactions in the case of large anharmonicities, since the preceding expansion is independent of the size of the anharmonicities.

5. Conclusion

The present method circumvents possible degeneracy complications and also difficulties that would arise for high quantum numbers in a matrix element perturbation approach. Also the evaluation of highly involved series for the case of such perturbation potential energy as v_1 (1.1a), which would render the task of finding the partition function rather desperate, is evaded. The present method is systematic and reduces the problem of finding the final results to a matter of routine exercise. We think that the functional approach to the evaluation of the partition function of anharmonic oscillators prevails in elegance and efficiency over the ordinary perturbation method.

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References

Feynman, R. P., and Hibbs, A. R., 1965, *Quantum Mechanics and Path Integrals* (New York: McGraw-Hill) pp. 58–61, 294.
Goldstein, H., 1953, *Classical Mechanics* (Cambridge Mass.: Addison-Wesley), p. 331.
Papadopoulos, G. J., 1968, *J. Phys.* A, (*Proc. Phys. Soc.*), [2], **1**, 431–46.
Tarski, I., 1967, *Lectures in Theoretical Physics* (Boulder: University of Colorado Press).
Yaglom, A. M., 1956, *Theory of Probability and Applications*, Vol. 1 (English translation from Russian), (Philadelphia, Pennsylvania: Society for Industrial and Applied Mathematics), p. 145.