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On Vibrational Contributions to the Thermodynamics of Imperfect Crystals. A Propagator Viewpoint

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A many-body perturbation treatment of the harmonically vibrating crystal lattice, containing a fixed distribution of imperfections, is presented. Using the fact that Lifshitz' Green's functions can be replaced by double-time thermal Green's functions of displacement, and invoking the connection between the space Fourier transforms of the latter functions and the finite temperature, phonon propagator basic expressions of the Lifshitz theory are recovered by the method of Feynmann diagrams. Thus, the Dyson equation for the defective lattice Green's function matrix and a series expansion of the Helmholz free energy are obtained by graphical summations to infinite order. In view of the formal exactness of the Lifshitz method, the imperfect crystal is found to provide an example of final results of infinite order perturbation theory, which can be rigorously proved to remain valid despite the occurrence of divergencies in underlying series. It is proposed that a partial summation version of the propagator treatment may furnish a useful approximation scheme in certain cases of non-local force field alterations.

I. INTRODUCTION

We discuss in this paper some effects of *fixed* distributions of mass changes and force constant alterations on a harmonically vibrating crystal lattice. Green's function techniques originated by Lifshitz[1] and subsequently extended and elaborated by several authors[2,3] have played a crucial role in many studies[4,5] dealing with phenomena conditioned by the dynamics of non-perfect solids. Leaving aside an interesting and sometimes highly pertinent interpretation in terms of formal scattering theory[1,6–8] the Lifshitz method may be characterized as an elegant version of classical normal mode algebra which utilizes Green's functions to overcome the loss of translational invariance. (The severity of this loss may readily be appreciated by recalling that lattice dynamics invariably relies on translational symmetry in reducing the mathematical description of a perfect lattice to manageable proportions.) The transition to quantum mechanics is usually introduced as a final step

awaiting a successful completion of the normal mode analysis. In principle this approach suffices to account for a wide variety of defect induced properties. This formal power notwithstanding, the theory in its rigorous form is not amenable to numerical analysis when non-local imperfections come into play. It is convenient, therefore, to adopt an alternative viewpoint which relates the Lifshitz method to the more general formalism of current many-body theory within the framework of which several systematic approximation schemes have been developed. As brought to attention by Elliot and Taylor [9] Lifshitz's Green's functions may be replaced by double-time thermal Green's functions of displacement.[10] Applying a quantum mechanical formulation from the outset these authors recovered the fundamental expressions of the Lifshitz theory by taking as their starting point the equations governing the time development of retarded and advanced Green's functions. It seems natural to assume the perturbation expansion of the phonon propagator to provide an alternative way of handling the situation. The object of the present paper is to corroborate this conjecture. A related problem has been studied by Maradudin [11] who investigated the effects of mass disorder and also, as a particular case, the effects of an isolated mass defect on the propagator. The propagator treatment of mass imperfections was related, mainly, to the construction of correlation functions. In another part of the paper, devoted to the elucidation of fixed defect configurations, equilibrium properties were discussed from the standpoint of the Lifshitz theory (or rather an elaborated version contributed, in part, by Maradudin). Including force constant perturbations but leaving aside situations where an averaging over defect configurations is called for, we shall adopt a somewhat different viewpoint by regarding many-body perturbation theory as an alternative route to defective lattice double-time thermal Green's functions. We thus rederive also those pivotal relations of the Lifshitz formalism which pertain to equilibrium properties, *i.e.* location of modified mode frequencies, thermodynamic state functions *etc.* On the practical level this procedure might be of some value in connection with defects which are non-local in the direct lattice space, since it immediately suggests that we exploit occasional occurrences of quasilocalization in **k** space by invoking selective summation techniques.

II. DOUBLE-TIME GREEN'S FUNCTIONS AND THEIR CONNECTION WITH THE PHONON PROPAGATOR

With a slight deviation from Zubarev's notation [10] the retarded and advanced Green's functions for any pair of Heisenberg operators

$$\begin{aligned} A(t) &= \exp(itH)A\exp(-itH) \\ B(t') &= \exp(it'H)B\exp(-it'H) \end{aligned} \tag{II-1}$$

may be written as

$$\begin{aligned} G(A,B;tt')_{r,a} &= 2\pi\langle\langle A(t);B(t')\rangle\rangle_{r,a} \\ \langle\langle A(t);B(t')\rangle\rangle_r &= -i\theta(t-t')\langle[A(t),B(t')]\rangle \\ \langle\langle A(t);B(t')\rangle\rangle_a &= i\theta(t'-t)\langle[A(t),B(t')]\rangle \end{aligned} \tag{II-2}$$

where

$$[A,B]=AB-\eta BA,\ \ \eta=\pm 1$$
$$\theta(t)\ \ =1,\ t>0;\ \ \theta(t)=0,\ t<0$$

and where $\langle\ldots\rangle$ denotes the expectation value of an operator averaged over the appropriate ensemble, which in our case is the canonical ensemble. Since we shall deal exclusively with Bose operators, $\eta=1$. In writing (II – 1) we have, for typographic simplicity, set $\hbar=1$. Identifying $A(t)$ and $B(t')$ with operators representing atomic excursions

$$A(t)=u_\alpha(l\varkappa,t);\quad B(t')=u_\beta(l'\varkappa',t')$$

the fundamental equations *

$$\mathbf{G}_0(\omega)(\mathbf{M}_0\omega^2-\boldsymbol{\Phi}_0)=\mathbf{G}_0(\omega)\mathbf{L}_0(\omega)=\mathbf{1} \tag{II-3a}$$
$$\mathbf{G}(\omega)(\mathbf{M}\omega^2-\boldsymbol{\Phi})=\mathbf{G}(\omega)[\mathbf{L}_0(\omega)-\delta\mathbf{L}(\omega)]=\mathbf{G}(\omega)\mathbf{L}(\omega)=\mathbf{1} \tag{II-3b}$$

and thereby also

$$\mathbf{G}=\mathbf{G}_0+\mathbf{G}_0\delta\mathbf{L}\mathbf{G}\langle=\rangle\mathbf{G}=[\mathbf{1}-\mathbf{G}_0(\omega)\delta\mathbf{L}(\omega)]^{-1}\mathbf{G}_0(\omega) \tag{II-3c}$$

(where $\mathbf{M}_0(\mathbf{M})$ is the perfect (defective) lattice diagonal mass matrix, $\boldsymbol{\Phi}_0(\boldsymbol{\Phi})$ is a $3nN\times 3nN$ perfect (defective) real and symmetric force constant matrix, and where n is the number of atoms in each of the N unit cells contained in the cyclic lattice under consideration)

may be derived by

(i) subjecting the equations of motion for $G_0(A,B;tt')_{r,a}$ and $G(A,B;tt')_{r,a}$ to an additional time differentiation followed by a time Fourier transformation [9]

and by subsequently

(ii) continuing $G_0(A,B;\omega)_{r(a)}$ and $G(A,B;\omega)_{r(a)}$ analytically into the upper (lower) half of the ω-plane and setting [10] **

$$G_{(0)}(A,B;\omega)=G_{(0)}(A,B;\omega)_r,\ Im(\omega)>0$$
$$G_{(0)}(A,B;\omega)=G_{(0)}(A,B;\omega)_a,\ Im(\omega)<0 \tag{II-4}$$

In the version of the Lifshitz theory most frequently encountered [2,3] $\mathbf{L}_{(0)}(\omega)$ is introduced by writing down the classical time-independent equations of motion while (II-3a,b) is taken as the defining relation(s) for $\mathbf{G}_{(0)}$.
As noted by Elliot and Taylor [9] the prescription

$$G_{(0)}(A,B;\omega+i\delta)-G_{(0)}(A,B;\omega-i\delta)=-2\pi i[\exp(\beta\omega)-1]J_{(0)}(A,B;\omega)$$
$$\beta=1/(kT),\ \omega\ \text{real} \tag{II-5}$$

for obtaining correlation functions

* In the following ω is complex unless otherwise indicated. Furthermore, time Fourier transforms will be written as $G(\omega)$, while space Fourier transforms will appear as small letters, *i.e.* $g(tt')$ or $g(\omega)$.

** In (II-4) and below the symbol (0) will be employed as subscript(s) in general expressions and statements pertaining to perfect and imperfect lattice quantities alike.

$$D^{<}_{(0)}(A,B;t,t') = \langle B(t')A(t)\rangle_{(0)} = \int_{-\infty}^{\infty} J_{(0)}(A,B;\omega)\exp[-i\omega(t-t')]\mathrm{d}\omega \tag{II-6a}$$

$$D^{>}_{(0)}(A,B;t,t') = \langle A(t)B(t')\rangle_{(0)} = \int_{-\infty}^{\infty} J_{(0)}(A,B;\omega)\exp(\beta\omega)\exp[-i\omega(t-t')\mathrm{d}\omega$$

$$\omega \text{ real} \tag{II-6b}$$

from $G_{(0)}(A,B;\omega)$, a theme elegantly expounded by Zubarev,[10] renders superfluous the complicated transformations from sums to integrals occurring in the Lifshitz method. Posing the problem in reverse, *i.e.* setting out to calculate $G_{(0)}$ from $D^{>}_{(0)}$, $D^{<}_{(0)}$, we arrive at another way of obtaining (II-3). A brief outline of the reasoning involved serves to summarize some expressions which will be needed later on. In matrix notation $\mathbf{G}_{(0)}$, $\mathbf{D}^{>}_{(0)}$, and $\mathbf{D}^{<}_{(0)}$ may be written in terms of their $\mathbf{k}$ space analogues

$$\begin{aligned} g_{(0)}(\mathbf{k}j,\mathbf{k}'j',tt')_{r(a)} &= 2\pi\langle\langle \mathcal{A}_{\mathbf{k}j}(t);\mathcal{A}^{\dagger}_{\mathbf{k}'j'}(t')\rangle\rangle_{(0)r(a)} \\ d^{>}_{(0)}(\mathbf{k}j,\mathbf{k}'j';tt') &= \langle \mathcal{A}_{\mathbf{k}j}(t)\mathcal{A}^{\dagger}_{\mathbf{k}'j'}(t')\rangle_{(0)} \\ d^{<}_{(0)}(\mathbf{k}j,\mathbf{k}'j';tt') &= \langle \mathcal{A}^{\dagger}_{\mathbf{k}'j'}(t')\mathcal{A}_{\mathbf{k}j}(t)\rangle_{(0)} \\ \mathcal{A}_{\mathbf{k}j}(t) &= a_{\mathbf{k}j}(t) + a^{\dagger}_{-\mathbf{k}j}(t), \mathcal{A}^{\dagger}_{\mathbf{k}j}(t') = a_{\mathbf{k}j}{}^{\dagger}(t') + a_{-\mathbf{k}j}(t'); \end{aligned} \tag{II-7}$$

$a^{\dagger}_{\mathbf{k}j}$ and $a_{\mathbf{k}j}$ being the usual phonon creation and destruction operators.[2] as

$$\mathbf{G}_{(0)}(t,t')_{r(a)} = \tfrac{1}{2}\mathbf{M}_0^{-\frac{1}{2}}\boldsymbol{\varepsilon}\boldsymbol{\omega}^{-\frac{1}{2}}\mathbf{g}_{(0)}(t,t')_{r(a)}\boldsymbol{\omega}^{-\frac{1}{2}}\boldsymbol{\varepsilon}^{\dagger}\mathbf{M}_0^{-\frac{1}{2}} \tag{II-8a}$$

$$\mathbf{D}^{>}_{(0)}(t,t') = \tfrac{1}{2}\mathbf{M}_0^{-\frac{1}{2}}\boldsymbol{\varepsilon}\boldsymbol{\omega}^{-\frac{1}{2}}\mathbf{d}^{>}_{(0)}(t,t')\boldsymbol{\omega}^{-\frac{1}{2}}\boldsymbol{\varepsilon}^{\dagger}\mathbf{M}_0^{-\frac{1}{2}} \tag{II-8b}$$

$$\mathbf{D}^{<}_{(0)}(t,t') = \tfrac{1}{2}\mathbf{M}_0^{-\frac{1}{2}}\boldsymbol{\varepsilon}\boldsymbol{\omega}^{-\frac{1}{2}}\mathbf{d}^{<}_{(0)}(t,t')\boldsymbol{\omega}^{-\frac{1}{2}}\boldsymbol{\varepsilon}^{\dagger}\mathbf{M}_0^{-\frac{1}{2}} \tag{II-8c}$$

with similar equations for the time Fourier transforms.

In the above equations $\boldsymbol{\varepsilon}$ is a unitary matrix the columns of which are discrete analogues of waves which span the null spaces of $\{\mathbf{1}\omega_{\mathbf{k}j}^2 - \mathbf{M}_0^{-\frac{1}{2}}\boldsymbol{\Phi}_0\mathbf{M}_0^{-\frac{1}{2}};\mathbf{k}\in$ irreducible part of the first Brillouin zone$\}$. The dimensionality of each of these spaces equals the number of distinct wave vectors in the star of the associated $\mathbf{k}$. In explicit form

$$\varepsilon(\mathbf{k}j;l\varkappa\alpha) = N^{-\frac{1}{2}}e_{\alpha}(\varkappa|\mathbf{k}j)\exp[i\mathbf{k}\cdot\mathbf{x}(l\varkappa)]$$

where $\mathbf{e}(\mathbf{k}j)$ is the polarization vector with wave vector $\mathbf{k}$ and branch index j and where $\mathbf{x}(l\varkappa)$ is the site vector of the $\varkappa$th atom in the lth unit cell. $\boldsymbol{\omega}$ is a diagonal matrix composed of phonon frequencies $\omega_{\mathbf{k}j}$. For the moment we confine the interest to the perfect lattice quantities. A straightforward and standard argument produces the following explicit expressions for the Fourier transforms of

$$d_0{}^{>(<)}(\mathbf{k}j,\mathbf{k}'j';t,t') = \Delta(\mathbf{k}-\mathbf{k}')\delta_{jj'}d^{>(<)}(\mathbf{k}j;t,t') \tag{II-9}$$

$$d^{>}{}_0(\mathbf{k}j;\omega) = j_0(\mathbf{k}j;\omega)\exp(\beta\omega) \tag{II-10a}$$

$$\omega \text{ real}$$

$$d^{<}{}_0(\mathbf{k}j;\omega) = j_0(\mathbf{k}j;\omega) \tag{II-10b}$$

where the spectral density function j_0 is given by

$$j_0(\mathbf{k}j;\omega) = \exp(-\beta\omega)\{[1+N_{\mathbf{k}j}{}^0]\delta(\omega-\omega_{\mathbf{k}j}) + N_{\mathbf{k}j}{}^0\delta(\omega+\omega_{\mathbf{k}j})\} \tag{II-11}$$

$$N_{\mathbf{k}j}{}^0 = \langle a^{\dagger}_{\mathbf{k}j}a_{\mathbf{k}j}\rangle_0 = [\exp(\beta\omega_{\mathbf{k}j})-1]^{-1},\ \omega \text{ real}$$

With recourse to Zubarev's work [10] we may write

$$g_0(\mathbf{k}j;\omega)_{r(a)} = \int_{-\infty}^{\infty} [\exp(\beta\omega')-1]j_0(\mathbf{k}j;\omega')\mathrm{d}\omega'/[(\omega \pm i\delta)-\omega'] \qquad \text{(II-12a)}$$

$$\omega,\omega' \text{ real}, \; r=>+, a=>-$$

The temperature dependent terms cancel out, as they should in a gas of noninteracting phonons, whereupon

$$g_0(\mathbf{k}j;\omega)_{r(a)} = 2\omega_{\mathbf{k}j}/[(\omega \pm i\delta)^2-\omega_{\mathbf{k}j}^2], \; \omega \text{ real} \qquad \text{(II-12b)}$$

Substituting the latter expression into the time Fourier transform of (II-8a) and making use of the above step (ii) we find

$$\begin{aligned}\mathbf{G}_0(\omega) &= \mathbf{M}_0^{-\frac{1}{2}}(\boldsymbol{\varepsilon}\{\mathrm{diag}[(\omega^2-\omega_i^2)^{-1};i=\mathbf{k}j=1,3nN]\}\boldsymbol{\varepsilon}^\dagger)\mathbf{M}_0^{-\frac{1}{2}} \\ &= \mathbf{M}_0^{-\frac{1}{2}}(\boldsymbol{\varepsilon}\{\mathbf{1}\omega^2-\mathrm{diag}[\omega_i^2;i=1,3nN]\}\boldsymbol{\varepsilon}^\dagger)^{-1}\mathbf{M}_0^{-\frac{1}{2}} \qquad \text{(II-13)} \\ &= \mathbf{M}_0^{-\frac{1}{2}}(\mathbf{1}\omega^2-\mathbf{M}_0^{-\frac{1}{2}}\boldsymbol{\Phi}_0\mathbf{M}_0^{-\frac{1}{2}})^{-1}\mathbf{M}_0^{-\frac{1}{2}} = (\mathbf{M}_0\omega^2-\boldsymbol{\Phi}_0)^{-1} = \mathbf{L}_0(\omega)^{-1}\end{aligned}$$

which obviously implies (II-3a). In explicit form the first of the relations contained in (II-13) reads

$$\begin{aligned}G_0(l\varkappa\alpha,l'\varkappa'\beta;\omega) &= N^{-1}(M_{0\varkappa}M_{0\varkappa'})^{-\frac{1}{2}}\sum_{\mathbf{k}j} e_\alpha(\varkappa|\mathbf{k}j)e_\beta^*(\varkappa'|\mathbf{k}j)\times \\ &(\omega^2-\omega_{\mathbf{k}j}^2)^{-1}\exp[i\mathbf{k}\cdot\{\mathbf{x}(l\varkappa)-\mathbf{x}(l'\varkappa')\}] \qquad \text{(II-14)}\end{aligned}$$

which is the well known bilinear expansion of $\mathbf{G}_0(\omega)$ normally obtained [2] by arguments which, essentially, correspond to a reversion of the sequence of relations (II-13). Except for an obvious change of notation the perturbed lattice equation (II-3b), and hence (II-3c), follows in an entirely similar manner by temporarily interpreting the columns of $\boldsymbol{\varepsilon}$ as the set of orthonormal (molecular type) eigenvectors of $\mathbf{M}^{-\frac{1}{2}}\boldsymbol{\Phi}\mathbf{M}^{-\frac{1}{2}}$. The fact that we do not know *a priori* the explicit form of these eigenvectors is of no consequence to a formal argument since their existence is guaranteed by general and well known theorems of linear algebra. In conformity with the usual terminology [12] we define the finite temperature propagator, $\mathcal{G}_{(0)}(i\omega_n)$, by the relations

$$\mathcal{G}_{(0)}(A,B;i\omega_n) = (\tfrac{1}{2}\beta^{-1})\int_{-\beta}^{\beta}\exp(-i\omega_n\tau)\mathcal{G}_{(0)}(A,B;\tau)\mathrm{d}\tau \qquad \text{(II-15a)}$$

$$\mathcal{G}_{(0)}(A,B;\tau) = \sum_n \exp(i\omega_n\tau)\mathcal{G}_{(0)}(A,B;i\omega_n) \qquad \text{(II-15b)}$$

where $\tau = it$, and where

$$\mathcal{G}_{(0)}(A,B;\tau) = \langle TA(\tau)B(0)\rangle_{(0)} \qquad \text{(II-16)}$$

is the causal Green's function analytically continued to the interval $(-i\beta,i\beta)$[13,14] and periodically repeated along the imaginary time axis. T is the Dyson time ordering operator. In the Bose case the cyclic trace property implies

$$\mathcal{G}_{(0)}(A,B;\tau+\beta) = \mathcal{G}_{(0)}(A,B;\tau), -\beta<\tau<0 => \omega_n = 2\pi n/\beta \qquad \text{(II-17)}$$

In order to establish a link between $G_{(0)}$ and $\mathcal{G}_{(0)}$ we consider the relation

$$\mathcal{G}_{(0)}(A,B;\tau) = D^{>}{}_{(0)}(A,B;t,0) = \int_{-\infty}^{\infty}\exp(-\tau\omega')D^{>}{}_{(0)}(A,B;\omega')\mathrm{d}\omega', \tau>0 \qquad \text{(II-18)}$$

Insertion of (II-18) into the first of the equations (II-15) yields

$$\mathcal{G}_{(0)}(A,B;i\omega_n)=(1/\beta)\int_0^\beta \exp(-i\omega_n\tau)\int_{-\infty}^{\infty}\exp(-\tau\omega')D^{>}_{(0)}(A,B;\omega')\mathrm{d}\omega'\mathrm{d}\tau$$
$$=-(1/\beta)\int_{-\infty}^{\infty}[\exp(\beta\omega')-1]J_{(0)}(A,B;\omega')\mathrm{d}\omega'/[(-i\omega_n)-\omega'] \tag{II-19}$$

Calling to mind (II-4) and comparing with (II-12a) one obtains

$$G_{(0)}(A,B;\omega)=-\beta\mathcal{G}_{(0)}(A,B;-i\omega_n\rightarrow\omega) \tag{II-20a}$$

and a similar relation for $g_{(0)}(A_{\mathbf{k}j},A^{\dagger}_{\mathbf{k}'j'};\omega)\equiv g_{(0)}(\mathbf{k}j,\mathbf{k}'j';\omega)$, *viz.*

$$g_{(0)}(\mathbf{k}j,\mathbf{k}'j';\omega)=-\beta g_{(0)}(\mathbf{k}j,\mathbf{k}'j';-i\omega_n\rightarrow\omega) \tag{II-20b}$$

We shall refer to $g_{(0)}(\mathbf{k}j,\mathbf{k}'j';i\omega_n)$ as the phonon propagator. Alternatively one could give explicit recognition to the $a^{\dagger}a$ and $aa^{\dagger}$ components of $\mathcal{A}\mathcal{A}^{\dagger}$ and work with two propagators; one for backward propagation, $a^{\dagger}a$, and one for forward propagation, $aa^{\dagger}$. This, in fact, is the convention adopted by Maradudin [11] in the aforementioned treatment of mass disorder. For mathematical simplicity, but at the expense of some pictorial connotation in the perturbation expansion to appear shortly, we have chosen to employ the combined $\mathcal{A}\mathcal{A}^{\dagger}$ propagator, which form is frequently encountered in works on anharmonic lattices.[15,16] Both procedures are utilized concurrently by Mattuck [17] in his $T=0$ discussion of the dressing of Einstein phonons brought about by the turning on of interatomic correlations in a linear chain.
An expression for the perfect lattice phonon propagator

$$g_0(\mathbf{k}j,\mathbf{k}'j';i\omega_n)=\Delta(\mathbf{k}-\mathbf{k}')\delta_{jj'}g_0(\mathbf{k}j;i\omega_n) \tag{II-21}$$

is readily obtained by contour integration,[18] or by applying (II-15a) to $\langle T\mathcal{A}_{\mathbf{k}j}(\tau)\mathcal{A}^{\dagger}_{\mathbf{k}j}(0)\rangle_0$. Alternatively, one could also make use of (II-12b) in a reserved (II-20b). In any case

$$g_0(\mathbf{k}j;i\omega_n)=\frac{-2\omega_{\mathbf{k}j}}{\beta}\frac{1}{(i\omega_n)^2-\omega_{\mathbf{k}j}^2}=\frac{2\omega_{\mathbf{k}j}}{\beta}\frac{1}{\omega_n^2+\omega_{\mathbf{k}j}^2} \tag{II-22}$$

III. EXPANSION OF THE DEFECTIVE LATTICE PROPAGATOR

Although we are primarily interested in the Fourier components $g(\mathbf{k}j,\mathbf{k}'j';i\omega_n)$ it is convenient to expand $g(\mathbf{k}j,\mathbf{k}'j';\tau)$ in powers of the defect induced interactions and to read off the Fourier components afterwards. The expansion in mind, which is a general recipe of many-body (and field) theory, is carried out in the interaction representation, *viz.*

$$g(\mathbf{k}j,\mathbf{k}'j';\tau)=\langle T\mathcal{A}_{\mathbf{k}j}(\tau)\mathcal{A}^{\dagger}_{\mathbf{k}'j'}(0)\rangle=$$
$$=\sum_{n=0}^{\infty}\frac{(-1)^n}{n!}\int_0^\beta \mathrm{d}\tau_1\cdots\int_0^\beta \mathrm{d}\tau_n\langle T\{\overline{H}_1(\tau_1)\cdots\overline{H}_1(\tau_n)\overline{\mathcal{A}}_{\mathbf{k}j}(\tau)\overline{\mathcal{A}}^{\dagger}_{\mathbf{k}'j'}(0)\}\rangle_0/ \tag{III-1}$$
$$/\sum_{n=0}^{\infty}\frac{(-1)^n}{n!}\int_0^\beta \mathrm{d}\tau_1\cdots\int_0^\beta \mathrm{d}\tau_n\langle T\{\overline{H}_1(\tau_1)\cdots\overline{H}_1(\tau_n)\}\rangle_0$$

where H_1 is the defect part of the Hamiltonian and where $\bar{O}$ is an operator in the interaction picture, *i.e.* $\bar{O}(\tau)=\exp(\tau H_0)O\exp(-\tau H_0)$. The derivation of this expansion (for general field operators) has been discussed in detail by several authors [12,17] and need not be repeated here. The Hamiltonian of the imperfect lattice may be expressed in terms of direct lattice operators as

$$H=H_0+H_1=H_0+V_1+T_1 \tag{III-2}$$

$$H_0=\tfrac{1}{2}\sum_{l\varkappa\alpha} p_\alpha{}^2(l\varkappa)/M_{0\varkappa}+\tfrac{1}{2}\sum_{l\varkappa\alpha}\sum_{l'\varkappa'\beta}\Phi_0(l\varkappa\alpha;l'\varkappa'\beta)u_\alpha(l\varkappa)u_\beta(l'\varkappa') \tag{III-2a}$$

$$V_1=\tfrac{1}{2}\sum_{l\varkappa\alpha}\sum_{l'\varkappa'\beta}\delta\Phi(l\varkappa\alpha;l'\varkappa'\beta)u_\alpha(l\varkappa)u_\beta(l'\varkappa') \tag{III-2b}$$

$$T_1=\tfrac{1}{2}\sum_{l\varkappa\alpha}p_\alpha{}^2(l\varkappa)(1/M(l\varkappa)-1/M_{0\varkappa})=\tfrac{1}{2}\sum_{l\varkappa\alpha}p_\alpha{}^2(l\varkappa)[\chi(l\varkappa)/(1-\chi(l\varkappa))]/M_{0\varkappa} \tag{III-2c}$$

where $M(l\varkappa)=[1-\chi(l\varkappa)]M_{0\varkappa}$. For notational convenience we introduce a diagonal matrix $\boldsymbol{\Lambda}$ the elements of which are defined as

$$\lambda(l\varkappa\alpha;l'\varkappa'\beta)=\delta_{ll'}\delta_{\varkappa\varkappa'}\delta_{\alpha\beta}(-\tfrac{1}{2})\chi(l\varkappa)/[1-\chi(l\varkappa)] \tag{III-3a}$$

and a matrix $\boldsymbol{\Psi}$ with elements

$$\psi(l\varkappa\alpha;l'\varkappa'\beta)=\tfrac{1}{2}\delta\Phi(l\varkappa\alpha;l'\varkappa'\beta)(M_{0\varkappa}M_{0\varkappa'})^{-\frac{1}{2}} \tag{III-3b}$$

Then after a space Fourier transformation we may write

$$V_1=\tfrac{1}{2}\sum_{\mathbf{k}j}\sum_{\mathbf{k}'j'}v_1(\mathbf{k}j|\mathbf{k}'j')\mathcal{A}^\dagger{}_{\mathbf{k}j}\mathcal{A}_{\mathbf{k}'j'} \tag{III-4a}$$

$$T_1=\tfrac{1}{2}\sum_{\mathbf{k}j}\sum_{\mathbf{k}'j'}t_1(\mathbf{k}j|\mathbf{k}'j')\mathcal{B}^\dagger{}_{\mathbf{k}j}\mathcal{B}_{\mathbf{k}'j'} \tag{III-4b}$$

where

$$\mathbf{v}_1=\boldsymbol{\omega}^{-\frac{1}{2}}\boldsymbol{\varepsilon}^\dagger\boldsymbol{\Psi}\boldsymbol{\varepsilon}\boldsymbol{\omega}^{-\frac{1}{2}} \text{ and } \mathbf{t}_1=\boldsymbol{\omega}^{+\frac{1}{2}}\boldsymbol{\varepsilon}^\dagger\boldsymbol{\Lambda}\boldsymbol{\varepsilon}\boldsymbol{\omega}^{+\frac{1}{2}} \tag{III-5}$$

and where

$$\mathcal{B}_{\mathbf{k}j}=a^\dagger{}_{-\mathbf{k}j}-a_{\mathbf{k}j} \text{ and } \mathcal{B}^\dagger{}_{\mathbf{k}j}=a^\dagger{}_{\mathbf{k}j}-a_{-\mathbf{k}j} \tag{III-6}$$

Omitting the zero point energy we also have $H_0=\sum_{\mathbf{k}j}\omega_{\mathbf{k}j}a^\dagger{}_{\mathbf{k}j}a_{\mathbf{k}j}$. We now proceed to a graphical treatment of (III-1). To evalutate the thermal averages we make use of Wick's theorem [17] and take the sum over products of all possible contractions (a contraction $=\langle\cdots\rangle_0$ value of a "time" ordered product of two phonon field operators $\mathcal{A}$ or $\mathcal{B}$), each product being depicted by a Feynmann diagram consisting of free phonon lines (contractions) beginning and/or terminating at vertices $\bar{H}_1(\tau_k)$ on a vertical τ-axis. Since the disconnected parts of disconnected diagrams associated with the numerator of (III-1) contribute independently their sum becomes a multiplicative factor which cancels the thermalized vacuum amplitude in the denominator (linked cluster theorem for the propagator [17]). It is sufficient therefore to take into account only the connected numerator diagrams. In order to get at the Fourier components $g(\mathbf{k}j,\mathbf{k}'j';i\omega_n)$ we expand each contraction in a Fourier series (see II-15b), as is customary,[12] and make use of the vertex conservation of ω_n's imposed by the τ-integrations, *viz.*

$$\int_0^\beta \exp(2\pi ilt/\beta)\mathrm{d}t=\delta_{l0}\beta, \text{ for } l=\text{some integer} \tag{III-7}$$

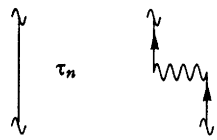
For convenience we start by considering separately the two restricted imperfections

$$\text{A: } H_1 = V_1, T_1 = 0 \text{ and B: } H_1 = T_1, V_1 = 0$$

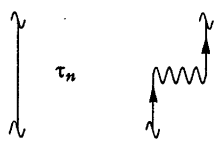
Subsequently the desired $H_1 = V_1 + T_1$ results will be derived by substituting for the free phonon lines in the case A diagrams with clothed case B propagators.

A. Phonons interacting via force field perturbations

To calculate $\mathcal{g}(\mathbf{k}j,\mathbf{k}'j';i\omega_n)$ we draw all possible distinct and connected diagrams in which a $(\mathbf{k}j)$ line leaves at the top and a $(\mathbf{k}'j')$ line enters from the bottom. We note that since there are only two $\bar{\mathcal{A}}$ operators associated with each v_1 element there will be only two lines connected with each vertex. For reasons to become apparent shortly we choose to depict the introduction of a V_1 term into a diagram in either of two ways as displayed in Fig. 1. Since



$$v_1(\mathbf{k}_1j_1|\mathbf{k}_2j_2)\mathcal{A}^\dagger_{\mathbf{k}_1j_1}(\tau_n)\mathcal{A}_{\mathbf{k}_2j_2}(\tau_n) \qquad \text{(a)}$$



$$\begin{aligned} &v_1(-\mathbf{k}_2j_2|-\mathbf{k}_1j_1)\mathcal{A}^\dagger_{\mathbf{k}_2j_2}(\tau_n)\mathcal{A}_{-\mathbf{k}_1j_1}(\tau_n) \\ &= v_1(-\mathbf{k}_2j_2|-\mathbf{k}_1j_1)\mathcal{A}_{\mathbf{k}_2j_2}(\tau_n)\mathcal{A}^\dagger_{\mathbf{k}_1j_1}(\tau_n) \end{aligned} \qquad \text{b)}$$

Fig. 1. Equivalent vertex arrangements.

the defective crystal is no longer invariant under a rigid body translation through one of the perfect lattice translation vectors, there will be no wave vector conservation at the vertices. The rules for calculating the contribution of any particular diagram may be summarized as follows:

1) For each vertex with lines $(\mathbf{k}_1j_1)$ leaving, $(\mathbf{k}_2j_2)$ entering, there is a factor $\frac{1}{2}v_1(\mathbf{k}_1j_1|\mathbf{k}_2j_2)$ from (III-4a), a factor (-1) from (III-1), and a factor β from the τ-integrations.

2) For each phonon line $(\mathbf{k}j)$ there is a factor $\mathcal{g}_0(\mathbf{k}j;i\omega_n)$.

3) At each vertex the sum of ω_n's leaving should equal the sum of ω_n's entering; since we consider only connected diagrams, and since there are only two lines associated with every vertex, there will be no summation over independent n's.

4) For each nth order diagram there is a factor $(n!)^{-1}$ from (III-1).

As it happens all connected diagrams obtainable from the numerator of (III-1) may be summed to infinite order in closed form. To verify this assertion it suffices to consider a few low order diagrams. The zeroth order contribution

is exhausted by the diagonal perfect lattice propagator (II-21). To the first order one obtains two diagrams which may be identified with the graphs in Fig. 1 provided that one sets: $\mathbf{k}_1=\mathbf{k}, j_1=j, \mathbf{k}_2=\mathbf{k}', j_2=j'$. According to the above rules, 1) to 4), Fig. 1 a) and b) then give rise to the contributions

$$\mathcal{g}_0(\mathbf{k}j;i\omega_n)(-\tfrac{1}{2}\beta)v_1(\mathbf{k}j|\mathbf{k}'j')\mathcal{g}_0(\mathbf{k}'j';i\omega_n) \tag{III-8a}$$

$$\mathcal{g}_0(\mathbf{k}j;i\omega_n)(-\tfrac{1}{2}\beta)v_1(-\mathbf{k}'j'|-\mathbf{k}j)\mathcal{g}_0(\mathbf{k}'j';i\omega_n) \tag{III-8b}$$

By definition $\mathbf{v}_1$ is hermitean (see (III-5)). Thus $v_1(\mathbf{k}j|\mathbf{k}'j')$ equals $v_1(-\mathbf{k}'j'|-\mathbf{k}j)$. Consequently one may allow for first order perturbation by discarding (III-8b) and suppressing the factor $\frac{1}{2}$ appearing in (III-8a). There are eight diagrams stemming from second order perturbations, four of which are shown in Fig. 2. Translation of Fig. 2 a) to d) yields

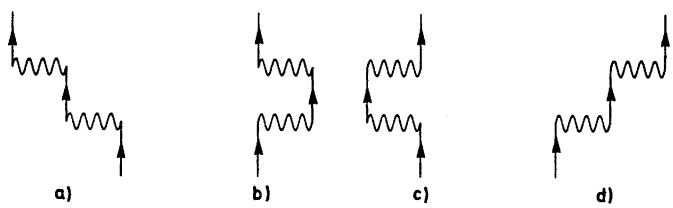


Fig. 2. Second order propagator diagrams.

$$\tfrac{1}{2}\mathcal{g}_0(\mathbf{k}j;i\omega_n)\sum_{\mathbf{k}_1j_1}(-\tfrac{1}{2}\beta)v_1(\mathbf{k}j|\mathbf{k}_1j_1)\mathcal{g}_0(\mathbf{k}_1j_1;i\omega_n)(-\tfrac{1}{2}\beta)v_1(\mathbf{k}_1j_1|\mathbf{k}'j')\mathcal{g}_0(\mathbf{k}'j';i\omega_n) \tag{III-9a}$$

$$\tfrac{1}{2}\mathcal{g}_0(\mathbf{k}j;i\omega_n)\sum_{\mathbf{k}_1j_1}(-\tfrac{1}{2}\beta)v_1(\mathbf{k}j|\mathbf{k}_1j_1)\mathcal{g}_0(\mathbf{k}_1j_1;i\omega_n)(-\tfrac{1}{2}\beta)v_1(-\mathbf{k}'j'|-\mathbf{k}_1j_1)\mathcal{g}_0(\mathbf{k}'j';i\omega_n) \tag{III-9b}$$

$$\tfrac{1}{2}\mathcal{g}_0(\mathbf{k}j;i\omega_n)\sum_{\mathbf{k}_1j_1}(-\tfrac{1}{2}\beta)v_1(-\mathbf{k}_1j_1|-\mathbf{k}j)\mathcal{g}_0(\mathbf{k}_1j_1;i\omega_n)(-\tfrac{1}{2}\beta)v_1(\mathbf{k}_1j_1|\mathbf{k}'j')\mathcal{g}_0(\mathbf{k}'j';i\omega_n) \tag{III-9c}$$

$$\tfrac{1}{2}\mathcal{g}_0(\mathbf{k}j;i\omega_n)\sum_{\mathbf{k}_1j_1}(-\tfrac{1}{2}\beta)v_1(-\mathbf{k}_1j_1|-\mathbf{k}j)\mathcal{g}_0(\mathbf{k}_1j_1;i\omega_n)(-\tfrac{1}{2}\beta)v_1(-\mathbf{k}'j'|-\mathbf{k}_1j_1)\times \times\mathcal{g}_0(\mathbf{k}'j';i\omega_n) \tag{III-9d}$$

By virtue of the hermiteicity of $\mathbf{v}_1$ each of the expressions (III-9b, c, d) is identical to (III-9a). The four remaining diagrams may be obtained from Fig. 2a) to d) by transposing the vertical order of the interaction lines, which process does not alter the contributions of any of the four diagrams. Thus, the entire second order contribution is given by

$$\mathcal{g}_0(\mathbf{k}j;i\omega_n)\sum_{\mathbf{k}_1j_1}(-\beta)v_1(\mathbf{k}j|\mathbf{k}_1j_1)\mathcal{g}_0(\mathbf{k}_1j_1;i\omega_n)(-\beta)v_1(\mathbf{k}_1j_1|\mathbf{k}'j')\mathcal{g}_0(\mathbf{k}'j';i\omega_n) \tag{III-10}$$

In the nth order case there will be a total of $n!2^n$ diagrams all of which are equivalent. The term $n!$ stems from the $n!$ different ways of permuting the $\overline{V}_1(\tau_1)\cdots\overline{V}_1(\tau_n)$ on the τ-axis, while 2^n comes about because every vertex of the Fig 1a) type may be replaced by the Fig. 1b) type and *vice versa*. It is sufficient therefore to consider only one nth order diagram provided that its

contribution is augmented by omission of the factor $\frac{1}{2}$ associated with every $v_1(\mathbf{k}_1 j_1|\mathbf{k}_2 j_2)$ term (see 1) above), and by neglection of the above rule 4). Hence

$$\begin{aligned}
&\mathcal{g}_0(\mathbf{k}j,\mathbf{k}'j';i\omega_n)=\Delta(\mathbf{k}-\mathbf{k}')\delta_{jj'}\mathcal{g}_0(\mathbf{k}j;i\omega_n)+\mathcal{g}_0(\mathbf{k}j;i\omega_n)(-\beta)v_1(\mathbf{k}j|\mathbf{k}'j')\times\\
&\mathcal{g}_0(\mathbf{k}'j';i\omega_n)+\mathcal{g}_0(\mathbf{k}j;i\omega_n)\sum_{\mathbf{k}_1 j_1}(-\beta)v_1(\mathbf{k}j|\mathbf{k}_1 j_1)\mathcal{g}_0(\mathbf{k}_1 j_1;i\omega_n)(-\beta)\times\\
&v_1(\mathbf{k}_1 j_1|\mathbf{k}'j')\mathcal{g}_0(\mathbf{k}'j';i\omega_n)+\mathcal{g}_0(\mathbf{k}j;i\omega_n)\sum_{\mathbf{k}_1 j_1}(-\beta)v_1(\mathbf{k}j|\mathbf{k}_1 j_1)\times\\
&\mathcal{g}_0(\mathbf{k}_1 j_1;i\omega_n)\sum_{\mathbf{k}_2 j_2}(-\beta)v_1(\mathbf{k}_1 j_1|\mathbf{k}_2 j_2)\mathcal{g}_0(\mathbf{k}_2 j_2;i\omega_n)(-\beta)v_1(\mathbf{k}_2 j_2|\mathbf{k}'j')\times\\
&\mathcal{g}_0(\mathbf{k}'j';i\omega_n)+\cdots\cdots
\end{aligned}\tag{III-11}$$

or in matrix notation

$$\begin{aligned}
\boldsymbol{g}(i\omega_n)=&\boldsymbol{g}_0(i\omega_n)+\boldsymbol{g}_0(i\omega_n)(-\beta)\mathbf{v}_1\boldsymbol{g}_0(i\omega_n)+\boldsymbol{g}_0(i\omega_n)(-\beta)\mathbf{v}_1\boldsymbol{g}_0(i\omega_n)\times\\
&(-\beta)\mathbf{v}_1\boldsymbol{g}_0(i\omega_n)+\cdots\cdots
\end{aligned}\tag{III-12}$$

which is an iterative solution to the Dyson equation

$$\boldsymbol{g}(i\omega_n)=\boldsymbol{g}_0(i\omega_n)+\boldsymbol{g}_0(i\omega_n)(-\beta)\mathbf{v}_1\boldsymbol{g}(i\omega_n)\tag{III-13}$$

with $(-\beta)\mathbf{v}_1$ as the self energy part. Solving for $\boldsymbol{g}(i\omega_n)$ one obtains

$$\boldsymbol{g}(i\omega_n)=[\mathbf{1}-\boldsymbol{g}_0(i\omega_n)(-\beta)\mathbf{v}_1]^{-1}\boldsymbol{g}_0(i\omega_n)\tag{III-14}$$

In order to establish contact with direct lattice Lifshitz theory we subject (III-13) to the process indicated by (II-20b) to get

$$\mathbf{g}(\omega)=\mathbf{g}_0(\omega)+\mathbf{g}_0(\omega)\mathbf{v}_1\mathbf{g}(\omega)\tag{III-15}$$

Insertion of this expression into the time Fourier transform of (II-8a) yields

$$\mathbf{G}(\omega)=\mathbf{G}_0(\omega)+\mathbf{G}_0(\omega)\mathbf{M}_0^{\frac{1}{2}}\boldsymbol{\varepsilon}\boldsymbol{\omega}^{\frac{1}{2}}2\mathbf{v}_1\boldsymbol{\omega}^{\frac{1}{2}}\boldsymbol{\varepsilon}^{\dagger}\mathbf{M}_0^{\frac{1}{2}}\mathbf{G}(\omega)\tag{III-16}$$

In view of the definition of $\mathbf{v}_1$, (III-5), (III-16) may be rewritten as

$$\begin{aligned}
\mathbf{G}(\omega)&=\mathbf{G}_0(\omega)+\mathbf{G}_0(\omega)\mathbf{M}_0^{\frac{1}{2}}2\boldsymbol{\Psi}^{\dagger}\mathbf{M}_0^{\frac{1}{2}}\mathbf{G}(\omega)\\
&=\mathbf{G}_0(\omega)+\mathbf{G}_0(\omega)\delta\boldsymbol{\Phi}\mathbf{G}(\omega)\langle=\rangle\mathbf{G}(\omega)=[\mathbf{1}-\mathbf{G}_0(\omega)\delta\boldsymbol{\Phi}]^{-1}\mathbf{G}_0(\omega)
\end{aligned}\tag{III-17}$$

which is the $T_1=0$ restriction of (II-3c). In principle (III-17) suffices to determine the perturbed frequency spectrum. By taking into account (II-13) and a corresponding equation for $\mathbf{G}(\omega)$ the familiar (distributional) relation

$$F_{(0)}(\omega^2)=(3nN)^{-1}\sum_{i=1}^{3nN}\delta(\omega^2-\omega^2_{(0)i})=(3nN\pi)^{-1}Im\sum_i(\omega_-{}^2-\omega^2_{(0)i})^{-1}$$

($\omega_-{}^2$ means that we approach the real ω^2 axis from below.)
for the normalized spectrum of squared frequencies ω_i^2 may be expressed as

$$F_{(0)}(\omega^2)=(3nN\pi)^{-1}Im\{Tr\mathbf{M}^{\frac{1}{2}}_{(0)}\mathbf{G}_{(0)}(\omega_-{}^2)\mathbf{M}_{(0)}{}^{\frac{1}{2}}\}$$

where the invariance of trace against a similarity transformation has been exploited. Consequently, defect induced changes in thermodynamic state functions may be discussed on the basis of (III-17). It is not without interest, however, to attempt a direct perturbative attack on the Helmholz free energy

$$\Omega=-\beta^{-1}\ln z\tag{III-18}$$

where z is the partition function $Tr\ \exp(-H\beta)$. In accordance with a by now well known prescription of many-body theory * we define an operator $S(\beta)$ by writing the density matrix $\varrho(\beta)$ as

$$\varrho(\beta)=\exp(-[H_0+H_1]\beta)=\exp(-H_0\beta)S(\beta) \tag{III-19}$$

Since $\varrho(\beta)$ is determined by the Bloch equation

$$-\partial\varrho/\partial\beta=(H_0+H_1)\varrho \tag{III-20}$$

$S(\beta)$ must satisfy

$$\partial S/\partial\beta=-\overline{H}_1(\beta)S \tag{III-21}$$

where

$$\overline{H}_1(\beta)=\exp(H_0\beta)H_1\exp(-H_0\beta) \tag{III-22}$$

Integrating from 0 to β with allowance for the initial condition $S(0)=1$, iterating the result, and transforming all upper integration limits to β by using the Dyson ordering operator one finally obtains

$$z=\exp(-\beta\Omega_0)\{1+\sum_{n=1}^{\infty}\frac{(-1)^n}{n!}\int_0^\beta d\tau_1\cdots\int_0^\beta d\tau_n\langle T\{\overline{H}_1(\tau_1)\cdots\overline{H}_1(\tau_n)\}\rangle_0\} \tag{III-23}$$

As in the propagator case we represent the various terms in (III-23) by diagrams.[12] However, presently there will be no external lines since the $\overline{\mathcal{A}}_{\mathbf{k}j}(\tau)\overline{\mathcal{A}}^\dagger_{\mathbf{k}'j'}(0)$ operators in the numerator of (III-1) do not appear in (III-23). Since Ω is our primary concern we exploit the effect of taking the logarithm of z which is to eliminate all unlinked diagrams,[12] whence

$$\Delta\Omega=\Omega-\Omega_0=-\beta^{-1}\mathcal{L}(\beta) \tag{III-24}$$

where $\mathcal{L}(\beta)$ is the sum of all linked parts. The first, second, and third order linked diagrams are shown in Fig. 3a, Fig. 3b, and in Fig. 4, respectively. By the suitably modified rules 1) to 4) the contribution of the first order "oyster" to $\Delta\Omega$ becomes

$$(-\beta)^{-1}\sum_{m=-\infty}^{\infty}\sum_{\mathbf{k}j}\mathcal{g}_0(\mathbf{k}j;i\omega_m)(-\tfrac{1}{2}\beta)\mathbf{v}_1(\mathbf{k}j|\mathbf{k}j)=(-2\beta)^{-1}\sum_{m=-\infty}^{\infty}Tr\{(-\beta)g_0(i\omega_m)\mathbf{v}_1\}$$

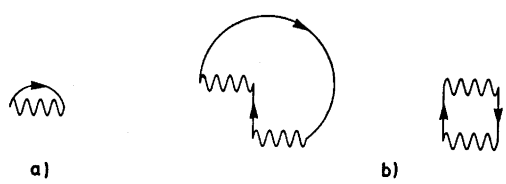


Fig. 3a. Instantaneous phonon (=quantum of collective motion) contributing to the Helmholz free energy. *b.* Second order linked $\Delta\Omega$ graphs.

* The approach briefly outlined below, (III-19 to 24), is usually formulated in terms of a grand canonical ensemble.[12] The formally simple system of interest here can be conveniently dealt with by using a canonical ensemble which, incidentally, was the ensemble employed in the initial and decisive work of Matsubara.[19]

Again in view of the hermiteicity of $\mathbf{v}_1$ each of the two second order diagrams in Fig. 3b gives rise to one half of the total second order term

$$(-2\beta)^{-1}\sum_{m=-\infty}^{\infty}(\tfrac{1}{2})\sum_{\mathbf{k}j}\mathcal{g}_0(\mathbf{k}j;i\omega_m)(-\beta)\sum_{\mathbf{k}_1j_1}v_1(\mathbf{k}j|\mathbf{k}_1j_1)\mathcal{g}_0(\mathbf{k}_1j_1;i\omega_m)(-\beta)v_1(\mathbf{k}_1j_1|\mathbf{k}j)$$

$$=(-2\beta)^{-1}\sum_{m=-\infty}^{\infty}Tr(\tfrac{1}{2})\{(-\beta)\boldsymbol{g}_0(i\omega_m)\mathbf{v}_1\}^2$$

Similarly, each of the topologically equivalent third order diagrams in Fig. 4 contributes one eighth of

$$(-2\beta)^{-1}\sum_{m=-\infty}^{\infty}Tr(1/3)\{(-\beta)\boldsymbol{g}_0(i\omega_m)\mathbf{v}_1\}^3$$

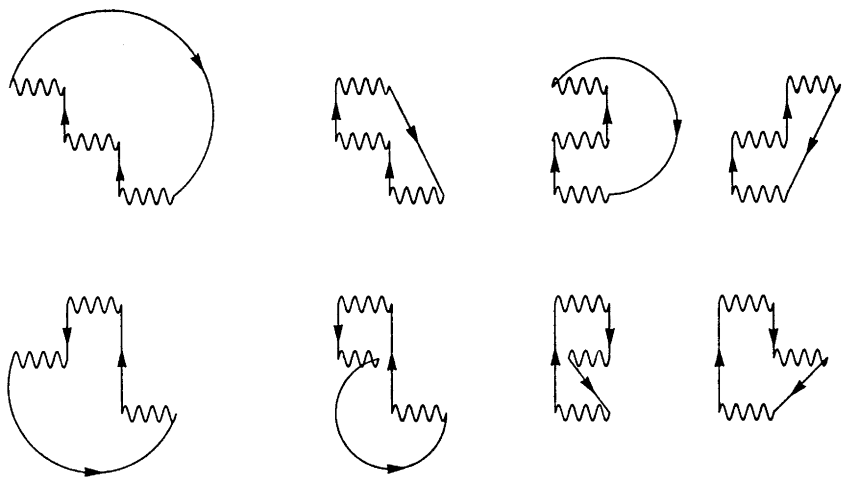


Fig. 4. Third order linked $\Delta\Omega$ graphs.

In the general nth order case it is a matter of trivial combinatorics to show that there are $(n-1)!2^{n-1}$ diagrams, each one contributing

$$\frac{1}{n!}(-\beta)^{-1}\sum_{m=-\infty}^{\infty}Tr\{\left(-\frac{\beta}{2}\right)\boldsymbol{g}_0(i\omega_m)\mathbf{v}_1\}^n=\frac{1}{n!}2^{-(n-1)}(-2\beta)^{-1}\sum_{m=-\infty}^{\infty}Tr\{(-\beta)\boldsymbol{g}_0(i\omega_m)\mathbf{v}_1\}^n$$

Consequently the total nth order therm becomes

$$(-2\beta)^{-1}\sum_{m=-\infty}^{\infty}Tr\left(\frac{1}{n}\right)\{(-\beta)\boldsymbol{g}_0(i\omega_m)\mathbf{v}_1\}^n$$

whence

$$\Delta\Omega=(2\beta)^{-1}\sum_{m=-\infty}^{\infty}Tr\sum_{n=1}^{\infty}\left(-\frac{1}{n}\right)\{(-\beta)\boldsymbol{g}_0(i\omega_m)\mathbf{v}_1\}^n \qquad \text{(III-25)}$$

Assuming the $\sum_{n=1}^{\infty}$ series to converge and keeping in mind that

$$\ln(1-x) = -x - \tfrac{1}{2}x^2 - \cdots - \frac{1}{n}x^n - \cdots (|x| < 1)$$

we rewrite (III-25) as

$$\begin{aligned} \Delta\Omega &= (2\beta)^{-1} \sum_m Tr \ln(\mathbf{1} + \beta \boldsymbol{g}_0(i\omega_n)\mathbf{v}_1) \\ &= (2\beta)^{-1} \sum_{\mathbf{m}} \ln|\mathbf{1} + \beta \boldsymbol{g}_0(\mathrm{i}\omega_{\mathrm{n}})\mathbf{v}_1| \end{aligned} \tag{III-26}$$

The value of a determinant is left unchanged upon a similarity transformation performed on the associated matrix. Thus (see (II-13), (II-22), and (III-5))

$$\begin{aligned} \Delta\Omega &= (2\beta)^{-1} \sum_m \ln|\mathbf{1} + \boldsymbol{\varepsilon}\boldsymbol{\omega}^{-\frac{1}{2}} \mathrm{diag}\{2\omega_{\mathbf{k}j}/[\omega_m{}^2 + \omega_{\mathbf{k}j}{}^2]\}\boldsymbol{\omega}^{-\frac{1}{2}}\boldsymbol{\varepsilon}^\dagger \boldsymbol{\Psi}\boldsymbol{\varepsilon}\boldsymbol{\omega}^{-\frac{1}{2}}\boldsymbol{\omega}^{\frac{1}{2}}\boldsymbol{\varepsilon}^\dagger| \\ &= (2\beta)^{-1} \sum_m \ln|\mathbf{1} - (\mathbf{M}_0{}^{-\frac{1}{2}}\boldsymbol{\varepsilon}\, \mathrm{diag}\{[-\omega_m{}^2 - \omega_{\mathbf{k}j}{}^2]^{-1}\}\boldsymbol{\varepsilon}^\dagger \mathbf{M}_0{}^{-\frac{1}{2}})\delta\boldsymbol{\Phi}| \\ &= (kT/2) \sum_m \ln|\mathbf{1} - \mathbf{G}_0(i\omega_m)\delta\boldsymbol{\Phi}| \end{aligned} \tag{III-27}$$

which is the $T_1 = 0$ restriction of an expression obtained in a nonperturbative manner by Maradudin,[20] who made use of an infinite product representation for $\sinh(x)$.

B. Phonons interacting *via* mass defects

The effects of mass changes on the propagator and on Ω may be evaluated in a fashion almost identical to the one encountered in the preceding subsection. We shall therefore dwell rather briefly on the $V_1 = 0$ case. With allowance for the following relations

$$\begin{aligned} &\langle T\mathcal{A}^\dagger{}_{\mathbf{k}j}\mathcal{B}_{\mathbf{k}j}; i\omega_n\rangle_0 = \langle T\mathcal{A}_{\mathbf{k}j}\mathcal{B}^\dagger{}_{\mathbf{k}j}; i\omega_n\rangle_0 = \\ &= -\langle T\mathcal{B}_{\mathbf{k}j}\mathcal{A}^\dagger{}_{\mathbf{k}j}; i\omega_n\rangle_0 = -\langle T\mathcal{B}^\dagger{}_{\mathbf{k}j}\mathcal{A}_{\mathbf{k}j}; i\omega_n\rangle_0 = \\ &= \frac{2(i\omega_n)}{\beta}\frac{1}{(i\omega_n)^2 - \omega_{\mathbf{k}j}{}^2} = -\frac{(i\omega_n)}{\omega_{\mathbf{k}j}} g_0(\mathbf{k}j; i\omega_n) \\ &\langle T\mathcal{B}^\dagger{}_{\mathbf{k}j}\mathcal{B}_{\mathbf{k}j}; i\omega_n\rangle_0 = \langle T\mathcal{B}_{\mathbf{k}j}\mathcal{B}^\dagger{}_{\mathbf{k}j}; i\omega_n)_0 = -g_0(\mathbf{k}j; i\omega_n) \end{aligned}$$

one finds for the propagator

$$\begin{aligned} &g(\mathbf{k}j,\mathbf{k}'j'; i\omega_n) = \Delta(\mathbf{k}-\mathbf{k}')\delta_{jj'}g_0(\mathbf{k}j; i\omega_n) - (i\omega_n)\omega_{\mathbf{k}j}{}^{-1}g_0(\mathbf{k}j; i\omega_n) \times \\ &(-\beta)t_1(\mathbf{k}j|\mathbf{k}'j')g_0(\mathbf{k}'j'; i\omega_n)\omega_{\mathbf{k}'j'}{}^{-1}(i\omega_n) + (i\omega_n)\omega_{\mathbf{k}j}{}^{-1}g_0(\mathbf{k}j; i\omega_n) \times \\ &\sum_{\mathbf{k}_1 j_1}(-\beta)t_1(\mathbf{k}j|\mathbf{k}_1 j_1)g_0(\mathbf{k}_1 j_1; i\omega_n)(-\beta)t_1(\mathbf{k}_1 j_1|\mathbf{k}'j')g_0(\mathbf{k}'j'; i\omega_n)i\omega_{\mathbf{k}'j'}{}^{-1}(i\omega_n) + \cdots \end{aligned} \tag{III-28}$$

or in matrix notation

$$\begin{aligned} \boldsymbol{g}(i\omega_n) &= \boldsymbol{g}_0(i\omega_n) + \sum_{m=1}^{\infty}(-1)^m(i\omega_n)\boldsymbol{\omega}^{-1}\{\boldsymbol{g}_0(i\omega_n)(-\beta)\mathbf{t}_1\}^m\boldsymbol{g}_0(i\omega_n)\boldsymbol{\omega}^{-1}(i\omega_n) \\ &= \boldsymbol{g}_0(i\omega_n) + (i\omega_n)\boldsymbol{\omega}^{-1}(\sum_{m=0}^{\infty}\{\boldsymbol{g}_0(i\omega_n)(\beta)\mathbf{t}_1\}^m)\boldsymbol{g}_0(i\omega_n)\boldsymbol{\omega}^{-1}(i\omega_n) - \\ &\quad - (i\omega_n)\boldsymbol{\omega}^{-1}\boldsymbol{g}_0(i\omega_n)\boldsymbol{\omega}^{-1}(i\omega_n) \\ &= \boldsymbol{g}_0(i\omega_n) + (i\omega_n)\boldsymbol{\omega}^{-1}([\mathbf{1} - \boldsymbol{g}_0(i\omega_n)(\beta)\mathbf{t}_1]^{-1} - \mathbf{1})\boldsymbol{g}_0(i\omega_n)\boldsymbol{\omega}^{-1}(i\omega_n) \end{aligned} \tag{III-29}$$

In view of (II-20b) and (III-29)

$$\mathbf{g}(\omega)=\mathbf{g}_0(\omega)+\omega^2\boldsymbol{\omega}^{-1}([\mathbf{1}+\mathbf{g}_0(\omega)\mathbf{t}_1]^{-1}-\mathbf{1})\mathbf{g}_0(\omega)\boldsymbol{\omega}^{-1} \tag{III-30}$$

If only a few diagonal elements of Λ differ from zero (by definition, (III-3a), the off diagonal elements vanish) it is advantageous to replace the above indicated matrix inversion by a corresponding process in direct lattice space. If we set $\mathbf{t}_1=\mathbf{EF}$, where $\mathbf{E}=\boldsymbol{\omega}^{\frac{1}{2}}\boldsymbol{\varepsilon}^{\dagger}\boldsymbol{\Lambda}$ and $\mathbf{F}=\boldsymbol{\varepsilon}\boldsymbol{\omega}^{\frac{1}{2}}$, and rearrange, (III-30) becomes*

$$\begin{aligned}\mathbf{g}(\omega)&=\mathbf{g}_0(\omega)-\omega^2\boldsymbol{\omega}^{-1}\mathbf{g}_0(\omega)\mathbf{E}(\mathbf{1}+\mathbf{F}\mathbf{g}_0(\omega)\mathbf{E})^{-1}\mathbf{F}\mathbf{g}_0(\omega)\boldsymbol{\omega}^{-1}\\&=\mathbf{g}_0(\omega)-\omega^2\boldsymbol{\omega}^{-1}\mathbf{g}_0(\omega)\mathbf{E}(\mathbf{1}+\boldsymbol{\varepsilon}\omega^2\boldsymbol{\omega}^{-\frac{1}{2}}\mathbf{g}_0(\omega)\boldsymbol{\omega}^{-\frac{1}{2}}\boldsymbol{\varepsilon}^{\dagger}\boldsymbol{\Lambda})^{-1}\mathbf{F}\mathbf{g}_0(\omega)\boldsymbol{\omega}^{-1}\\&=\mathbf{g}_0(\omega)-\omega^2\boldsymbol{\omega}^{-1}\mathbf{g}_0(\omega)\mathbf{E}(\mathbf{1}+\{\mathbf{M}_0^{-\frac{1}{2}}\boldsymbol{\Phi}_0\mathbf{M}_0^{-\frac{1}{2}}\}\{\mathbf{M}_0^{\frac{1}{2}}\mathbf{G}_0(\omega)\mathbf{M}_0^{\frac{1}{2}}\}2\boldsymbol{\Lambda})^{-1}\mathbf{F}\mathbf{g}_0(\omega)\omega^{-1}\\&=\mathbf{g}_0(\omega)-\omega^2\boldsymbol{\omega}^{-1}\mathbf{g}_0(\omega)\mathbf{E}(\mathbf{1}+[\omega^2\{\mathbf{M}_0^{\frac{1}{2}}\mathbf{G}_0(\omega)\mathbf{M}_0^{\frac{1}{2}}\}-\mathbf{1}]2\boldsymbol{\Lambda})^{-1}\mathbf{F}\mathbf{g}_0(\omega)\boldsymbol{\omega}^{-1}\end{aligned} \tag{III-31}$$

the total expression still referring to **k** space. To complete the transformation to position representation we insert (III-31) into a time Fourier transformed (II-8a), thereby arriving at

$$\begin{aligned}\mathbf{G}(\omega)&=\mathbf{G}_0(\omega)-\omega^2\mathbf{G}_0(\omega)\mathbf{M}_0^{\frac{1}{2}}2\boldsymbol{\Lambda}(\mathbf{1}+[\omega^2\{\mathbf{M}_0^{\frac{1}{2}}\mathbf{G}_0(\omega)\mathbf{M}_0^{\frac{1}{2}}\}-\mathbf{1}]2\boldsymbol{\Lambda})^{-1}\mathbf{M}_0^{\frac{1}{2}}\mathbf{G}_0(\omega)\\&=\mathbf{G}_0(\omega)-\omega^2\mathbf{G}_0(\omega)2\boldsymbol{\Lambda}[(\mathbf{1}-2\boldsymbol{\Lambda})\mathbf{M}_0^{-1}+\omega^2\mathbf{G}_0(\omega)2\boldsymbol{\Lambda}]^{-1}\mathbf{G}_0(\omega)\\&=\mathbf{G}_0(\omega)+\omega^2\mathbf{G}_0(\omega)(\mathbf{M}_0-\mathbf{M})[\mathbf{1}-\omega^2\mathbf{G}_0(\omega)(\mathbf{M}_0-\mathbf{M})]^{-1}\mathbf{G}_0(\omega)\\&=\mathbf{G}_0(\omega)+\mathbf{G}_0(\omega)\omega^2(\mathbf{M}_0-\mathbf{M})\{\mathbf{1}+\mathbf{G}_0(\omega)\omega^2(\mathbf{M}_0-\mathbf{M})+\\&\quad+\cdots\cdot[\mathbf{G}_0(\omega)\omega^2(\mathbf{M}_0-\mathbf{M})]^n+\cdots\}\mathbf{G}_0(\omega)\\&=\mathbf{G}_0(\omega)+\mathbf{G}_0(\omega)\omega^2(\mathbf{M}_0-\mathbf{M})\mathbf{G}_0(\omega)+\mathbf{G}_0(\omega)\omega^2(\mathbf{M}_0-\mathbf{M})\mathrm{X}\\&\quad\mathrm{X}\mathbf{G}_0(\omega)\omega^2(\mathbf{M}_0-\mathbf{M})\mathbf{G}_0(\omega)+\cdots\cdots\\&=\mathbf{G}_0(\omega)+\mathbf{G}_0(\omega)\{\omega^2(\mathbf{M}_0-\mathbf{M})\}\mathbf{G}(\omega)\\&=[\mathbf{1}-\mathbf{G}_0(\omega)\{\omega^2(\mathbf{M}_0-\mathbf{M})\}]^{-1}\mathbf{G}_0(\omega)\end{aligned} \tag{III-32}$$

(III-32) is readily recognized as the $\mathrm{V}_1=0$ restriction of (II-3c). The analogue of (III-25) becomes

$$\Delta\Omega=(2\beta)^{-1}\sum_{m=-\infty}^{\infty}Tr\sum_{n=1}^{\infty}\left(-\frac{1}{n}\right)\{\beta\boldsymbol{g}_0(i\omega_m)\mathbf{t}_1\}^n \tag{III-33}$$

which expression may be rearranged as follows

$$\begin{aligned}\Delta\Omega&=(2\beta)^{-1}\sum_m Tr\ln(\mathbf{1}-\beta\boldsymbol{g}_0(i\omega_m)\mathbf{t}_1)=(2\beta)^{-1}\sum_m\ln|\mathbf{1}-\beta\boldsymbol{g}_0(i\omega_m)\mathbf{t}_1|\\&=(2\beta)^{-1}\sum_m\ln|\mathbf{1}-\boldsymbol{\varepsilon}\boldsymbol{\omega}^{\frac{1}{2}}\mathrm{diag}\{\omega_{kj}/[\omega_m{}^2+\omega_{kj}{}^2]\}\boldsymbol{\omega}^{\frac{1}{2}}\boldsymbol{\varepsilon}^{\dagger}2\boldsymbol{\Lambda}|\\&=(2\beta)^{-1}\sum_m\ln|\mathbf{1}+\boldsymbol{\varepsilon}\boldsymbol{\omega}^2\mathrm{diag}\{[-\omega_m{}^2-\omega_{kj}{}^2]^{-1}\}\boldsymbol{\varepsilon}^{\dagger}2\boldsymbol{\Lambda}|\\&=(2\beta)^{-1}\sum_m\ln|\mathbf{1}+\boldsymbol{\varepsilon}\boldsymbol{\varepsilon}^{\dagger}\mathbf{M}_0^{-\frac{1}{2}}\boldsymbol{\Phi}_0\mathbf{M}_0^{-\frac{1}{2}}\boldsymbol{\varepsilon}\ \mathrm{diag}\{[-\omega_m{}^2-\omega_{kj}{}^2]^{-1}\}\boldsymbol{\varepsilon}^{\dagger}2\boldsymbol{\Lambda}|\\&=(2\beta)^{-1}\sum_m\ln|\mathbf{1}+\boldsymbol{\Phi}_0\mathbf{G}_0(i\omega_m)2\boldsymbol{\Lambda}|\\&=(2\beta)^{-1}\sum_m\ln|\mathbf{1}+(\mathbf{M}_0(i\omega_m)^2\mathbf{G}_0(i\omega_m)-\mathbf{1})2\boldsymbol{\Lambda}|\end{aligned} \tag{III-34}$$

* A rearranged (III-15) similar to (III-31) can be obtained by an analogous "splitting" of $\mathbf{v}_1$.

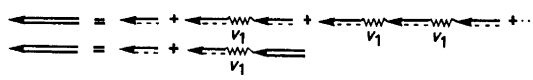
$$= (2\beta)^{-1} \sum_m \ln|\mathbf{M}_0\mathbf{M}^{-1} - \mathbf{G}_0(i\omega_m)(i\omega_m)^2(\mathbf{M}_0 - \mathbf{M}_1)\mathbf{M}_0\mathbf{M}^{-1}|$$

$$= (\mathrm{kT}/2) \sum_m \ln \frac{|\mathbf{M}_0|}{|\mathbf{M}|} |\mathbf{1} - \mathbf{G}_0(i\omega_m)(i\omega_m)^2(\mathbf{M}_0 - \mathbf{M})|$$

(III-34) is the $V_1 = 0$ counterpart of (III-27).

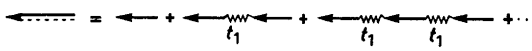
C. Combined effect of mass changes and force constant alterations

With the preceding results in hand we turn to the case of a simultaneous switching on of mass and force constant perturbations. This time there will be a total of $n!2^n \sum_{m=0}^{n} \binom{n}{m}$ nth order connected propagator diagrams. The reason for the term $n!2^n$ has already been stated in subsection A. The sum $\sum_{m=0}^{n}$ comes about because the nth order diagrams differ among themselves in the number of v_1 vertices, m, and in the number of t_1 vertices, $n-m$, included. For any specific choice of m $(0 \leqq m \leqq n)$ and for some fixed arrangement of free phonon lines there are $n!/[(n-m)!m!]$ ways of permuting the m v_1 labels and the $(n-m)$ t_1 labels on the vertices. Hence the appearance of binomial coefficients. If we group the diagrams according to their m-order (as opposed to the previous n-order grouping) it becomes possible to sum all diagrams to infinite order by simply substituting for the free phonon lines in the $T_1 = 0$, $V_1 \neq 0$ diagrams with clothed $V_1 = 0$, $T_1 \neq 0$ propagators. Symbolically



(III-35)

where



Translation of (III-35) yields

$$\begin{aligned} g(i\omega_n) &= g_t(i\omega_n) + g_t(i\omega_n)\mathbf{v}_1 g_t(i\omega_n) + \cdots\cdots \\ &= g_t(i\omega_n) + g_t(i\omega_n)\mathbf{v}_1 g(i\omega_n) \\ &= (\mathbf{1} - g_t(i\omega_n)\mathbf{v}_1)^{-1} g_t(i\omega_n) \end{aligned} \tag{III-36}$$

where g_t $(i\omega_n)$ is the propagator matrix (III-29) relabelled. By substitution of (III-29) into (III-36) one easily sees that the latter expression implies a correct number of nth order diagrams, for all n's, and that any particular diagram is represented once and only once. In view of (III-17) and (III-32) we obtain from (III-36)

$$\begin{aligned} \mathbf{G}(\omega) &= \mathbf{G}_t(\omega) + \mathbf{G}_t(\omega)\delta\boldsymbol{\Phi}\mathbf{G}_t(\omega) + \cdots\cdots \\ &= [\mathbf{1} - \mathbf{G}_t(\omega)\delta\boldsymbol{\Phi}]^{-1}\mathbf{G}_t(\omega) \end{aligned} \tag{III-37}$$

where $\mathbf{G}_t(\omega)$ is to be identified with the displacement-displacement Green's function matrix in the $V_1=0$ case. To recover the $V_1\neq 0$, $T_1\neq 0$ result of the Lifshitz theory we rewrite (III-37) as follows

$$\begin{aligned}\mathbf{G}(\omega) &= [\mathbf{1}-\mathbf{G}_t(\omega)\delta\boldsymbol{\Phi}]^{-1}[\mathbf{1}-\mathbf{G}_0(\omega)\omega^2(\mathbf{M}_0-\mathbf{M})]^{-1}\mathbf{G}_0(\omega)\\ &= \{[\mathbf{1}-\mathbf{G}_0(\omega)\omega^2(\mathbf{M}_0-\mathbf{M})][\mathbf{1}-\mathbf{G}_t(\omega)\delta\boldsymbol{\Phi}]\}^{-1}\mathbf{G}_0(\omega)\\ &= \{\mathbf{1}-\mathbf{G}_0(\omega)\omega^2(\mathbf{M}_0-\mathbf{M})-[\mathbf{G}_t(\omega)-\mathbf{G}_0(\omega)\omega^2(\mathbf{M}_0-\mathbf{M})\mathbf{G}_t(\omega)]\delta\boldsymbol{\Phi}\}^{-1}\mathbf{G}_0(\omega)\\ &= \{\mathbf{1}-\mathbf{G}_0(\omega)\omega^2(\mathbf{M}_0-\mathbf{M})-\mathbf{G}_0(\omega)\delta\boldsymbol{\Phi}\}^{-1}\mathbf{G}_0(\omega)\\ &= [\mathbf{1}-\mathbf{G}_0(\omega)\{\omega^2(\mathbf{M}_0-\mathbf{M})+\delta\boldsymbol{\Phi}\}]^{-1}\mathbf{G}_0(\omega) \qquad \text{(III-38)}\end{aligned}$$

which expression coincides with (II-3c). We divide the linked Ω graphs into two classes. The first encompasses all diagrams which contain only t_1-vertices. Below $\Delta\Omega_t$ denotes the associated contribution, given by (III-34), The diagrams in the second class are conveniently grouped into subsets according to their m-order ($m=1, 2,\cdots\infty$) where, again, m is the number of v_1-vertices. By partitioning of integers and a simple combinatorial argument it may be shown that the contribution from any subset can be obtained exactly as in subsection A provided that the free phonon lines are replaced by fully dressed $T_1\neq 0$, $V_1=0$ propagators. To fix the ideas let us consider the nth order diagrams in the mth subset. The diagrams in question, which contain m v_1-vertices and $(n-m)$ t_1-vertices, can be separated into $\binom{n-1}{m-1}$ groups in one-to-one correspondence with partitions $\{P_k^n\}=\{k_1,k_2,\cdots,k_m;\ \sum_{i=1}^{m} k_i=(n-m)\}$. We first reduce the contents of each group by exploiting the hermiteicity of $\mathbf{v}_1$ and $\mathbf{t}_1$ to get rid of $(n-1)$ of the n factors $(\frac{1}{2})$ belonging to the n matrix elements. As before the remaining factor $(\frac{1}{2})$ is to be lumped in with the term $(-\beta)^{-1}$ appearing in (III-24). All vertices are now of the Fig. 1a type, say. Then the common characteristic of all graphs in the same P_k^n group (corresponding to some fixed combination $k_1,\cdots,k_m$, thus) may be formulated as follows:

Pick out an arbitrary v_1-vertex. Upon leaving the wiggly line from the left and going through the "circuit" by staying on free phonon lines or interaction wiggles at all times the number of t_1-vertices encountered between the ith and the $(i+1)$th v_1-vertex equals k_i; the first and the $(m+1)$th v_i-vertex both referring to the one from which we departed.

Translating the diagrams into algebraic expressions and summing over $(\mathbf{k}j)$ labels it follows at once that all diagrams with a common P_k^n designation are equivalent. (Diagrams belonging to different P_k^n groups may, by virtue of the cyclic trace property, or may not, if so mainly because of different numbers of mixed $\mathcal{AB}$ contractions, be equivalent.) To calculate the entire contribution of all the $\binom{n-1}{m-1}$ groups we consequently select representatives with different P_k^n labels and multiply each representative by the number of diagrams, P_k^nN, in its associated group. The set $\{P_k^nN;P_k^n=1,\cdots,\binom{n-1}{m-1}\}$ is determined in the following way: Irrespective of the partition at

hand there is a factor $(m-1)!\binom{n}{m}$ stemming from the different ways of combining the m v_1 and the n τ_j designations, and from the various orders of appearance of the m $v_1(\tau_j)$-(fixed j's)-vertices encountered when going through the diagrams. Given a fixed and ordered v_1-τ_j combination, and a fixed partition, $P_k{}^n$, then upon going along the closed "circuit" of phonon lines and interaction wiggles as previously described the number of different and allowable arrangements of phonon lines encountered between the first and the second v_1-vertex is $\binom{n-m}{k_1}k_1!$. $\binom{n-m}{k_1}$ represents the various ways of picking out k_1 t_1-vertices among the $(n-m)$ vertices which have not already been attributed v_1 labels, and $k_1!$ takes into account the different ways of getting from one v_1-vertex to another by threading k_1 t_1-vertices. Similarly there is a factor $\binom{n-m-k_1}{k_2}k_2!$ associated with those diagram parts that must be threaded to get from the second to the third v_1-vertex. Altogether

$$P_k{}^nN=(m-1)!\binom{n}{m}\left[\prod_{i=1}^{m-1}\left\{\binom{n-m-\sum i}{k_i}k_i!\right\}\right]k_m!$$

where $\sum i=\sum_{j=1}^{i-1}kj, \quad i>1$

$\sum i=0, \quad i=1$

By writing out the binomial coefficients explicitly and by keeping in mind that $k_m=(n-m)-\sum m$, one sees that $P_k{}^nN$ simplifies to

$$P_k{}^nN=\frac{n!}{m!}(m-1)!=\frac{n!}{m}$$

In view of the term $(n!)^{-1}$ appearing in (III-23) the "effective" multiplicative factor to be associated with each $P_k{}^n$ group representative is $(P_k{}^nN/n!)=m^{-1}$. Thus the "effective" factor depends only on the m-order, and this is exactly what must be the case to justify our making use of previous results in the manner stated above and depicted in Fig. 5. Consequently

$$\Delta\Omega=\Delta\Omega_t+(2\beta)^{-1}\sum_{m=-\infty}^{\infty}Tr\sum_{n=1}^{\infty}\left(-\frac{1}{n}\right)\{(-\beta)\boldsymbol{g}_t(i\omega_m)\mathbf{v}_1\}^n$$

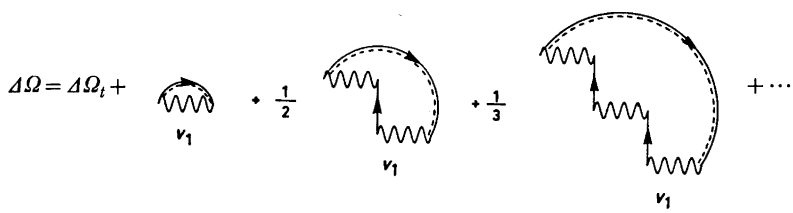


Fig. 5. Linked diagrammatic expansion of $\Delta\Omega$ ($V_1\neq0$, $T_1\neq0$) expressed in terms of fully dressed ($V_1=0$) propagators.

$$
\begin{aligned}
&= \Delta\Omega_t + (2\beta)^{-1}\sum_m \ln|\mathbf{1} + \beta \boldsymbol{g}_t(i\omega_m)\mathbf{v}_1| \\
&= \Delta\Omega_t + (2\beta)^{-1}\sum_m \ln|\mathbf{1} - \mathbf{G}_t(i\omega_m)\delta\boldsymbol{\Phi}| \\
&= (2\beta)^{-1}\sum_m \ln \frac{|\mathbf{M}_0|}{|\mathbf{M}|}\,|\{\mathbf{1} - \mathbf{G}_0(i\omega_m)(i\omega_m)^2(\mathbf{M}_0 - \mathbf{M})\}\{\mathbf{1} - \mathbf{G}_t(i\omega_m)\delta\boldsymbol{\Phi}\}|
\end{aligned}
\tag{III-39}
$$

To transform (III-39) into a somewhat more revealing form we copy the matrix manipulations occurring in the last few lines preceding (III-38), and find

$$
\Delta\Omega = (kT/2)\sum_m \ln \frac{|\mathbf{M}_0|}{|\mathbf{M}|}\,|\mathbf{1} - \mathbf{G}_0(i\omega_m)\{(i\omega_m)^2(\mathbf{M}_0 - \mathbf{M}) + \delta\boldsymbol{\Phi}\}| \tag{III-40}
$$

which expression constitutes the desired generalization of (III-27) and (III-34).

IV. QUESTIONS OF CONVERGENCE

The preceding section contains a considerable amount of hazardous reasoning in view of the apparent carelessness exhibited while treating the various infinite series resulting from graphical summations to infinite order. We shall not attempt to justify the dubious manipulations by setting out to prove the convergence of the series referred to. On the contrary, we intend to give a counter-example in which two of the expansions *diverge*. Consider the case of an isolated substitutional impurity atom imbedded in a cubic Bravais lattice. For the geometric progression

$$
\begin{aligned}
(\mathbf{1} - \{\boldsymbol{g}_0(i\omega_n)(\beta)\mathbf{t}_1\})^{-1} = ?\,\mathbf{1} + \{\boldsymbol{g}_0(i\omega_n)(\beta)\mathbf{t}_1\} + \{\boldsymbol{g}_0(i\omega_n)(\beta)\mathbf{t}_1\}^2 + \cdots \\
+ \{\boldsymbol{g}_0(i\omega_n)(\beta)\mathbf{t}_1\}^k + \cdots
\end{aligned}
\tag{IV-1}
$$

and the Taylor expansion

$$
\begin{aligned}
\ln(\mathbf{1} - \{\boldsymbol{g}_0(i\omega_n)(\beta)\mathbf{t}_1\}) = ?\,-\{\boldsymbol{g}_0(i\omega_n)(\beta)\mathbf{t}_1\} - \tfrac{1}{2}\{\boldsymbol{g}_0(i\omega_n(\beta)\mathbf{t}_1\}^2 \cdots \\
\cdots - \frac{1}{k}\{\boldsymbol{g}_0(i\omega_n)(\beta)\mathbf{t}_1\}^k \cdots
\end{aligned}
\tag{IV-2}
$$

to converge it is necessary (and sufficient) that all eigenvalues of

$$
\boldsymbol{g}_0(i\omega_n)(\beta)\mathbf{t}_1 = [\mathrm{diag}(\omega_{\mathbf{k}j}/[\omega_n^2 + \omega_{\mathbf{k}j}^2])](\boldsymbol{\omega}^{\frac{1}{2}}\boldsymbol{\varepsilon}^\dagger(2\boldsymbol{\Lambda})\boldsymbol{\varepsilon}\boldsymbol{\omega}^{\frac{1}{2}})
$$

be less than one in modulus.[21] As it stands this matrix is inconvenient for investigating whether it fulfills, or fails to comply with, the necessary condition. However, since the eigenvalues of a matrix are left unaltered by a similarity transformation we may alternatively look into the matrix

$$
\mathbf{Q} = \boldsymbol{\varepsilon}\boldsymbol{\omega}^{\frac{1}{2}}\{\boldsymbol{g}_0(i\omega_n)(\beta)\mathbf{t}_1\}\boldsymbol{\omega}^{-\frac{1}{2}}\boldsymbol{\varepsilon}^\dagger = [\boldsymbol{\varepsilon}\ \mathrm{diag}\{\omega_{\mathbf{k}j}^2/[\omega_n^2 + w_{\mathbf{k}j}^2]\}\boldsymbol{\varepsilon}^\dagger](2\boldsymbol{\Lambda})
$$

Recalling the definition of $\boldsymbol{\Lambda}$, (III-3a), invoking the orthonormality of the vectors $\{\mathbf{e}(\mathbf{k}j);\ \text{fixed } \mathbf{k}; j = 1,3\}$, and making use of a simple space group argument one easily verifies that the eigenvalue condition

$$
|\mathbf{1}\mu - \mathbf{Q}| = 0
$$

is satisfied for

$$
\mu = \{(1/3N)\sum_{\mathbf{k}j}(\omega_{\mathbf{k}j}^2/[\omega_n^2 + \omega_{\mathbf{k}j}^2])\}\{-\chi/[1-\chi]\}
$$

By choosing χ in the interval $(\frac{1}{2},1)$ the quantity $\chi/[1-\chi]$ can be made to assume any value between 1 and $+\infty$. Thus, replacing one of the perfect lattice constituents by a suitably chosen impurity atom of mass smaller than the one possessed by the host lattice atoms, $|\mu|$ can be made to exceed unity (whether this thought experiment is physically realizable for any ω_n and some given perfect lattice frequency spectrum is immaterial in the present context), in which case (IV-1) and (IV-2) both diverge. This, in turn, would seem to invalidate the reasoning in subsections III B and III C. Moreover it may be shown in a similar manner that the expansions encountered in subsection III A cannot generally be assumed to converge. This situation is not alien to many-body and field theory where one is often compelled to run the risk of extrapolating end results into regions wherein underlying expansions actually diverge.[17,22] By virtue of the formal exactness of the Lifshitz theory our present calculation furnishes an example of final results which can be rigorously proved to remain valid despite the occurrence of divergencies.

V. CONCLUDING REMARKS

The applications of many-body concepts in physics and in physical chemistry are multitudinous. The present rederivation of some of the basic formulas of the Lifshitz theory presumably constitutes a simple illustration; the propagator technique being put to work on a comparatively transparent solid state problem. However, the author hopes that the usefulness of the viewpoint presently adopted may to some extent transcend the mere provision of a treatment being suitable for illustration purposes. It is probably expressing a truism to state that the vibrating crystal lattice containing defects (other than fixed distributions of a few truly isotopic substitutions) remains a challenge and is likely to do so for some time to come. Despite the advent of high-speed computers a detailed investigation of a defective lattice, as represented by a reasonably realistic crystal model, still poses non-trivial problems. In most cases calculations become prohibitively difficult unless simplifications are invoked, and at present the development of systematic approximation schemes appears to be attracting considerable attention. Hitherto, however, it seems that the major efforts within the framework of Green's function methods have been made to overcome the inherent complications of mass disordered lattices (see the paper of Leath and Goodman[23] and references contained therein), so that there remain unsolved difficulties in taking account of force field perturbations even in connection with isolated "point" defects. As a consequence of this, no doubt, a reasonably diligent search of the literature did not bring to light any published work on the latter type of imperfections where the Lifshitz theory proper is applied to perturbations extending beyond one or two shells of atoms surrounding an impurity or vacancy site. Although highly localized model defects still require a considerable effort if an extensive description is aimed at,* such cases have by now become tractable. However, by

* This point may be appreciated from a recent and highly interesting article written by Lakatos and Krumhansl,[24] which paper we take to be representative of the art in its present status.

restricting the range of applicability of the Lifshitz method to local imperfections one obtains only a short-lived reprieve. Warranted elaborations of localized model defects (*e.g.* incorporation of the long-range relaxation effects which are likely to appear in response to the introduction of even "mild" lattice misfits,[25] and refinements in the depiction of the electronic structure of imperfections [26,27] would in many cases seem to call for recognition of defect induced interactions receiving non-negligible contributions from extensive regions of the system in question. Sometimes a space Fourier transformation of a slowly varying part of the perturbation would lead to the projection of predominant and numerically obtainable contributions on a limited region in $\mathbf{k}j$-space. In other cases a restriction of the scope of the investigation to particular aspects of the defect problem would make it plausible to assume the most important part of the relevant interactions to be localized in $\mathbf{k}j$-space.[28] In general, if for some reason or other it makes sense to account for the long-range part (the precise definition of which would depend on the capacity of the computer at hand) of a "point" defect by writing

$$\delta\boldsymbol{\Phi}^{\mathrm{l}(=\text{long-range})} = \delta\boldsymbol{\Phi} - \delta\boldsymbol{\Phi}^{\mathrm{s}(=\text{short-range})}$$

$$\boldsymbol{\Psi}^{\mathrm{l}} = \tfrac{1}{2}\mathbf{M}_0^{-\frac{1}{2}}\delta\boldsymbol{\Phi}^{\mathrm{l}}\mathbf{M}_0^{-\frac{1}{2}}$$

and by subsequently neglecting suitable portions of

$$\mathbf{v}_1^{\mathrm{l}} = \boldsymbol{\omega}^{-\frac{1}{2}}\boldsymbol{\varepsilon}^{\dagger}\boldsymbol{\Psi}^{\mathrm{l}}\boldsymbol{\varepsilon}\boldsymbol{\omega}^{\frac{1}{2}} \text{ (some elements of which would occasionally vanish for symmetry reasons)}$$

then one might

i) retain the phonon representation as the basic reference frame while treating the effects of $(\mathbf{M}_0 - \mathbf{M})$ and $\delta\boldsymbol{\Phi}^{\mathrm{s}}$ on $\boldsymbol{g}(i\omega_n)$ in an exact manner by inverting ($\sim$ diagonalizing) a low order matrix referring to position representation (see (III-31) and footnote on page 2386); and

ii) continue the modifying of the already partially clothed propagator(s) by invoking a selective summation adaptation of the argument in section III C, thereby including also the effects of a simplified $\mathbf{v}_1^{\mathrm{l}}$.

Thus one could, possibly, exploit the propagator viewpoint to arrive at useful approximations which, although obtainable without the use of many-body methodology, would seem unwarranted from the standpoint of the standard normal mode problem. The author intends to pursue this point further by presenting the results of numerical calculations on specific defect systems in a subsequent paper. In conlusion of the present one it should be added that the propagator method may readily be extended to recover also Wagner's generalization [29] of the Lifshitz theory to defects which do not conserve the total number of degrees of freedom. Such cases have been omitted here since their inclusion would have increased the bookkeeping without adding appreciably to the underlying theme.

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REFERENCES

1. Lifshitz, E. M. *Nuovo Cimento Suppl. 10* **3** (1956) 716.
2. Maradudin, A. A., Montroll, E. W. and Weiss, G. H. *Theory of Lattice Dynamics in the Harmonic Approximation*, Academic, N. Y., London 1963.
3. Maradudin, A. A. *Rept. Progr. Phys.* **28** (1965) 331.
4. Maradudin, A. A. *Solid State Phys.* **18** (1966) 273.
5. Maradudin, A. A. *Solid State Phys.* **19** (1966) 1.
6. Klein, M. V. *Phys. Rev.* **131** (1963) 1500.
7. Takeno, S. *Progr. Theor. Phys., Japan* **29** (1963) 191.
8. Callaway, J. *J. Math. Phys.* **5** (1964) 783.
9. Elliot, R. J. and Taylor, D. W. *Proc. Phys. Soc.* **83** (1964) 189.
10. Zubarev, D. N. *Sov. Phys. Uspekhi* **3** (1960) 320.
11. Maradudin, A. A. *Astrophysics and the Many Body Problem*, Benjamin, N. Y. 1963, p. 109.
12. Parry, W. and Turner, R. *Rept. Progr. Phys.* **27** (1964) 23.
13. Kadanoff, L. P. and Baym, G. *Quantum Statistical Mechanics*, Benjamin, N. Y. 1962.
14. Baym, G. and Mermin, N. D. *J. Math. Phys.* **2** (1961) 232.
15. Maradudin, A. A. and Fein, A. E. *Phys. Rev.* **128** (1962) 2589.
16. Cowley, R. A. *Advan. Phys.* **12** (1962) 421.
17. Mattuck, R. D. *A Guide to Feynmann Diagrams in the Many-Body Problem*, McGraw, London 1967.
18. Luttinger, J. M. and Ward, J. C. *Phys. Rev.* **118** (1960) 1417.
19. Matsubara, T. *Progr. Theor. Phys., Japan* **14** (1955) 351.
20. Maradudin, A. A. *Phonons and Phonon Interactions*, Benjamin, N. Y. 1964, p. 424.
21. Pease, M. C. *Methods of Matrix Algebra*, Academic, N. Y., London 1965.
22. Gell-Mann, M. and Brueckner, K. A. *Phys. Rev.* **106** (1957) 364.
23. Leath, P. L. and Goodman, B. *Phys. Rev.* **185** (1968) 963.
24. Lakatos, K. and Krumhansl, J. A. *Phys. Rev.* **175** (1968) 841.
25. Hardy, J. R. *J. Phys. Chem. Solids* **23** (1962) 113.
26. Wood, R. F. and Öpik, U. *Phys. Rev.* **162** (1967) 736.
27. Wood, R. F. and Gilbert, R. L. *Phys. Rev.* **162** (1967) 746.
28. Krumhansl, J. A. *J. Appl. Phys. Suppl.* **33** (1962) 307.
29. Wagner, M. *Phys. Rev.* **131** (1963) 2520.

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