Displacement Correlations and Frequency Spectra for Mass-Disordered Lattices*

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The general form of the multiple-occupancy polynomials $P_n(c)$, shown by Langer to be necessary in the perturbation expansion of the Green's function of a mass-disordered lattice, is derived and its use is illustrated by the summation to all orders in the concentration of the self-energy diagrams involving one vertex. Different Green's functions must be used for the displacement correlations and for the frequency spectrum, and numerical calculations for a linear chain show that the two Green's functions can differ considerably in certain regions of frequency. Some problems of convergence are discussed.

I. INTRODUCTION

THE vibrational contribution to the thermodynamic properties of an alloy is determined by the frequency spectrum $\langle \rho(\omega) \rangle$ averaged over all atoms or, equivalently, averaged over an ensemble of atomic configurations representing the composition and order of the system. The interaction with external radiation is determined by the averaged displacement correlations $\langle u(n\alpha)u(m\beta) \rangle$ for specified types of atoms (say A or B for a binary alloy) at the sites n and m (α, β are Cartesian components). Each of the above quantities can be obtained from an appropriate Green's function but, when the mass located at any site may take on different values, there appears to be no simple connection between the different averaged Green's functions.

A diagram expansion technique for calculation of the frequency spectra of these disordered systems was introduced several years ago by Langer.[1] The present work completes the formalism by deriving the form of the multiple-occupancy correction polynomial factors which permit calculation of the contribution from arbitrarily complex diagrams. The expansion technique is applied to displacement correlations as well as frequency spectra.

The Green's functions are introduced in Sec. II, thus fixing the notation, and some of their properties are given. In Sec. III the average over all configurations of, say, atoms of type B with concentration c is discussed for the displacement Green's function. The restriction to at most one B atom per site leads to the multiple-occupancy factor $P_n(c)$ associated with an nth-order vertex in the perturbation series. The complete polynomials are presented in Sec. III, and their derivation is given in the Appendix. The one-vertex contributions to the self-energy can be summed to all orders of the concentration in closed form (Sec. IV). The resulting self-energy has an infinite number of poles most of which are spurious and will be cancelled by the two- and higher vertex contributions. A similar analysis of

the conjugate Green's function, which gives the frequency spectrum, is presented in Sec. V.

II. GREEN'S FUNCTIONS

The displacement correlations are obtained from the usual displacement Green's function[2] of which the retarded form is used here:

$$D(n\alpha, m\beta; t-t')$$
$$\equiv (i\hbar)^{-1} \langle [u(n\alpha,t),u(m\beta,t')] \rangle_T \theta(t-t'), \quad (1)$$

where $u(n\alpha,t)$ is the Cartesian displacement α of atom n at time t, $\theta(t) = (1$ for $t>0$; 0 for $t<0)$, and the subscript T denotes a thermal average. The average over different atomic configurations will be introduced in Sec. III. In words, the above definition of D says that $-\epsilon D$ is the displacement $\langle u(n\alpha,t) \rangle_T$ when an impulsive force $f(m\beta,t) = \epsilon\delta(t-t')$ (ϵ small) is applied to atom m of the system initially in thermal equilibrium. The left-hand member of (1) will be regarded as the $(n\alpha,m\beta)$ element of $\mathbf{D}(t-t')$ in the position representation. The Fourier time transform of $\mathbf{D}$ is defined by

$$\mathbf{D}(\omega) \equiv \int_{-\infty}^{\infty} dt e^{i\omega t} \mathbf{D}(t). \quad (2)$$

Strictly, (2) should be understood as the limit as $z \to \omega$ (real) from the upper z half-plane. The displacement correlations may be written in terms of $\mathbf{D}(z)$ in the following way[2]:

$$\langle u(n\alpha,t)u(m\beta) \rangle_T = -\lim_{\epsilon \to +0} \int_0^{\infty} d\omega \big((\hbar\pi^{-1} \coth(\hbar\omega/2kT))$$

$$\times \cos\omega t - i\hbar\pi^{-1} \sin\omega t \big)$$

$$\times \text{Im}[D(n\alpha, m\beta; \omega+i\epsilon)]. \quad (3)$$

Relation (3) does not require the assumption of harmonicity. For a harmonic system, the verbal definition

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[1] J. S. Langer, J. Math. Phys. 2, 584 (1961).

[2] See for example: D. N. Zubarev, Usp. Fiz. Nauk. 71, 71 (1960). [English transl.: Soviet Phys.—Usp. 3, 320 (1960)].

following Eq. (1) implies

$$\left[M\frac{\partial^2}{\partial t^2}+V\right]D(t)=-I\delta(t), \quad D=\frac{\partial D}{\partial t}=0 \text{ for } t<0, \quad (4)$$

where M is the mass matrix with diagonal elements $M(n\alpha,n\alpha)=M_n$, and V is the force-constant matrix. The solution of (4) is

$$D(n\alpha,m\beta;t)$$

$$=-\left[\left(M\frac{\partial^2}{\partial t^2}+V\right)^{-1}\right](n\alpha,m\beta;t) \quad (5a)$$

$$=-\{\sum_s u_s(n\alpha)u_s^*(m\beta)\omega_s^{-1}\sin(\omega_s t)\}\theta(t), \quad (5b)$$

independently of temperature, where $M_n^{1/2}u_s(n\alpha)$ are the orthonormal modes with frequency ω_s; so that

$$D(z)=(Mz^2-V)^{-1} \quad (6a)$$

$$=\sum_s u_s u_s^\dagger(z^2-\omega_s^2)^{-1}. \quad (6b)$$

The frequency distribution ascribable to a system is not unique and depends on the means of excitation. The following prescription leads in the harmonic case to the usual definition $\rho(\omega)\equiv\sum_s\delta(\omega-\omega_s)$: Apply a small periodic force to atom m, $f(m\beta,t)=\epsilon\exp(-i\omega t)$, and observe the momentum displacement

$$\langle\delta p(n\alpha,t)\rangle_T\equiv\epsilon P(n\alpha,m\beta;\omega)\exp(-i\omega t).$$

The real part of the amplitude $\pi^{-1}P(n\alpha,n\alpha;\omega)$ is the frequency distribution of atom n, and the average over all atoms,

$$\langle\rho(\omega)\rangle_T\equiv 2(3\pi N)^{-1}\sum_{n\alpha}\mathrm{Re}[P(n\alpha;n\alpha;\omega)], \quad (7)$$

is the normalized frequency distribution of the system.[3] From its definition $F(n\alpha,m\beta;\omega)\equiv-iP(n\alpha,m\beta;\omega)$ is the Fourier transform of the conjugate Green's function[4]

$$F(n\alpha, m\beta; t-t')\equiv\hbar^{-1}\langle[p(n\alpha,t),u(m\beta,t')]\rangle_T\theta(t-t'). \quad (8)$$

In matrix form this function can be written in terms of the displacement Green's function

$$F(t)=iMdD(t)/dt, \quad (9a)$$

or

$$F(z)=zMD(z). \quad (9b)$$

For the case of a harmonic system, it follows from either form (8) or (6a and 9b) that, for $\omega>0$,[3]

$$\rho\langle(\omega)\rangle_T=-\lim_{\epsilon\to+0}2(3\pi N)^{-1}\mathrm{Im}[\mathrm{Tr}\{F(\omega+i\epsilon)\}]. \quad (10)$$

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[3] This definition is equivalent to that introduced in the theory of neutron scattering from liquids by A. Rahman, K. S. Singwi, and A. Sjölander, Phys. Rev. 126, 986 (1962).

[4] D. W. Taylor [Ph.D. thesis, Oxford University, 1965 (unpublished)] has used the time-ordered $\langle up\rangle$ Green's function in discussing the frequency spectrum of the mass-disordered alloy.

The displacement Green's function $d(\omega)$ for the perfect lattice satisfies

$$(M\omega^2 I-V)d(\omega)=I, \quad (11)$$

where M is the fixed scalar atomic mass. For the system with impurity masses, this relation becomes

$$(M\omega^2 I-V)D(\omega)=I+M\omega^2\epsilon D(\omega), \quad (12)$$

where ϵ is the fractional mass change matrix defined by $M=M(I-\epsilon)$. Then one obtains

$$D(\omega)=d(\omega)+d(\omega)\mathfrak{y}D(\omega), \quad (13)$$

where $\mathfrak{y}=M\omega^2\epsilon$. The perturbation expansion for D in powers of the mass change is obtained by iteration, which gives

$$D(\omega)=d(\omega)+d(\omega)\mathfrak{y}d(\omega)+d(\omega)\mathfrak{y}d(\omega)\mathfrak{y}d(\omega)+\cdots. \quad (14)$$

III. CONFIGURATION AVERAGE

We consider the random binary alloy consisting of atoms of type A and B. The concentration of B atoms is c. The displacement correlations $\langle u(n\alpha)u(m\beta)\rangle$ are determined by $\langle D(\omega)\rangle$, the average of $D(\omega)$ over atomic configurations. This can be written in the form

$$\langle D(\omega)\rangle=d(\omega)+d(\omega)\langle\mathfrak{y}\rangle d(\omega)$$
$$+d(\omega)\langle\mathfrak{y}d(\omega)\mathfrak{y}\rangle d(\omega)+\cdots. \quad (15)$$

It is instructive to review a few of the low-order terms.[5] The second term in (15) involves

$$\langle\mu(n\alpha,m\beta)\rangle=\langle\mu(n)\rangle\delta_{nm}\delta_{\alpha\beta}=\mu c\delta_{nm}\delta_{\alpha\beta}, \quad (16)$$

where $\mu=(M-M')\omega^2$, and M and M' are the masses of the A and B atoms, respectively. The third term in Eq. (15) involves $\langle\mu(n)\mu(m)\rangle$ which has the value μ^2c^2 if $n\neq m$ and μ^2c if $n=m$, so that

$$\langle\mu(n)\mu(m)\rangle=\mu^2[c^2+(c-c^2)\delta_{nm}]. \quad (17)$$

The sth term of Eq. (15) is

$$\sum_{\substack{l_1\gamma_1, l_2\gamma_2, \\ \cdots, l_s\gamma_s}} d(n\alpha,l_1\gamma_1;\omega)d(l_1\gamma_1,l_2\gamma_2;\omega)\cdots$$

$$\times d(l_s\gamma_s,m\beta;\omega)\langle\mu(l_1)\mu(l_2)\cdots\mu(l_s)\rangle. \quad (18)$$

The averages can be written in the form

$$\langle\mu(l_1)\mu(l_2)\cdots\mu(l_s)\rangle$$

$$=\mu^s[c\delta(l_1l_2\cdots l_s)+c^2\sum_{\substack{(2)'\\ \text{partitions}}}\delta(l_1\cdots)\delta(l_i\cdots)$$

$$+c^3\sum_{\substack{(3)'\\ \text{partitions}}}\delta(l_1\cdots)\delta(l_i\cdots)\delta(l_j\cdots)+\cdots], \quad (19)$$

where $\delta(l_1l_2\cdots l_s)=(1$ for $l_1=l_2=\cdots=l_s;$ 0 otherwise).

The sum in Eq. (19) is over all partitions of the site indices l_1, l_2, $\cdots$, l_s into one, two, three, etc., groups.

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[5] The discussion is given here in the position (n) representation which seems to be more direct for the present purposes than the k representation used by Langer (Ref. 1).
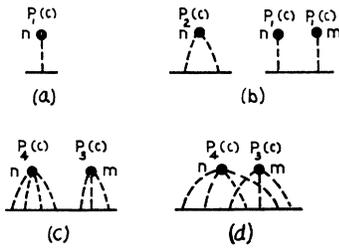
FIG. 1. Some diagrams occurring in the perturbation expansion of $\langle D(\omega) \rangle$, with the associated vertex factors.

The prime signifies the exclusion of those cases where two or more δ's in a product refer to the same site. This restriction on a given partition sum can be removed by adding to it the excluded terms and subtracting them from the sums with *fewer* partitions. As was first indicated by Langer,[1] this procedure leads to multiple-occupancy corrections which are polynomials $P_k(c)$ $=c+\cdots$, of degree k, multiplying each $\delta(l_{i(1)}\cdots l_{i(k)})$. Then (19) becomes

$$\langle \mu(l_1)\cdots\mu(l_s)\rangle = \mu^s[P_s(c)\delta(l_1l_2\cdots l_s)$$

$$+ \sum_{\substack{\text{partitions}\\ p+q=s}}^{(2)} P_p(c)P_q(c)\delta(l_1\cdots)\delta(l_i\cdots)$$

$$+ \sum_{\substack{\text{partitions}\\ p+q+r=s}}^{(3)} P_p(c)P_q(c)P_r(c)\delta(l_1\cdots)$$

$$\times\delta(l_i\cdots)\delta(l_j\cdots)+\cdots], \quad (20)$$

which terminates with $\mu^s(P_1(c))^s$ (or $\mu^s c^s$) corresponding to s distinct lattice sites. It has been assumed implicitly, but can easily be proven, that the polynomials $P_p(c)$, etc., are independent of the total number of sites s and depend only on the number of sites in the corresponding δ function. From Eqs. (16) and (17) and the above, it is clear that $P_1(c)=c$ and $P_2(c)=c-c^2$.

The derivation of the $P_k(c)$ is expedited by a diagram representation of the expansion (15). In Fig. 1 let the solid circles represent lattice sites which interact with the phonon through the dashed lines, each of which carries the factor μ. The horizontal line segment between two successive interactions with, say, sites n and m carries the factor $d(n\alpha, m\beta; \omega)$, the unperturbed phonon propagator. A lattice site which is the vertex of k interaction lines is assigned the factor $P_k(c)$. Figures 1(a) and (b) represent the second and third terms on the right-hand side of Eq. (15). Figures 1(c) and (d) show two terms for $s=7$ with $p=4$ and $q=3$ in the second sum of Eq. (20) where the propagators have been included. The contribution of an unlabeled diagram is obtained by summing the internal lattice sites and Cartesian indices over all values.
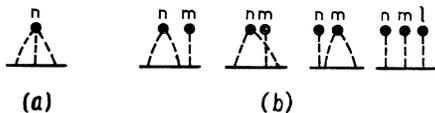

(a)   (b)

FIG. 2. A third-order vertex (a) and diagrams (b) whose vertex confluence determines $P_3(c)$.

TABLE I. Multiple-occupancy polynomials $P_k(c)$ for $k \leqslant 6$.

$$P_1(c)=c$$
$$P_2(c)=c-c^2$$
$$P_3(c)=c-3c^2+2c^3$$
$$P_4(c)=c-7c^2+12c^3-6c^4$$
$$P_5(c)=c-15c^2+50c^3-60c^4+24c^5$$
$$P_6(c)=c-31c^2+180c^3-390c^4+360c^5-120c^6$$

To illustrate the origin of the $P_k(c)$, we consider the third-order vertex $P_3(c)$ in Fig. 2(a). The terms of higher order than c should correct for the confluence of site indices in the diagrams with more partitions, shown in Fig. 2(b), which themselves are already corrected for the confluence of first-order vertices. The correction factor $P_3(c)$ so constructed is

$$P_3(c)=c-3[P_1(c)P_2(c)]-P_1^3(c)=c-3c^2+2c^3. \quad (21)$$

The results for $P_k(c)$ up to $k=6$ are presented in Table I.

The general term is shown in the Appendix to have the simple form

$$P_k(c)=\sum_{m=1}^{k} (-1)^{m-1}(m-1)!S(k,m)c^m, \quad (22)$$

where $S(k,m)$ are Stirling numbers of the second kind.[6-8] A combinatorial interpretation is that $S(k,m)$ is the number of ways that k distinct objects can be put into m indistinguishable boxes with *no box empty*. Langer[1] gave the coefficient of c^2 to be $2^{k-1}-1$ which agrees with $S(k,2)$.[7]

Since the summations in two parts of a diagram separated by a d line are independent when the $P_k(c)$ are used, the usual notion of reducibility is applicable. Thus Figs. 1(c) and (d) show a reducible and an irreducible diagram, respectively. The Dyson equation is

$$\langle D(\omega) \rangle = d(\omega) + d(\omega)\Pi(\omega)\langle D(\omega) \rangle, \quad (23)$$

where $\Pi(n\alpha, m\beta; \omega)$ is the proper self-energy, that is,

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[6] The notation used here for the Stirling numbers is that of J. Riordan, *An Introduction to Combinatorial Analysis* (John Wiley & Sons, Inc., New York, 1958), p. 32.

[7] A better reference than Ref. 6 for the identities and numerical tables of the Stirling numbers is *National Bureau of Standards, Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A. Stegun (U. S. Government Printing Office, Washington, D. C., 1964), Appl. Math. Ser. 55, Chap. 24.

[8] *Note*: After this work was completed, a derivation of $P_k(c)$ in terms of cumulants was announced by T. Matsubara and F. Yonezawa, in a letter: Progr. Theoret. Phys. (Kyoto) **34**, 871 (1965). The connection with Stirling numbers was not made. This was important in our obtaining Eqs. (30) and (36), using the identity (28). However, they did give a generating function

$$g(x; c) = \sum_k P_k(c)x^k/k! = \ln(1-c+c\exp(x)).$$

That this generating function agrees with the Stirling number representation is easily verified by expanding $P_k(c)$ according to Eq. (22), formally interchanging orders of summation, and using the identity

$$(\exp(x)-1)^m = m! \sum_{n=m}^{\infty} S(n,m)x^n/n!$$

of Ref. 7. The relationship between Stirling numbers and cumulant coefficients may be of interest in other connections.

the sum of all irreducible parts. The formal solution of (23) is

$$\langle \mathbf{D}(\omega) \rangle = [\mathbf{I} - \mathbf{d}(\omega)\mathbf{\Pi}(\omega)]^{-1}\mathbf{d}(\omega), \qquad (24a)$$

or

$$\langle \mathbf{D}(\omega) \rangle = [\mathbf{d}^{-1}(\omega) - \mathbf{\Pi}(\omega)]^{-1}. \qquad (24b)$$

IV. ONE-VERTEX CONTRIBUTION TO THE SELF-ENERGY

Figure 3 shows the self-energy diagrams with one vertex. Their total contribution, using Eq. (22), will be a power series in c, beginning with the first power. Self-energy diagrams with two vertices will contribute from c^2 on, and so forth. Thus, the contributions to the c^p term in the self-energy come from all diagrams with $r \leqslant p$ vertices. The one-vertex diagrams can be summed in closed form. This may be of use in considering the convergence of the perturbation series.

The one-vertex self-energy $\mathbf{\Pi}^{(1)}(\omega)$ is diagonal in the lattice indices. For simplicity, we assume here and in the next section that we have a Bravais lattice and that the point group includes tetrahedral symmetry, so that

$$\Pi^{(1)}(n\alpha,m\beta;\omega) = \Pi^{(1)}(\omega)\delta_{nm}\delta_{\alpha\beta}. \qquad (25)$$

It follows from Eq. (24b) that $\mathbf{D}^{(1)}(\omega)$, the $\mathbf{\Pi}^{(1)}(\omega)$ approximation to $\langle \mathbf{D}(\omega) \rangle$, is related to $\mathbf{d}(\omega)$ by

$$\mathbf{D}^{(1)}(\omega) = \mathbf{d}([\omega^2 - M^{-1}\Pi^{(1)}(\omega)]^{1/2}). \qquad (26)$$

The diagram rules give

$$\Pi^{(1)}(\omega) = \sum_{k=1}^{\infty} \mu^k d_0(\omega)^{k-1} P_k(c), \qquad (27)$$

where $d_0(\omega) = d(0\alpha,0\alpha;\omega)$. Using Eq. (22) and the identity[7]

$$\sum_{n=p}^{\infty} S(n,p)x^n = x^p[(1-x)(1-2x)\cdots(1-px)]^{-1} \qquad (28)$$

for $|x| < p^{-1}$ gives for the coefficient of c^p in Eq. (27)

$$(p-1)!\mu(-\mu d_0(\omega))^{p-1}$$
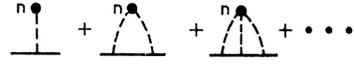$$\times [(1-\mu d_0)(1-2\mu d_0)\cdots(1-p\mu d_0)]^{-1}, \qquad (29)$$

if $|\mu d_0(\omega)| < p^{-1}$. Summing the c^p terms over p gives

$$\Pi^{(1)}(\omega) = \frac{\mu c}{1 - \mu d_0(\omega)}{}_2F_1\left(1,1;2 - \frac{1}{\mu d_0(\omega)};c\right), \qquad (30)$$

which converges as a power series in c for all $c < 1$. The hypergeometric function has poles at all nonpositive integral values of the third argument, i.e., at $\mu d_0(\omega) = r^{-1}$, $r = 2, 3, \cdots$, which shows that the form (27) of $\Pi^{(1)}(\omega)$ as a power series in $\mu d_0(\omega)$ has zero radius of convergence and should be regarded only formally while Eq. (30) is its proper analytic form.

The pole of $\Pi^{(1)}(\omega)$ at $\mu d_0(\omega) = 1$ is the condition for a localized mode for an isolated B atom; the high-frequency localized modes have real ω_p above the con-

tinuum and the in-band modes have complex ω_p. The poles of the hypergeometric function at $(r\mu)d_0(\omega) = 1$, $r = 2, 3, \cdots$ represent the overlapping of more than one mass perturbation μ at a single site and are nonphysical. The nonphysical nature is especially evident when M' is slightly smaller than M so that $r\mu$ may correspond to a very light impurity with a high-frequency localized mode in a region where there is clearly none. Langer[9] has shown that the $r = 2$ pole multiplying c^2 in $\Pi^{(1)}(\omega)$ is replaced by a different singularity on combination with the c^2 contribution of $\Pi^{(2)}(\omega)$, the two-vertex part of the self-energy. Presumably the $r > 2$ poles of $\Pi^{(1)}(\omega)$ will be similarly affected by contributions from $\Pi^{(2)}(\omega)$ to $\Pi^{(r)}(\omega)$.

It is important to note that in the diagrams for $\Pi(\omega)$ the overlapping of mass defects is not completely compensated as it is in $\langle \mathbf{D}(\omega) \rangle$. Figure 2 illustrates this point in that only Fig. 2(a) and the second diagram in Fig. 2(b) are irreducible and included in $\Pi(\omega)$, whereas all five diagrams are needed for compensation. This may have the consequence that $\Pi(\omega)$ has singularities of a nonphysical type, that is, not corresponding to any possible cluster of atoms.

The result of a numerical calculation of the imaginary part of $\mathbf{D}^{(1)}(\omega)$ for a linear chain with nearest-neighbor forces, where $d_0(\omega) = (\omega^2 - \omega_M^2)^{-1/2}(M\omega)^{-1}$, is shown in Fig. 4 for $c = 0.1$ and $M' = \frac{1}{2}M$. For the particular case chosen, the condition $r\mu d_0(\omega) = 1$ for a pole in $\Pi^{(1)}(\omega)$ on the positive real axis is satisfied only for $r = 1$ and just *one* impurity band appears.

The way in which this impurity band appears can be seen from Eq. (26). If $\Pi^{(1)}(\omega)$ has a simple pole for some real $\omega > \omega_M$, then near this pole $(\omega^2 - M^{-1}\Pi^{(1)}(\omega))^{1/2}$ can
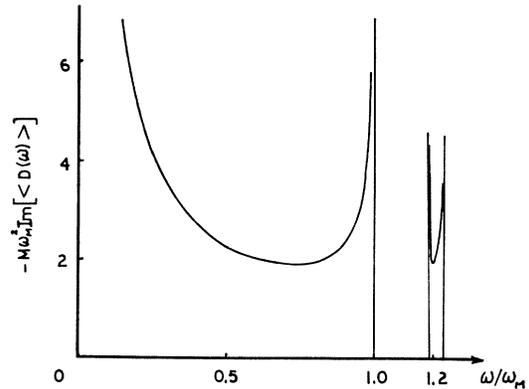
FIG. 4. The negative imaginary part of $D^{(1)}(n\alpha,n\alpha,\omega)$ versus ω, Eqs. (26) and (30), for a linear chain with $c = \frac{1}{10}$ and $M' = \frac{1}{2}M$. The spectral density of the displacements is obtained by multiplication with the factor $\hbar\pi^{-1}\coth(\hbar\omega/2kT)$ of Eq. (3).

[9] In Ref. 1 Langer considered the quantity $-\omega^{-1}\langle F^T(\omega) \rangle$ in the $\mathbf{k}$ representation [his $D_k(\omega^2)$], but $\langle \mathbf{D}(\omega) \rangle$ can be discussed similarly.
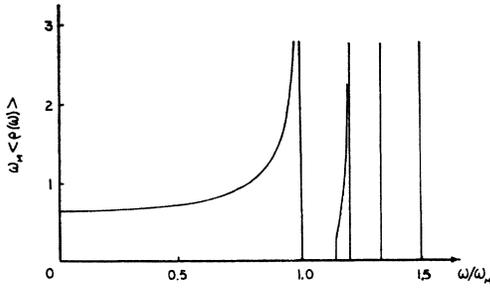
FIG. 5. The frequency spectrum $\langle\rho^{(1)}(\omega)\rangle$, versus ω, Eqs. (36) and (38), for a linear chain with $c=\frac{1}{10}$ and $M'=\frac{1}{2}M$.

sweep through the interval $(0,\omega_M)$ where the imaginary part of $d_0(\omega)$ is nonzero. This gives an impurity band near the pole of $\pi^{(1)}(\omega)$ which is a nonuniform lateral compression of the perfect lattice band.

V. CONJUGATE GREEN'S FUNCTION

The equation for $\mathbf{F}(\omega)$ from the substitution of Eq. (6a) into Eq. (9b),

$$\mathbf{F}(\omega)[\omega^2-\mathbf{V}\mathbf{M}^{-1}]=\omega,$$

leads to the Dyson equation

$$\mathbf{F}(\omega)=\mathbf{f}(\omega)+\mathbf{F}(\omega)\mathbf{V}\lambda(M\omega)^{-1}\mathbf{f}(\omega), \tag{31}$$

where

$$\mathbf{M}^{-1}=M^{-1}(\mathbf{I}+\lambda), \quad \text{and} \quad \mathbf{f}(\omega)=M\omega\mathbf{d}(\omega). \tag{32}$$

Iterating in Eq. (31) and performing the configuration average gives an expansion in $(1/M'-1/M)$:

$$\langle\mathbf{F}(\omega)\rangle=\mathbf{f}(\omega)+\mathbf{f}'(\omega)\langle\lambda\rangle\mathbf{f}(\omega)$$
$$+\mathbf{f}'(\omega)\langle\lambda\mathbf{f}'(\omega)\lambda\rangle\mathbf{f}(\omega)+\cdots, \tag{33}$$

where

$$\mathbf{f}'(\omega)=\mathbf{f}(\omega)\mathbf{V}(M\omega)^{-1}=\omega\mathbf{f}(\omega)-\mathbf{I}. \tag{34}$$

Since $\lambda(n\alpha,m\beta)=\lambda(n)\delta_{nm}\delta_{\alpha\beta}$ is nonzero only at B sites, the configuration average and diagram representation in Sec. III are applicable with the modifications that (a) $\lambda=(M-M')/M'$ replaces μ as the interaction strength, (b) $\mathbf{f}'(\omega)$ replaces $\mathbf{d}(\omega)$ as the propagator, except for the external propagator at one end which is $\mathbf{f}(\omega)$. In terms of $\mathbf{\Pi}_F(\omega)$, the self-energy, the equation for $\langle\mathbf{F}(\omega)\rangle$ is

$$\langle\mathbf{F}(\omega)\rangle=\mathbf{f}(\omega)+\langle\mathbf{F}(\omega)\rangle\mathbf{V}(M\omega)^{-1}\mathbf{\Pi}_F(\omega)\mathbf{f}(\omega), \tag{35a}$$

which has the solution

$$\langle\mathbf{F}(\omega)\rangle=[\mathbf{f}^{-1}(\omega)-(M\omega)^{-1}\mathbf{V}\mathbf{\Pi}_F(\omega)]^{-1}. \tag{35b}$$

The one-vertex part of $\mathbf{\Pi}_F(\omega)$ has the diagonality of Eq. (25). The diagonal elements $\Pi_F^{(1)}(\omega)$ can be found, using the diagram rules, to be

$$\Pi_F^{(1)}(\omega)$$

$$=\lambda\sum_{p=1}^{\infty}\frac{(p-1)!c^p(-\lambda f_0'(\omega))^{p-1}}{[1-\lambda f_0'(\omega)][1-2\lambda f_0'(\omega)]\cdots[1-p\lambda f_0'(\omega)]},$$

which can be written in the closed form

$$\Pi_F^{(1)}(\omega)=\frac{\epsilon c}{1-\mu d_0(\omega)}{}_2F_1\left(1,1;2-\frac{1}{\lambda f_0'(\omega)};c\right), \tag{36}$$

where $f_0'(\omega)=f'(0\alpha,0\alpha;\omega)$ and $\epsilon=(M-M')/M$. The first pole $\mu d_0(\omega)=1$ of $\Pi_F^{(1)}(\omega)$ is the same as that for $\Pi^{(1)}(\omega)$ but the other poles are not. The c and c^2 terms of Eq. (36) agree with the corresponding terms given by Langer.[1] From Eq. (35b) and the diagonality of $\Pi_F^{(1)}(\omega)$, one gets

$$\mathbf{F}^{(1)}(\omega)=(1+\Pi_F^{(1)}(\omega))^{-1/2}\mathbf{f}(\omega(1+\Pi_F^{(1)}(\omega))^{-1/2}), \tag{37}$$

so that the frequency spectrum of the alloy in the $\Pi_F^{(1)}(\omega)$ approximation is

$$\langle\rho^{(1)}(\omega)\rangle=-\frac{2}{\pi}\lim_{\epsilon\to+0}\text{Im}[(1+\Pi_F^{(1)}(z))^{-1/2}$$

$$\times\text{Tr}\{\mathbf{f}(z(1+\Pi_F^{(1)}(z)))^{-1/2}\}]_{z=\omega+i\epsilon}. \tag{38}$$

Figure 5 shows $\langle\rho^{(1)}(\omega)\rangle$ for the linear chain with nearest-neighbor forces and $c=0.1$, $M'=\frac{1}{2}M$. As in Fig. 4, the first high-frequency band is a distortion of the unperturbed band but now *each* of the poles $r\lambda f_0'(\omega)=1$, $r\geq 2$, occurs on the positive real axis and gives a side band. The latter are not of physical significance, as discussed in Sec. IV, and decrease rapidly in weight.

VI. DISCUSSION

The formulas in this paper hold in three dimensions; the calculations using Eqs. (26) and (37) were done for a linear chain in order to illustrate simply the features of the perturbation method. The expansions (15) and (33) of $\langle\mathbf{D}(\omega)\rangle$ and $\langle\mathbf{F}(\omega)\rangle$ are similar but not identical and Figs. 4 and 5 for $\mathbf{D}^{(1)}(\omega)$ and $\mathbf{F}^{(1)}(\omega)$, respectively, differ significantly in the region $\omega>\omega_M$. It is important to recognize that, in $\langle\mathbf{F}(\omega)\rangle=\omega\langle\mathbf{MD}(\omega)\rangle\neq\omega\langle\mathbf{M}\rangle\langle\mathbf{D}(\omega)\rangle$, the factoring of the average may not hold even approximately in some regions of ω. Thus, for example, even if the scattering lengths and temperature factors of the A and B atoms are nearly the same, the neutron inelastic scattering cross sections give the spectral density of $\langle\mathbf{D}(\omega)\rangle$ rather than the frequency spectrum. However, the relation $\omega\langle\mathbf{MD}\rangle=\omega^{-1}[\mathbf{V}\langle\mathbf{D}\rangle-\mathbf{I}]$ does give a useful connection between $\langle\mathbf{F}\rangle$ and $\langle\mathbf{D}\rangle$ in the $\mathbf{k}$ representation in low orders of the perturbation c when changes of the phonon polarization vectors are neglected.[4]

The scattering of radiation by lattice vibrations involves the quantities $\langle u_{n\alpha}{}^A u_{m\beta}{}^B\rangle$ and $\langle u_{n\alpha}{}^A u_{m\beta}{}^A\rangle$, the displacement correlations for distinguished atom types of n and m. Taylor[4] has given an approximate treatment of these functions for a mass-disordered lattice, and Dzyub[10] has discussed the perturbation expansion to

[10] I. P. Dzyub, Fiz. Tverd. Tela **6**, 1866 (1964); **6**, 3691 (1964) [English transls.: Soviet Phys.—Solid State **6**, 1469 (1964); **6**, 2955 (1965)].

order c^2 in the Green's function without the benefit of the multiple-occupancy factors. These factors can be incorporated by modifying the coefficients for the distinguished vertices by differentiation with respect to c. The details will be presented elsewhere.

The two-vertex contribution to the self-energy can also be reduced using the properties of the Stirling numbers but the result is more complicated than Eqs. (30) or (36) because it is no longer diagonal in n. This contribution has been evaluated and will be discussed elsewhere.

APPENDIX

The proof of Eq. (22) is by induction. Assume for $k < n$ that $P_k(c)$ is as given in (22). This is clearly true for $k = 1$ since $S(1,1) = 1$. Then $P_n(c)$ is calculated by the procedure used in obtaining Eq. (21), namely,

$$P_n(c) = c - \left\{ \begin{array}{l} \text{The sum of the } P_k(c) \text{ products} \\ \text{for all diagrams with 2 lattice} \\ \text{sites and } n \text{ interactions} \end{array} \right\} \quad (A1)$$
$$- \{ \cdots 3 \text{ lattice sites } \cdots \} - \cdots$$
$$- \{ \cdots n \text{ lattice sites } \cdots \}.$$

The $(j-1)$st bracket is

$$P_n(c,j) = \frac{1}{j!} \sum_{k_{j-1}=1}^{n-(j-1)} \cdots \sum_{k_2=1}^{(n_2-2)} \sum_{k_1=1}^{(n_1-1)}$$
$$\times \frac{n! P_{k_1}(c) P_{k_2}(c) \cdots P_{k_j}(c)}{k_1! k_2! \cdots k_{j-1}! k_j!}, \quad (A2)$$

where $n_i = n - k_{i+1} - k_{i+2} - \cdots - k_{j-1}$, and $k_j = n_1 - k_1$. The factor

$$\frac{1}{j!} \left(\frac{n!}{k_1! k_2! \cdots k_j!} \right) = \frac{1}{j!} \binom{n}{k_{j-1}} \binom{n_{j-2}}{k_{j-2}} \cdots \binom{n_1}{k_1}$$

is the number of ways in which n successive interactions of a phonon can be assigned in groups of $k_1, k_2, \cdots, k_j$ to j unordered lattice sites (in an unlabeled diagram). The innermost sum in Eq. (A2),

$$\sum_{k_1=1}^{n_1-1} P_{k_1}(c) P_{n_1-k_1}(c) \binom{n_1}{k_1}, \quad (A3)$$

can be performed by expanding $P_k(c)$ according to Eq. (22), noting that the sum there can be extended to infinity since $S(k,m) = 0$ for $m > k$, and using the following identity[7]:

$$\sum_{k=1}^{n-1} \binom{n}{k} S(k,m_1) S(n-k, m_2)$$
$$= \binom{m_1 + m_2}{m_1} S(n, m_1 + m_2). \quad (A4)$$

Thus, (A3) becomes

$$\sum_{r_1 \geq 2} (-1)^{r_1} r_1! S(n_1, r_1) c^{r_1} \sum_{m_1=1}^{r_1-1} \frac{1}{m_1(r_1 - m_1)}, \quad (A5)$$

which is similar in form to $P_{n_1}(c) = P_{n_2-k_2}(c)$, so that the sum over k_2 in (A2) can be performed in the same manner, giving

$$\sum_{r_2 \geq 3} (-1)^{r_2-1} r_2! S(n_2, r_2) c^{r_2} \sum_{m_2=2}^{r_2-1} \sum_{m_1=1}^{m_2-1}$$
$$\times \frac{1}{m_1(m_2 - m_1)(r_2 - m_2)}, \quad (A6)$$

which in turn can be summed over k_3, and k_4, and so forth, until all the successive sums in Eq. (A2) are completed, leaving

$$P_n(c,j) = \frac{(-1)^j}{j!} \sum_{r \geq j} (-1)^r r! S(n,r) c^r$$
$$\times \sum_{\{m_j\}} \frac{1}{m_1 m_2 \cdots m_j}, \quad (A7)$$

where $\{m_j\}$ denotes the summation over all sets of j positive integers satisfying $m_1 + m_2 + \cdots + m_j = r$. Thus, from Eq. (A1),

$$P_n(c) = c - \sum_{j=2}^{n} P_n(c,j)$$

$$= c + \sum_{r=2}^{n} (-1)^{r-1} r! S(n,r) c^r$$
$$\times \sum_{j=2}^{r} \frac{(-1)^j}{j!} \sum_{\{m_j\}} \frac{1}{m_1 m_2 \cdots m_j}. \quad (A8)$$

The sum over j is equal to $1/r$, which proves Eq. (22). The assertion about the sum over j follows from the relation

$$\sum_{j=1}^{r} \frac{(-1)^j}{j!} \sum_{\{m_j\}} \frac{1}{m_1 m_2 \cdots m_j} = 0 \quad (A9)$$

for $r \geq 2$, since the left-hand number of (A9) is the coefficient of x^r in the series expansion about $x = 0$ of $\exp[\ln(1-x)] = 1 - x$. Thus the sum starting from $j = 2$ is equal to $1/r$.

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