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Evaluation of Integrals over the Brillouin Zone*

I. Houston-Moment-Singularity Method for Counting Frequencies of Lattice Vibrations

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Frequency distributions (FD) of crystal lattices cannot be determined by a direct application of the Houston method, because no matter how many terms of expansion are used spurious singularities cannot be eliminated. However, it yields closely proximate values to the integrated frequency distributions (IFD) when sufficient number of terms of expansion is used.

This property enables us to compute moments of IFD as well as those of FD for any desired number. Then following the method due to Phillips or due to Lax and Lebowitz and to Rosenstock, a good approximation to FD can be obtained from a combination of a few number of moments with the relevant information about the nature of various critical points in k-space.

The method presented in this paper has a merit that FD and therefore its moments can be divided into segments, each segment corresponding to a different frequency range. Owing to this merit, unknowns involved in the simultaneous linear equations for determining FD can be reduced to a small number.

I. INTRODUCTION AND THE HOUSTON METHOD WITH MANY TERMS EXPANSION

IN solid state physics, various kinds of quantities, such as densities of states of electronic systems, magnetic susceptibilities, dielectric response functions, frequency distributions of phonon systems, thermodynamic quantities and cross sections of solid state scattering, can be represented by the integrals of the following type:

$$I=\int F(\mathbf{k})d\mathbf{k}=\int_0^{\pi}\sin\theta d\theta\int_0^{2\pi}d\phi J(\theta,\phi), \qquad (1),\ (2)$$

where

$$J(\theta,\phi)=\int F(k,\theta,\phi)k^2dk, \qquad (3)$$

and the integration in k-space is taken over the entire volume of the first Brillouin zone. Generally **F(k)** has cubic symmetry and is a function of eigenvectors and/or eigenvalues of the crystal Hamiltonian. The calculation of F(k) would require evaluation of a truncated secular determinant.

A simple method for evaluating the integral I was given by Houston. This method gives good results for the frequency distributions (abbreviated as FD) of phonon systems at very low frequencies, and therefore is most valuable for a calculation of low temperature thermodynamic properties. Houston approximated the integral to

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$$I=4\pi\int k^2 a_1(k)dk, \tag{4}$$

where $a_1(k)$ is the first coefficient of the expansion of the function F(k) in terms of the cubic harmonics $K_j(\theta,\phi)$ of van der Lage and Bethe, i.e.

$$F(k,\theta,\phi)=\sum_{j=1}^{n} a_j(k)K_j(\theta,\phi). \tag{5}$$

a_j can be evaluated from the matrix equation

$$\mathcal{F}_i=\sum_{j=1}^{n}\mathcal{K}_{ij}a_j, \tag{6}$$

where $\mathcal{K}_{ij}=K_j(\theta_i,\phi_i)$, $\mathcal{F}_i=F(k,\theta_i,\phi_i)$, $i=1, 2, \cdots$, n., and n is the number of selected directions (θ_i,ϕ_i) along which the secular equation can be solved exactly for frequencies as a function of k.

Houston[1] terminated the expansion in (5) with only three terms ($n=3$) and obtained

$$a_1^{(3)}=\frac{4\pi}{35}[10F_{100}+16F_{110}+9F_{111}],$$

where $a_1^{(n)}$ is the n-term approximation for a, and F_{klm} is the value of functions F(k) in the direction (k, I, m). The expansion was extended by Betts, Bhatia and Wyman[2] for 6 terms ($n=6$), and later by Betts[3] for 9 and 15 terms ($n=9$ and $n=15$). Recently Singhal[4] has presented the expansion up to 16 terms (n-16). In general, $a_1^{(n)}$ has the form (See Appendix),

$$a_1^{(n)}=\sum_{r=1}^{n} C_r(F_{klm})_r. \tag{6}'$$

Of course, the approximation for the integral beomes better and better, as more terms are added in the expansion. However, spurious singularities are introduced into the approximate I when the integrand J in Eq. (2) involves derivatives of k with respective to the frequency or to the energy, such as in the frequency distributions (FD) of phonon systems or in the state densities of electronic systems. Unfortunately, no matter how many terms of expansion are used, these singularities cannot be eli:nenated. The analysis of van Hove[5] clarified exact behaviors of singularities of FD, and led to a caution that the use of the Houston method in its original, unmodified form is to be avoided. Nakamura[6] and the present author[7] independently attempted to modify the Houston method. The latter used a graphical interpolation scheme for determining contours of constant frequency intermediate to those which can be exactly calculated. The combination with an exact handling of singularities gave excellent agreement with known FD.

In this paper, an alternative method for avoiding the occurrence of spurious singularities in the integrals I is presented. This method need not use graphical computations, and is far more convenient than the previous one. It originates from an observation that many terms expansion in the original Houston method gives a closely proximate value to the integral Z when the integrand J in Eq. (2) does not involve the derivatives of k with respective to the frequency or the energy. The many terms expansion enables us further to compute moments of integral Z for any desired number. Then, following the method due to Phillips[8] or due to Lax and Lebowitz[9] and to Rosenstock[10] good

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(3) D. D. Betts, Canad. J. Phys. 39, 233 (1961).
(4) S.P. Singhal, Phys. Rev. B4, 2497 (1971), S.P. Singhal, J. Computational Phys. 10, 316 (1972).
(5) L. van Hove, Phys. Rev. 89, 1189 (1953).
(6) T. Nakamura, Progr. Theoret. Phys. (Kyoto) 5, 213 (1950).
(7) J.L. Hwang, Phys. Rev. 99, 1098 (1955), J. L. Hwang and C. S. Wang, J. Chem. Phys. 37, 1655 (1962).
(8) J.C. Phillips, Phys. Rev. 104, 1263 (1956).
(9) M. Lax and J. Lebowitz, Phys. Rev. 96, 594 (1954).
(10) H. B. Rosenstock, Phys. Rev. 97, 290 (1955).

results can be derived from the combination of a few number of moments with the relevant information about the nature of various critical points in k-space.

II. APPLICATIONS TO PHONON SYSTEMS AND TO ELECTRONIC SYSTEMS

In the theory of Lattice dynamics, the number of vibrational modes of phonon systems $N(\omega^2)$ with squared frequencies less than or equal to ω^2 is given by

$$N(\omega^2)=\int_0^{\pi}\sin\theta d\theta\int_0^{2\pi}d\phi\left(\sum_s\frac{1}{3}k_s^3(\omega^2,\ \theta,\ \phi)\right),$$

where the summation is taken over each branch s. If not specially stated, we will use hereafter a convension that ω^2 ranges from 0 to 1. We define $G(\omega^2)d\omega^2$ as the fraction of squared frequencies in the interval $(\omega^2, \omega^2+d\omega^2)$ in the limit as $d\omega^2\to 0$. $G(\omega^2)$ is called the frequency distribution (FD) in this paper, and it is clearly related to $N(\omega^2)$ by

$$G(\omega)=\frac{dN(\omega^2)}{d\omega^2}=\int_0^{\pi}\sin\theta d\theta\int_0^{2\pi}d\phi\left(\sum k_s^2\frac{dk_s}{d\omega^2}\right). \tag{8}$$

$N(\omega^2)$ is called an integrated FD hereafter.

Comparing Eqs. (7) and (8) with Eqs. (1)-(3), it is readily seen that

$$J(\theta,\ \varphi)=\frac{1}{3}\sum_s k_s^3(\omega^2,\ \theta,\ \varphi) \tag{9}$$

and

$$F(\mathbf{k}_s)=\sum_s Y(\omega^2-\omega^2(\mathbf{k}_s)) \tag{10}$$

for the expression of $N(\omega^2)$, and

$$J(\theta,\ \varphi)=\sum_s k_s^2\frac{dk_s}{d\omega^2} \tag{11}$$

and

$$F(\mathbf{k}_s)=\sum_0\delta(\omega^2-\omega^2(\mathbf{k}_s)) \tag{12}$$

for $G(\omega^2)$, where Y(x) and $\delta(x)$ are respectively the step function and the b-function. The dispersion relation $\omega^2=\omega^2(\mathbf{k}_s)$ specifes a surface of the constant frequency in the Erst Brillouin zone. The spurious singularities introduced to the FD $G(\omega^2)$ are the results due to the derivatives $dk_s/d\omega^2$.

$G(\omega^2)$ in Eqn. (8) can be written in a familiar form

$$G(\omega^2)=\sum_s\iint_{\omega^2(\mathbf{K}s)=\omega^2}\frac{dS(\omega^2)}{|\operatorname{grad}_{\mathbf{K}s}\omega^2(\mathbf{k}_s)|}. \tag{13}$$

Formulas analogous to Eqs. (7)-(13) were known in the electron theory of metals. The densities of states of electron $g(E)$ is given by

$$g(E)=\frac{2}{(2\pi)^3}\sum_n\iint\frac{dS(E)}{|\operatorname{grad}_{\mathbf{K}n}E(\mathbf{k}_n)|}, \tag{14}$$

Therefore, in principle, both theories can be treated with the same manner. There is, however, a difficulty for a practical calculation in the latter theory, that is, a large number of critical points, as many as 250, can occur in the irreducible first Brillouin zone. On the other hand. Only six or seven normally are present in the FD of phonon systems. For this reason, the phonon system will -be taken as an illustrative example in the following argument.

As an example, we consider a monoatomic simple cubic lattice with three force parameters. This lattice was investigated by H. B. Rosenstock and H. M. Rosenstock[11]. The FD of one of its three branches can be calculated exactly by a direct integration, and enables us to examine the accuracy of appro..imate methods. The FD of the other two branches were determined by the present authors with graphical interpolation scheme as mentioned earlier[7]. The secular equation for determing frequencies involves a 3 x 3 determinant with diagonal elements

$$f_{ij}=1-C_i+\sigma(2-C_iC_j-C_iC_k)+\tau(1-C_iC_jC_k)-(m\omega^2/2\alpha), \quad (15)$$

and the off diagonal elements

$$f_{ij}=S_iS_j(\sigma+\tau C_k), \quad (16)$$

where $C_i=\cos k_i$, $S_i=\sin k_i$, $\sigma=\beta/\alpha$, $\tau=4\gamma/3\alpha$, (k_1, k_2, k_3) is the components of a wave vector, and α, β and γ represent respectively the force constants of the interaction between the lst, 2nd and 3rd neighbors. When $\sigma=3/7$ and $\tau=2/7$, the solution of this secular equation seperates into

$$\omega_1^2=(2\alpha/7m)[21-\sum_i C_i-4\sum_{i>j} C_iC_j-6C_1C_2C_3] \quad (17)$$

and

$$\omega_{2,3}^2=(2\alpha/7m)\left\{12-3\sum_i C_i-\sum_{i>j} C_iC_j\pm\left[\frac{1}{2}\sum_{i\neq j\neq k}(1-C_i)^2(C_j-C_k)^2\right]^{1/2}\right\}. \quad (18)$$

The maximum frequency for these three branches is found to be $\omega_L^2=30(2\alpha/7m)$.

The integrated FD $N(\omega^2)$ and FD $G(\omega^2)$ of the above lattice with $\sigma=3/7$ and $\tau=2/7$ are calculated from Eqs. (4) and (6)′ by means of the Singhal formulas for $n=3$, 8, 12 and 16 (See Appendix). The results are shown in Figs. l(a)-(f) and are compared with those of Rosenstock and Rosenstock and the graphical interpolation scheme. For $n=3$ which corresponds to the original Houston method, neither of $N(\omega^2)$ nor $G(\omega^2)$ can give a close approximation, Spurious singularities appearing in $G(\omega^2)$ never be eliminated for any value of n. However, the proximity of $N(\omega^2)$ to the exact value is satisfactory for $n=8$, 12 and 16, and improvement of accuracy for larger n already becomes gradual in this stage. This behavior of approximate $N(\omega^2)$ leads us to suggest that its moments

$$\eta_n=\int_0^1 N(\omega^2)\omega^{2n}d\omega^2 \quad (19)$$

would also be a good approximation.

III. MOMENTS OF INTEGRATED FREQUENCY DISTRIBUTIONS AND OF FREQUENCY DISTRIBUTIONS

The moments η_n of $N(\omega^2)$ may be calculated directly from Eqn. (19) after $N(\omega^2)$ is determined from Eqs. (4) and (6)′. The moments of FD

$$\mu_n=\int_0^1 G(\omega^2)\omega^{2n}d\omega^2 \quad (20)$$

cannot be calculated by using Eqs. (4) and (6)′, since such $G(\omega^2)$ always involves spurious singularities. Fortunately, μ_n can be derived directly from the moments η_n of $N(\omega^2)$. On integrating Eqn. (19) by parts we readily obtain

$$\eta_n=\frac{1}{n+1}[N(1)-\mu_{n+1}]. \quad (21)$$

Then with noting the normalization property of $G(\omega^2)$, i.e.

$$N(1)=\int_0^1 G(\omega^2)d\omega^2=\mu_0=1, \quad (22)$$

(11) H. B. Rosenstock and H. M. Rosenstock, J. Chem. Phys. 21, 1608 (1953).

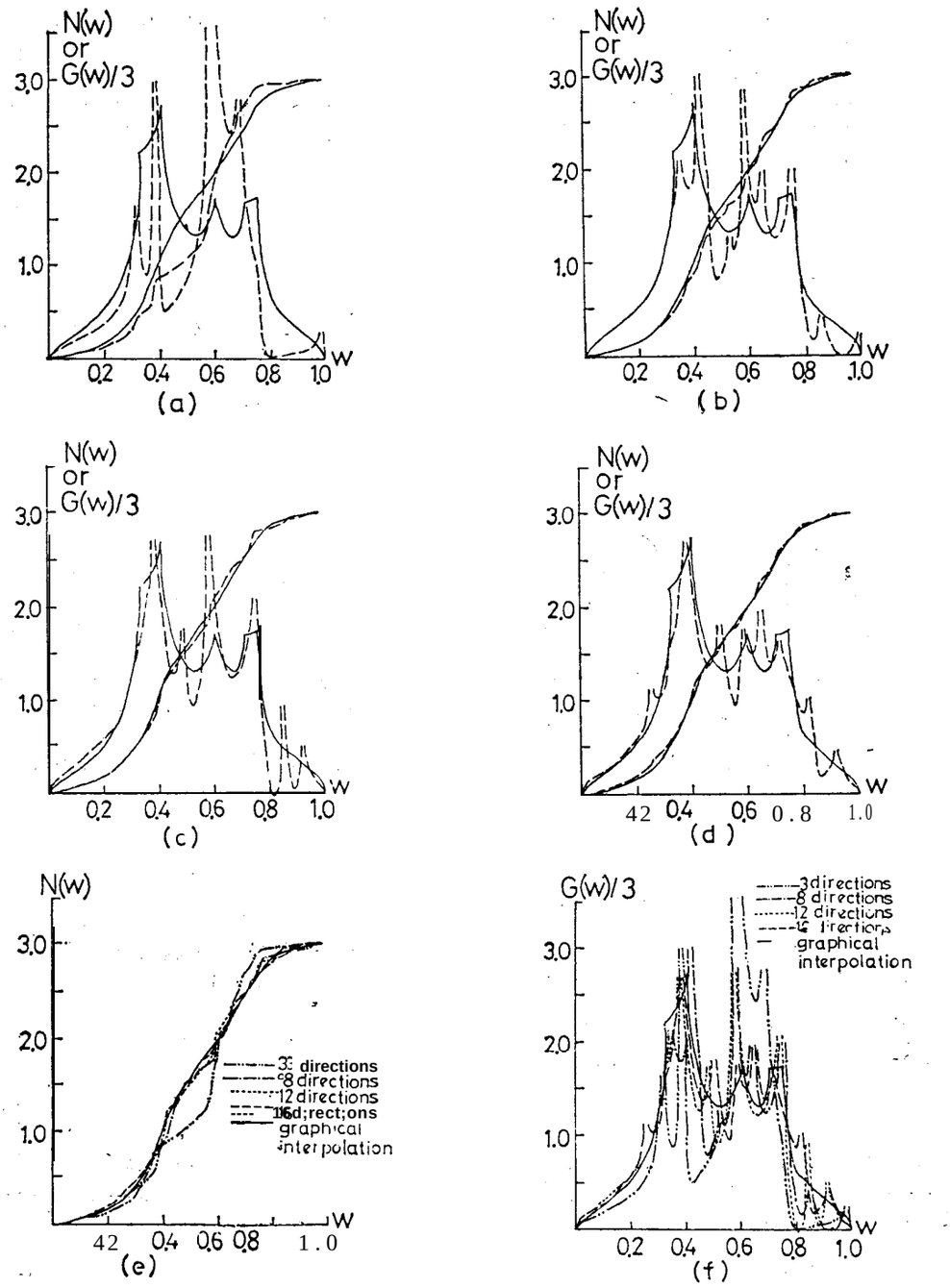

Fig. 1. The integrated frequency distribution $N(\omega^2)$ and the total frequency distribution $G(\omega^2)$ calculated from the Singhal ' s formulas for the monoatomic simple cubic lattice studied earlier by Rosenstock and Rosenstock and the present authors. Solid lines represent results of the present authors obtained by the graphical interpolation scheme. (a), (b), (c) and (d) illustrate respectively the results of 3, 8, 12 and 16 directions formulas. (e) shows a comparison of these results for $N(\omega^2)$. (f) shows a comparison of these results for. $G(\omega^2)$.

we arrive at

$$\eta_n=\frac{1}{n+1}(\mu_0-\mu_{n+1}) \quad \text{or} \quad \mu_{n-1}=1-(n+1)\eta_n. \tag{23}$$

In Table I are listed the moments η_n and μ_n of the each branch.

Table I. Moments η_n of $N(\omega^2)$ and μ_n of $G(\omega^2)$ for each branch

n	the first branch		the second branch		the third branch	
	η_n	μ_n	η_n	μ_n	η_n	μ_n
0	0.301	1.000	0.561	1.000	0.639	1.000
1	0.246	0.699	0.393	0.439	0.429	0.361
2	0.207	0.509	0.296	0.214	0.314	0.142
3	0.178	0.380	0.235	0.111	0.244	0.0591
4	0.155	0.289	0.193	0.0597	0.198	0.0256
5	0.138	0.223	0.164	0.0331	0.166	0.0115
6	0.123	0.175	0.141	0.0187	0.142	0.00536
7	0.111	0.140	0.124	0.0107	0.125	0.00256
8	0.101	0.113	0.111	0.00623	0.111	0.00125

IV. MOMENT SINGULARITY METHOD FOR DETERMINING FREQUENCY DISTRIBUTIONS

When appropriate number of moments μ_n's of FD $G(\omega^2)$ are calculated[12], the actual form of $G(\omega^2)$ can be determined with use of the knowledge about the location and shapes of the singularities. The location of most of the critical points can be inferred, as was firstly done by Rosenstock[10], from the behavior of $\omega^2(\mathbf{k})$ at the cornors, along the edges, and on the faces of the irreducible first Brillouin zone. The shapes of the singularities can be known from the work of analysis, particularly by van Hove[5], Rosenstock[10], Phillips(B) and others.

Following the treatment of Phillips, suppose that $G(\omega^2)$ can be written as

$$G(\omega^2)=G_q(\omega^2)+G_a(\omega^2), \tag{24}$$

where

$$G_q(\omega^2)=\sum_i a_i Q_i(|\omega^2-\omega_c^2|) \tag{25}$$

is the singular part and

$$G_a(\omega^2)=\sum_j b_j\omega^{2j} \tag{26}$$

is analytic. Functions $Q_i(|\omega^2-\omega_c^2|)$ characterize the behavior of singularities in the vicinity of critical points $\omega^2=\omega_c^2$. a_i's and b_j's are then solved from a set of simultaneous linear equations of the type

$$\mu_n=\sum_i a_i\int_0^1 Q_i(|\omega^2-\omega_c^2|)\omega^{2n}d\omega^2+\sum_j b_j\int_0^1\omega^{2j+2n}d\omega^2, \qquad n=0,\ 1,\ 2\cdots. \tag{27}$$

In the first branch of our example, it needs six terms for $G_s(\omega^2)$, and two or three for $G_a(\omega^2)$. Therefore, eight or nine unknowns are involved in the simultaneous system Eqs. (27). In each of the other

(12) The method of calculation described here should not be confused with tht moment trace method due to E. W. Montroll [J. Chem. Phys. **10,** 218 (1942); 11, 481 (1943); **12,** 98 (1944)].

two branches, four terms are needed in $G_s(\omega^2)$, and totally six or seven unknowns exist in Eqs. (27). It is quite laborious to solve the equations with such many unknowns, unless use is made of electronic computers.

In the present method, however, this tedious procedure for solutions can be diminished to the least extent. Unlike other methods, $G(\omega^2)$ as well as its moments μ_n in Eqn. (20) can be divided into several segments, each segment corresponding to a different frequency range. For instance, in the last branch $G(\omega^2)$ may be divided into three segments, and each segment is approximated respectively to

$$\begin{aligned}
&a_1^{\mathrm{I}} m(|\omega^2-0|)+a_2^{\mathrm{I}} S_1(|\omega^2-\omega_1^2|)+b_0^{\mathrm{I}}+b_1^{\mathrm{I}}\omega^2=G_{\mathrm{I}}(\omega^2), && 0\le\omega^2\le\omega_1^2\\
&b_0^{\mathrm{II}}+b_1^{\mathrm{II}}\omega^2+b_2^{\mathrm{II}}\omega^4=G_{\mathrm{II}}(\omega^2), && \omega_1^2\le\omega^2\le\omega_2^2\\
&a_1^{\mathrm{III}} S_2(|\omega^2-\omega_2^2|)+a_2^{\mathrm{III}} M(|\omega^2-\omega_L^2|)+b_0^{\mathrm{III}}+b_1^{\mathrm{III}}\omega^2=G_{\mathrm{III}}(\omega^2), && \omega_2^2\le\omega^2\le\omega_L^2,
\end{aligned} \tag{28}$$

with[13] $b_0^{\mathrm{I}}=-a_-^{\mathrm{I}} S_1(|0-\omega_-^2|)$ and $b_0^{\mathrm{III}}=-a_1^{\mathrm{III}} S_2(|\omega_L^2-\omega_2^2|)-b_1^{\mathrm{III}}\omega_L^2$, where different segments are distinguished by I, II and III, and the functions $Q_i(|\omega^2-\omega_c^2|)$ are taken to be

$$\begin{aligned}
&m(|\omega^2-\omega_c^2|)=|\omega^2-\omega_c^2|^{1/2}[1+\mathrm{sgn}(\omega^2-\omega_c^2)] && \text{(minimum)}\\
&S_1(|\omega^2-\omega_c^2|)=|\omega^2-\omega_c^2|^{1/2}[-1+\mathrm{sgn}(\omega^2-\omega_c^2)] && \text{(saddle point, } S_1\text{)}\\
&S_2(|\omega^2-\omega_c^2|)=-|\omega^2-\omega_c^2|^{1/2}[1+\mathrm{sgn}(\omega^2-\omega_c^2)] && \text{(saddle point, } S_2\text{)}\\
&M(|\omega^2-\omega_c^2|)=|\omega^2-\omega_c^2|^{1/2}[1-\mathrm{sgn}(\omega^2-\omega_c^2)] && \text{(maximum),}
\end{aligned} \tag{28}'$$

Table ZZ. An example of fit to $G(\omega^2)$ for branch

The First Branch

Segment I. $0.8224\,|\omega^2-0|^{1/2}-1.778\,\omega^2+2.693\,\omega^4$
Segment II. $16.80\,|\omega^2-0.6000|^{1/2}-19.63\,|\omega^2-0.6667|^{1/2}+58.25-87.72\,\omega^2$
Segment III. $-12.43\,|\omega^2-0.7067|^{1/2}+29.04-33.68\,\omega^2$
Segment IV. $-4.555+13.86\,\omega^2$
Segment V. $-16.60\,|\omega^2-0.750|^{1/2}+2.049\,|\omega^2-1.000|^{1/2}-8.882+17.18\,\omega^2$

The Second Branch

Segment I. $0.7836\,|\omega^2-0.000$ (“8-3.818 $|\omega^2-0.3333|^{1/2}+2.204\,\omega^2-2.030\,\omega^4$
Segment II. $14.77-65.29\,\omega^2+80.80\,\omega^4$
Segment III. $-31.67\,|\omega^2-0.600|^{1/2}+21.68\,|\omega^2-0.6667|^{1/2}-82.37+136.4\,\omega^2$

The Third Branch

Segment I. $2.044\,|\omega^2-0.000|^{1/2}-14.77\,|\omega^2-0.3333|^{1/2}+8.526\,\omega^2-15.89\,\omega^4$
Segment II. $74.69-406.2\,\omega^2+586.2\,\omega^4$
Segment III. $-21.11\,|\omega^2-0.4000|^{1/2}+5.228\,|\omega^2-0.6000|^{1/2}-7.967+29.03\,\omega^2$

Table ZZZ. Comparison of approximate $G(\omega)^2$ for the first branch with exact one

ω^2	present method	graphical	exact	ω^2	present method	graphical	exact
0.2	0.120	0.117	0.118	0.707	5.24	5.16	4.95
0.3	0.159	0.170	0.170	0.73	5.56	5.10	4.89
0.4	0.210	0.244	0.242	0.75	5.02	5.23	4.98
0.5	0.366	0.357	0.348	0.775	2.78	2.81	2.78
0.55	0.447	0.438	0.432	0.8	2.07	2.03	2.04
0.6	0.540	0.540	0.555	0.9	0.816	0.807	0.816
0.63	2.33	2.26	2.25	0.95	0.477	0.482	0.477
0.667	4.10	3.93	3.96	1.00	0.000	0.000	0.000
0.69	4.26	4.29	4.20				

(13) These values of b_0^{I} and b_0^{III} guarantee respectively $G_{\mathrm{I}}(0)=0$ and $G_{\mathrm{III}}(\omega_L^2)=0$.

with sgn $x = +1$ if $x > 0$ and sgn $x = -1$ if $x < 0$. Each segment of $G(\omega^2)$ thus can be determined by solving the simultaneous linear equations of several (at most four) unknowns. The other two branches may also be treated in an analogous manner. An example of such determination is illustrated in Table II and Table III.

V. MODIFICATION OF THE METHODS DUE TO LAX AND LEBOWITZ AND TO ROSENSTOCK

It is also possible to obtain a simple variant of the method due independently to Lax and Lebowitz and to Rosenstock, if combining it with the foregoing modification of Phillips' method. Originally the method of Lax and Lebowitz assumes that the singular part $G_q(\omega^2)$ can be found exactly from a study of critical points in the k-space. However, the study of critical points gives only the shape of singularities, but not their magnitude. Thus the original method seems not practical, although it has a merit by which an improvement of the approximation may be observed step by step with adding a higher moment one by one.

If we cast away the coefficients b_i's of the analytical part and only leave the coefficients a_i's of the singular part $G_q(\omega^2)$ determined from the Eqs. (28), then the analytical part $G_a(\omega^2)$ *defined newly through the whole frequency range* $0 \leq \omega^2 \leq 1$ can be approximated by a series of Legendre polynomials,

$$G_a(\omega^2) = \sum_{k=0}^{N} A_k P_k(x), \tag{29}$$

where $x = \omega^2$ and

$$A_k = (2k+1)\int_0^1 [G(x) - G_s(x)] P_k(x) dx \tag{29'}$$

are the coefficients of expansion. A_k ($k = 0, 1, 2, \cdots, N$) can be constructed from the moments of $G(\omega^2)$ and $G_q(\omega^2)$. This method is particularly useful when all branches are added in the same time to yield the total FD, in which the anlytical part can be determined with only one step.

VI. CONCLUDING REMARKS

After the advent of large-scale computers, two powerful methods were invented respectively by Gilat and Raubenheimer[14] and Mueller and his collaborators[15]. The former is called the linear interpolation scheme, originally designed to calculate FD of a Born-von Kármán force constant model; the latter is called the quadratic interpolation scheme (QUAD), specifically suitable for the study of electronic systems. Afterwards, Cooke and Wood[16] unified both methods into one, and showed that it is very useful for different kinds of problems. Thus, the evaluation of integrals over the Brillouin zone becomes realizable in principle. However, such powerful methods seems still not so popular. Some papers appeared recently in the literature still leave out the final determination of FD, though they have already derived interesting and valuable forms of dynamical secular equations. A presumed reason is that the facilities are very expensive and are still not in a state of general use. Another reason might be that their too mechanistic operation makes a monotonous feeling. The motivation of the present series of work to search for more facile methods comes mainly from this situation.

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(15) F. M. Mueller, J. W. Garland, M.H. Cohen and K. H. Bennemann, Ann. Phys. 67, 19 (1971), F.M. Mueller, Phys. Rev. 153, 659 (1967), F. M. Mueller and J. C. Phillips, Phys. Rev. 157, 600 (1967).

(16) J. F. Cooke and R. F. Wood, Phys. Rev. **B5**, 1276 (1972).

APPENDIX 1

We normalize the frequency distribution for the s-branch to 1,

$$\int_0^{(\omega_L^2)_s} G_s(\omega^2)d\omega^2 = 1, \tag{A-1}$$

where $(\omega_L^2)_s$ is the largest frequency in that branch, so that the total frequency distribution becomes

$$\int_0^1 G(\omega^2)d\omega^2 = \sum_{s=1}^{3}\int_0^{(\omega_L^2)_s} G_s(\omega^2)d\omega^2 = 3, \tag{A-2}$$

where the maximum frequency for three branches is equal to 1 since we have used the convension that ω^2 ranges from 0 to 1.

The volume in the first Brillouin zone calculated from the secular equation, or the integrated frequency distribution, should be divided by $8\pi^3$ in accordance with normalization Eqn. (A-l).

APPENDIX 2

The Singhal formulas for $n=3$, 8, 12 and 16 are cited in the following:

$$\begin{aligned}
a_1^{(3)} &= 1.012831F(100)+1.620529F(110)+0.911548F(111),\\
a_1^{(8)} &= 0.221613F(100)+0.110091F(110)+0.294637F(111)\\
&\quad +0.635562F(321)+1.083847F(831)+0.137543F(210)\\
&\quad +0.474521F(211)+0.587092F(441),\\
a_1^{(12)} &= 0.138472F(100)+0.351457F(110)+0.234507F(111)\\
&\quad +1.246640F(321)-0.230632F(831)+0.875489F(210)\\
&\quad +0.184069F(211)-0.0332286F(441)-0.341204F(741)\\
&\quad +0.679635F(411)+0.225170F(221)+0.214534F(410),\\
a_1^{(16)} &= 0.101332F(100)+0.191861F(110)+0.109811F(111)\\
&\quad +0.326929F(321)+0.0450450F(831)+0.0395619F(210)\\
&\quad +0.342493F(211)+0.255739F(441)+0.783543F(741)\\
&\quad +0.603400F(411)+0.216117F(221)+0.605269F(410)\\
&\quad +0.0208283F(732)-0.0269079F(651)-0.378570F(821)\\
&\quad +0.308456F(543).
\end{aligned}$$

These formulas should be multiplied by $(4\pi)^{1/2}=3.544908$ in accordance with the Eqn. (4).