Vibration Frequency Spectra of Disordered Lattices. I. Moments of the Spectra for Disordered Linear Chains*

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By using the theory of random walks on lattices, a combinatorial expression has been obtained for the even moments of the vibrational frequency spectrum of a randomly disordered, two-component, isotopic linear chain as functions of the concentrations of the two kinds of particles and of their mass ratio. Expressions for the even moments up to μ_{20} are presented.

1. INTRODUCTION

CONSIDERABLE progress has been made in the theory of the vibration spectra of regular crystalline solids in recent years. Exact information is available regarding the nature of the singularities,[1] exact calculations have been carried out for simple models[2] which illustrate how these singularities arise in one, two, and three dimensions, and high-powered computational methods have been developed when exact solutions are not available.[3] However, the methods used for deriving those results are intimately connected with the periodicity of the crystalline solids, and cannot be applied to solids containing impurities, or to mixed crystals. For this latter class of problems much less exact information is available, and no practical computational methods have been developed to enable spectra to be calculated.

For lattices containing isolated impurities Montroll and Potts[4] developed methods for determining the frequencies of the localized modes. They applied these methods to one-, two-, and three-dimensional models, but did not deal with finite concentrations of impurities.

The problem of calculating the frequency spectrum of a lattice containing isotopes of different masses in a finite ratio of concentrations is quite formidable mathematically, even in one dimension, and has excited some theoretical attention.

In 1953 Dyson[5] considered the problem of a linear chain of atoms of arbitrary masses connected by arbitrary spring constants. Making certain assumptions about the probability distributions of masses and spring constants, he obtained a formal solution for the frequency distribution function as a solution of an integral equation; in the case of practical interest of a random mixture of two isotopes of different masses, this reduces to a functional equation. Although Dyson states that a moderate amount of numerical work should provide an estimate of the spectrum for any ratio of masses and any concentration, it seems to us that he has underestimated the computational difficulties. We were unable to make use of his results for practical calculations. Similarly, the subsequent papers of Lifshitz and Stepanova,[6] Schmidt,[7] and Hori and Asahi,[8] although they contain features of considerable mathematical elegance, do not seem to provide a basis for practical calculation of spectra. A more detailed account of these approaches has been given in a recent review article.[9]

The methods of Montroll and Potts[4] depended on the expression of additive functions of the frequencies as contour integrals. Recently some of us attempted to apply this approach to random mixtures of isotopes, and the results of this investigation have been described elsewhere.[10] We developed the properties of the random mixture as a perturbation expansion in powers of the deviation from a "mean" mass, and we were able to derive several results of physical interest. The perturbation approach is useful in the long-wave region of the spectrum, but cannot be applied to short waves, and the method thus cannot be used for the complete determination of spectra.

In the present paper we have used the method of moments to provide an approximation to the vibrational frequency spectrum. This method was first used by Montroll[11] in connection with vibrations of homogeneous

[1] L. Van Hove, Phys. Rev. 89, 1189 (1953).
[2] See, e.g., E. W. Montroll, *Proceedings of the Third Berkeley Symposium on Mathematical Statistics and Probability* (University of California Press, Berkeley, 1955), p. 209.
[3] E. H. Jacobson, Phys. Rev. 97, 654 (1955); C. B. Walker, Phys. Rev. 103, 547 (1956).
[4] E. W. Montroll and R. B. Potts, Phys. Rev. 100, 525 (1955); 102, 72 (1956).
[5] F. J. Dyson, Phys. Rev. 92, 1331 (1953).

[6] I. M. Lifshitz and G. I. Stepanova, J. Exptl. Theoret. Phys. U.S.S.R. 30, 938 (1956) [translation: Soviet Phys. JETP 3, 656 (1956)].
[7] H. Schmidt, Phys. Rev. 105, 4025 (1957).
[8] J. Hori and T. Asahi, Progr. Theoret. Phys. (Kyoto) 17, 523 (1957).
[9] A. A. Maradudin and G. H. Weiss, J. Soc. Indust. Appl. Math. 6, 302 (1958).
[10] G. H. Weiss and A. A. Maradudin, J. Phys. Chem. Solids 7, 327 (1958).
[11] E. W. Montroll, J. Chem. Phys. 10, 218 (1942); 11, 481 (1943).

lattices, and a preliminary account of its application to the random chain was discussed in a recent paper.[12] We have now developed a more powerful technique for evaluating the moments and have consequently been able to calculate all even moments μ_{2n} up to $n=10$ for a linear chain. Certain asymptotic properties of these moments have enabled us to discuss the behavior of the spectrum at its upper end.

In this paper we describe the method used for the evaluation of the even moments of the vibrational frequency spectra of a disordered linear chain.

The techniques which we have developed should also be applicable to two- and three-dimensional models, and we hope to deal with these applications subsequently.

In a recent paper Pirenne[13] has described a general theoretical approach to this problem using the method of moments. His method seems to be a perturbation expansion in terms of deviations from a mean mass. Since he has not yet applied his theory to detailed calculations, we have been unable to compare his results with ours.

2. MOMENTS OF THE SPECTRUM. USE OF THE RANDOM WALK PROBLEM

The equation of motion of the pth atom, in a linear chain of N atoms, is given by

$$m_p \ddot{u}_p = -\alpha_{p-1}(u_p - u_{p-1}) - \alpha_p(u_p - u_{p+1})$$
$$= \alpha_{p-1}u_{p-1} - (\alpha_{p-1} + \alpha_p)u_p + \alpha_p u_{p+1}. \quad (1)$$

Here m_p is the mass of the pth atom, u_p its displacement from equilibrium, and α_p is the spring constant between the pth and $(p+1)$st atoms of the chain. We assume that the atoms are joined in a ring, so that the Nth atom is connected with the first. The secular equation which determines the normal mode frequencies of the chain can thus be written in the form

$$|A - \omega^2 I| = 0, \quad (2)$$

where A is a Jacobi matrix whose elements a_{pq} are all zero unless p equal q, $q-1$ or $q+1$. Montroll's method of calculation[11] consisted in determining $\sum \omega^2$, $\sum \omega^4$, $\sum \omega^6$, $\cdots$, the sums being taken over all normal modes, from the relations

$$\text{Trace } A = \sum \omega^2,$$
$$\text{Trace } A^2 = \sum \omega^4, \quad (3)$$
$$\text{Trace } A^3 = \sum \omega^6.$$

There was little point in using this method for a one-dimensional homogeneous chain, for which an exact solution is readily obtained, but in two and three dimensions it rapidly and easily provided useful information on the form of the spectrum. Montroll did not use the original secular matrix of order N (= number of normal modes); taking account of the cyclic boundary
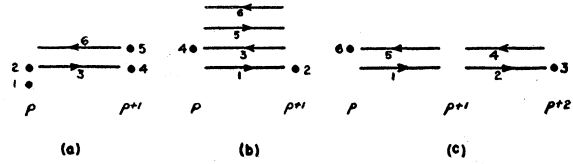

FIG. 1. Typical graphs for one-dimensional random walks of six steps which return to the starting point.

condition, he decomposed this matrix into submatrices corresponding to different directions of propagation in the crystal, following the standard treatment of Born.[14] This decomposition is no longer possible for a disordered lattice, and we must revert to the original secular matrix.

If we now consider the trace of A^n, it consists of the sum of all n-cycles $a_{p_1 p_2} a_{p_2 p_3} \cdots a_{p_n p_1}$, where p_1, p_2, $\cdots$, p_n take on all N possible values. However, since $a_{pq}=0$ unless $q-p=0$, ± 1, only a small fraction of the N^n terms will be nonzero, and any nonzero term can be represented by a graph on the linear chain: $a_{p\ p+1}$ is represented by $\rightarrow$, $a_{p\ p-1}$ by $\leftarrow$, and a_{pp} by $\bullet$. Typical graphs for 6 cycles are shown in Fig. 1. It will be readily seen that each nonzero graph corresponds to a random walk on the chain, in which each step consists of 0 or ± 1 units, and in which the walker must return to his starting position after n steps. For each graph it is easy to write down the corresponding term in trace A^n; thus in Fig. 1 for (a) it is $a_{pp}{}^2 a_{p+1\ p+1}{}^2 a_{p\ p+1} a_{p+1\ p}$; for (b), $a_{pp} a_{p+1\ p+1} a_{p\ p+1}{}^2 a_{p+1\ p}{}^2$; and for (c), $a_{p+1\ p+2} a_{p+2\ p+1} a_{pp} a_{p+2\ p+2} a_{p\ p+1} a_{p+1\ p}$. For any particular set of masses and spring constants we must sum over all types of graphs corresponding to n steps, and over all points p of the chain.

When the atomic masses and spring constants are independent random variables, a considerable simplification arises. All points of the chain are equivalent, and the terms corresponding to each graph are replaced by stochastic mean values, each α_p, $m_p{}^{-1}$ being an independent random variable. These mean values can readily be determined for any graph in terms of the moments of the m^{-1} and α distributions. From Eq. (1), $a_{pp}=(\alpha_{p-1}+\alpha_p)/m_p$, $a_{p\ p-1}=\alpha_{p-1}/m_p$, and $a_{p\ p+1}=\alpha_p/m_p$. We shall denote the sth moments of the m^{-1} and α distributions by ν_s and γ_s, respectively.

The graphs can be considerably simplified by drawing a single line to correspond to a forward and backward step, since any such step must be traversed in both directions for the random walker to return to his starting point. The resulting graphs then appear as in Fig. 2.
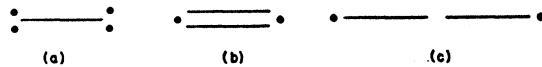

FIG. 2. Condensed graphs for the same six-step random walks shown in Fig. 1. Each line in these graphs now corresponds to a doubled step.

[12] Maradudin, Mazur, Montroll, and Weiss, Revs. Modern Phys. **30**, 175 (1958).
[13] J. Pirenne, Physica **24**, 73 (1958).
[14] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1954), Chap. II.

A simple recipe can now be given for writing down mean values. For the terms in m^{-1} each dot, and each end of a line, should be replaced by m_p^{-1} at the appropriate position;

$$\text{(a)} \quad \frac{1}{m_p{}^3}\frac{1}{m_{p+1}{}^3}; \quad \text{(b)} \quad \frac{1}{m_p{}^3}\frac{1}{m_{p+1}{}^3};$$

$$\text{(c)} \quad \frac{1}{m_p{}^2}\frac{1}{m_{p+1}{}^2}\frac{1}{m_{p+2}{}^2}. \tag{4}$$

For terms in α a dot at point p should be replaced by $(\alpha_{p-1}+\alpha_p)$ and a line connecting points p and $p+1$ should be replaced by $\alpha_p{}^2$:

$$\text{(a)} \quad \alpha_p{}^2(\alpha_{p-1}+\alpha_p)^2(\alpha_p+\alpha_{p+1})^2;$$

$$\text{(b)} \quad \alpha_p{}^4(\alpha_{p-1}+\alpha_p)(\alpha_p+\alpha_{p+1}); \tag{5}$$

$$\text{(c)} \quad (\alpha_{p-1}+\alpha_p)\alpha_p{}^2\alpha_{p+1}{}^2(\alpha_{p+1}+\alpha_{p+2}).$$

The mean values for each graph can be written down relatively easily according to the following rule: a term $m_{i_1}{}^{-j_1}m_{i_2}{}^{-j_2}\cdots\alpha_{n_1}{}^{k_1}\alpha_{n_2}{}^{k_2}\cdots$ with $i_1\neq i_2\neq\cdots$ and $n_1\neq n_2$ $\neq\cdots$ gives a contribution of $\nu_{j_1}\nu_{j_2}\cdots\gamma_{k_1}\gamma_{k_2}\cdots$ to the moments. Thus, for example, the mean values corresponding to the graphs in Fig. 1 are given by

$$\text{(a)} \quad \nu_3{}^2(\gamma_6+4\gamma_5\gamma_1+2\gamma_4\gamma_2+4\gamma_4\gamma_1{}^2+4\gamma_3\gamma_2\gamma_1+\gamma_2{}^3);$$

$$\text{(b)} \quad \nu_3{}^2(\gamma_6+2\gamma_5\gamma_1+\gamma_1{}^2\gamma_4); \tag{6}$$

$$\text{(c)} \quad \nu_2{}^3(\gamma_3{}^2+2\gamma_3\gamma_2\gamma_1+\gamma_2{}^2\gamma_1{}^2).$$

The main problem is the determination of the number of possible paths in a random walk which corresponds to any graph. We shall consider this problem in detail in the next section, and shall derive an exact combinatorial expression for this number.

We shall confine our attention to the simplified problem of a random mixture of isotopes in which the spring constants are all equal, and only the masses are independent random variables. In this case γ_s and ν_s, the moments of the α_p and m_p^{-1} distributions, become

$$\gamma_s=\alpha^s, \quad \nu_s=\tau/m^s+(1-\tau)/M^s,$$

where τ is the probability that an atom with mass m occupies a given lattice point and $1-\tau$ is the corresponding probability for a particle with mass M. It will be convenient to adopt a system of units in which $\alpha=1$.
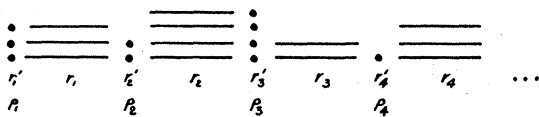

FIG. 3. The general graph for an n-step walk. The dashed letters correspond to pauses and the undashed letters to doubled steps, so that $(r_1'+r_2'+\cdots)+2(r_1+r_2+\cdots)=n$.

More general cases of both masses and spring constants randomly distributed, or of any particular type of correlation between them, can be treated by the same methods.

When the spring constants are random and the masses equal, it is found that the moments are identical with those of a random isotopic mixture with equal spring constants and random masses. It is easy to show by an elementary transformation (Appendix B) that the problems are effectively equivalent.

3. EVALUATION OF THE MOMENTS

The general graph of the type described at the end of Sec. 2 can be represented as in Fig. 3. Dashed letters correspond to pauses and undashed letters to doubled steps, so that for a walk of n steps $(r_1'+r_2'+r_3'+\cdots)$ $+2(r_1+r_2+r_3+\cdots)=n$. With each graph we will associate two combinatorial factors, $F_0(r_1',r_1,r_2',r_2,\cdots)$ representing the number of possible walks corresponding to the graph which start at the left hand end and end at the initial point, and $F(r_1',r_1,r_2',r_2,\cdots)$ representing the total number of possible walks which start at any of the
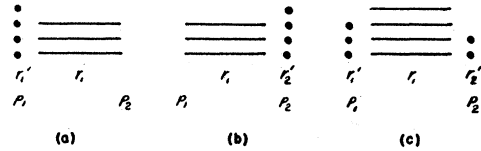

FIG. 4. Graphs which arise in determining the combinatorial factor $F(r_1',r_1,r_2')$, which depends on the auxiliary factor $F_0(r_1'r_1,r_2')$. In (a) and (b) two subgraphs of the total graph (c) determining $F_0(r_1'r_1,r_2')$ are shown.

points of the graph. We shall start with the simplest case of graphs corresponding to one link of the chain, and bounded by two atoms; we shall then proceed to graphs corresponding to two links and containing three atomic positions, and so on; we shall thus be led to a general formula the validity of which can be established by induction.

Let us first consider the simple graph of Fig. 4(a). It is clear that pauses can be fitted in at any r_1' of the total of (r_1+r_1') occasions when the walker is at his starting point and about to take a step to the right. Thus $F_0(r_1',r_1)=(r_1'+r_1)!/r_1'!r_1!$. However, for the graph in Fig. 4(b) the walker must start by stepping to the right at p_1 and must terminate by returning to his starting place, and there remain $r_1+r_2'-1$ occasions when he is at p_2 of which any r_2' can be selected for pauses; thus $F_0(0,r_1,r_2')=(r_1+r_2'-1)!/(r_1-1)!r_2'!$.

If we now proceed to determine $F_0(r_1',r_1,r_2')$ for the graph in Fig. 4(c), we can start with any one of the $F_0(r_1',r_1,0)$ walks, and we have the freedom to fit in r_2' pauses at p_2 on any of $(r_1+r_2'-1)$ occasions. The factor r_1-1 appears because the random walker must finally

return to his starting point. Hence,

$$F_0(r_1',r_1,r_2') = F_0(r_1',r_1,0)\frac{(r_1+r_2'-1)!}{(r_1-1)!r_2'!}$$

$$= \frac{(r_1'+r_1)!}{r_1'!r_1!}\frac{(r_1+r_2'-1)!}{(r_1-1)!r_2'!}. \qquad (7)$$

Clearly $F(r_1',r_1,r_2')$ will arise from summing possible walks starting at the left or right hand of the graph, and we have

$$F(r_1',r_1,r_2') = F_0(r_1',r_1,r_2') + F_0(r_2',r_1,r_1')$$

$$= \frac{(r_1'+r_1-1)!}{r_1'!r_1!}\frac{(r_1+r_2'-1)!}{(r_1-1)!r_2'!}(r_1'+r_1+r_1+r_2')$$

$$= n\frac{(r_1'+r_1-1)!}{r_1'!r_1!}\frac{(r_1+r_2'-1)!}{(r_1-1)!r_2'!}, \qquad (8)$$

since $2r_1+r_1'+r_2'=n$ by definition.

We next consider the graph in Fig. 5(a), and to determine $F_0(r_1',r_1,r_2',r_2,r_3')$, we decompose the graph into the two graphs shown in Figs. 5(b) and (c). $F_0(r_1',r_1,r_2',r_2,r_3')$ can be made up of combinations of $F_0(r_1',r_1,0)$ and $F_0(r_2',r_2,r_3')$, but these can be fitted together at the point of decomposition p_2 in $\begin{pmatrix} r_1-1+r_2+r_2' \\ r_1-1 \end{pmatrix}$ ways. Hence,

$$F_0(r_1',r_1,r_2',r_2,r_3')$$

$$= F_0(r_1',r_1,0)F_0(r_2',r_2,r_3')\frac{(r_1+r_2'+r_2-1)!}{(r_1-1)!(r_2'+r_2)!}$$

$$= \frac{(r_1'+r_1)!}{r_1'!r_1!}\frac{(r_1+r_2'+r_2-1)!}{(r_1-1)!r_2'!r_2!}\frac{(r_2+r_3'-1)!}{(r_2-1)!r_3'!}. \qquad (9)$$

It is clear that $F(r_1',r_1,r_2',r_2,r_3')$ is made up of walks which start at the ends p_1, p_3, and walks which start at the central point p_2 and which can be decomposed as above. Hence

$$F(r_1',r_1,r_2',r_2,r_3')$$

$$= F_0(r_1',r_1,r_2',r_2,r_3') + F_0(r_3',r_2,r_2',r_1,r_1')$$

$$+ \begin{pmatrix} r_1+r_2'+r_2 \\ r_1 \end{pmatrix}F_0(r_1',r_1,0)F_0(r_2',r_2,r_3')$$

$$= n\frac{(r_1'+r_1-1)!}{r_1'!r_1!}\frac{(r_1+r_2'+r_2-1)!}{(r_1-1)!r_2'!r_2!}\frac{(r_2+r_3'-1)!}{(r_2-1)!r_3'!}. \qquad (10)$$

By comparing (10) and (8) it is easy to write down the general form of the combinatorial factor $F(r_1',r_1,r_2',r_2,\cdots)$, and the result can be established by induction. The mean value corresponding to the general graph is $\nu_{r_1'+r_1}\nu_{r_1+r_2'+r_2}\nu_{r_2+r_3'+r_3}\cdots$ since $\nu_{r_j+r_{j+1}'+r_{j+1}}$
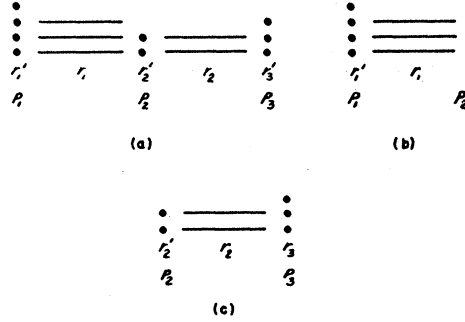

FIG. 5. Graphs which arise in determining the combinatorial factor $F(r_1',r_1,r_2',r_2,r_3')$. The graph in (a) determines the auxiliary combinatorial factor $F_0(r_1',r_1,r_2',r_2,r_3')$. This factor is a combination of the factors $F_0(r_1',r_1,0)$ and $F_0(r_2',r_2,r_3')$, and the graphs corresponding to these two factors are shown in (b) and (c).

represents all the contributions from a given m_p. The $2n$th moment μ_{2n} of the vibration spectrum of the chain can be written in the form

$$\mu_{2n} = \sum_{r_1',r_1,r_2',\cdots} 2^{r'}F(r_1',r_1,r_2',\cdots)$$

$$\times \nu_{r_1'+r_1}\nu_{r_1+r_2'+r_2}\nu_{r_2+r_3'+r_3}\cdots. \qquad (11)$$

The sum is to be taken over all distinct values of r_1, r_2, $\cdots$, r_1', r_2', $\cdots$, such that $2(r_1+r_2+\cdots)+r_1'+r_2'+\cdots=n$; r' is written for $r_1'+r_2'+\cdots$ and the factor $2^{r'}$ arises from the factor 2 along the main diagonal of A corresponding to each pause in the random walk. The factor $F(r_1')$ corresponds to all pauses and no steps and is clearly unity. The problem of evaluating the moment is thus reduced to enumerating partitions of n given by the above condition, and for the first few moments, this can be done simply and rapidly. However, for higher moments the enumeration, although straightforward, becomes rather tedious. It is therefore useful to devise an alternative method of evaluating the $F(r_1',r_1,r_2',r_2,\cdots)$.

We consider the successive generating functions

$$\Phi_1(x_1') = \sum_{r_1'=1}\frac{1}{r_1'}(x_1')^{r_1'},$$

$$\Phi_{12}(x_1',x_1,x_2')$$

$$= \sum_{r_1',r_2'=0}\sum_{r_1=1}\frac{1}{n}F(r_1',r_1,r_2')(x_1')^{r_1'}(x_2')^{r_2'}(x_1)^{2r_1}, \qquad (12)$$

$$\Phi_{123}(x_1',x_1,x_2',x_2,x_3')$$

$$= \sum_{r_1',r_2',r_3'=0}\sum_{r_1,r_2=1}\frac{1}{n}F(r_1',r_1,r_2',r_2,r_3')$$

$$\times (x_1')^{r_1'}(x_2')^{r_2'}(x_3')^{r_3'}(x_1)^{2r_1}(x_2)^{2r_2}.$$

Thus Φ_1 corresponds to graphs using one atom of the chain, Φ_{12} to graphs using two atoms, Φ_{123} to three atoms, and so on. We proceed to evaluate the first few generating functions, and we shall then establish a general relation between successive generating functions from which they can readily be determined.

We have immediately that $\Phi_1 = -\ln(1-x_1')$. For the remaining functions we can easily sum over the r_i' variables, using the relation

$$\sum_{s=0}^{\infty} \frac{(s+r-1)!}{s!} t^s = (r-1)!(1-t)^{-r}. \tag{13}$$

Thus we obtain

$$\Phi_{12} = \sum_{r_1',r_2'=0}^{\infty} \sum_{r_1=1}^{\infty} \frac{(r_1'+r_1-1)!}{r_1'!r_1!}$$

$$\times \frac{(r_1+r_2'-1)!}{(r_1-1)!r_2'!}(x_1')^{r_1'}(x_2')^{r_2'}(x_1)^{2r_1}$$

$$= \sum_{r_1=1}^{\infty} (r_1-1)!(1-x_1')^{-r_1}(r_1-1)!$$

$$\tag{14}$$

$$\times (1-x_2')^{-r_1}\frac{(x_1)^{2r_1}}{r_1!(r_1-1)!}$$

$$= \sum_{r_1=1}^{\infty} \frac{1}{r_1}u_{12}{}^{r_1} = -\ln(1-u_{12}),$$

$$u_{12} = \frac{x_1{}^2}{(1-x_1')(1-x_2')}.$$

Similarly

$$\Phi_{123} = \sum_{r_1,r_2=1}^{\infty} \frac{(r_1+r_2-1)!}{r_1!r_2!}u_{12}{}^{r_1}u_{23}{}^{r_2},$$

$$\tag{15}$$

$$u_{23} = \frac{x_2{}^2}{(1-x_2')(1-x_3')},$$

$$\Phi_{1234} = \sum_{r_1,r_2,r_3=1}^{\infty} \frac{(r_1+r_2-1)!}{r_1!r_2!}\frac{(r_2+r_3-1)!}{(r_2-1)!r_3!}u_{12}{}^{r_1}u_{23}{}^{r_2}u_{34}{}^{r_3},$$

$$\tag{16}$$

$$u_{34} = \frac{x_3{}^2}{(1-x_3')(1-x_4')}.$$

Hence all the generating functions other than the zeroth are functions of u_{12}, u_{23}, $\cdots$, only. It should be noted that the sums over r_1, r_2, r_3, $\cdots$ are to be taken from 1 to ∞; however, if any particular value of r_i could be taken from 0 to ∞, then relation (13) could be applied and the sum carried out. Now if we put $r_2=0$ in the expression for Φ_{123} we obtain Φ_{12}; thus we have

$$\Phi_{123}(u_{12},u_{23})+\Phi_{12}(u_{12})$$

$$= \sum_{r_1=1}^{\infty} \sum_{r_2=0}^{\infty} \frac{(r_1+r_2-1)!}{r_1!r_2!}u_{12}{}^{r_1}u_{23}{}^{r_2}$$

$$= \sum_{r_1=1}^{\infty} \frac{(r_1-1)!}{r_1!}u_{12}{}^{r_1}(1-u_{23})^{-r_1} = \Phi_{12}\left(\frac{u_{12}}{1-u_{23}}\right). \tag{17}$$

Therefore

$$\Phi_{123}(u_{12},u_{23}) = -\Phi_{12}(u_{12})+\Phi_{12}\left(\frac{u_{12}}{1-u_{23}}\right). \tag{18}$$

Similarly

$$\Phi_{1234}(u_{12},u_{23},u_{34})$$

$$= -\Phi_{123}(u_{12},u_{23})+\Phi_{123}\left(u_{12},\frac{u_{23}}{1-u_{34}}\right), \tag{19}$$

and so on. We see that the successive generating functions can readily be expressed in the form of continued fractions

$$\Phi_{12} = -\ln(1-u_{12}),$$

$$\Phi_{123} = -\ln\left(1-\frac{u_{12}}{1-}\frac{u_{23}}{1}\right)+\ln(1-u_{12}),$$

$$\tag{20}$$

$$\Phi_{1234} = -\ln\left(1-\frac{u_{12}}{1-}\frac{u_{23}}{1-}\frac{u_{34}}{1}\right)+\ln\left(1-\frac{u_{12}}{1-}\frac{u_{23}}{1}\right),$$

and the sum of all the generating functions $\Phi_{12}+\Phi_{123}+\Phi_{1234}+\cdots$ is the function

$$-\ln\left(1-\frac{u_{12}}{1-}\frac{u_{23}}{1-}\frac{u_{34}}{1-}\cdots\right). \tag{21}$$

The expression (10) for the combinatorial factor is similar to one obtained by Dyson,[5] and the last expression (21) for the sum of the generating functions as a continued fraction is also reminiscent of his results. However, since we have preferred to use the original matrix of the vibrating frequencies rather than the transformed matrix of Dyson, we have not tried to establish a direct connection between his results and ours. The methods which we have used can be generalized to two- and three-dimensional models, although the topological problems of enumerating possible graphs are considerably more complicated. Some help can be obtained from corresponding work on the Ising model in two and three dimensions, and we hope to deal with this generalization in a subsequent paper.

We have used the formulas (18) and (19) for the generating functions as a means of writing down expressions for the moments. The generating functions are expanded as power series in the u's and hence in the x's and x''s. Corresponding to each term in the expansion of a given order there will be a mean value and a term in the expression for the moment. By this means the values of the even moments from μ_2 to μ_{20} have been derived; some further details of the calculations, and the resulting expressions, are reproduced in Appendix A. Previously the moments up to μ_{14} have been obtained by an alternative method[12]; the present results check with those obtained previously, but because of the greater simplicity of the present method, the calculations can be carried much further.

When the lattice is homogeneous all the u's are equal, and it can be verified that the infinite continued fraction given above leads to the correct result.

APPENDIX A. EVALUATION OF THE MOMENTS

We shall illustrate the method described in Sec. 3 by deriving in detail the moments up to μ_{10}, and quoting the results for μ_{12} to μ_{20}.

We have from Eqs. (12), (18), and (19):

$$\Phi_1(x_1') = -\ln(1-x_1') = x_1' + \tfrac{1}{2}x_1'^2 + \tfrac{1}{3}x_1'^3 + \cdots,$$

$$\Phi_{12}(u_{12}) = -\ln(1-u_{12}) = u_{12} + \tfrac{1}{2}u_{12}^2 + \tfrac{1}{3}u_{12}^3 + \cdots,$$

$$\Phi_{123}(u_{12},u_{23})$$

$$= -\Phi_{12}(u_{12}) + \Phi_{12}\left(\frac{u_{12}}{1-u_{23}}\right)$$

$$= u_{12}u_{23} + (u_{12}u_{23}^2 + u_{12}^2 u_{23})$$

$$+ (u_{12}u_{23}^3 + \tfrac{3}{2}u_{12}^2 u_{23}^2 + u_{12}^3 u_{23}) + \cdots,$$

$$\Phi_{1234}(u_{12},u_{23},u_{34})$$

$$= -\Phi_{123}(u_{12},u_{23}) + \Phi_{123}\left(u_{12},\frac{u_{23}}{1-u_{34}}\right)$$

$$= u_{12}u_{23}u_{34} + (u_{12}u_{23}u_{34}^2$$

$$+ u_{12}^2 u_{23}u_{34} + 2u_{12}u_{23}^2 u_{34}) + \cdots.$$

We must now expand $u_{12} = x_1^2/(1-x_1')(1-x_2')$, $\cdots$, as power series in x_1', x_2', $\cdots$, sum $\Phi_1 + \Phi_{12} + \Phi_{123} + \cdots$, and collect together all terms of order r in all the x's and x''s for the $2r$th moment. We obtain for the first five terms:

$$x_1' + (\tfrac{1}{2}x_1'^2 + x_1^2) + (\tfrac{1}{3}x_1'^3 + x_1^2 x_1' + x_1^2 x_2')$$
$$+ [\tfrac{1}{4}x_1'^4 + x_1^2(x_1'^2 + x_1'x_2' + x_2'^2) + \tfrac{1}{2}x_1^4 + x_1^2 x_2^2]$$
$$+ [\tfrac{1}{5}x_1'^5 + x_1^2(x_1'^3 + x_1'^2 x_2' + x_1'x_2'^2 + x_2'^3)$$
$$+ \tfrac{1}{2}x_1^4(2x_1' + 2x_2') + x_1^2 x_2^2(x_1' + x_3' + 2x_2')].$$

Each term in the polynomial must now be replaced by its appropriate average as described in Sec. 3. The resulting moments are

$$\mu_0 = 1,$$

$$\mu_2 = \tfrac{1}{4}(2\nu_1),$$

$$\mu_4 = \frac{1}{16}(4\nu_2 + 2\nu_1^2),$$

$$\mu_6 = \frac{1}{64}(8\nu_3 + 12\nu_1\nu_2),$$

$$\mu_8 = \frac{1}{256}(16\nu_4 + 32\nu_3\nu_1 + 18\nu_2^2 + 4\nu_2\nu_1^2),$$

$$\mu_{10} = \frac{1}{1024}(32\nu_5 + 80\nu_4\nu_1 + 100\nu_3\nu_2 + 20\nu_3\nu_1^2 + 20\nu_2^2\nu_1),$$

$$\mu_{12} = \frac{1}{4096}(64\nu_6 + 192\nu_5\nu_1 + 264\nu_4\nu_2 + 72\nu_4\nu_1^2 + 146\nu_3^2$$
$$+ 156\nu_3\nu_2\nu_1 + 24\nu_2^3 + 6\nu_2^2\nu_1^2),$$

$$\mu_{14} = \frac{1}{16\,384}(128\nu_7 + 448\nu_6\nu_1 + 672\nu_5\nu_2 + 812\nu_4\nu_3 + 224\nu_5\nu_1^2$$
$$+ 532\nu_4\nu_2\nu_1 + 280\nu_3^2\nu_1 + 252\nu_3\nu_2^2 + 56\nu_3\nu_2\nu_1^2 + 28\nu_2^3\nu_1),$$

$$\mu_{16} = \frac{1}{65\,536}(256\nu_8 + 1024\nu_7\nu_1 + 1664\nu_6\nu_2 + 2176\nu_5\nu_3$$
$$+ 1186\nu_4^2 + 640\nu_6\nu_1^2 + 1664\nu_5\nu_2\nu_1 + 1872\nu_4\nu_3\nu_1$$
$$+ 844\nu_4\nu_2^2 + 832\nu_3^2\nu_2 + 192\nu_4\nu_2\nu_1^2 + 366\nu_3\nu_2^2\nu_1$$
$$+ 144\nu_3^2\nu_1^2 + 32\nu_2^4 + 8\nu_2^3\nu_1^2),$$

$$\mu_{18} = \frac{1}{262\,144}(512\nu_9 + 2304\nu_8\nu_1 + 4032\nu_7\nu_2 + 5664\nu_6\nu_3$$
$$+ 6660\nu_5\nu_4 + 1728\nu_7\nu_1^2 + 4896\nu_6\nu_2\nu_1 + 5904\nu_5\nu_3\nu_1$$
$$+ 2700\nu_5\nu_2^2 + 3132\nu_4^2\nu_1 + 5472\nu_4\nu_3\nu_2 + 864\nu_3^3$$
$$+ 576\nu_5\nu_2\nu_1^2 + 1080\nu_4\nu_3\nu_1^2 + 1116\nu_4\nu_2^2\nu_1 + 1368\nu_3^2\nu_2\nu_1$$
$$+ 468\nu_3\nu_2^3 + 108\nu_3\nu_2^2\nu_1^2 + 36\nu_2^4\nu_1),$$

$$\mu_{20} = \frac{1}{1\,048\,576}(1024\nu_{10} + 5120\nu_9\nu_1 + 9600\nu_8\nu_2 + 14\,400\nu_7\nu_3$$
$$+ 18\,120\nu_6\nu_4 + 9762\nu_5^2 + 4480\nu_8\nu_1^2 + 13\,760\nu_7\nu_2\nu_1$$
$$+ 17\,760\nu_6\nu_3\nu_1 + 8280\nu_6\nu_2^2 + 20\,020\nu_5\nu_4\nu_1$$
$$+ 17\,640\nu_5\nu_3\nu_2 + 8920\nu_4^2\nu_2 + 8320\nu_4\nu_3^2 + 1600\nu_6\nu_2\nu_1^2$$
$$+ 3520\nu_5\nu_3\nu_1^2 + 3360\nu_5\nu_2^2\nu_1 + 2190\nu_4^2\nu_1^2 + 9520\nu_4\nu_3\nu_2\nu_1$$
$$+ 1520\nu_4\nu_2^3 + 1760\nu_3^3\nu_1 + 2570\nu_3^2\nu_2^2 + 360\nu_4\nu_2^2\nu_1^2$$
$$+ 520\nu_3^2\nu_2\nu_1^2 + 580\nu_3\nu_2^3\nu_1 + 40\nu_2^5 + 10\nu_2^4\nu_1^2).$$

It is worth pointing out that checks are available for the coefficients in the expressions for the moments. For example, the sum of all the coefficients in μ_{2n} must be equal to the value for the homogeneous lattice, $(2n)!/[4^n(n!)^2]$. Such checks are of great practical importance for the higher moments since the calculations become involved. A final source of error (not eliminated by such checks) is writing down the wrong average for a given configuration; this is much less likely to occur than other errors, and was eliminated by performing the calculations independently on different occasions.

APPENDIX B. THE CASE OF EQUAL MASSES AND RANDOM FORCE CONSTANTS

The equation of motion of the $(p-1)$th atom of a chain of random masses and equal spring constants is, from (1),

$$\frac{d^2 u_{p-1}}{dt^2} = \frac{\alpha}{m_{p-1}}[u_{p-2}-2u_{p-1}+u_p]$$

$$= \frac{\alpha}{m_{p-1}}[u_{p-2}-u_{p-1}] - \frac{\alpha}{m_{p-1}}[u_{p-1}-u_p]$$

$$= \frac{\alpha}{m_{p-1}}w_{p-1} - \frac{\alpha}{m_{p-1}}w_p, \qquad (B.1)$$

where

$$w_p = u_{p-1}-u_p.$$

Similarly

$$\frac{d^2 u_p}{dt^2} = \frac{\alpha}{m_p}w_p - \frac{\alpha}{m_p}w_{p+1}. \qquad (B.2)$$

Substracting we obtain

$$\frac{d^2 w_p}{dt^2} = \frac{\alpha}{m_{p-1}}w_{p-1} - \left(\frac{\alpha}{m_{p-1}}+\frac{\alpha}{m_p}\right)w_p + \frac{\alpha}{m_p}w_{p+1}, \qquad (B.3)$$

and this is of exactly the same form as (1) with constant m and random α.

Vibration Frequency Spectra of Disordered Lattices. II. Spectra of Disordered One-Dimensional Lattices*

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By using a combination of the moment-trace method and a new method, the "delta-function" method, the vibrational frequency spectrum of a randomly disordered, two-component, isotopic, linear chain has been computed for a wide range of the concentrations of the two kinds of particles and of their mass ratios. In addition the particular case of a chain in which the mass of one of the isotopic constituents becomes infinite can be treated exactly, and the results of this analysis shed light on the form of the spectra for lattices with large but finite mass ratios for the two constituents. The spectra are characterized by the disappearance of the square-root singularity at the maximum frequency which is found in ordered one-dimensional lattices, and by the appearance of impurity bands, the nature of which is discussed. Finally, the zero-point energy of a randomly disordered lattice is calculated and compared with the zero-point energy of an ordered lattice and of the separated phases.

1. INTRODUCTION

IN a previous paper[1] a method for obtaining the moments of the vibrational frequency spectrum of a disordered two-component linear chain was described, and explicit expressions for the even moments up to μ_{20} were given. In the present paper we apply these results to the construction of frequency spectra of disordered isotopic linear chains for a wide variety of concentrations of the two kinds of particles and of the ratios of their masses. In obtaining these spectra the moments are used in two different ways: In the first method,

the spectrum is expanded in an infinite series of Legendre polynomials whose coefficients are linear combinations of the moments; in the second method, which is believed to be new, polynomial approximations to a Dirac delta-function are used to give the value of the spectrum at any point as a linear combination of the moments.

We begin by considering a particular one-dimensional disordered lattice problem which can be solved exactly, namely the case in which the mass of one atomic species becomes infinite, and obtain the distribution of normal mode frequencies for this case. We then obtain spectra for the finite-mass case by the two methods mentioned above. The zero-point energy of a randomly disordered linear chain is also calculated. In an Appendix the relation between asymptotic properties of the moments and the high- and low-frequency behavior of the spectrum is discussed.

[1] Domb, Maradudin, Montroll, and Weiss, preceding paper [Phys. Rev. 115, 18 (1959)].