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Vibrational spectra of binary disordered linear chains with short-range order*

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We consider the generation of binary disordered linear chains with short-range order by using the theory of Markov processes. We generate second-order Markov chains in which specific correlations are introduced to first- and second-nearest neighbors. We find the density of vibrational states for several second-order chains in which one of the two kinds of atoms is twice as heavy as the other, but the nearest-neighbor force constants are unchanged. Properties of these spectra can be related to the chain structures, but pair correlation functions do not provide an adequate measure of structure to specify details of the spectra. We derive an expression for the integrated density of states at special frequencies for second-order chains and find that chains with quite different structures may have identical integrated spectra at all special frequencies.

I. INTRODUCTION

This paper is the first of three papers on the vibrations of a disordered harmonic linear chain. In this paper we discuss computer experiments for the vibrational density of states of chains with arbitrary concentrations of two kinds of atoms. In the second paper we present a cluster self-consistent-field theory, analogous to the coherent-potential approximation, and compare theoretical densities of states for disordered chains with those determined by computer experiments. In the third paper we discuss the localization of the eigenstates of such a disordered system.

In this paper we present the results of computer experiments for the densities of states for long (10 000 atoms) chains. The experimental method follows the pioneering work of Dean[1] and co-workers, and of Payton and Visscher.[2] The significant new aspect of our experiments for the density of states is the systematic inclusion of short-range order (Sec. II) among the constituents, by means of the theory of Markov chains. The Markov theory (Sec. III) permits the introduction of specific correlations to any number of neighbors, and provides a statistical framework for the construction and identification of "good chains." In practice, we confine our attention to first- and second-order Markov chains, in which specific correlations are introduced between, respectively, the first- and the first-two-nearest neighbors. The short-range order introduced by other authors[3] has corresponded to that of a first-order Markov chain. Although the later papers in the series will contain spectra and localization lengths for first-order chains, this paper includes spectra only for second-order chains (Sec. IV). In particular we show that two chains with identical pair correlation functions may have completely different vibrational spectra. We also derive a formula for the second-order chain to determine the exact integrated density of states to special frequencies. Here we find that second-order chains with different structure and different spectra may yet have identical integrated densities of states to the special frequencies (Sec. V).

For all our calculations we use the following model: a linear chain with equal nearest-neighbor force constants between all atoms, and arbitrary concentrations of two kinds of atoms, heavy host atoms of mass m_h and lighter atoms, which we call defects, of mass m_d. Because other authors have thoroughly investigated the effect of different mass ratios we always take $m_h/m_d = 2$. This model is the simplest possible model for a vibrating disordered system.

For the harmonic vibrations of a chain with nearest-neighbor force constants, the equation of motion governing the displacement u_l of the atom at site l with mass m_l is

$$\sum_{l'} (m_l \omega^2 \delta_{ll'} - \Phi_{ll'}) u_{l'} = 0 , \qquad (1.1)$$

where the force-constant matrix $\Phi_{ll'}$ is translationally invariant,

$$\Phi_{ll'} = \Phi_{l-l'} = \gamma(2\delta_{l,l'} - \delta_{l,l'+1} - \delta_{l,l'-1}) . \qquad (1.2)$$

II. SHORT-RANGE ORDER

Whereas most previous work on disordered systems has been for random systems, we wish to investigate the effects of short-range order among the constituents of a binary system in some detail. A study of short-range order in three dimensions usually begins with pair correlation functions such as $\rho^{d,d}_{l,l'}$, defined as the probability that, if there is a defect (d) at site l, then there is a defect at site l'. For a homogeneous system, $\rho^{d,d}_{l,l'} = \rho^{d,d}(\vec{R}_l - \vec{R}_{l'})$, where $\vec{R}_l$ is the position of atom l. Similarly one may define higher-order correlation functions such as $\rho^{d,dd}_{l,l'l''}$, the probability that if there is a defect at site l, then there are defects both at site l' and at site l''.

For real systems, the pair correlation function, for example, is

$$c_d\,\rho^{d,d}(\vec{L}) = N^{-1}\sum_{ll'}\theta^d_l\theta^d_{l'}\,\delta_{\vec{R}_l,\vec{R}_{l'}+\vec{L}}\ , \tag{2.1}$$

where c_d is the concentration of defects; $\theta^d_l = 1$ if there is a defect at site l; and $\theta^d_l = 0$ if there is a host atom at site l. The sum on l and l' runs over all the N lattice sites of a real system. Theoretically, one typically assumes that because of homogeneity, the correct pair correlation functions are equal to the ensemble average (configuration average $\langle\cdots\rangle$) of the occupancies for any two sites,

$$c_d\,\rho^{d,d}(\vec{L}) = \langle\theta^d_{\vec{R}_l}\theta^d_{\vec{R}_l+\vec{L}}\rangle\ . \tag{2.2}$$

Short-range order is said to exist if either of these expressions (2.1) or (2.2) differs from the random value of c^2_d ($\vec{L}\neq 0$), or if any other correlation function of any order differs from its random value. Furthermore, the term "short-range order" is typically reserved for situations in which long-range order, in the Bragg-Williams sense, is not present.[4]

Experimentally, short-range order may be identified by x-ray or neutron-diffraction measurements.[5] Because these scattering cross sections are analyzed in the Born approximation, in which the scattering potentials on individual sites occur only in pairs, the scattering experiments provide information only about the correlation between pairs of atoms. A convenient notation for the analysis of such experiments is provided by the Warren-Cowley[6] short-range order parameters α_L, defined by

$$\rho^{d,d}(\vec{L}) = c_d + (1 - c_d)\alpha_{\vec{L}}\ . \tag{2.3}$$

The scattered intensity then consists of the sum of a coherent scattering term, in which the Bragg peaks occur at the superlattice reflection points, with amplitude proportional to the configuration-averaged scattering length $(c_h f_h + c_d f_d) \equiv \langle f\rangle$, plus an incoherent term

$$I_{\text{inc}}(k) \sim c_d c_h(\langle f^2\rangle - \langle f\rangle^2)\alpha(k),$$
$$\alpha(k) = \sum_L \alpha_L\, e^{i\vec{k}\cdot\vec{L}}\ . \tag{2.4}$$

Because of the short-range order, the incoherent scattering is not independent of the wave vector $\vec{k}$.

It is now interesting to ask how short-range order can be included in calculations of such dynamical aspects of disordered systems as phonon or electron scattering from disorder. So long as one treats the disordered scattering only by second-order perturbation theory (adequate for x-ray or neutron scattering), the pair correlation functions provide an adequate representation of the short-range order.[7] More generally, however, one must include in some approximate way all orders of scattering, which then involve all orders of correlation functions. One may begin by writing higher-order correlation functions as simple functions of pair correlation functions. For example, Hartmann[8] considered the lattice dynamics of dilute alloys with arbitrary pair correlations among strong scatterers by writing all correlation functions as simple products of pair correlation functions. Kramer[9] has used the same approximation in his study of the optical properties of amorphous semiconductors. The inadequacy of any approach to the high-concentration strong-scattering problem which involves only pair correlation functions will be demonstrated in Sec. IV.

In order to study the effects of short-range order on lattice dynamics with computer experiments on linear chains, we need to generate chains with short-range order. To extend these experiments beyond the simple chains in which only pair correlation functions are significant, we require a systematic means of introducing short-range order into a binary chain. We therefore turn to the theory of Markov processes; the remainder of this paper is specialized to one-dimensional systems.

III. MARKOV CHAINS

The Markov theory[10] provides the mathematical foundations which allow us to specify short-range order which depends on next-nearest neighbors, as well as on nearest neighbors. Generalizations to generate chains with any number of constituents specifying short-range order among any number of neighbors are also possible.

Using Markov theory, we build a chain by starting at some point and adding atoms only to one end of the chain. This directionality is essential for constructing Markov chains, but cannot be identified once the construction is complete. A stochastic process is a Markov process if the probability that the system will be in a given state at a particular position or time x_2 can be deduced from the state of the system at a previous position or time x_1, and is independent of the state of the system before x_1. The Markov process is particularly suitable for generating a chain in which the position is associated with lattice sites, and the state is the type of atom. To specify the probability relationships, we define the unconditional probability (row) vector

$$s_j(l) \text{ for all states } j \ ,$$

and the transition probability matrix

$$J_{j,k}(l_1, l_2) \text{ for all states } j \text{ and } k$$

and $l_1 < l_2$, where

$$J_{j,k}(l_1, l_2) \geq 0 \tag{3.1}$$

and

$$\sum_k J_{j,k}(l_1, l_2) = 1 \ . \tag{3.2}$$

The elements of the unconditional probability vector are the probabilities of each of the possible states of the system at position l. The elements of the transition probability matrix are the probabilities of a transition to state k at position l_2, given that state j occurs at position l_1. For a homogeneous chain, the transition probability matrix will depend on l_2 and l_1 only through their difference, $n = l_2 - l_1$. For convenience, we call the one-step transition probability matrix $\underline{\mathrm{J}}(1) \equiv \underline{\mathrm{p}}$. The transition probability matrix satisfies the Chapman-Kolomogorov equation,

$$\underline{\mathrm{J}}(n) = \underline{\mathrm{J}}(m)\underline{\mathrm{J}}(n-m) \text{ where } m < n \ . \tag{3.3}$$

From these definitions, we see that

$$\underline{\mathrm{s}}(l) = \underline{\mathrm{s}}(0)\underline{\mathrm{J}}(l) = \underline{\mathrm{s}}(0)\underline{\mathrm{p}}^l \ . \tag{3.4}$$

We require the chain we construct to be an ergodic Markov chain. An ergodic Markov chain has three fundamental properties:

(i) The chain must be homogeneous; $\underline{\mathrm{J}}(l_1, l_2) = \underline{\mathrm{J}}(n)$, where $n \equiv l_2 - l_1$.

(ii) The chain is irreducible and all states are recurrent; that is, it is possible to make a transition from any state of the system to all states of the system. Clearly, if this were not true, some of the constituents of a chain would have a concentration tending to zero with increasing chain length.

(iii) The chain must be aperiodic; that is, there must exist a value of n such that $J_{j,k}(n) > 0$ for all states j and k. Certain periodic chains which are special limits of the aperiodic chain also satisfy the following equations.

Theorem: An ergodic Markov chain has a *unique* long-run distribution π_k where

$$\lim_{n\to\infty} J_{j,k}(n) = \pi_k \text{ with } \pi_k > 0 \ . \tag{3.5}$$

The long-run distribution of an ergodic Markov chain is the unique solution of

$$\pi_k = \sum_j \pi_j p_{j,k}, \quad \text{satisfying } \sum_k \pi_k = 1 \ . \tag{3.6}$$

Since the long-run distribution π_k is independent of the starting state, the long-run distribution is equal to the concentrations of the constituents c_k. In addition to proving the above theorem, we have proved that the converse is also true.[11]

Converse: If a Markov chain has a long-run distribution π_k with $\sum_k \pi_k = 1$, $\pi_k = \sum_j \pi_j p_{j,k}$, and $0 < \pi_k < 1$, then the chain is ergodic.

The simplest application of the above Markov theory is to a binary chain with host atoms h and defect atoms d with only nearest-neighbor correlations. The unconditional probability vector is

$$\underline{\mathrm{s}}(l) = [\, s_h(l), \, s_d(l)] \tag{3.7}$$

and the transition probability matrix is

$$\underline{\mathrm{p}} = \begin{bmatrix} p_{h,h} & p_{h,d} \\ p_{d,h} & p_{d,d} \end{bmatrix} . \tag{3.8}$$

From Eq. (3.6) we have

$$[c_h, c_d] = [c_h, c_d] \begin{bmatrix} p_{h,h} & p_{h,d} \\ p_{d,h} & p_{d,d} \end{bmatrix} , \tag{3.9}$$

where

$$c_h + c_d = 1 \ , \tag{3.10a}$$

$$p_{h,h} + p_{h,d} = 1 \ , \tag{3.10b}$$

and

$$p_{d,d} + p_{d,h} = 1 \ . \tag{3.10c}$$

It follows that

$$c_d p_{d,h} = c_h p_{h,d} \ . \tag{3.10d}$$

We are left with two independent specifications which we take to be c_d (the concentration of defects) and $p_{d,d}$ (the probability that if the present atom is a defect, the next atom will be a defect). The choice $p_{d,d} = c_d$ will generate a random chain. For a given c_d, we cannot allow all $0 < p_{d,d} \leq 1$. Demanding that $0 \leq p_{h,d} \leq 1$, we see that $(2 - 1/c_d) < p_{d,d} < 1$. By induction, we can show that the n-step transition probability matrix is

$$\underline{\mathrm{J}}(n) = \underline{\mathrm{p}}^n = \begin{bmatrix} (1-c_d) & c_d \\ (1-c_d) & c_d \end{bmatrix} + \left(\frac{p_{d,d} - c_d}{1 - c_d} \right)^n \begin{bmatrix} c_d & -c_d \\ (c_d - 1) & (1 - c_d) \end{bmatrix} . \tag{3.11}$$

We call a Markov chain generated by nearest-neighbor correlations a first-order Markov chain. We can now find all pair correlation functions for the binary ergodic first-order Markov chain. In general we find that

$$\rho^{i,j}(n) = J_{i,j}(|n|) \ . \tag{3.12}$$

It is this convenient property of first-order Markov chains which has allowed previous authors to generate correct chains with short-range order nonrigorously, by using the $\rho^{i,j}$. We demonstrate

Eq. (3.12) for the particular case of $\rho^{d,d}(n)$, the conditional probability of having a defect $|n|$ sites away from another defect. The initial unconditional probability vector would be

$$\underline{s}(l)=[0,1]$$

and

$$\rho^{dd}_{l,l'}=\rho^{d,d}(n)\equiv s_d(|n|)=s(0)\,p^{|n|}\,|_d=J_{d,d}(|n|)$$

$$=c_d+(1-c_d)\left(\frac{p_{d,d}-c_d}{1-c_d}\right)^{|n|}$$

or

$$\rho^{d,d}(n)=c_d+(1-c_d)\alpha_n=c_d+(1-c_d)\alpha_1^{|n|}\ , \qquad (3.13)$$

where $n=l'-l$. The Fourier transform of the short-range order parameter can be found analytically to be

$$\alpha(k)=\frac{1-\alpha_1^2}{1-2\alpha_1\cos(ka)+\alpha_1^2}\ , \qquad (3.14)$$

where a is the lattice parameter. $\alpha(k)$ has a peak at $k=0$ for $\alpha_1>0$ (clustering), and a peak at $k=\pi/a$ for $\alpha_1<0$ (anticlustering).

Previous computer experiments on the effects of short-range order on dynamical properties have corresponded to such a first-order Markov chain. Yet the short-range order introduced by a first-order chain is rather special. Not only are all pair correlation functions strictly determined by a single nearest-neighbor pair correlation parameter $p_{d,d}$, but any correlation function of arbitrary order is strictly determined by the pair correlation functions, as we now demonstrate. First we note that we can express all higher-order correlation functions in terms of the set of ordered unconditional correlation functions, defined as

$$c_i\,\rho^{i,jk\cdots st}_{l_1,l_2l_3\cdots l_{n-1}l_n}\,,$$

where $i,\ j,\ k\cdots s, t$ can be h or d, $l_1<l_2\cdots<l_{n-1}<l_n$, and we associate i with l_1, j with l_2, etc. An arbitrary correlation function can be written in the ordered form because

$$c_i\,\rho^{i,\cdots j\cdots k\cdots t}_{l_1,\cdots l_m\cdots l_p,\cdots l_n}=c_i\,\rho^{i,\cdots k\cdots j\cdots t}_{l_1,\cdots l_p,\cdots l_m\cdots l_n}$$

and

$$c_i\,\rho^{i,\cdots j\cdots t}_{l_1,\cdots l_m\cdots l_n}=c_j\,\rho^{j,\cdots i\cdots t}_{l_m,\cdots l_1\cdots l_n}\ .$$

However, because of the first-order property, every ordered unconditional higher-order correlation function can be expressed as an ordered product of pair correlation functions, i.e.,

$$c_i\,\rho^{i,jk\cdots st}_{l_1,l_2l_3\cdots l_{n-1}l_n}$$

$$=c_i\,\rho^{i,j}_{l_1,l_2}\,\rho^{j,k}_{l_2,l_3}\cdots\rho^{s,t}_{l_{n-1},l_n}\ . \qquad (3.15)$$

Note that although the approximation of Ref. 8 is one in which a higher-order correlation function is given as a single product of pair correlation functions, the approximation is still not correct for a first-order Markov chain because the correlation functions are not properly ordered in the approximation. Consider, for example, the correlation function $\rho^{d,dd}_{0,91}$. The approximation of Ref. 8 sets this equal to $\rho^{d,d}_{0,9}\rho^{d,d}_{9,1}$, greatly different from the first-order Markov value $\rho^{d,d}_{0,1}\rho^{d,d}_{1,9}$.

Because the first-order Markov process generates such a special sort of short-range order, we think it worthwhile to consider chains in which correlations are specifically introduced between an atom and both its first and second neighbors. We call such a chain a second-order Markov chain. For the second-order chain, the transition probabilities are of the form $p_{ij,k}$, which we define as the probability of a transition from a two-atom state ij to a state k. Since we are going from a state with two atoms to a state with one atom, the second-order chain as stated cannot be a Markov chain in the strict sense. We can make it a Markov chain by the following transformation:

$$p_{ij,k}=p_{ij,jk}\ \text{and}\ p_{ij,rk}=0\ \text{for}\ r\neq j\ . \qquad (3.16)$$

For the binary chain we now have four states instead of two. The preceding theorem gives [Eq. (3.6)]

$$[c_{hh},c_{hd},c_{dh},c_{dd}]=[c_{hh},c_{hd},c_{dh},c_{dd}]\begin{bmatrix} p_{hh,h} & p_{hh,d} & 0 & 0\\ 0 & 0 & p_{hd,h} & p_{hd,d}\\ p_{dh,h} & p_{dh,d} & 0 & 0\\ 0 & 0 & p_{dd,h} & p_{dd,d}\end{bmatrix}, \qquad (3.17)$$

and $p_{hh,h}+p_{hh,d}=1$, $p_{hd,h}+p_{hd,d}=1$, $p_{dh,d}+p_{dh,h}=1$, $p_{dd,d}+p_{dd,h}=1$, and $c_{dd}+c_{dh}+c_{hd}+c_{hh}=1$. We can relate these pair concentrations to the constituent concentrations by $c_d+c_h=1$ and $c_d=c_{dd}+\frac{1}{2}(c_{hd}+c_{dh})$. From Eq. (3.17) we can easily prove the chain reversibility condition $c_{dh}=c_{hd}$.

For this system, we have four independent parameters which we take to be c_d, $p_{dd,d}$, $p_{dh,d}$, and $p_{hd,d}$. Taking $p_{dd,d}=p_{hd,d}$ and $p_{dh,d}=c_d(1-p_{dd,d})/(1-c_d)$ generates a first-order Markov chain. For a given c_d, the three independent probabilities cannot take on arbitrary values in the unit interval;

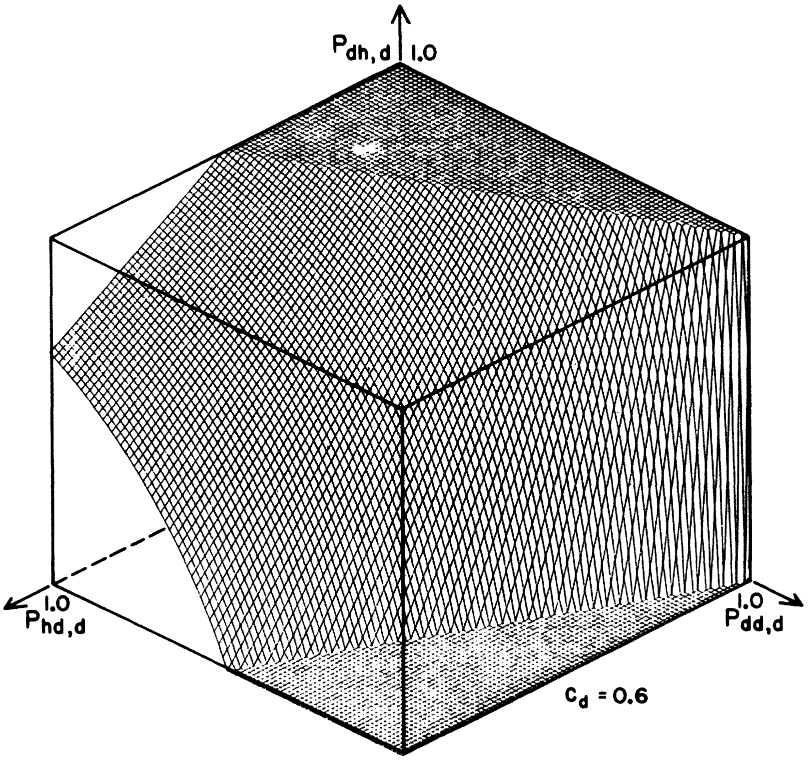

FIG. 1. Allowed values of the three independent parameters for a second-order two-constituent Markov chain occur in the volume of the unit cube which is above and in front of the surface shown for a defect concentration $c_d = 0.6$.

only for $c_d < \frac{1}{3}$ are they unrestricted. Figure 1 shows the allowed values of the probabilities for $c_d = 0.6$. Only the volume above and in front of the surface is allowed.

The pair correlation functions can now be computed for the second-order Markov chain. For example, for $\rho^{d,d}(n)$, the initial unconditional probability vector is

$$\underline{s}(0) = [0, c_{hd}, 0, c_{dd}]/c_d$$

and the pair correlation function is

$$\begin{aligned}\rho^{d,d}(n) &= s_{dd}(|n|) + s_{hd}(|n|)\\ &= c_{hd}[J_{hd,hd}(|n|) + J_{hd,dd}(|n|)]/c_d\\ &\quad + c_{dd}[J_{dd,hd}(|n|) + J_{dd,dd}(|n|)]/c_d\ . \qquad (3.18)\end{aligned}$$

Higher-order correlation functions for the second-order Markov chain are easy to describe but often quite difficult to calculate. For example, $\rho^{d,hd}_{l_1,l_2 l_3}$, where $l_1 < l_2 < l_3$, can be found by starting with $\vec{s}(l_1) = [0, c_{hd}, 0, c_{dd}]/c_d$. Then, for the complete probability vector at site l_2, for a defect at site l_1, we have $\vec{s}(l_2) = \vec{s}(l_1)\vec{J}(l_2 - l_1)$. The probability that there is both a host atom at site l_2 and a defect on site l_3 can be found by making the transition to $\vec{s}(l_3)$ from a restricted vector $\vec{s}\,'(l_2)$,

$$\vec{s}\,'(l_2) = [s_{hh}(l_2), 0, s_{dh}(l_2), 0]\ .$$

Then by calculating

$$\vec{s}\,'(l_3) = \vec{s}\,'(l_2)\vec{J}(l_3 - l_2)$$

we can find

$$\rho^{d,hd}_{l_1,l_2 l_3} = s'_{hd}(l_3) + s'_{dd}(l_3)\ ,$$

because the transition to site l_3 from vectors with defect atoms at l_2 has been excluded by setting $s'_{hd}(l_2)$ and $s'_{dd}(l_2)$ equal to zero.

We will examine two particularly interesting second-order Markov chains.

Case 1: $p_{dd,d} = p_{dh,d}$ and $p_{hh,d} = p_{hd,d}$. Therefore, it follows that

$$c_d(1 - p_{dd,d})/(1 - c_d) = p_{hd,d}\ . \qquad (3.19)$$

For this case, the short-range order parameter is

$$\alpha_{2l} = \left(\frac{p_{dd,d} - c_d}{1 - c_d}\right)^{|l|} \text{ and } \alpha_{2l+1} = 0\ . \qquad (3.20)$$

The Fourier transform of the short-range order parameter is

$$\alpha(k) = \frac{1 - \alpha_2^2}{1 - 2\alpha_2\cos(2ka) + \alpha_2^2}\ .$$

For $\alpha_2 > 0$, $\alpha(ak)$ is symmetric about $\frac{1}{2}\pi$, with peaks at 0 and π. For $\alpha_2 < 0$, $\alpha(ak)$ is symmetric about $\frac{1}{2}\pi$ with the peak occurring at $\frac{1}{2}\pi$.

For this type of order the transition probability matrix elements indicate that a given atom is not correlated with its nearest neighbors, but is correlated only with every second atom, counting from the given atom. The resulting chain looks like two mutually independent interpenetrating correlated chains.

Case 2:

$$p_{dd,d} = p_{hh,d}$$

and

$$p_{hd,d} = p_{dh,d} = 1 - p_{dd,d} \; . \qquad (3.21)$$

The relationships of this case can only hold if $c_d = 0.5$. The short-range order parameter is

$$\begin{aligned} \alpha_{3l} &= (1 - 2p_{dd,d})^{2|l|} , \\ \alpha_{3l+1} &= 0 , \qquad (3.22) \\ \alpha_{3l+2} &= 0 , \end{aligned}$$

and its Fourier transform is

$$\alpha(k) = \frac{1 - \alpha_3^2}{1 - 2\alpha_3 \cos(3ka) + \alpha_3^2} \; . \qquad (3.23)$$

The short-range order parameter is always greater than, or equal to, zero, and $p_{dd,d} = u$ and $p_{dd,d} = 1 - u$ give identical pair correlation functions, but quite different triple correlation functions. Also, $\alpha(ak)$ always displays a peak at 0 and $\frac{2}{3}\pi$.

IV. EXPERIMENTAL SPECTRA OF CHAINS

In this section we describe vibrational spectra determined by computer experiments on finite chains with various types of short-range order. The densities of states $D(\omega^2)$ which we present are all normalized to 1, i.e.,

$$\int_0^\infty D(\omega^2)\, d\omega^2 = 1 \; . \qquad (4.1)$$

The computation is begun by generating a chain of host and defect atoms with a random-number generator biased by the defect concentration and by the first- or second-order Markov transition probabilities discussed in Sec. III. An error analysis for these chains is discussed in Appendix A. Our chain has fixed boundary conditions. Although the boundary conditions have an effect on the eigenvectors of the vibrational states, as discussed in the third paper of this series, the boundary conditions have a negligible effect on the density of states. As noted by Maradudin *et al.*,[12] Ledermann's theorem guarantees that the various boundary conditions (periodic, fixed, free, or mixed) will not change the spectral distribution of modes in any frequency interval by more than four modes for a linear chain.

We find the vibrational density of states of these chains by the Sturm sequence method. Rosenstock and McGill[13] have shown that for a given value of ω^2, the u_l's in the equation of motion, Eqs. (1.1) and (1.2),

$$u_{l+1} = (2 - m_l \omega^2/\gamma)\, u_l - u_{l-1}$$

$(u_0 = 0,\ u_1 = 1)$ form a Sturm sequence. The number of sign changes for consecutive u_l is the number of

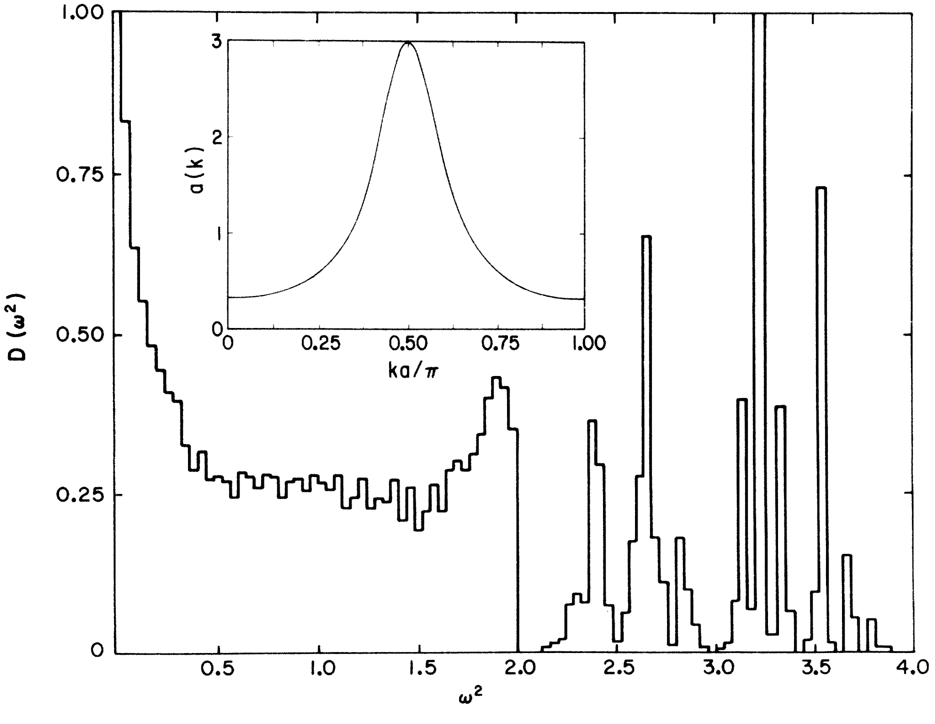

FIG. 2. Vibrational spectrum of a second-order chain of 10 000 atoms, with $m_h/m_d = 2$, with $c_d = 0.5$, and the short-range order of *case* 1 with $p_{dd,d} = p_{dh,d} = 0.25$, and $p_{hd,d} = 0.75$. The Fourier transform of the short-range order parameter is shown in the inset.

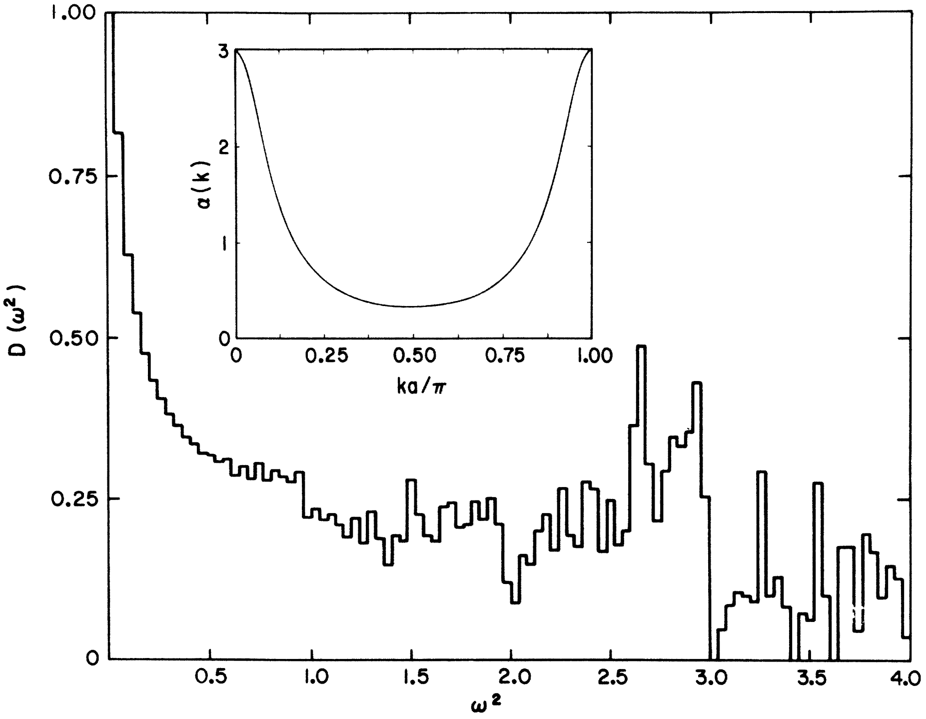

FIG. 3. Vibrational spectrum of a second-order Markov chain of 10 000 atoms with $m_h/m_d = 2$, with $c_d = 0.5$, and the short-range order of *case* 1 with $p_{dd,d} = p_{dh,d} = 0.75$ and $p_{hd,d} = 0.25$. The Fourier transform of the short-range order parameter is shown in the inset.

eigenvalues strictly less than ω^2. By counting sign changes we get an integrated density of states from which a histogram for the density of states may be derived with no loss of precision.

Figures 2 and 3 are second-order Markov chain spectra for *case* 1, $c_d = 0.5$, with $N = 10\,000$ atoms and $p_{dd,d} = 0.25$ and 0.75, respectively. The Fourier transform of the short-range order parameter is shown in the inserts for each case. The spectrum for $p_{dd,d} = 0.25$ is not radically different from that for a random chain. The major effects are a reduction in the spectrum at the single-defect mode frequency ($\omega^2 = 2.66$), because $p_{hd,h} = 0.25$; and a corresponding increase in the nearest-neighbor-pair defect mode strength ($\omega^2 = 3.24$), because $p_{hd,d} = 0.75$. The spectrum for $p_{dd,d} = 0.75$ is, however, quite different. The host band edge at $\omega^2 = 2$ is not visible. Since $p_{dh,d} = p_{hd,h} = 0.75$, the chain has a structure rather like the ordered binary alternating chain (with $p_{dh,d} = p_{hd,h} = 1$), but because $p_{dd,d} = p_{hh,h} = 0.75$, this structure includes some long clusters of similar atoms.

Figures 4 and 5, with $c_d = 0.5$ and $N = 10\,000$, are for *case* 2 with $p_{dd,d} = 0.25$ and 0.75, respectively. These two figures show quite different density-of-states plots, but identical pair correlation functions. The major difference between the two chains is that isolated defects are more probable for $p_{dd,d} = 0.75$, and nearest-neighbor defect pairs are considerably more probable for $p_{dd,d} = 0.25$. Figure 6 shows the density of states for $c_d = 0.2$, $p_{dd,d} = 0$, $p_{dh,d} = 0.4$, and $p_{hd,d} = 0.8$, along with the Fourier transform of the short-range order parameter in the insert. The structure of this chain is one in which there will be no defect clusters longer than 2 atoms ($p_{dd,d} = 0$), with defects generally coming in pairs ($p_{hd,d} = 0.8$) or separated by a single host ($p_{dh,d} = 0.4$), and with few isolated defects. The density of states shows the large defect-pair peak $\omega^2 = 3.26$, with a small single-defect peak $\omega^2 = 2.66$. The short-range order parameter shows a local maximum between $0 < k < \pi/a$.

V. INTEGRATED DENSITY OF STATES

Matsuda[14] proved that there are special frequencies at which the density of states of a binary disordered chain is zero, so long as the ratio of the two masses exceeds a certain value. These special frequencies are given by

$$\omega^2(s, t) = \omega^2_{\max} \cos^2(\pi s/2t) \tag{5.1}$$

where $\omega^2_{\max}$ is the maximum frequency of a perfect chain of light atoms (in our case, $\omega^2_{\max} = 4$), and s and t are integers prime to each other. The integers s and t must satisfy the condition[15]

$$m_h/m_d \geq 1 + \cot(\pi/2t)\tan(s\pi/2t) \,. \tag{5.2}$$

For a mass ratio $m_h/m_d = 2$, only $s = 1$ is allowed.

Matsuda and Teramoto[16] generalized a result of Borland[17] to find the integrated density of states to

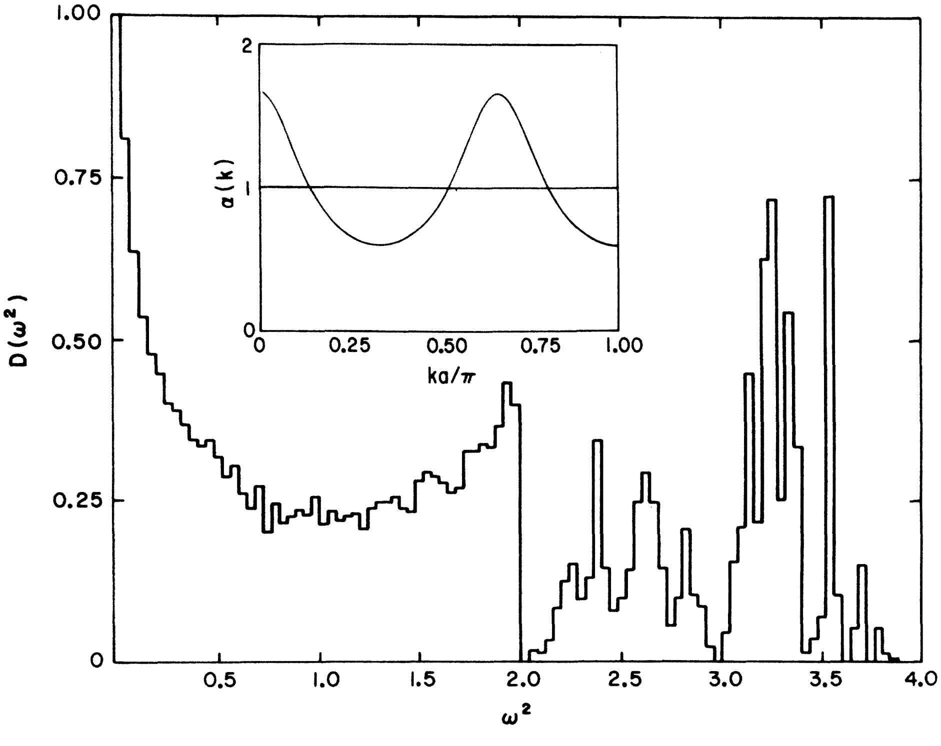

FIG. 4. Vibrational spectrum of a second-order Markov chain of 10 000 atoms with $m_h/m_d=2$ and the short-range order of *case* 2 with $c_d=0.5$, $p_{dd,d}=0.25$, and $p_{dh,d}=p_{hd,d}=0.75$. The Fourier transform of the short-range order parameter is shown in the inset, and is identical with that of Fig. 5.

these special frequencies, and they presented a specific formula for a first-order Markov chain. In this section we find a similar formula for a second-order Markov chain.

The integrated density of states to special frequencies is found by first noting that, since the normal mode frequencies are smooth monotone functions of the heavy host mass m_h, no modes

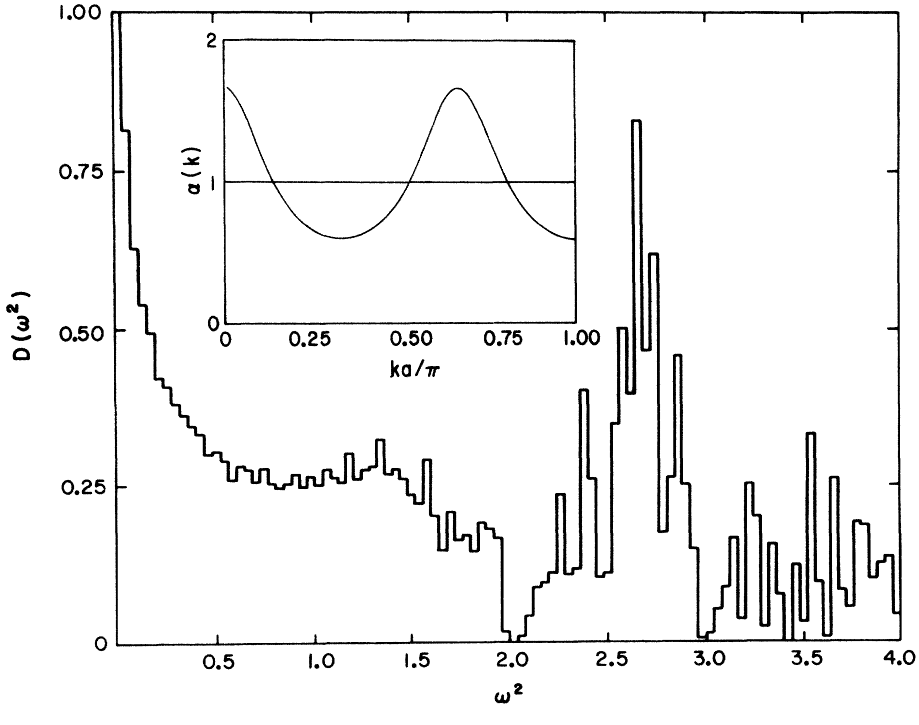

FIG. 5. Vibrational spectrum of a second-order Markov chain of 10 000 atoms with $m_h/m_d=2$, and the short-range order of *case* 2 with $c_d=0.5$, $p_{dd,d}=0.75$, and $p_{dh,d}=p_{hd,d}=0.25$. The Fourier transform of the short-range order parameter is shown in the inset, and is identical with that of Fig. 4.

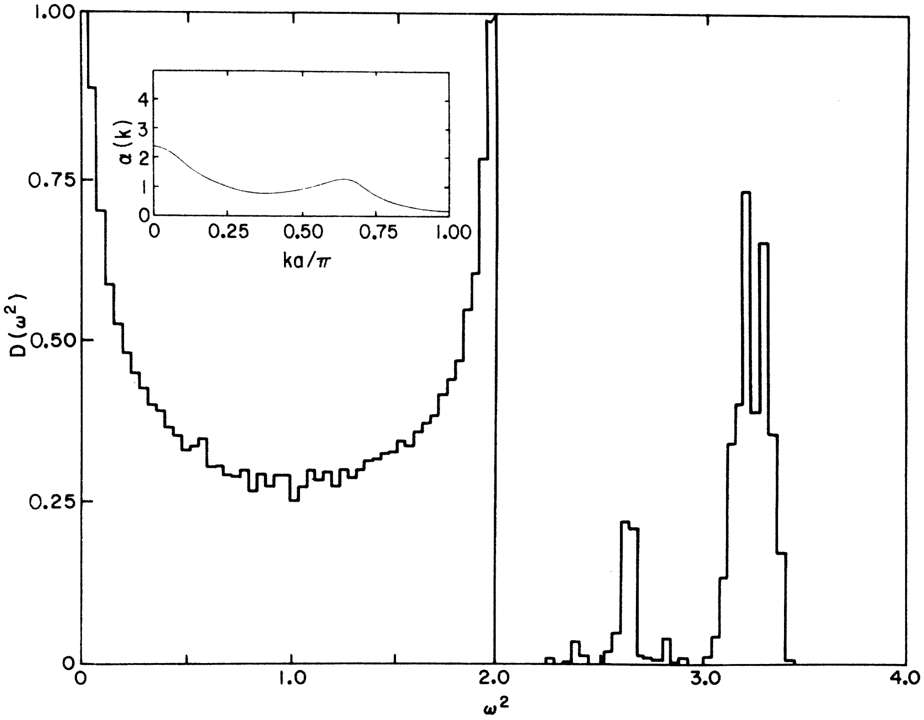

FIG. 6. Vibrational spectrum of a second-order Markov chain of 10 000 atoms with $m_h/m_d=2$, $c_d=0.2$, $p_{dd,d}=0$, $p_{hd,d}=0.8$, and $p_{dh,d}=0.4$.

will cross a gap at a special frequency if m_h is increased. In the limit $m_h\rightarrow\infty$, the chain becomes a series of light defect chain segments with fixed boundary conditions. For such a chain, the integrated density of states $\overline{D}(s,t)$ to special frequencies $\omega^2(s,t)$ can be calculated and, by the preceding argument, it must be equal to the integrated density of states, for the same s and t values, for the original disordered chain. Matsuda and Teramoto find

$$\overline{D}(s,t)=1-\frac{\sum_{J=0}^{\infty}I(s(J+1)/t)P(J)}{\sum_{J=0}^{\infty}(J+1)P(J)}, \tag{5.3}$$

where $P(J)$ is the probability that a chain segment of J atoms contains only light defect atoms. The function $I(x)$ is equal to the largest integer not greater than x. For a first-order Markov chain

$$\overline{D}(1,t)=1-c_d(1-p_{d,d})p_{d,d}^{t-2}/(1-p_{d,d}^{t})\ . \tag{5.4}$$

We may find the values of $P(J)$ for a second-order Markov chain from the correlation functions of Sec. III. With the simplified notation

$$p_{dd,d}\equiv u,\quad p_{dh,d}\equiv v,\quad p_{hd,d}\equiv w\ , \tag{5.5}$$

we find

$$\begin{aligned}c_h P(0)&=c_{hh}=1-c_d[w+2(1-u)]/(1+w-u),\\ c_h P(1)&=c_{hd}p_{hd,h}\\ &=c_d(1-u)(1-w)/(1+w-u),\\ c_h P(J)&=c_{hd}p_{hd,d}(p_{dd,d})^{J-2}p_{dd,h}\\ &=c_d(1-u)^2wu^{J-2}/(1+w-u),\quad (J>1)\ .\end{aligned} \tag{5.6}$$

The denominator of Eq. (5.3) is the mean length of a defect string, and is equal to $(1-c_d)^{-1}$, independent of short-range order. We evaluate the numerator by rewriting it, for $s=1$, as

$$\sum_{r=0}^{\infty}r[P(tr-1)+P(tr)+\cdots P(tr+t-2)]\ .$$

Summing this series, and treating the case $t=2$ separately, we find in general

$$\overline{D}(1,t)=1-\frac{c_d(1-u)u^{t-3}}{(1+w-u)(1-u^t)}\times[w+\delta_{t,2}(1-u^2)(u-w)]\ . \tag{5.7}$$

Because we have taken $s=1$, Eq. (5.7) is valid only for $m_h/m_d\leq 3$. For a second-order Markov chain which is equivalent to a first-order chain, the parameters u and w are equal. In that case Eq. (5.7) reduces to the Matsuda-Teramoto result of Eq. (5.4).

An interesting point to note is that whereas the structure of a second-order Markov chain is determined by four parameters, c_d, u, v, and w, the integrated density of states to special frequencies depends upon only c_d, u, and w. Because the probabilities $P(J)$ are independent of v, the integrated density of states $\overline{D}(s,t)$ is independent of

$p_{dh,d}$ for any ratio m_h/m_d. Therefore, chains with quite different structure and quite different spectra have the same values of the $\overline{D}(s,t)$ for all s and t.

In Table I we compare the predictions of the analytic expression Eq. (5.7) with numerical results from the computer experiments on the 10 000-atom chains of Figs. 2 and 4. The values of the special frequencies $\omega^2(1,t)$ are functions only of m_h/m_d, and are the same for all chains considered in this paper. In Fig. 2, the first five gaps can be clearly seen in the histogram. In Table II we compare the predictions of Eq. (5.7) with numerical results from the computer experiments on the 10 000-atom chains of Figs. 3 and 5. Both tables illustrate the lack of dependence of $\overline{D}(s,t)$ on the structure parameter $p_{dh,d}$. Although the spectra of all four chains are clearly quite different, the numerical values of $\overline{D}(1,t)$ for the chains compared are equal to within the experimental accuracy.

TABLE I. Integrated densities of states to special frequencies $\omega^2(1,t)$. For the chain of Fig. 2, $m_h/m_d=2$, $c_d=0.5$, $p_{dd,d}=p_{dh,d}=0.25$, $p_{hd,d}=0.75$; and for the chain of Fig. 4, $m_h/m_d=2$, $c_d=0.5$, $p_{dd,d}=0.25$, $p_{dh,d}=p_{hd,d}=0.75$. The analytic result is determined from Eq. (5.7) and the numerical results are determined by the computer experiments on 10 000-atom chains. To within experimental error, the three values of $\overline{D}(1,t)$ in each row are equal.

			$\overline{D}(1,t)$	
t	$\omega^2(1,t)$	Analytic	Numerical (Fig. 2)	Numerical (Fig. 4)
2	2.000	0.700 00	0.6980	0.6913
3	3.000	0.809 52	0.8114	0.8096
4	3.414	0.952 94	0.9545	0.9517
5	3.618	0.988 27	0.9890	0.9890
6	3.732	0.997 07	0.9973	0.9971
7	3.802	⋯	⋯	⋯

TABLE II. Integrated densities of states to special frequencies. For the chain of Fig. 3, $m_h/m_d=2$, $c_d=0.5$ $p_{dd,d}=p_{dh,d}=0.75$, $p_{hd,d}=0.25$; and for the chain of Fig. 5, $m_h/m_d=2$, $c_d=0.5$, $p_{dd,d}=0.75$, $p_{dh,d}=p_{hd,d}=0.25$. The analytic result is determined from Eq. (5.7), and the numerical results are determined by computer experiments on 10 000-atom chains. To within experimental error, the three numbers in each row are equal.

		$D(1,t)$	
t	(Analytic)	Numerical (Fig. 3)	Numerical (Fig. 5)
2	0.642 86	0.6382	0.6421
3	0.891 89	0.8912	0.8875
4	0.931 43	0.9327	0.9295
5	0.953 91	0.9531	0.9530
6	0.967 92	0.9691	0.9689
7	0.977 18	0.9770	0.9765

VI. CONCLUSION

We have shown how general short-range order may be systematically included in a disordered chain by means of Markov theory. Physically reasonable chains are required to be ergodic Markov chains, and this requirement leads to the conditions for the Markov transition probabilities $p_{j,k}$. The most significant condition is Eq. (3.6)

$$c_k=\sum_j c_j p_{j,k},$$

where j and k are states of the chain. These states may be single-site occupancies, or pair occupancies, etc. We showed how the Markov transition probabilities can be related to pair and higher-order correlation functions, but we found that simple closed-form expressions could be obtained only for the pair correlation functions. We examined the density of vibrational states for several second-order Markov chains, and showed that features of these spectra can be related to the probabilities of various atomic clusters as determined by the short-range order parameters. We noted that pair correlation functions do not provide an adequate measure of short-range order to determine the spectra, except for first-order Markov chains, for which all possible correlation functions are completely determined by only two parameters. This unsurprising observation casts some doubt on the validity of strong-scattering theories in which short-range order is included only by means of pair correlation functions.[18] However, higher-order correlation functions can be included in self-consistent theories for strong-scattering systems which we discuss in the second paper of this series.

APPENDIX A: CHAIN STATISTICS

For the first-order two-constituent Markov chain, a simple error analysis can be performed to indicate the likelihood that the actual correlations in a finite chain of N atoms will equal those of the corresponding infinite chain. The pair correlation function $\rho^{i,j}(n)=J_{i,j}(|n|)$ is a binomial statistic with a mean number of occurances of constituents i and j separated by $n-1$ sites given by

$$\mu=NJ_{i,j}(|n|) \tag{A1}$$

and a variance of

$$\sigma^2=NJ_{i,j}(|n|)[1-J_{i,j}(|n|)], \tag{A2}$$

where N is the chain length. For a confidence level C, expressed as a certain number of standard deviations $C=a\sigma$, the maximum relative error is

$$E_r = \frac{(\mu + C) - \mu}{\mu} = a[N^{-1} J^{-1}_{i,j}(|n|)]^{1/2} . \qquad \text{(A3)}$$

From this expression we can determine the correctness of a finite chain. For example, for $c_d = 0.5$ and $p_{d,d} = 0.1$, we note that since $p_{d,d} < c_d$, the smallest $J_{d,d}$ and largest relative errors occur for the smallest values of n. Table III gives the exact values of $J_{d,d}(|n|)$ as well as the observed values for specific chains of 10 000 and 100 000 atoms. The errors in the statistical relationships are quite small in each case.

Solving Eq. (A3) for N, we can calculate the chain length required in the above example to be 99% confident of generating a chain with no relative error greater than 1%. Then $a = 2.58$, and the chain length is 600 000 atoms. The $c_d = 0.5$ random chain will always give the best over-all relative errors for any given chain length.

APPENDIX B: SECOND-ORDER THREE-CONSTITUENT MARKOV CHAIN

We briefly examine the second-order three-constituent Markov chain to show how it can be reduced to a first-order saltlike chain. Generally, the transition probability matrix is $3^2 \times 3^2$ with 81 elements, of which 27 can be nonzero. The governing equations for the ergodic chain are

$$\sum_{i,j=1,2,3} c_{ij} = 1 , \qquad \text{(B1)}$$

$$\sum_j c_{ji} p_{ji,k} = c_{ik} , \qquad \text{(B2)}$$

$$\sum_k p_{ij,k} = 1 , \qquad \text{(B3)}$$

and

$$\begin{aligned} c_1 &= c_{11} + \tfrac{1}{2}(c_{12} + c_{21} + c_{31} + c_{13}) , \\ c_2 &= c_{22} + \tfrac{1}{2}(c_{12} + c_{21} + c_{32} + c_{23}) , \\ c_1 &+ c_2 + c_3 = 1 , \end{aligned} \qquad \text{(B4)}$$

where i, j, and k indicate the states, or atom types, ($\{i, j, k\} = \{1, 2, 3\}$), and c_{ji} is the pair concentration.

We now examine the special case in which nearest-neighbor atoms may not be of the same type. Then

$$c_{ii} = 0 ; \quad p_{ij,j} = 0 . \qquad \text{(B5)}$$

This condition reduces the number of equations, and reduces the number of variables from 39 to 21. For example, Eq. (B2) reduces to

$$\begin{aligned} c_{12} p_{12,1} + c_{32} p_{32,1} &= c_{21} , \\ c_{13} p_{13,1} + c_{23} p_{23,1} &= c_{31} , \\ c_{21} p_{21,2} + c_{31} p_{31,2} &= c_{12} . \end{aligned} \qquad \text{(B6)}$$

For this case, we also find that $p_{13,1}$ and $p_{21,2}$ are proportional to $p_{23,1}$ and $p_{31,2}$, respectively, giving a total of 15 equations among 21 unknowns, leaving six parameters to specify the chain, c_1, c_2, $p_{12,1}$, $p_{32,1}$, $p_{13,1}$, and $p_{21,2}$.

For the further special case in which atoms 2 and 3 cannot be nearest neighbors, we have a saltlike chain $1\, 2_{1-x}\, 3_x$, in which one of two sublattices contains only atoms of type 1, and the other sublattice is occupied only by atoms of types 2 and 3. Then $c_1 = 0.5$, and the set of equations is reduced to 11 equations, 7 of which are trivial, in 13 unknowns. We then have

$$\begin{aligned} c_2 + c_3 &= 0.5 , \\ p_{21,2} + p_{21,3} &= 1 , \\ p_{31,2} + p_{31,3} &= 1 , \\ c_2 p_{21,3} &= c_3 p_{31,2} , \end{aligned} \qquad \text{(B7)}$$

four equations in six unknowns, leaving two parameters to be specified. We can now show that, for the special case of a saltlike chain, the second-order Markov chain on an atomic basis can be reduced to a first-order Markov chain on a diatomic basis. Let the two states of the diatomic molecular chain be the ordered pairs (21) and (31). We may write the first-order transition probabilities for the molecular chain in terms of second-order atomic transition probabilities, in general

TABLE III. Exact correlation $J_{d,d}(|n|)$ for an infinite first-order Markov chain with $c_d = 0.5$ and $p_{d,d} = 0.1$, compared to the numerically determined values for these correlations $\rho^{d,d}(n)$ for such chains of 10 000 and 100 000 atoms. The experimental relative errors (expt.) are compared with the maximum relative error acceptable at the 99% confidence limit (acc.) determined from Eq. (A3).

		100 000 atoms			10 000 atoms		
n	$J_{d,d}(n)$	$\rho^{d,d}(n)$	Er(acc.)	Er(expt.)	$\rho^{d,d}(n)$	Er (acc.)	Er(expt.)
1	0.100 00	0.098 18	0.0245	0.0182	0.101 12	0.0774	0.0112
2	0.820 00	0.822 78	0.0038	0.0034	0.814 18	0.0121	0.0071
3	0.244 00	0.241 44	0.0144	0.0105	0.249 55	0.0454	0.0227
4	0.704 80	0.707 87	0.0053	0.0044	0.696 78	0.0167	0.0114
5	0.336 16	0.333 37	0.0115	0.0083	0.344 15	0.0366	0.0238

$$p_{(i1),(j1)} = p_{j1,i}\, p_{1i,1}\,, \tag{B8}$$

where i and j can be 2 or 3. But for the saltlike chain, $p_{1i,1} = 1$ and

$$p_{(i1),(j1)} = p_{j1,i}\,. \tag{B9}$$

Now we substitute Eq. (B9) into the last three equations of (B7). If we let h stand for molecule (21), and d stand for molecule (31), then $c_h = 2c_2$ and $c_d = 2c_3$; and Eq. (B7) becomes identical with the four equations (3.10) for the first-order Markov chain.

APPENDIX C: CORRESPONDENCE WITH THE ONE-ELECTRON PROBLEM

It is interesting to compare the equation of motion, Eq. (1.1) with diagonal disorder, to the one-band Anderson model[19] frequently used in the study of the one-electron properties of disordered systems,[20]

$$\sum_{l'} [(\epsilon_l - \epsilon)\delta_{ll'} - t_{ll'}]\, a_{l'} = 0\,, \tag{C1}$$

where a_l is the amplitude of the one-electron wave function on site l with a local energy ϵ_l and transfer matrix element $t_{ll'}$, usually considered to be translationally invariant. The lattice-dynamics problem and the electron problem, each with diagonal disorder, are similar, and similar Green's-function methods may be used for approximate solutions of both. But because the disordered variable in the lattice-dynamics equation of motion, $m_l\omega^2$, involves the eigenvalues, the two problems are not identical. We may recast the equation of motion [Eq. (1.1)] into the form of Eq. (C1) with the substitutions

$$\epsilon = \omega^2\,,$$

$$a_l = \sqrt{m_l}\, u_l\,,$$

$$\epsilon_l = 2\gamma/m_l\,,$$

$$t_{ll'} = \tfrac{1}{2}(\epsilon_l \epsilon_{l'})^{1/2}(\delta_{l,l'+1} + \delta_{l,l'-1})\,. \tag{C2}$$

Therefore, the lattice-dynamics equation of motion with diagonal disorder corresponds to the one-band Anderson equation with a very particular sort of off-diagonal disorder. The transfer matrix elements are related to the diagonal energies, and for atoms of types h and d,

$$t_{hd} = t_{dh} = (t_{hh}\, t_{dd})^{1/2}\,. \tag{C3}$$

Equation (C3) is a common approximation in the treatment of off-diagonal disorder.[21] In the simplest treatments of overlap effects, it is assumed that the localized states $|l\rangle$ are both solutions of an atomic Hamiltonian, and are orthogonal on different sites. These mutually exclusive simplifications can be retained in the disordered problem, while leaving the Hamiltonian Hermitian, by writing the hopping terms $l \neq l'$ as $\langle l | p^2/2m | l' \rangle$. Let us assume that Gaussian wave functions will characterize the essential decay of $\langle r | l \rangle$ with decay length (l_h or l_d). Let us also assume that the overlap terms are small compared to the diagonal terms, i.e., the narrow-band limit. Then in one dimension, if the decay lengths differ greatly, then t_{hd} is dominated by the slower decay, as is the arithmetic mean $\frac{1}{2}(t_{hh} + t_{dd})$. The geometric mean, however, is dominated by the faster decay. If the decay lengths differ only slightly, $|l_h^{-2} - l_d^{-2}| \equiv \delta \ll a^{-2}$, where a is the interatomic separation, then the relative error in the arithmetic mean is $O(\delta a^2)$, but the relative error in the geometric mean is only $O(\delta^2 a^2 l_h^2)$. Therefore, as a simple approximation to t_{hd}, we expect the arithmetic mean to be better for gross disorder, and the geometric mean to be better for weak disorder.

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