Numerical studies of the harmonic modes of a disordered zigzag chain

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We describe the results of a simulation of a model of a random chain embedded as a self-avoiding walk on a diamond lattice. The dynamic model is the same as that of Kirkwood. The equation-of-motion method that we use permits such functions as $S(k,\omega)$ the dynamic structure factor, to be calculated as easily as the density of states. We describe the method in some detail and present results on the density of states and $S(k,\omega)$ for chains of 1000 monomers. The results show that a depression appears in the density of states around $\omega=0$ when the chain is disordered. We discuss the possible origin of this hole and its possible significance for studies of polymer conformation.

I. INTRODUCTION

Many people have simulated the harmonic behavior of polymers including particularly the work of Zerbi and his group. In the present paper we introduce a new numerical method for use in such studies. While the advantages of this method are not great for studying the density of states, we believe that if one is interested in other quantities, which in the traditional approaches are calculated using the eigenvectors of the dynamical matrix, then our method has significant computational advantages. The method is known in other, related, fields of condensed matter physics as the equation-of-motion method and it has been used successfully for study of spin waves, localization, and phonons in disordered media. In the present paper we will review the method with emphasis on its application to the polymer problem and will apply it to a particularly simple model of polymer dynamics, that of the disordered Kirkwood chain. While the model is too simple to describe the high-frequency modes of any polymer, we will argue that we can use it to study dynamics of polyethylene in the frequency range 50–500 cm$^{-1}$ and will compare our calculations of the incoherent neutron scattering function with experiments on that quantity. Our results show some interesting low-frequency behavior in both the density of states and other quantities for this model which does not seem to have been noticed before. We will discuss the possible physical meaning of this structure and its possible significance for studies of polymer morphology.

The second section of the paper describes the formal aspects of the method. The third section applies the formalism to the Kirkwood model. Sec. IV contains numerical results and Sec. V presents a theoretical discussion of the possible origins of the low-frequency response which we find. The last section gives conclusions and discussion.

II. EQUATION-OF-MOTION METHOD FOR PHONONS

The equation-of-motion method for phonons can be formulated in terms of the classical equations of motion for the particle displacements $u_i^\alpha$ of the particles in the polymer as long as one ignores zero point effects. Here $i$ labels the monomer and $\alpha$ labels one of its Cartesian components. We formulate the method in terms of a general linear response function

$$G^{\beta}_{i;j}(t) = -i \Theta(t) \langle [u^\beta_j(t),u^\alpha_i(0)] \rangle. \tag{1}$$

Here $[\ ,\ ]$ indicates a commutator, $\Theta$ is the Heaviside unit step function, $i=\sqrt{-1}$, and $\langle \cdots \rangle$ indicates a thermal average. The subscript $r$ on the function $G^{\beta}_{i;j}(t)$ indicates that it is the “retarded” response function (sometimes called a “Green’s function”) in the condensed matter literature which is discussed in many monographs and textbooks. It is not hard to establish that this function is directly and linearly related to many quantities which are measured directly in condensed matter systems. Here we will be interested in the coherent neutron scattering function $S(k,\omega)$ defined as

$$S(k,\omega) = (1/2\pi) \int_{-\infty}^{+\infty} dt e^{-i\omega t} \sum_{i,j} e^{-ik\cdot r_i(0)} e^{ik\cdot r_j(t)}, \tag{2}$$

in the incoherent neutron scattering function defined as
\[ S_\omega(k_0) = (1/2\pi) \int_{-\infty}^{+\infty} dt \ e^{-\text{i}\omega t} \sum_l \epsilon_l \left\{ e^{-\text{i}k_{\omega} x} e^{\text{i}k_{\omega} y} \right\} \text{(3)} \]

and in the density of states defined as
\[ N(\omega) = \sum_\lambda \delta(\omega - \epsilon_\lambda/\hbar). \text{(4)} \]

\[ S(k,\omega) = \sum_{i,j} e^{\text{i}k_{\omega} (x_i - x_j)} B_i B_j \left[ \delta(\omega) + \frac{1}{\pi(1 - e^{-\beta\hbar\omega})} \sum_{a,b} k_{\alpha} k_{\beta} \text{Im} \int_0^\infty \frac{G_{r,i,j}^{a,b} e^{-\text{i}\omega t} dt}{G_{r,i,j}^{a,b} e^{-\text{i}\omega t} dt} \right], \text{(5)} \]

\[ S_\omega(k_0) = \sum_i B_i^2 \left[ \delta(\omega) + \frac{1}{\pi(1 - e^{-\beta\hbar\omega})} \sum_{a,b} k_{\alpha} k_{\beta} \text{Im} \int_0^\infty G_{r,i,j}^{a,b} e^{-\text{i}\omega t} dt \right], \text{(6)} \]

\[ N(\omega) = (2M\omega/\hbar\pi) \int_0^\infty \sum_{i,j} G_{r,i,j}^{a,b} (t) \sin(\omega t) \ dt. \text{(7)} \]

In these expressions
\[ B_i = e^{-(\{\eta_i(0)^2\}^2)/2} \text{(8)} \]
is a form of the Debye-Waller factor which takes account of the fact that the monomers are moving during the scattering due to both thermal and zero-point motion. In deriving these expressions we have made repeated use of the assumption that the Hamiltonian is harmonic. We note that the desired quantities have been written in terms of time Fourier transforms of the time representation of the generalized response function. The reason for this is that the equation-of-motion method solves the harmonic problem of the disordered system in the time domain and then Fourier transforms the result at the end, in contrast to other methods, which diagonalize the problem in the frequency domain.

To express the problem of finding the response function \( G_{r,i,j}^{a,b} \) in terms of an equation of motion one needs a differential equation for the response function as well as initial conditions. For \( t > 0 \) and any harmonic Hamiltonian, the equation of motion takes the form
\[ d^2G_{r,i,j}^{a,b}/dt^2 = -\sum_{k,\gamma} M_{a,k}^{\gamma} G_{r,k,j}^{\gamma,b}. \text{(9)} \]
The matrix \( M \) is a form of the dynamical matrix and will be written in Appendix A for the particular model of interest here. The initial conditions on \( G_{r,i,j}^{a,b} \) are
\[ G_{r,i,j}^{a,b}(0) = 0, \text{(10)} \]
\[ dG_{r,i,j}^{a,b}/dt(0) = (-\hbar/M)\delta_{i,j}\delta_{a,b}. \]

We can combine equations (5)—(7) with (9) and (10) to obtain expressions for the quantities of interest which lend themselves to numerical calculation in the time domain. The function \( S(k,\omega) \) for \( \omega \) different from zero is
\[ S(k,\omega) = \sum_{a,b} \left[ k_{\alpha} k_{\beta} / (\pi e^{-\beta\hbar\omega} - 1) \right] \times \sum_j e^{\text{i}k_{\omega} x} B_j \int_0^\infty F_{j}^{a,b} \sin(\omega t) dt, \text{(11)} \]
where
\[ F_{j}^{a,b}(t) = \sum_i e^{-\text{i}k_{\omega} x} B_i G_{r,i,j}^{a,b}(t) \text{(12)} \]
defines the function \( F_{j}^{a,b} \). The equation-of-motion for this function is exactly the same as that for \( G_{r,i,j}^{a,b} \) [Eq. (9)] but the second initial condition is
\[ dF_{j}^{a,b}/dt(0) = (-\hbar/M)B_j e^{-\text{i}k_{\omega} x} \delta_{a,b}. \text{(13)} \]

For the incoherent neutron scattering factor \( S_\omega(k,\omega) \) one obtains identical expressions if the phase factors in Eqs. (11) and (12) are chosen to have random phases chosen with equal weight from the interval 0 to 2\( \pi \). To get the density of states one makes these changes and also sets \( B_j \to 1 \), the temperature \( \to 0 \), and \( q_{a,b} \to \delta_{a,b} \) and multiplies the result by \( 2M\omega/\hbar \). Notice that, using this method, no sum on \( k \) vectors is required in order to obtain the density of states.

We note that because \( B_i \) in Eq. (8) depends on the dynamics of the system, the equations are not linear but must be solved self-consistently (except in the case of the density of states). These Debye-Waller factors can be included in the calculation by iterating the equations and they can be quite important in systems of low effective dimensionality such as polymers. In the calculations to be presented here, however, we will only present results in which the \( B_i \) have been set equal to 1. This is a good ap-
proximation when the chain is highly disordered. (See, however, the discussion in Sec. VI.)

III. MODEL

To illustrate the utility of the method, we will present calculations on the Kirkwood model of harmonic interactions on a chain embedded on a diamond lattice. The model can be written as

\[ H = \frac{1}{2M} \sum_i p_i^2 + \frac{1}{2} \sum_{ij} (\Delta r_{ij})^2 + \frac{a^2 K_b}{2} \sum_{ijk} (\Delta \gamma_{ijk})^2. \]  

(14)

Here \( \Delta r_{ij} \) is the difference between separation of two nearest neighbors \( ij \) in the chain and their equilibrium separation. \( \Delta \gamma_{ijk} \) is the deviation of the angle \( \gamma_{ijk} \) between the "bonds" (straight lines) between nearest neighbors \( ij \) and nearest neighbors \( jk \) from its equilibrium, tetrahedral value \( \gamma_0 \) \( (\cos \gamma_0 = -\frac{1}{2}) \). \( a \) is the equilibrium bond length. \( K_b \) makes the model nontrivial. With \( K_b \rightarrow 0 \), the density of states is independent of the way the chain is embedded on the lattice.\(^\text{10}\) For \( K_b = 0 \), the low-lying band of normal modes which is of primary interest here also collapses to a delta function at \( \omega = 0 \). For a straight zigzag chain (corresponding to all trans bonds) the phonon spectrum was calculated by Kirkwood.\(^\text{6}\) It consists of four phonon branches (using the conventional zone scheme; Kirkwood used a Brillouin zone twice as big as the conventional one). The qualitative form of the resulting dynamics depends to some extent on the relative values of \( K_s \) and \( K_b \). We will suppose that \( K_s \) is several times \( K_b \), as it will be, for example, when the parameters are chosen to approximately describe polyethylene (see below). Then the density of states of the straight zigzag chain displays two broad frequency bands (see Fig. 1): a low-frequency band from the two acoustic phonon branches and a higher-frequency "optical" band arising from the upper two phonon branches. In crystalline polyethylene,\(^\text{10}\) this simple model fails to adequately describe the high-frequency region even qualitatively (partly because C-H stretching and wagging begins to become important). The lower-frequency band, however, does appear to provide a reasonable representation of the low-frequency dynamics of crystalline polyethylene, as long as the frequency is high enough (\( \geq 50 \text{ cm}^{-1} \)) so that chain interactions and out-of-plane vibrations are not important. In our simulations, we therefore use parameters appropriate\(^\text{11}\) to a description of polyethylene in this spectral range. A somewhat more detailed discussion of the usefulness of this model in describing polyethylene appears in Ref. 12. The values we use for the parameters are\(^\text{12,13}\)

\[ K_s = 4.532 \times 10^{-3} \text{ dyn/Å}, \]

\[ a^2 K_b = 1.032 \times 10^{-3} \text{ dyn Å/(rad)^2}, \]

\[ a = 1.54 \text{ Å}. \]

(15)

Using Eq. (14), it is straightforward to work out the values of the elements of the dynamical matrix \( M_{ij}^{ab} \) defined implicitly in Eq. (9). This is done in Appendix A when, as we assume here, the equilibrium position of the monomers are given by sites of a self-avoiding random walk on a diamond lattice.

IV. NUMERICAL RESULTS

We tested the equation-of-motion program by calculating the density of states and the inelastic neutron scattering function \( S(k,\omega) \) for the straight chain. Numerical results are compared with the exact results from Kirkwood’s solution in Fig. 1 and in Table I. Within the frequency resolution of the simulations, the results for the simulation are in excellent agreement with the Kirkwood calculation. Some details of the calculations of the Kirkwood solution appear in Appendix B.

We recall in particular that the Kirkwood model contains\(^\text{6}\) a transverse mode with frequency \( \omega_2 \approx q^2 \) near \( q = 0 \). This unusual but completely physical and well-known result arises because the model allows transverse motions with a stiffness (associated with \( K_b \) in the model) in a model which is otherwise one dimensional. The transverse mode with \( \omega \approx q^2 \) gives rise to a singularity proportional to the inverse square root of the frequency which is clearly visible in Fig. 1. (In Appendix B, the \( \omega \approx q^2 \) mode is evident if one notes that, because the model has been
TABLE I. Intensities of peaks in $S(k,\omega)$ (see Appendix B).

<table>
<thead>
<tr>
<th>$k$</th>
<th>$l,\sigma$</th>
<th>Exact</th>
<th>Simulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\left[\frac{1}{\sqrt{12}}, \frac{1}{\sqrt{12}}, 0\right] \frac{2\pi}{L}$</td>
<td>1, $-$</td>
<td>0.105</td>
<td>0.13</td>
</tr>
<tr>
<td>2, $-$</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>2, +</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>1, +</td>
<td>0.895</td>
<td>0.87</td>
<td></td>
</tr>
<tr>
<td>$\left[\frac{1}{\sqrt{12}}, \frac{1}{\sqrt{12}}, 1 \right] \frac{2\pi}{L}$</td>
<td>1, $-$</td>
<td>0.0019</td>
<td>0.0</td>
</tr>
<tr>
<td>2, $-$</td>
<td>0.015</td>
<td>0.0192</td>
<td></td>
</tr>
<tr>
<td>2, +</td>
<td>0.4041</td>
<td>0.441</td>
<td></td>
</tr>
<tr>
<td>1, +</td>
<td>0.5814</td>
<td>0.543</td>
<td></td>
</tr>
<tr>
<td>$\left[\frac{\sqrt{3}}{8}, \frac{\sqrt{3}}{8}, \frac{\sqrt{3}}{8}\right] \frac{2\pi}{L}$</td>
<td>1, $-$</td>
<td>0.1302</td>
<td>0.18</td>
</tr>
<tr>
<td>2, $-$</td>
<td>0.0015</td>
<td>0.0192</td>
<td></td>
</tr>
<tr>
<td>2, +</td>
<td>0.4041</td>
<td>0.441</td>
<td></td>
</tr>
<tr>
<td>1, +</td>
<td>0.8698</td>
<td>0.82</td>
<td></td>
</tr>
</tbody>
</table>

solved in an extended zone, $q$ is equivalent to $\pi - q$). It can easily be shown quite generally that any onedimensional model with a transverse degree of freedom will have transverse modes at long wavelengths which go as $q^2$.

To introduce disorder into the model we produce a numerical realization of a self-avoiding walk on a diamond lattice in which the probability of a trans bond at each step is $\mathcal{W}$ while the probability of a gauche bond is $1 - \mathcal{W}$. We then integrate the equation of motion (12) forward in time numerically with the lattice positions $r_j(0)$ given by the positions of the sites of the realization of the self-avoiding random walk. By choice of appropriate initial conditions we can then generate $S(k,\omega)$ or $N(\omega)$ from Eq. (11) by fast Fourier transform in time using Eq. (11). The chains used in the realizations were 1000 monomer units long and the results varied very little from one realization to another.

In Fig. 2 we show the density of states for disordered chains with fractions $(1 - \mathcal{W}) = \frac{1}{3}$ and $\frac{2}{3}$ of gauche bonds. The striking feature of these results is the dramatic decrease in the density of states at low frequencies with increasing disorder. We discuss a possible origin of this effect in Sec. V below.

In Fig. 3 we compare an experimental\textsuperscript{14} incoherent neutron scattering cross section for “stretched” polyethylene with a simulation with $\mathcal{W} = \frac{1}{3}$. The results are closely similar in the region from $50-500$ cm$^{-1}$ where we expect this model to be a reasonable model of polyethylene as discussed above. On the other hand, the experimental results are very different from the results of simulation with $\mathcal{W}$ nearer to 1 (see, e.g., Fig. 1). We believe that by making such comparisons we can estimate the number of gauche bonds in a sample to within about 5%. In the particular case shown in Fig. 3 such a comparison indi-

**FIG. 2.** (a) Density of states with $\mathcal{W} = \frac{1}{3}$ for a chain with 1000 monomers. (b) Density of states with $\mathcal{W} = \frac{2}{3}$.

**FIG. 3.** (a) Incoherent neutron scattering function $S_N(k,\omega)/\omega$ as calculated from the simulation with $\mathcal{W} = \frac{1}{3}$. (b) Experimental incoherent neutron scattering function for “aligned” polyethylene.
states that the number of gauche bonds is significantly larger than was suggested by the characterization of the sample as "aligned" in Ref. 14.

V. DISCUSSION OF THE LOW-FREQUENCY STRUCTURE

The most striking feature of the results reported in the last section is the large depression which appears in the density of states (and to some extent in other response functions) when the chain is disordered. Qualitatively, the existence of zero density of states at small \omega in the disordered chain can be understood as follows: In a chain of \textit{N} atoms there will, in general, be 3\textit{N} finite phonon frequencies. In the Kirkwood model, however, the chain can be disordered without changing the elastic energy of Eq. (14) as long as 2\textit{N} constraints are satisfied, namely that the length of each bond and the angle \gamma_{l,j} should be fixed for each monomer. As a consequence, there are \textit{N} zero-frequency modes (which are seen in the simulation) in the absence of dihedral restoring forces. For the same reason, the elastic constants of the disordered chain in this model will be identically zero. Thus we expect that the density of states at low frequencies will consist of a delta function of weight \textit{N} at \omega=0 followed by a region with no or very small density at finite but small \omega. The absence of any elastic restoring forces to \textit{N} of the 3\textit{N} independent deformations suggests that \omega cannot be proportional to any power of the wave number \textit{q} at long wavelengths and thus that \textit{N}(\omega)\to0 faster than any power of \omega. In the next paragraph we briefly describe a simple analytical model which has all these features and appears to contain at least some of the physics associated with the low-frequency depression in the density of states of disordered chains. In the model, the chain consists of disconnected "straight" (trans) pieces lying between gauche bonds and the model neglects the "leakage" of modes propagating down straight portions of the chain into the next straight part of the chain.

We will assume that \textit{W} is near 1 so that the lowest frequency modes in these "straight" segments have wavelengths much longer than the monomer spacing. For a given wave vector \textit{q} on the "straight" segment we will then suppose, consistent with the long-wavelength features of any straight chain model as discussed in the second paragraph of Sec. II, that there are two finite frequency modes at frequencies \textit{r}=1 means longitudinal; \textit{r}=2 means transverse)

\begin{equation}
\omega_1(q) = c_1 q
\end{equation}

and

\begin{equation}
\omega_2(q) = (c_2 q)^2
\end{equation}
as well as a mode at frequency \omega=0 (corresponding to out-of-plane vibrations; this will also have a frequency proportional to \textit{q}^2 when the dihedral force constants are made nonzero). Denoting half the unit-cell length in the "straight" segment by \textit{d} \begin{bmatrix} d = a \cos(\gamma_0/2) \end{bmatrix} where \textit{a} is the bond length and \gamma_0 is the tetrahedral bond angle, and assuming that the monomers at the gauche bonds do not move, we have allowed wavelengths \lambda on a segment of length \textit{nd} given by

\begin{equation}
\lambda = 2\pi d / \textit{m},
\end{equation}

where \textit{m} is an integer. Thus the frequencies of the low-lying modes are

\begin{equation}
\omega_1 = \omega_{1,0}(m / \textit{n}),
\end{equation}

\begin{equation}
\omega_2 = \omega_{2,0}(m / \textit{n})^2,
\end{equation}
in which

\begin{equation}
\omega_{1,0} = c_1 \pi / \textit{d},
\end{equation}

\begin{equation}
\omega_{2,0} = (c_2 \pi / \textit{d})^2.
\end{equation}
The probability \textit{P}(n) that a "straight" segment will have length \textit{nd} is

\begin{equation}
\textit{P}(n) = \textit{N}(1 - \textit{W})^2 \textit{W}^n
\end{equation}

and the density of states of the two finite frequency modes at low frequency is

\begin{equation}
N_r(\omega) = \sum_{\textit{n}=1}^{\infty} \sum_{\textit{m}=1}^{\infty} \textit{P}(n) \delta(\omega - \omega_{r,0}(m / \textit{n})^r),
\end{equation}

where \textit{r}=1,2 for the longitudinal (\textit{l}) and transverse (\textit{t}) cases, respectively. (One easily checks that

\begin{equation}
\int N_r(\omega)d\omega = \textit{NW}
\end{equation}

which is correct because this model omits one mode at each gauche bond.) For small \omega, the upper limit on the sum on \textit{m} can be replaced by \infty. Changing the sum on \textit{n} to an integral we find

\begin{equation}
N_r(\omega) = \sum_{\textit{m}=1}^{\infty} \int_0^{\infty} \textit{dn} \textit{W}^{\textit{n}} \delta(\omega - \omega_{r,0}m / \textit{n})^r) N(1 - \textit{W})^2
\end{equation}

\begin{equation}
= [N(1 - \textit{W})^2 / \omega \ln \textit{W}] \sum_{\textit{m}=1}^{\infty} 2\textit{ym} e^{-2\textit{ym}},
\end{equation}
in which

\begin{equation}
\textit{y} = (\ln \textit{W} / 2)(\omega_{0,0} / \omega)^{1/r}.
\end{equation}
The density of states \textit{N}_0(\omega) of the straight chain is in the same approximation

\begin{equation}
N_{0,0}(\omega) = (N / \omega)^{(1 / r)}.
\end{equation}
Using this in the preceding expression and doing the sum gives

\begin{equation}
N_r(\omega) = N_{0,0}(\textit{y} / \sinh \textit{y})^2,
\end{equation}
where we have used \textit{lnW} = 1 - \textit{W} assuming \textit{W} is near 1. From Eq. (27) one sees that the straight chain density of states is dominated by the 1/(\sinh \textit{y})^2 factor for small \omega where it forces the density of states to zero as

\begin{equation}
\textit{W}^{-1}(\omega_0 / \omega)^{2/r}.
Thus this model exhibits a depression in the density of states of the sort observed in the simulations. We show graphs of Eq. (27) in Figs. 4 - 6. Because of the square-root singularity in $N_{0,1}(n)$, the density of states at small $\omega$ is completely dominated by the transverse modes. The physical origin of the depression in this model is clearly in the cutoff of the long-wavelength modes arising from the disorder as we discussed physically in Ref. 5. In the same figures we show densities of states from simulations with $W=0.90, 0.86$, and $0.80$ for comparison. The simulations are in qualitative accord with the calculation of this section but quantitative details are not consistent: The gap is changing magnitude more slowly with $W$ than predicted here and is consistently larger than the picture given here would suggest for small $1-W$. While some of the discrepancy might arise from a failure to count all the modes at low frequency, we do not believe that this can fully account for the discrepancy evident in Figs. 4 - 6: The simulation densities of states were summed and gave two modes per monomer to within a few percent in all cases (for example, for $W=0.9$ the sum for the run shown in Fig. 4 was 1.98.) The discrepancy must therefore arise from the effects of “leakage” which are left out of this model as discussed at the beginning of this section.

VI. DISCUSSION AND CONCLUSIONS

We have presented results on the harmonic simulation of the disordered Kirkwood chain using the equation-of-motion method. The most striking results are (i) that a depression appears around $\omega=0$ in the density of states and other response functions and (ii) that the simulations of the coherent inelastic neutron scattering function for highly disordered ($W = \frac{1}{2}$) chains look much like experiments on ostensibly more aligned polyethylene.

We have suggested (Sec. V) that the depression arises from the cutoff of long-wavelength modes associated with the disorder and have presented a simple model which gives results much like the simulations. It is clear, however, that one gets a zero in the density of states at $\omega = 0$ in this simple model only because the frequency of the out-of-plane vibrational band was set equal to zero (as it was in the simulation.) If we were to reintroduce dihedral forces, one expects the three-dimensional character of the harmonic spectrum to be restored in the sense that the longitudinal and transverse sound waves would be linear in wave vector at sufficiently long wavelengths. In such a case, the form of the density of states would be similar but the out-of-plane modes would contribute a finite density of states inside the depression.

In our present calculation, the fact that the density of states $\rightarrow 0$ as $\omega \rightarrow 0$ (apparently quite rapidly) means that the Debye-Waller factors have no infrared divergence. If, on the other hand, adding dihedral forces introduced a normal phonon spectrum with three branches linear in wave vector and a state density

$$N(\omega) \sim \omega^{d-1},$$

where $d = \frac{5}{4}$ (the dimension of the self-avoiding walk), then the Debye-Waller factors would acquire an infrared
divergence at finite temperature of the form

$$\int \omega^{-4/3} d\omega$$

and the conformation would change so that its fractal dimension $d$ was 2 or greater. Such a chain, with slightly tighter coiling than that of the self-avoiding walk, would also have a finite Debye-Waller factor and a spectral response similar to that found by leaving the Debye-Waller factors out altogether.

**APPENDIX A: DYNAMICAL MATRIX $M_{ij}^{a,\beta}$**

For $t > 0$, the equation of motion for $G_{r;r,j}^{a,\beta}$ is

$$d^2 G_{r;r,j}^{a,\beta}/dt^2 = (i/\hbar)\Theta(t)\{[[u^\beta(t),H],H],u^\alpha(0)\},$$

which, by repeated use of Eq. (14), gives Eq.(9) with

$$M_{ij}^{a,\beta} = (1/M)\{K_4(\hat{r}_j^\alpha \hat{r}_j^\beta + \hat{r}_j^\alpha \hat{r}_{j+1}^\beta) + (K_b/\sin^2 \gamma_0)[(\hat{r}_j - \cos \gamma \hat{r}_{j-1})\rho(\hat{r}_j + \cos \gamma \hat{r}_j) - (\hat{r}_{j+1} + \cos \gamma \hat{r}_j)\rho(\hat{r}_{j+1} - \hat{r}_j)],$$

$$\ldots$$

$$M_{ij}^{a,\beta} = (-1/M)(K_b/\sin^2 \gamma_0)(\hat{r}_{j+1} + \cos \gamma \hat{r}_{j+2})\rho(\hat{r}_{j+2} + \cos \gamma \hat{r}_{j+1}),$$

$$M_{ij}^{a,\beta} = (-1/M)(K_b/\sin^2 \gamma_0)(\hat{r}_j + \cos \gamma \hat{r}_{j-1})\rho(\hat{r}_j - \cos \gamma \hat{r}_j),$$

where $\hat{r}_j$ is a unit vector from site $j - 1$ to site $j$.

**APPENDIX B: SOLUTIONS FOR ALL TRANS ZIGZAG CHAIN**

The equation of motion for the straight chain is written in terms of the variables

$$x_q = \sum_n x_n e^{i\eta n}, \quad y_q = \sum_n y_n e^{i\eta n} \quad (B1)$$

as

$$\begin{pmatrix} M\omega^2 & 0 \\ 0 & M\omega^2 \end{pmatrix} \begin{pmatrix} x_q \\ y_q \end{pmatrix} = \begin{pmatrix} D_{11} & -iD \\ iD & D_{22} \end{pmatrix} \begin{pmatrix} x_q \\ y_q \end{pmatrix} \quad (B2)$$

in which the coordinates $x_n, y_n$ are defined in Fig. 7 and the values of $q$ go from $-\pi$ to $\pi$ (so that we here use the "Kirkwood zone" which is twice as large as the true Brillouin zone.) The quantities $D_{11}, D_{22}$, and $D$ are

$$D_{11} = K_s(1 - \cos q)(1 + \cos \gamma_0),$$

$$+ 2K_b(1 + \cos q)(1 - \cos \gamma_0),$$

$$D_{22} = K_s(1 + \cos q)(1 + \cos \gamma_0),$$

$$+ 2K_b(1 + \cos q)(1 + \cos \gamma_0)(1 - \cos \gamma_0). \quad (B3)$$

$$D = K_s \sin q \sin \theta - 2K_b a^2(1 + \cos q) \sin q \sin \gamma_0.$$
FIG. 7. Definitions of coordinates used in Appendix B.

\[ \omega^4 - 2\omega^2\omega^2 + \omega^4 = 0 \]

or

\[ \omega_{+, -}^2 = \omega_0^2 + (\omega_0^4 - \omega_p^4)^{1/2} , \]

in which

\[ \omega_0^2 = \frac{(K_y / M)(1 + \cos \gamma_0 \cos q)}{1 + \cos \gamma_0 \cos q} \]

\[ + (2K_y / M)(1 - \cos \gamma_0 \cos q), \]  

\[ \omega_p^4 = 8K_y K_b (1 + \cos q) \sin^2 q. \]  

The density of states shown in Fig.1 was evaluated using (B4) and (B5). To find the eigenvectors we write

\[ x_q = \sin \beta_q, \quad y_q = \cos \beta_q \]

so that

\[ (m\omega^2 - D_{11}) \sin \beta_q = D \cos \beta_q , \]

\[ (m\omega^2 - D_{22}) \cos \beta_q = D \sin \beta_q , \]  

and

\[ \tan \beta_{q, +, -} = \frac{M \omega_{+, -}^2 - D_{22}}{D} . \]  

To find the intensities of peaks in \( S(k, \omega) \) we note, using Eq. (2) in the harmonic approximation and confining attention to one-phonon processes that (at \( T = 0 \))

\[ S(k, \omega) = \sum_m \left| \left\langle 0 \left| \sum_n e^{ik \cdot R_n} k \cdot u_n \right| m \right\rangle \right|^2 \delta(\omega - (\omega_m - \omega_o)) , \]

where \( \left| m \right\rangle \) are the one-phonon excitations of the chain, characterized by \( q_i(0, +, -) \) and given by the solutions of Eqs. (B4) and (B6). Denoting \( \sigma = (+, -) \) we have

\[ S(k, \omega) = \sum_{q, \sigma} \sum_n e^{ik \cdot R_n} \left| \left\langle 0 \left| k \cdot u_n \right| q, \sigma \right\rangle \right|^2 \delta(\omega - \omega_{q, \sigma}). \]  

The matrix elements \( \left\langle 0 \left| u_n \right| q, \sigma \right\rangle \) are related to the \( (q, \sigma) \)th eigenvector of Eq. (B3). The proportionality constant can be eliminated by use of a version of the \( f \)-sum rule

\[ \int_0^{\omega_o} \omega S(k, \omega)d\omega = \sum_m \left( \left| \left\langle 0 \left| \sum_n e^{ik \cdot R_n} u_n \right| m \right\rangle \right|^2 \delta(\omega_m - \omega_o) \right) = N\hbar k^2 / 2M. \]  

Combining (B9) and (B10), the function

\[ \tilde{S}(k, \omega) = \frac{\omega S(k, \omega)}{\int_0^{\omega_o} \omega S(k, \omega)d\omega} \]

integrates to one and the predicted weight integrated over one peak is

\[ \int_{\omega_{o, +}^0}^{\omega_{o, -}^0} \omega S(k, \omega)d\omega = 2M\omega_{q, \sigma} \left( \left| \left\langle 0 \left| \sum_n e^{ik \cdot R_n} u_n \right| q, \sigma \right\rangle \right|^2 \right) / (N\hbar k^2) . \]  

Finally,

\[ \left| \left\langle 0 \left| k \cdot \sum_n e^{ik \cdot R_n} u_n \right| q, \sigma \right\rangle \right|^2 = | \hat{k} \cdot \hat{u}_{q, \sigma} |^2 \hbar N / 2M\omega_{q, \sigma} . \]  

where \( \hat{u}_{q, \sigma} \) is a unit vector satisfying (B6) so that the weight of the peak characterized by \( q, \sigma \) is \( | \hat{k} \cdot \hat{u}_{q, \sigma} |^2 \). For each value of \( \sigma \) and \( k \), there will be two values of \( q \) for which a finite contribution to \( \tilde{S}(k, \omega) \) is obtained for some \( \omega \). Denoting these two values of \( q \) by \( q_1 \) and \( q_2 \) one thus finds \( [q_1 = k a; q_2 = q_1 + \pi; b \equiv a \cot(\frac{1}{2} \gamma_0)] \)

\[ \tilde{S}(k, \omega) = \sum_{l=1}^{2} \sum_{\sigma = +, -} | \hat{k} \cdot \hat{u}_{q, \sigma} |^2 \delta(\omega - \omega_{q, \sigma}) \]

\[ = (\hat{k}_x \sin \beta_{q_1} \cos k_x b + \hat{k}_y \cos \beta_{q_1} \sin k_x b)^2 \delta(\omega - \omega_{q_1, +}) + (\hat{k}_x \sin \beta_{q_1} \cos k_x b + \hat{k}_y \cos \beta_{q_1} \sin k_x b)^2 \delta(\omega - \omega_{q_1, -}) \]

\[ + (\hat{k}_x \sin \beta_{q_2} \sin k_y b + \hat{k}_y \cos \beta_{q_2} \cos k_y b)^2 \delta(\omega - \omega_{q_2, +}) + (\hat{k}_x \sin \beta_{q_2} \sin k_y b + \hat{k}_y \cos \beta_{q_2} \cos k_y b)^2 \delta(\omega - \omega_{q_2, -}). \]  

(B14)
To compare this result with the simulation, we computed $S(k,\omega)$ in the simulation, multiplied by $\omega$ and normalized to 1 to form $\tilde{S}(k,\omega)$ according to (B11) and then integrated the result over each of the four peaks corresponding to the solutions $\omega_{q_i\sigma}$ for a given wave vector $k$ and compared the results with the four coefficients in Eq. (B14). The results are shown in Table I.