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Effect of correlations on the low-frequency behavior of random one-dimensional systems

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We study the motion of a particle or elementary excitation that hops between nearest neighbors in a one-dimensional array of traps. The trap depths and transition probabilities are random, but they may show correlations over short distances. When certain averages of the inverse transition rates exist, the low-lying eigenvalues of the master equation for the system are distributed like those of some equivalent regular chain. However, the nature of this equivalent regular chain depends on the degree of correlation of the random transition rates. Moreover, for a chain with periodic boundary conditions the degeneracy of the eigenvalues in the regular chain is lifted. The amount of this splitting depends on the degree of randomness and on the chain length. The density of low-lying eigenvalues is closely related to the asymptotic form of the probability for finding the particle at some large time at the same place where it started its random walk. Our results are obtained by studying the moments of the reciprocals of the eigenvalues, in which the distribution of low-lying eigenvalues leaves a characteristic "fingerprint."

I. INTRODUCTION AND SURVEY

In this paper we study the diffusive motion of a particle in a linear chain of N traps of random depth. The particle may jump only between nearest neighbors. The jump rate is allowed to vary from site to site, subject only to the constraint of detailed balance. The model has received much attention recently. We refer to a recent review by Alexander, Bernasconi, Schneider, and Orbach[1] for a history of the model and the different physical systems to which it may be applied. A typical example would be an amorphous polymer in which a particle or an electronic excitation may hop along the polymer chains, but not between them. The randomness may be provided either by substitutional disorder in the chains, as in a copolymer, or by the influence of neighboring chains on the in-chain hopping rates. The model is moreover closely related to the classical problem of the random harmonic chain.[2] We are particularly interested in the distribution $\rho(\lambda)$ of the eigenvalues of the master equation governing our system, especially in the limit of low λ. The quantity $\rho(\lambda)$ is related to the averaged probability $\langle G_{nn}(t)\rangle$ that the particle is found at time t at the same site where it was at $t=0$:

$$\lim_{N\to\infty}\langle G_{nn}(t)\rangle=\lim_{N\to\infty}\left[\frac{1}{N}\int_{-\infty}^{0}\rho(\lambda)e^{-|\lambda|t}d\lambda\right]. \tag{1.1}$$

Our results therefore bear upon the asymptotic behavior of $\langle G_{nn}(t)\rangle$ for large t.

The emphasis of our treatment differs somewhat from that of the work reviewed in Ref. 1. The authors of Ref. 1 consider only the leading term in $\rho(\lambda)$ for small $|\lambda|$ and treat the trap depths and jump rates at different sites as independent random variables. However, they provide a detailed treatment of the case that the average of the inverse jump rate does not exist; this means that the long-time behavior of the chain is dominated by bottlenecks. We confine ourselves to the case that the inverse jump rate does have a finite expectation value; this implies that the low-frequency behavior approaches that of an equivalent homogeneous chain. On the other hand, we consider corrections to the leading term in $\rho(\lambda)$ and we are able to include the effects of correlations, provided they are of reasonably short range. In addition we obtain some aspects of the distribution of relaxation times

that do not manifest themselves in the ensemble averaged $\rho(\lambda)$. When one imposes periodic boundary conditions, eigenvalues occur in almost degenerate pairs with spacings that exhibit a characteristic dependence on λ and the chain length.

The method used to obtain our results is a variant of the moment method devised by Domb, Maradudin, Montroll, and Weiss[3] for the random harmonic chain. Whereas these authors considered the regular moments, we consider the moments of their reciprocals

$$M_p=\sum_{i=2}^{N}(-\lambda_i)^{-p}, \tag{1.2}$$

where the sum runs over all nonzero eigenvalues (weighted by their multiplicity in case of degeneracy). The moments M_p are related to the first p coefficients in the characteristic polynomial

$$\Delta_N(\lambda)=\sum_{p=1}^{N}C_p\lambda^p \tag{1.3}$$

whose roots are the eigenvalues λ_i. The coefficients C_p, and hence the moments M_p, approach relatively simple forms in the limit of large chain length N. We explicitly calculate the leading terms and corrections up to relative order N^{-2} for a slightly simplified model, namely one in which the trap depths are random but the heights of the barriers between them are all equal. We can also treat the case when only the barrier heights fluctuate or when both parameters fluctuate independently of one another. Correlated fluctuations of trap depths and barrier heights, however, would require a modification of our scheme.

The first few moments contain significant contributions from eigenvalues outside the asymptotic region. Higher moments M_p settle into a pattern that can be recognized as the one generated by a specific eigenvalue distribution. This distribution is obtained by sampling a curve of the type

$$\lambda(q)=-D_1q^2-D_2q^4+\cdots \tag{1.4}$$

at the regularly spaced points $q_l=(2\pi l/N)$ and at certain additional points very close to the regularly spaced ones.

The paper is organized as follows: In Sec. II we define the model and determine the characteristic polynomial $\Delta_N(\lambda)$. We observe that this polynomial contains the parameters for the trap depths and barrier heights in a symmetric fashion. This feature is related to the existence of a unitary transformation that interchanges the role of the two types of parameter. We also give an explicit expression for the Green's function of the problem and show how its trace is related to the density of the eigenvalues.

In Sec. III we evaluate the coefficients in $\Delta_N(\lambda)$ asymptotically for large N; some of the combinatorics involved is relegated to Appendix A. In Sec. IV these results are converted into expressions for the moments M_n. Subsequently we show how these moments can be reproduced up to first order in N^{-1} by a sequence of regularly spaced almost degenerate pairs of eigenvalues. The pattern of spacings between the members of these almost degenerate pairs is equal to that of an exactly solvable case: a continuous diffusion model with a single strong inhomogeneity, approximated by a localized singularity. This model is discussed more fully in Appendix B. The results in Sec. IV do not lead to a change in the low-frequency eigenvalue density in the thermodynamic limit when compared with a homogeneous chain in which all transition probabilities are replaced by their averages. Such differences do appear when we carry our scheme one order further in N^{-1}. This cannot be done for the polynomial $\Delta_N(\lambda)$ itself, but only for its ensemble average. In Sec. V we first justify the use of this average for the specific problem we want to solve and subsequently apply the formalism of Sec. IV to find the averaged eigenvalue density $\rho(\lambda)$. Section VI contains a few concluding remarks.

II. PROPERTIES OF THE SECULAR MATRIX

We consider a circular array of N traps in which a particle can jump between neighboring traps. The rightward and leftward jump rates are $\alpha_n\beta_n$ and $\alpha_n\beta_{n-1}$, respectively, where α_n^{-1} is the equilibrium occupancy of the nth trap. This choice for the jump rates automatically fulfils detailed balance.[4] The occupation probability for the nth trap obeys the master equation

$$\frac{dp_n}{dt}=-\alpha_n(\beta_{n-1}+\beta_n)p_n+\alpha_{n-1}\beta_{n-1}p_{n-1}+\alpha_{n+1}\beta_np_{n+1}\,. \tag{2.1}$$

The system of equations (2.1) has a complete set of eigenvectors $\vec{\mathrm{p}}^{(j)}$ satisfying the orthogonality condition

$$(\vec{\mathrm{p}}^{(j)},\vec{\mathrm{p}}^{(j')})\equiv\sum_{n=1}^{N}p_n^{(j)}p_n^{(j')}\alpha_n=\delta_{jj'} \tag{2.2}$$

and corresponding eigenvalues λ_j that are the zeros of the determinant $\Delta_N(\lambda)$ of the secular matrix

$$\underline{S}_N(\lambda)=\begin{vmatrix} -\alpha_1(\beta_N+\beta_1)-\lambda & \alpha_2\beta_1 & 0 & \cdots & \alpha_N\beta_N \\ \alpha_1\beta_1 & -\alpha_2(\beta_1+\beta_2)-\lambda & \alpha_3\beta_2 & \cdots & 0 \\ 0 & \alpha_2\beta_2 & -\alpha_3(\beta_2+\beta_3)-\lambda & \cdots & 0 \\ 0 & 0 & \alpha_3\beta_3 & \cdots & 0 \\ \vdots & \vdots & \vdots & & \vdots \\ \alpha_1\beta_N & 0 & 0 & & -\alpha_N(\beta_{N-1}+\beta_N)-\lambda \end{vmatrix} . \tag{2.3}$$

All zeros of $\Delta_N(\lambda)$ are negative and real, except a single eigenvalue $\lambda_1=0$, corresponding to $p_n=\alpha_n^{-1}$. As a preliminary towards determining $\Delta_N(\lambda)$ we first consider

$$D_{nm}(\lambda)=\begin{vmatrix} -\alpha_{n+1}(\beta_n+\beta_{n+1})-\lambda & \alpha_{n+2}\beta_{n+1} & \cdots & 0 \\ \alpha_{n+1}\beta_{n+1} & -\alpha_{n+2}(\beta_{n+1}+\beta_{n+2})-\lambda & \cdots & 0 \\ 0 & \alpha_{n+2}\beta_{n+2} & \cdots & 0 \\ \vdots & \vdots & & \vdots \\ 0 & 0 & & -\alpha_{m-1}(\beta_{m-2}+\beta_{m-1})-\lambda \end{vmatrix} . \tag{2.4}$$

For $D_{nm}(0)$ one readily finds (e.g., by induction)

$$D_{nm}(0)=(-1)^{m+n+1}\prod_{j=n+1}^{m-1}\alpha_j\prod_{k=n}^{m-1}\beta_k B_{nm} \tag{2.5}$$

with

$$B_{nm}=\sum_{l=n}^{m-1}\beta_l^{-1} . \tag{2.6}$$

In order to evaluate $D_{nm}(\lambda)$ we first note that each term contributing to the coefficient of λ^p consists of a product of $p+1$ factors of type $D_{ij}(0)$. The result may be written as

$$D_{nm}(\lambda)=(-1)^{n+m+1}\prod_{j=n+1}^{m-1}\alpha_j\prod_{k=n}^{m-1}\beta_k B_{nm}(\lambda) \tag{2.7}$$

with

$$B_{nm}(\lambda)=B_{nm}+\sum_{p=1}^{m-n-1}B_{nm}^{(p)}\lambda^p ,$$

$$B_{nm}^{(p)}=\sum_{n<k_1<k_2\cdots<k_p<m}\times B_{nk_1}\alpha_{k_1}^{-1}B_{k_1k_2}\alpha_{k_2}^{-1}\cdots\alpha_{k_p}^{-1}B_{k_pm} , \tag{2.8}$$

Of course, the reduction process used to evaluate $D_{nm}(\lambda)$ works equally well for $\Delta_N(\lambda)$, for which we find

$$\Delta_N(\lambda)=(-1)^N\prod_{j=1}^{N}(\alpha_j\beta_j)\sum_{p=1}^{N}\lambda^p C_N^{(p)} \tag{2.9}$$

with

$$C_N^{(p)}=\sum_{1\le k_1<k_2\cdots<k_p\le N}\prod_{l=1}^{p}(\alpha_{k_l}^{-1}B_{k_lk_{l+1}}) , \tag{2.10}$$

where $k_{p+1}\equiv k_1+N$, $\beta_{N+i}\equiv\beta_i$. Note that $\Delta_N(0)$ vanishes due to the presence of the eigenvalue $\lambda_1=0$ (this is also readily verified explicitly).

The results (2.9) and (2.10) are the main results of this section and the starting point for the developments in the subsequent ones. We conclude the section with two observations. First, the technique used to calculate $\Delta_N(\lambda)$, which relies on the fact that only jumps to nearest neighbors are allowed in our model, can also be used to determine the resolvent matrix $\underline{S}^{-1}(z)$. It is the Laplace transform of the Green's function $G_{nm}(t)$, describing the probability that the particle is at n at time t when it was at m at $t=0$. One finds using Cramer's rule

$$\Delta_N(z)[S^{-1}(z)]_{nn}=(-1)^{N-1}\alpha_n^{-1}\prod_{j=1}^{N}(\alpha_j\beta_j)B_{n\,n+N}(z) , \tag{2.11a}$$

$$\Delta_N(z)[S^{-1}(z)]_{nm}=(-1)^{N-1}\alpha_n^{-1}\prod_{j=1}^{N}(\alpha_j\beta_j)[B_{nm}(z)+B_{m\,N+n}(z)] \quad (m>n) \tag{2.11b}$$

$$\alpha_m[S^{-1}(z)]_{mn}=\alpha_n[S^{-1}(z)]_{nm} , \tag{2.11c}$$

with the $B_{nm}(z)$ defined in (2.8). We employed the convention $\alpha_{l+N}\equiv\alpha_l$, $\beta_{l+N}=\beta_l$. Of particular interest is the residue of $\underline{S}^{-1}(z)$ at an eigenvalue, which equals[5]

$$\mathrm{Res}\{\,[S^{-1}(z)]_{nm}\,\}_{z=\lambda_j}=\alpha_m p_n^{(j)} p_m^{(j)}\,. \tag{2.12}$$

It now follows from (2.2) that the residue of the trace of $\underline{S}^{-1}(z)$ is unity. The inverse Laplace transform of $\mathrm{Tr}[S^{-1}(z)]$ is therefore equal to $\sum_j \exp(-|\lambda_j|t)$. This establishes the fact, mentioned in the Introduction, that the eigenvalue density and the trace of the Green's function form a Laplace transform pair. We note in passing that the relation (2.12) allows one in principle to determine the eigenvectors $\vec{\mathrm{p}}^{(j)}$ when the eigenvalues are known.

We conclude this section with the observation that the coefficients $C_N^{(p)}$ occuring in $\Delta_N(\lambda)$ [see (2.10)] may also be written, using (2.6), as

$$C_N^{(p)}=\sum_{1\le k_1\le l_1<k_2\le l_2\cdots<k_p\le l_p}\ \prod_{j=1}^{p}\alpha_{k_j}^{-1}\beta_{l_j}^{-1} \tag{2.13}$$

with $k_p\le N$, $k_p\le l_p<k_1+N$, i.e., as a string of alternating α^{-1} and β^{-1} factors. The symmetric way in which the α^{-1} and β^{-1} occur is easily understood. The variables

$$j_n\equiv\alpha_n p_n-\alpha_{n+1}p_{n+1} \tag{2.14}$$

obey the master equation

$$\frac{dj_n}{dt}=-\beta_n(\alpha_{n+1}+\alpha_n)j_n+\beta_{n-1}\alpha_n j_{n-1}$$
$$+\beta_{n+1}\alpha_{n+1}j_{n+1}\,. \tag{2.15}$$

Comparison with (2.1) shows that the transformation (2.14) switches the roles of the α and β coefficients (to reach complete equivalence one must also change one's convention as to "left" and "right"). The transformation (2.14) transforms the eigenvectors $\vec{\mathrm{p}}^{(i)}$ of (2.1) into eigenvectors $\vec{\mathrm{j}}^{(i)}$ of (2.15) obeying the orthogonality relation

$$((\vec{\mathrm{j}}^{(i)},\vec{\mathrm{j}}^{i'}))\equiv\sum_{n=1}^{N}j_n^{(i)}j_n^{(i')}\beta_n=\lambda_i\delta_{ii'}\,, \tag{2.16}$$

from which the unitary equivalence of the operators in the master equations follows. A slight complication arises with the $\lambda=0$ eigenvector $p_n^{(1)}=\alpha_n^{-1}$, which is mapped into zero by (2.14). One readily sees, however, that the vector $j_n^{(1)}=\beta_n^{-1}$ may be used to supplement the set of eigenvectors. A particular case of the unitary equivalence connected to the transformation (2.14) is that[1] between a model in which the α_n are all equal and the β_n are arbitrary (random barrier model) and the one for which the β_n are equal and the α_n arbitrary (random trap model).

III. THE COEFFICIENTS OF THE SECULAR EQUATION IN A LONG CHAIN

The purpose of this section is the evaluation of the coefficients $C_n^{(p)}$ of the secular equation

$$C_N(\lambda)=\sum_{p=1}^{N}\lambda^p C_N^{(p)}=0\,, \tag{3.1}$$

with $C_N^{(p)}$ given by (2.10) or (2.13) in the limit of large N and for $p<<N$. We treat the α_i^{-1} and β_i^{-1} as random variables with averages $\langle\alpha^{-1}\rangle$ and $\langle\beta^{-1}\rangle$. Furthermore we assume that the deviations δ_j^{α} and δ_j^{β} defined by

$$\alpha_j^{-1}=\langle\alpha^{-1}\rangle+\delta_j^{\alpha}\langle\beta^{-1}\rangle^{-1}\,,$$
$$\beta_j^{-1}=\langle\beta^{-1}\rangle+\delta_j^{\beta}\langle\alpha^{-1}\rangle^{-1} \tag{3.2}$$

are correlated at most over distances d short compared to N. If we substitute (3.2) into (2.13) and order the terms according to the number of factors δ_j^{α} or δ_j^{β} we obtain, using the combinatorial results of Appendix A,

$$C_N^{(p)}=\frac{N}{p}\binom{N+p-1}{2p-1}f_1^p$$
$$+\binom{N+p-1}{2p-1}f_1^{p-1}(\sigma_\alpha+\sigma_\beta)+\sum_{r=2}^{2p}C_N^{(p;r)}\,, \tag{3.3}$$

with $\binom{n}{m}$ the usual binomial coefficients and

$$f_1=\langle\alpha^{-1}\rangle\langle\beta^{-1}\rangle\,, \tag{3.4a}$$

$$\sigma_\alpha=\sum_{j=1}^{N}\delta_j^{\alpha}\,,\qquad \sigma_\beta=\sum_{j=1}^{N}\delta_j^{\beta}\,. \tag{3.4b}$$

The term $C_N^{(p;r)}$ consists of a $2p$-fold sum of terms containing r factors of type δ. To obtain an estimate of the range of variation of the $C_N^{(p;r)}$ we consider its mean square $\langle(C_N^{(p;r)})^2\rangle$. Inside the brackets we have a $4p$-fold sum containing $2r$ fac-

tors of type δ. Owing to our assumption that the δ_j are correlated only over a distance d, a term does not contribute to the sum unless each δ_j can find a partner no further than d steps away. Therefore we have

$$\langle (C_N^{(p;r)})^2 \rangle = O(N^{4p-r}) . \tag{3.5}$$

Thus we are justified in treating $C_N^{(p;r)}$ as a quantity of order $N^{-r/2}$ relative to the main term in (3.3), at least for low p. As we shall argue in the next section, the low-lying roots of (3.1) depend mainly on the lowest $C_N^{(p)}$, so it makes sense to try and determine them by truncating the series (3.3) at some low order r.

Truncating all $C_N^{(p)}$ after the first term amounts to replacing the random chain by a regular chain which all transition probabilities equal f_1^{-1}. The eigenvectors are sines and cosines and the eigenvalues are

$$\lambda_j = 2f_1^{-1}[\cos(2\pi j/N)-1] \quad (j=0,1,2,\ldots,[N/2]) , \tag{3.6}$$

with $[N/2]$ the largest integer not exceeding $N/2$. All except the lowest, and for even N the highest, are doubly degenerate. Including the second term in (3.3) does not alter the density of eigenvalues. If we denote the polynomial obtained by truncation at order $N^{-r/2}$ by $C_N^{[r]}(\lambda)$ then

$$C_N^{[1]}(\lambda) = C_N^{[0]}(\lambda) + \frac{\sigma_\alpha+\sigma_\beta}{Nf_1}\lambda\frac{d}{d\lambda}C_N^{[0]}(\lambda) . \tag{3.7}$$

At all double zeros of $C_N^{[0]}(\lambda)$ its first derivative vanishes and its second derivative is positive, as follows from its representation $\prod_{j=1}^{N}(\lambda-\lambda_j)$, where each double eigenvalue occurs twice in the product. Therefore, $C_n^{[1]}(\lambda)$ vanishes at all zeros of $C_N^{[0]}(\lambda)$ (except at the highest for even N), and its derivative has the sign opposite to that of $\sigma_\alpha+\sigma_\beta$. The latter fact implies that $C_N^{[1]}(\lambda)$ must have an additional zero between any two consecutive double zeros of $C_N^{[0]}(\lambda)$. Moreover all double zeros of $C_N^{[0]}(\lambda)$ are single zeros of $C_N^{[0]}(\lambda)$. In the next section we shall be able to obtain still more detailed information about the additional zeros. [Note that a correction term as in (3.7) will not change the eigenvalue density either, when the zeros of $C_N^{[0]}$ are simple. In that case the derivative has opposite sign at consecutive eigenvalues of $C_N^{[0]}$ and so has $C_N^{[1]}$. Therefore a zero of $C_N^{[1]}$ must lie between both consecutive zeros of $C_N^{[0]}$.]

IV. EIGENVALUE MOMENTS AND EIGENVALUE DISTRIBUTION

The coefficients $\tilde{C}_p$ of the polynomial

$$\tilde{\Delta}_N(\lambda) = 1 + \sum_{p=1}^{N-1} \tilde{C}_p \lambda^p \tag{4.1}$$

are related to the zeros $\tilde{\lambda}_i$ of $\tilde{\Delta}_N(\lambda)$ by means of the relations

$$\tilde{C}_p = \frac{(-1)^p}{p!} \sum_{i_1=1}^{N-1}{}' \sum_{i_2=1}^{N-1}{}' \cdots \sum_{i_p=1}^{N-1}{}' \prod_{q=1}^{p} \tilde{\lambda}_{i_q}^{-1} \tag{4.2}$$

where the primes at the summations indicate that each i_l must be different from all preceding ones. The coefficients $\tilde{C}_p$ are furthermore related to the moments

$$\tilde{M}_p = \sum_{i=1}^{N-1} (-\tilde{\lambda}_i)^{-p} \tag{4.3}$$

by means of simple relations. The first few are[6]

$$\begin{aligned} \tilde{M}_1 &= \tilde{C}_1 , \\ \tilde{M}_2 &= \tilde{C}_1^2 - 2\tilde{C}_2 , \\ \tilde{M}_3 &= \tilde{C}_1^3 - 3\tilde{C}_1\tilde{C}_2 + 3\tilde{C}_3 , \\ \tilde{M}_4 &= \tilde{C}_1^4 - 4\tilde{C}_1^2\tilde{C}_2 + 4\tilde{C}_1\tilde{C}_3 + 2\tilde{C}_2^2 - 4\tilde{C}_4 , \end{aligned} \tag{4.4a}$$

and the general expression is

$$\tilde{M}_n = n \sum_{\mathscr{P}(m_{\mathscr{P}};\{l_i\},\{n_i\})} (-1)^{n-l}(l-1)! \times \sum_{i=1}^{m_{\mathscr{P}}} \frac{(\tilde{C}_{n_i})^{l_i}}{l_i!} . \tag{4.4b}$$

The summation in (4.4b) runs over all partitions $\mathscr{P}$ of n objects into l groups ($1 \le l \le n$):

$$n=\sum_{i=1}^{m_{\mathscr{P}}} l_i n_i\ ,\quad l=\sum_{i=1}^{m_{\mathscr{P}}} l_i\ . \tag{4.4c}$$

[As an example: the partition (9) $\Rightarrow$(4)(2)(2)(1) has $n=9$, $m_{\mathscr{P}}=3$, $l=4$, $(l_1,l_2,l_3)=(1,2,1)$; $(n_1,n_2,n_3)=(4,2,1)$; its coefficient in (4.4b) would be -27. One may show that all coefficients are integers.]

Before one applies this formalism one must first eliminate the eigenvalue $\lambda=0$ by means of a division through $C_N^{(1)}$. The moments are then

$$M_p=\sum_{i=2}^{N}(\lambda_i)^{-p}\ . \tag{4.5}$$

They are obtained from (4.4) by substituting

$$\tilde{C}_p=C_N^{(p+1)}/C_N^{(1)}\ . \tag{4.6}$$

If this program is carried out with $C_N^{(p)}$ approximated by

$$[C_N^{(p)}]^{[1]}=\frac{2N^{2p}}{(2p!)}f_1^p\left[1+p\frac{\sigma_\alpha+\sigma_\beta}{Nf_1}\right]+O(N^{2p-2})\ . \tag{4.7}$$

We obtain a sequence of approximate moments starting with

$$M_1=2f_1\left[\frac{N}{2\pi}\right]^2\zeta(2)\times(1+\Sigma-\Sigma^2+\Sigma^3-\Sigma^4+\cdots)\ ,$$
$$M_2=2f_1^2\left[\frac{N}{2\pi}\right]^4\zeta(4)\times(1+2\Sigma+3\Sigma^2+8\Sigma^3+13\Sigma^4+\cdots)\ , \tag{4.8}$$
$$M_3=2f_1^3\left[\frac{N}{2\pi}\right]^6\zeta(6)\times(1+3\Sigma+\tfrac{15}{2}\Sigma^2-\tfrac{1}{2}\Sigma^3+24\Sigma^4+\cdots)\ ,$$

etc., with $\Sigma=(\sigma_\alpha+\sigma_\beta)/Nf_1$ and

$$\zeta(q)=\sum_{n=1}^{\infty}n^{-q} \tag{4.9}$$

the Riemann ζ function, which for even q assumes the values[7]

$$\zeta(2p)=\frac{2^{2p-1}|B_p|}{(2p)!} \tag{4.10}$$

with B_p the pth Bernoulli number.

For $3\le p\le 7$ the results we obtain satisfy the formula

$$M_p=f_1^p\left[\frac{N}{2\pi}\right]^{2p}\left\{\zeta(2p)\left[1+\binom{2p}{1}\Sigma+\binom{2p}{2}\Sigma^2+\binom{2p}{3}\Sigma^3+\binom{2p}{4}\Sigma^4\right]-\frac{1}{12}\left[\frac{2\pi}{N}\right]^2\zeta(2p-2)[2p\Sigma^3+2p(2p-1)\Sigma^4]+O(\Sigma^5)\right\}. \tag{4.11}$$

Of course, retaining the Σ^4 terms is not justified in view of the errors in (4.7). They have been retained merely to facilitate the pattern recognition. The pattern of zeros responsible for this sequence of moments is

$$\lambda_n=-f_1^{-1}k_n^2\quad(n=2,3,\ldots,\infty) \tag{4.12}$$

with k_n the solutions of the equation

$$\cos Nk+\tfrac{1}{2}Nk\Sigma\sin Nk=1\ , \tag{4.13}$$

which may be written in the form

$$k_{2n}=\frac{2\pi n}{N}\ , \tag{4.14}$$
$$k_{2n+1}=\frac{2\pi n}{N}\left[\frac{1}{1+\Sigma}+\frac{1}{12}\left[\frac{2\pi n}{N}\right]^2\frac{\Sigma^3}{1+\Sigma}+O(\Sigma^5)\right].$$

The pattern of zeros satisfies the general properties derived in Sec. III after (3.7). The dispersion relation (4.13) is derived in Appendix B for a specific model, namely diffusion along a circle with a single bottleneck. (The corresponding oscillation spectrum is that of a thin elastic bracelet with a single heavy point mass in it.) It is clear from (4.12) and (4.14) that $k_{2n+1}-k_{2n}$ is of order $nN^{-3/2}$, whereas $k_{2n}-k_{2n-2}$ is of order nN^{-1}. Therefore, the doublets become narrower with increasing N, even when one keeps nN^{-1} (and hence the value of λ) constant in the process. We conclude our discussion of the results (4.8) and (4.9) by noticing that all correction terms for M_1 and the last two in M_2 correspond to divergent expressions when the substitutions (4.14) are made. It is therefore not surprising that, but for the first one in M_1, they do not conform to the pattern (4.11).

V. THS EIGENVALUE DENSITY IN THE LOW-FREQUENCY REGION

The eigenvalue distribution (4.14) does not lead to an eigenvalue density different from the one obtained by retaining the term $C_N^{[0]}(\lambda)$ in (3.3). Thus, the results obtained in the preceding section, though of some interest in their own right and as an illustration of our moment method, are not very relevant for the behavior of our system in the thermodynamic limit. To obtain results which do have some relevance, we must consider higher-order terms in (3.7). However, then our program cannot be carried out for the $C_N(\lambda)$ themselves, but only for their ensemble average. Fortunately, this is all one needs for determining the low-frequency density of states, as we shall argue presently.

The expression for $C_N^{[2]}(\lambda)$ as defined before (3.7) cannot be cast in a simple form like the one derived from (3.3). However, as we show in Appendix A, the ensemble average of $C_N^{[2]}(\lambda)$ does have a simple form in the limit of high N; an explicit form is derived there for the case where all β_j are equal, and only the α_j are allowed to fluctuate.

The relevance of the ensemble-averaged polynomial for determining the averaged distribution of eigenvalues can be argued as follows.[8] From the considerations in Sec. II it is clear that the number of eigenvalues on a certain interval on the real line can be expressed in the contour integral of the trace of the resolvent along a curve encircling that interval. By comparing (2.8) and (2.10) (see Appendix A for further details), one sees readily that the sum over n of the right-hand side of (2.11a) is just the derivative of $\Delta_N(z)$ with respect to z. For large N and small $|z|$, and at some distance from their zeros, which all lie on the real line, both $\Delta_N(z)$ and its derivative have only small relative fluctuations. Thus, it is justified to replace the average of their quotient by the quotient of their averages. If we make that approximation along the entire contour, we obtain the number of zeros of $\langle \Delta_N(\lambda) \rangle$. The approximation breaks down when Imz becomes of the order of the spacing between the zeros of Δ_N; for large N this part of the contour becomes relatively unimportant. Note that our argument relies crucially on the smallness of $|z|$; for larger $|z|$ the "method of the average eigenvalue equation" can be justifiably criticized.[8]

If we expand the coefficients in $\langle C_N^{[2]} \rangle$ in powers of N^{-1} and retain only the first nonvanishing correction term, we obtain (see Appendix A)

$$\langle C_n^{(p)} \rangle = \frac{2N^{2p}}{(2p)!} f_1^p + \frac{N^{2p-2}}{(2p-3)!} f_1^{p-1} (f_2 - \tfrac{1}{12} f_1) + O(N^{2p-3}) \tag{5.1}$$

with

$$f_2 = \frac{f_1}{N^2} \sum_{i=1}^{N} \sum_{j=i}^{N} (j-i)(N+i-j) \langle \delta_i^\alpha \delta_j^\alpha \rangle \ . \tag{5.2}$$

Owing to the short range of the correlations only terms with $j-i \ll N$ or $N+i-j \ll N$ contribute to the sum, and f_2 is a quantity of order unity. The factor $j-i$ arises from the fact that factors α^{-1} and β^{-1} alternate in (2.13). For a similar term containing the correlation function $\langle \delta_i^\alpha \delta_j^\beta \rangle$, this restriction is irrelevant. The presence of such a correlation would lead to a term of order N between the brackets in the second term of (5.1). This would require an essential modification of the procedure to be used to derive the density of eigenvalues.

If we apply the procedure of Sec. IV with the averaged coefficients (5.1), we obtain for the first few averaged moments

$$M_1 = 2 \left[\frac{N}{2\pi} \right]^2 \frac{\pi^2}{6} f_1 + (f_2 - \tfrac{1}{12} f_1) \ ,$$

$$M_2 = 2 \left[\left[\frac{N}{2\pi} \right]^4 \frac{\pi^4}{90} f_1^2 - 2 \left[\frac{N}{2\pi} \right]^2 \frac{\pi^2}{6} f_1 (f_2 - \tfrac{1}{12} f_1) \right] + O(N) \ , \tag{5.3}$$

$$M_3 = 2 \left[\left[\frac{N}{2\pi} \right]^6 \frac{\pi^6}{945} f_1^3 - 3 \left[\frac{N}{2\pi} \right]^4 \frac{\pi^4}{90} f_1^2 (f_2 - \tfrac{1}{12} f_1) \right] + O(N^3) \ ,$$

which suggests the general expression

$$M_p = 2\left[\left(\frac{N}{2\pi}\right)^{2p}\zeta(2p)f_1^p - p\left(\frac{N}{2\pi}\right)^{2p-2}\zeta(2p-2)f_1^{p-1}(f_2-\tfrac{1}{12}f_1)\right] + O(N^{2p-3}) . \quad (5.4)$$

We did not prove (5.4) but verified it by explicit calculation for $2 \le p \le 7$. In particular, the emergence of $B_{12}=691/2370$ in M_6 and M_7 was comforting [cf. (4.10)]. The moments (5.4) for $p \ge 2$ can be reproduced by assuming for λ_i the values

$$\lambda_{2n}=\lambda_{2n+1}=-f_1^{-1}\left(\frac{2\pi n}{N}\right)^2 - f_1^{-2}(f_2-\tfrac{1}{12}f_1)\left(\frac{2\pi n}{N}\right)^4+\cdots \quad (5.5)$$

and substituting the Taylor expansion

$$(-\lambda_{2n})^p=\left(\frac{N}{2\pi n}\right)^{2p} f_1^p\left[1-\frac{pn^2}{4\pi^2}\frac{f_2-\frac{1}{12}f_1}{f_1}+\cdots\right] \quad (5.6)$$

in the expression

$$M_p=\sum_{j=2}^{\infty}(-\lambda_j)^{-p} . \quad (5.7)$$

Even the discrepancy for M_1 in (5.3) becomes understandable. Substitution of (5.6) in (5.7) yields a divergent result; the actual M_1 includes contributions from high-lying λ_n for which the approximation (5.5) is not adequate.

From the considerations earlier in this section it is clear that (5.5) need not be the actual zeros of any particular realization $\Delta_N(z)$. They do, however, lead to the correct average eigenvalue density. This density is given by

$$\rho(\lambda)=2\left[\frac{d\,|\lambda|}{dn}\right]^{-1}\rho(n) \quad (\lambda \le 0) , \quad (5.8)$$

where $\rho(n)$, the density of integers, is of course unity, and the factor 2 stems from the double degeneracy. Substituting (5.5) and converting to the variable λ yields

$$\rho(\lambda)=\frac{N}{\pi(f_1|\lambda|)^{1/2}}[1-\tfrac{3}{2}(f_2-\tfrac{1}{12}f_1)|\lambda|+\cdots] \quad (\lambda \le 0) , \quad (5.9)$$

which may be considered as the main result of our paper. The corresponding asymptotic decay of $\langle G_{nn}(t)\rangle$ is

$$\langle G_{nn}(t)\rangle \approx \frac{1}{(\pi f_1 t)^{1/2}}-\frac{3}{4}\frac{f_2-\frac{1}{12}f_1}{(\pi f_1 t^3)^{1/2}} . \quad (5.10)$$

For a random harmonic chain the variable $-\lambda_n$ corresponds to the square of the nth phonon frequency ω_n. The density $\rho(\omega)$ at a low ω is related, e.g., to the low-temperature specific heat of a chain. The leading term in (5.9) is well known.[1] The explicit expression (3.4a) for f_1 when both α_i and β_i are random may not have appeared in the literature, but its form is clearly indicated by the scaling considerations in Sec. IX of Ref. 1. The correction term in (5.9) is new.

VI. CONCLUDING REMARKS

The result (5.9) basically states that as far as the low-frequency density of states is concerned, a random chain behaves very much like a homogeneous one. The terms with f_1 in (5.9), and in (5.5) on which it is based, are simply the Taylor expansion of the expression (3.6) for a homogeneous chain. However, correlations do influence the first correction term. If the inhomogeneities are sufficiently large and positively correlated over some distance, they may even change the sign of this term. Of course all this presupposes that f_1 and f_2 do have a thermodynamic limit. Our discussion of this point in Sec. III did not cover the case when the α^{-1} and β^{-1} both fluctuate and have nonvanishing cross correlations. Similarly, it is not clear whether extending our calculations by including more terms from the expansion (3.3) will provide further well-behaved correction terms.

A particular case for which the corrections are well-behaved, albeit trivial, is that in which no correlations exist at all. Then all correction terms in (3.3) have vanishing expectation values and the density of states is exactly given by that implicit in (3.6):

$$\rho_0(\lambda)=\frac{N}{\pi[1-(1-\frac{1}{2}f_1|\lambda|)^2]^{1/2}} \quad (-4f_1^{-1} \le \lambda \le 0) . \quad (6.1)$$

Of course, the expression holds only for small $f_1|\lambda|$ since only terms in (3.3) with $p << N$ have the property that their mean square is small, which in turn is a requirement for the applicability of the

"averaged eigenvalue equation method." Indeed, numerical results[9] on the eigenvalue distributions in random chains show that the irregular peak structure characteristic for spectra of random chains sets in for "wave vectors" that are an appreciable fraction of the maximum wave vector of the corresponding homogeneous chain. (For any one-dimensional chain, regular or random, with periodic boundary conditions, the eigenvectors $\vec{p}_{2n}$ and $\vec{p}_{2n+1}$ have exactly $2n$ nodes, hence N/n may be interpreted as an average wavelength of this eigenvector in units of the distance between successive traps.)

The moment method used certainly has the disadvantage that the distribution of zeros must be guessed from the "fingerprint" they leave in the form of the moments M_p; no general methods are known to us. On the other hand, the method is free of approximations and it may at the least serve as a check on approximate methods. We note in this connection that the contour integral justification for the average eigenvalue equation method may be avoided. Instead[8] one may multiply the characteristic polynomials $\Delta_N^{(i)}(\lambda)$, $1 \le i \le M$, and determine the distribution of zeros of this polynomial of NMth degree using our moment method. Dividing the resulting eigenvalue density by M leads again to the results in Sec. V, under the assumption that M is large compared to N^2. This would be typical for three-dimensional samples in which excitations may diffuse along one-dimensional chains that are long on a molecular scale, but not quite as long as the dimensions of the sample.

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APPENDIX A: SOME COMBINATORIAL RESULTS

The first problem addressed here is how many ways are there to distribute $(p-1)$ α^{-1} at points k_j and p β^{-1} at points l_i subject to the restrictions (2.13) with $k_p = M+1$. To answer this, first choose $2p-1$ numbers from the set $(1,\ldots,M+p-1)$ and label them m_j in ascending order. Then set

$$l_i = m_{2i+1} - (i-1) ,$$

$$k_j = m_{2j+2} - j .$$

The set $\{ l_i, k_j \}$ obeys the restrictions imposed. The number of ways the m_j can be chosen is obviously

$$\mathcal{N}_M(p) = \binom{M+p-1}{2p-1} = \frac{M}{(2p-1)!} \prod_{q=1}^{p-1} (M^2 - q^2) . \tag{A1}$$

This explains the coefficient of σ_α in (3.3); the coefficient of σ_β is obtained by a minor modification of the same argument. To find the number of ways in which p α^{-1} and p β^{-1} can be arranged on a ring, first fix the label of one of the α^{-1}. The remaining labels can be distributed in $\mathcal{N}_N(p)$ ways. The α^{-1} singled out at first can occupy any of N places, but it may be any of the p α^{-1} in any given configuration, hence the additional factor N/p in the first term in (3.3). Expanding this factor in powers of N^{-2} using (A1), one obtains

$$\frac{N}{P}\binom{N+p-1}{2p-1} \simeq \frac{N^{2p}}{p(2p-1)!}\left[1 - \sum_{q=1}^{p-1} \frac{q^2}{N^2} + O(N^{-4})\right]$$

$$= \frac{2N^{2p}}{(2p)!}\left[1 - \frac{p(p-1)(2p-1)}{6N^2} + O(N^{-4})\right] = \frac{2N^{2p}}{(2p)!} - \frac{N^{2p-2}}{12(2p-3)!} + O(N^{2p-4}) , \tag{A2}$$

which explains the coefficients of the terms with f_1 in (5.1). The "cutting argument" used to relate the coefficients in (3.3) can also be used to show that the sum over n of the right-hand side of (2.11a) is the derivative of $\Delta_N(z)$ with respect to z. The coefficient of λ^p in this sum contains $\sum_n \alpha_n^{-1} B_{N+n}^{(p)}$. The sum of all terms in $C_N^{(p)}$ that correspond to taking a factor $(-\lambda)$ at the nth diagonal site con-

tains $\alpha_n^{-1}B_{n\,n+N}^{(p-1)}$. Summing this over n yields $pC_N^{(p)}$ since each term is counted p times. This establishes the required relationship.

To calculate the contribution to $C_N^{(p;2)}$ in (3.3) containing the product $\delta_i^\alpha\delta_j^\alpha$ we must find the number of ways one may distribute p β_k^{-1} and $(p-2)$ α_l^{-1} over the remaining sites. Both the inner and the outer gap must contain at least one β_k^{-1}, since α_l^{-1} and β_k^{-1} must alternate, including the two fixed α_l^{-1} at sites i and j. Thus one arrives at

$$C_N^{(p;2)}=f_1^{p-2}\sum_{i=1}^{N}\sum_{j=i}^{N}\sum_{q=1}^{p-1}\binom{j-i+q-1}{2q-1}\times\binom{N+i-j+p-q-1}{2p-2q-1}\times\delta_i^\alpha\delta_j^\alpha \tag{A3}$$

for the case when all δ_i^β vanish; the index q stands for the number of β_k^{-1} on the segment $[i,j)$. This is is not simply a multiple of the unaveraged version $\tilde{f}_2$ of f_2, defined in (5.2); it also contains terms proportional to

$$\tilde{f}_2^{(q)}=\frac{f_1}{N^2}\sum_{i=1}^{N}\sum_{j=i}^{N}(j-i)^q(N+i-j)^q\delta_i^\alpha\delta_j^\alpha \tag{A4}$$

for all q up to $p-1$. However, when one takes the ensemble average of (A3) and assumes short-range correlations, only the terms with $j-i$ small [or $N+i-j$ small, but this yields only a small correction, which is nevertheless recaptured in the second line of (A5)] survive, and for those the contribution with $q=1$ is by far the largest. Hence

$$\langle C_N^{(p;2)}\rangle\simeq\sum_{i=1}^{N}\sum_{j=i}^{N}(j-i)\binom{N+i-j+p-2}{2p-3}f_1^{p-2}\langle\delta_i^\alpha\delta_j^\alpha\rangle$$
$$\simeq\frac{N^{2p-4}}{(2p-3)!}f_1^{p-2}N^2f_1f_2=\frac{N^{2p-2}}{(2p-3)!}f_1^{p-1}f_2\ . \tag{A5}$$

This completes our derivation of (5.1).

APPENDIX B: DIFFUSION WITH A SINGLE BOTTLENECK

Consider a particle diffusing on the segment $(0,L)$. The time evolution of its probability density $p(x,t)$ is governed by

$$\frac{dp(x,t)}{dt}=D\frac{d^2p(x,t)}{dx^2}\ . \tag{B1}$$

The ends are connected via a "leaky valve" through which a current proportional to the concentration jump flows:

$$j(t)=-\gamma D[p(0,t)-p(L,t)]\ . \tag{B2}$$

Furthermore, one must have continuity of current:

$$j(t)=-D\left[\frac{dp(x,t)}{dt}\right]_{x=0}=-D\left[\frac{dp(x,t)}{dx}\right]_{x=L}\ . \tag{B3}$$

To find the eigenvalues of this system

$$\lambda_j=-Dk_j^2\ , \tag{B4}$$

we substitute the solution of (B1)

$$p(x,t)=e^{-|\lambda_j|t}(a_je^{ik_jx}+b_je^{-ik_jx}) \tag{B5}$$

in the equations (B3) and (B4). The determinant of the resulting system of equations equals

$$\Delta=2\gamma(1-\cos k_jL)-k_j\sin k_jL\ . \tag{B6}$$

Putting this equal to zero and setting $\gamma^{-1}=N\Sigma$ yields the equation (4.13).

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