Hubbard model for a disordered linear chain: Probability distribution of exchange*†

George Theodorou
Department of Physics and The James Franck Institute, The University of Chicago, Chicago, Illinois 60637
(Received 1 March 1976)

The Hubbard model for a disordered linear chain with a half-filled band is studied. At low temperatures ($T \lesssim U/4k$) and sufficiently small transfer integrals, the Hamiltonian via a perturbation expansion reduces to that of a disordered one-dimensional Heisenberg antiferromagnet. It is found that the coupling constant J has for $n \gg 1$ the behavior $J = Dn^{\alpha}\beta^{2n}$, where D, α, and β depend on the parameters of the Hamiltonian and n is the number of intermediate sites between localized spins, and is a random variable. An expression for the probability distribution $P(J)$ of exchange integral J is also obtained. For small J, $P(J) \propto 1/J^{1-c}|\ln(J/D)|^{ac}$. That is, $P(J)$ has a singularity at the origin for $c < 1$, where c depends on the parameters of the Hamiltonian.

I. INTRODUCTION

The study of one-dimensional systems is significant for several reasons. Because of their simplicity, they are easier to treat than the higher-dimensional ones. One can often obtain exact results without resorting to approximations and expects to be able to use this knowledge in treating more complex situations. In addition the one dimensionality in some cases leads to fascinating properties which are remarkably different from those of higher-dimensional systems. Furthermore, experimental investigations of a variety of compounds possessing quasi-one-dimensional structures have been reported.[1] The most prominent examples are some of the "mixed valence" complexes[2] of platinum and iridium, and certain salts of the organic ion-radical tetracyanoquinodimethane (TCNQ).[3] Bloch *et al.*[4] were the first to recognize the implications of the fact that x-ray crystallographic data[5,6] showed some of the above-mentioned quasi-one-dimensional compounds to be structurally disordered. One theoretical model extensively used in the study of the various properties of one-dimensional systems is the Hubbard model.[7] In view of the remarks of Bloch *et al.*[4] we expect that an investigation of the effects of disorder in the Hubbard Model will give results which will be proven applicable to a large class of one-dimensional systems. For relatively small transfer integrals t, and for low temperatures, the Hubbard model becomes equivalent[8] to a Heisenberg model as regards magnetic properties. We are particularly interested in the effect of disorder on magnetic properties of one-dimensional systems. Accordingly, in this paper we consider the probability distribution of the exchange interactions between localized spins arising in the Hubbard model of a disordered linear chain.

The simplest form of the Hubbard Hamiltonian for a disordered linear chain is

$$H = H_0 + V \ , \tag{1.1}$$

where

$$H_0 = \sum_{i,s} \epsilon_i a_{is}^{\dagger} a_{is} + U \sum_i a_{i\uparrow}^{\dagger} a_{i\uparrow} a_{i\downarrow}^{\dagger} a_{i\downarrow} \ ,$$
$$V = \sum_{i,j} t_{ij} a_{is}^{\dagger} a_{js} \ , \quad t_{ij} = t(\delta_{i,j+1} + \delta_{i,j-1}) \ . \tag{1.2}$$

Here $\{\epsilon_i\}$ are the single-site energies, which are considered to be independent random variables (with zero mean, and rms σ), t_{ij} is the transfer matrix element, and U is the Coulomb repulsion. We treat H_0 as the zero-order Hamiltonian and the electron-hopping term V as a perturbation, so that an appropriate perturbation expansion applies in the case $|t|$ sufficiently smaller than U, σ. The perturbation expansion results in an effective Hamiltonian of the form of the Heisenberg spin Hamiltonian, with nearest-neighbor interaction, and random coupling constant.

In Sec. II we present the formal theory of the perturbation expansion. Section III contains the evaluation of the expansion. In Sec. IV we derive the probability distribution of the random coupling constant for the cases (a) $t \ll U \ll \sigma$, and (b) $t \ll U \sim \sigma$. Finally in Sec. V we summarize our findings and give our conclusions. We reserve for subsequent publication study of various simple model Hamiltonians with that probability distribution of exchange and application to N-methylphenazinium-tetracyanoquinodimethanide (NMP-TCNQ). A preliminary account of the present study of the distribution of exchange interaction and of these latter applications has appeared.[9]

II. PERTURBATION EXPANSION

In one dimension, an infinitesimal amount of static disorder causes the states of noninteracting electrons to become localized.[10-12] In the strong-disorder limit the localization length becomes

smaller than the interatomic distance. In that case, we have to choose the zero-order Hamiltonian so as to reflect this property. The Hamiltonian H_0 describes a system of electrons localized on sites l, and satisfies the localization requirement on our zero-order Hamiltonian. As we shall see below, the ground state of H_0 contains singly occupied sites, that is localized spins. Spins sitting on different sites do not interact among themselves. As a result the zero-order ground-state energy does not depend on the orientation of the spin of the electrons sitting on singly occupied sites, and therefore the zero-order ground state is degenerate. For a configuration containing n singly occupied sites, the degeneracy of the zero-order ground state is 2^n. Our perturbation expansion must therefore take this degeneracy into account. In the absence of the Hubbard interaction, the localization property would assure the convergence of the perturbation expansion, as proven by Economou and Cohen.[13] As the interaction provides an additional localizing influence, we can expect the perturbation expansion to converge *a priori*. However, we have not attempted a proof because of the complications introduced by the interaction.

Before going on to the perturbation expansion, we shall diagonalize H_0. We examine the case in which the probability distribution of single-site energies is Gaussian with rms σ, and the band is half-filled. Although the chemical potential μ can be determined in the usual manner by fixing the average number of particles, we can set it immediately at $\frac{1}{2}U$ for the present case of a half-filled band. Electron-hole symmetry implies that μ is independent of temperature, and it is clear both physically, and by direct calculations that $\mu=\frac{1}{2}U$. As a result the occupancy at low temperatures, $kT \ll U$, is as follows[14]: Sites with energy $\epsilon_i < -\frac{1}{2}U$ are doubly occupied, those with energy $-\frac{1}{2}U<\epsilon_i<\frac{1}{2}U$ are singly occupied, and sites with energy $\epsilon_i>\frac{1}{2}U$ are empty (Fig. 1). Thus the probability for a site to be singly occupied at $T=0$°K is given by

$$p=\mathrm{erf}(U/2\sqrt{2}\,\sigma), \tag{2.1}$$

where erf is the error function. Generally the probability distribution of the single-site energies varies with the temperature. In the forthcoming analysis we are going to assume that the sites have their zero-temperature occupation. In order for this assumption to be meaningful the probability $p(T)$ for a site to be singly occupied must be close to that of (2.1). We define the critical temperature up to which our analysis is correct by the relation $p(T_c)\simeq 1.20p$, with p given by Eq. (2.1). This relation gives $T_c \simeq U/4k$.

We now proceed with the development of the perturbation formalism. We define P to be the projection operator to the space spanned by the zero-order ground states, and Q the projection operator to the complementary space. As projection operators, P and Q satisfy the relations

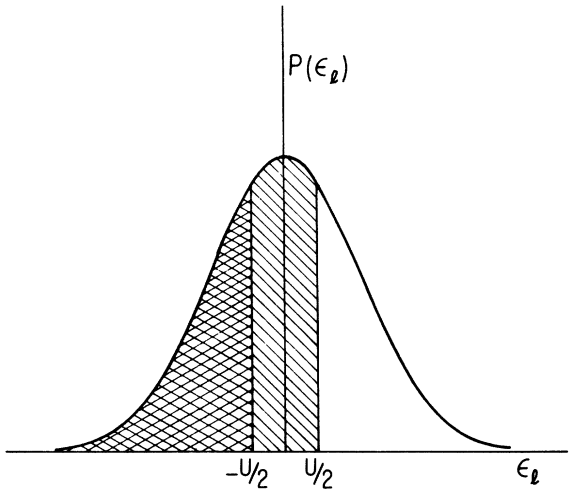

FIG. 1. Gaussian probability distribution for single-site energies. Sites with energy $\epsilon<-\frac{1}{2}U$ are doubly occupied, those with $-\frac{1}{2}U<\epsilon<\frac{1}{2}U$ are singly occupied, and sites with $\epsilon>\frac{1}{2}U$ are empty.

$$P+Q=1,\quad P^2=P,\quad Q^2=Q,\quad PQ=QP=0. \tag{2.2}$$

Using these properties of P and Q, the Schrödinger equation for the stationary states

$$(E-H)\psi=0$$

can be written as follows:

$$(E-H)(P+Q)\psi=0.$$

Premultiplication by P yields

$$(E-PHP)P\psi=(PHQ)Q\psi, \tag{2.3}$$

while premultiplication by Q yields

$$(E-QHQ)Q\psi=(QHP)P\psi. \tag{2.4}$$

Equation (2.4) may be inverted to give

$$Q\psi=(E-QHQ)^{-1}(QHP)P\psi, \tag{2.5}$$

and substituting $Q\psi$ into Eq. (2.3) we obtain that the equation for $P\psi$ is

$$[E-PHP-PHQ(E-QHQ)^{-1}QHP]P\psi=0, \tag{2.6}$$

which means that instead of solving the Schrödinger equation in the total space, we can solve it in the subspace spanned by the degenerate eigenfunctions of the zero-order ground state. In this subspace our system will be described by an effective Hamiltonian

$$H_{\mathrm{eff}}=PHP+PHQ(E-QHQ)^{-1}QHP. \tag{2.7}$$

Utilizing the usual Green's-function expansion

$$\frac{1}{E-QHQ} = \sum_{n=0}^{\infty} G_0(QVQG_0)^n,$$

with

$$G_0 = (E - QH_0Q)^{-1}, \tag{2.8}$$

we can rewrite Eq. (2.7) as

$$H_{eff} = PHP + PHQ \sum_{n=0}^{\infty} G_0(QVQG_0)^n QHP. \tag{2.9}$$

Let us now concentrate on our case, where the Hamiltonian is given by (2.1). The effect of V is to transfer an electron from site to site. Therefore, application of V to the ground state will cause the hopping of an electron from a singly occupied site to an empty one, or from a doubly occupied site either to a singly occupied site or to an empty one. All these processes cause the system to become excited. Similarly V operating on the excited states created by the hopping of *one* electron may cause a transition to the ground state. On the other hand, H_0 does not cause transitions from one state to another. The above mentioned physical arguments can be described mathematically by the following relations:

$$PHP = PH_0P, \quad PHQ = PVQ, \quad QHP = QVP. \tag{2.10}$$

Combining Eqs. (2.9) and (2.10) we obtain

$$H_{eff} = PH_0P + PVQ \sum_{n=0}^{\infty} G_0(QVQG_0)^n QVP. \tag{2.11}$$

We now proceed as follows: From the total system, consisting of an infinite number of empty, singly, and doubly occupied sites, randomly mixed, we isolate a subsystem composed of two singly occupied sites between which exists a random combination of empty and doubly occupied sites as shown in Fig. 2. In this particular case the degeneracy of the zero-order ground state is equal to 4. Thus the zero-order ground-state eigenvectors of this subsystem labelled according to the orientation of the end spin are

$$|1\rangle = |\uparrow\uparrow\rangle, \quad |2\rangle = |\downarrow\downarrow\rangle,$$
$$|3\rangle = |\uparrow\downarrow\rangle, \quad |4\rangle = |\downarrow\uparrow\rangle. \tag{2.12}$$

Expanding $P\psi$ in terms of the $|i\rangle$'s $i = 1, \ldots, 4$ we obtain

$$P\psi = \sum_{i=1}^{4} c_i |i\rangle,$$

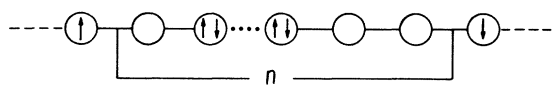

FIG. 2. Part of an infinite chain consisting of two singly occupied sites between which exist a total number n of empty and doubly occupied sites.

and writing the Schrödinger equation in matrix representation, we get that the eigenvalues of the Hamiltonian of the subsystem are the solutions of the secular equation:

$$\det(H_{eff} - EI) = 0.$$

Thus in order to obtain the eigenvalues of H_{eff} we must evaluate the matrix elements of H_{eff}. The matrix elements can be expressed as

$$\langle i|H_{eff}|j\rangle = E_0\delta_{ij} + \sum_{n=0}^{\infty} \langle i|PVQG_0(QVQG_0)^n QVP|j\rangle. \tag{2.13}$$

Each time that V operates it causes the hoping of an electron from a site to its nearest-neighbor site. Because of the fact that the initial and final states, $|i\rangle$ and $|j\rangle$, respectively, belong to the manifold of the zero-order ground state, one can see that it is necessary to have an *even* number of V applications present, otherwise the matrix element will be zero. Thus the expansion will contain only even-order terms. The presence of Q in the intermediate positions of Eq. (2.13), assures that no intermediate state can belong to the zero-order ground state.

From the perturbation expansion of H_{eff} we are interested to keep terms which contribute to the coupling of the end electrons. For a subsystem with n intermediate sites, all terms of the expansion of order less than $2(n+1)$ do not contribute to the coupling of end spins, that is their contribution is independent of the orientation of the end spins. The effect of all those terms is to renormalize the zero-order Green's functions. The lowest-order perturbation that contributes to the coupling of the end spins is $2(n+1)$. We also assume that terms of order higher than $2(n+1)$ make a fairly small contribution in comparison with the $(2n+2)$ term, and thus ignore them. In conclusion, for a subsystem with n intermediate sites the only term that we expect to contribute significantly to the coupling of the end spins is the $2(n+1)$ one. This is the reason we chose to isolate the subsystem of two spins and n intermediate empty or doubly occupied sites, and treated it separately. One can expect that this grouping, repeated for all possible pairs of nearest-neighbor singly occupied sites, will result in a fairly good approximation to the real physical system, namely that of an infinite chain, in the limit $t \ll U, \sigma$. In the present calculation we ignore interactions involving more than two spins, which would be present if the Hamiltonian were derived to consistent order in perturbation expansion.

From Eq. (1.2) one can see that V is a sum of terms. As a result, the matrix elements of H_{eff} are also sums of terms which originate from all

possible combinations of the various terms of V. In what follows any particular combination of such terms is going to be referred to as a *diagram*. Following Klein and Seitz[15] we represent a hopping from site i to site j by an arrow directed from i to j. Consequently, a diagram can be graphically presented as a set of arrows, each arrow representing an individual hopping. The arrows are ordered in such a way that the arrow representing the first hopping is located below the one representing the second hopping and so on (Fig. 3). In evaluating these diagrams one has to be careful not to violate Pauli's exclusion principle.

There is a subset of diagrams the contribution of which does not depend on the orientation of the end spins. Accordingly, such diagrams do not contribute to the coupling of end spins. We could eliminate them by renormalizing G_0, but, as they give a contribution to the exchange which is higher order in t, we neglect them instead. Elimination of these diagrams leads to

$$\langle 1|H_{eff}|1\rangle = \langle 2|H_{eff}|2\rangle = 0$$

and

$$\langle 3|H_{eff}|3\rangle = \langle 3|H_{eff}|4\rangle = \langle 4|H_{eff}|3\rangle = \langle 4|H_{eff}|4\rangle \equiv -H^{(2n+2)}.$$

The matrix elements $\langle 1|H_{eff}|j\rangle$; $j\neq 1$ and $\langle 2|H_{eff}|j\rangle$; $j\neq 2$ are equal to zero. This can be seen by making use of the symmetry of the system. A direct consequence of the symmetry is the conservation of the z component of the total spin. An example of the remaining diagrams for the system of Fig. 4 is given in Fig. 5. What we have managed to do is to reduce our original eigenvalue problem, the solution of which would have required the diagonalization of a 4×4 matrix, to that of a diagonalizing a 2×2 matrix with equal matrix elements. From Eq. (2.13) we note that for n even, there is an odd number of G_0's present. This, combined with the fact that all the G_0's are negative, gives $H^{(2n+2)}$ positive. The eigenvalues of H_{eff} are $-2H^{(2n+2)}$ and 0 with multiplicity one and three, respectively, corresponding to singlet and triplet states. Thus the effective Hamiltonian can be written

$$H_{eff} = -2H^{(2n+2)}(\tfrac{1}{4} - \vec{S}_1\cdot\vec{S}_2) = 2H^{(2n+2)}\vec{S}_1\cdot\vec{S}_2 + \text{const},$$

and since $H^{(2n+2)}>0$ the coupling between the end spins is antiferromagnetic. Therefore the Hamiltonian for the total system can be written as follows:

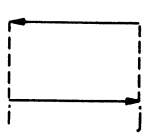

FIG. 3. Two-arrow diagram.

FIG. 4. Three-site system.

$$H_{eff} = \sum_i J_i \vec{S}_i\cdot\vec{S}_{i+1}, \tag{2.14}$$

with $J_i \geq 0$.

III. EVALUATION OF THE EXPANSION

The perturbation expansion we developed is of Brillouin-Wigner type, and the coupling constant J is calculated in terms of the eigenvalues of the total Hamiltonian, which are functions of J. Thus we have a typical self-consistent problem. For $t\ll U,\sigma$ the corrections to the zero-order energies are going to be small, and we can ignore them. Since we are interested in calculating the coupling constant at low temperatures, the system will be in its ground state, and therefore we can replace E in Eq. (2.8) by E_0, the zero-order ground state. The presence of Q in the denominator of G_0 prevents it from becoming infinite. We also ignore the renormalization effects, because we consider them to be minor for $t\ll U,\sigma$. Moreover, J depends on the separation of the spins and the single-site energies of the intermediate sites, all random variables. Therefore J is a random variable, and we must ultimately obtain its probability distribution. The latter is obtained in Sec. IV. The contribution to the magnetic properties at temperature

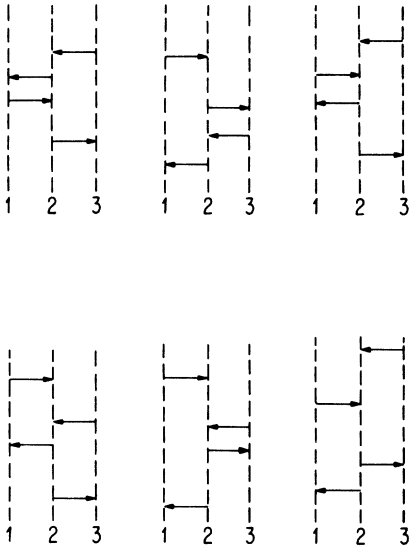

FIG. 5. Diagrams of the three-site system given in Fig. 4.

T is dominated by spins which are coupled by an exchange $J \lesssim kT$. Therefore our major concern in the present section is to calculate J in the asymptotic region, that is for a large number n of intermediate empty or doubly occupied sites, for which J is small and sharply distributed for fixed n.

From Eq. (2.13) one can easily derive the rules for evaluating diagrams; they are the following: (a) Each arrow contributes a factor t; and (b) each intermediate state contributes a factor $(E_0 - E_i)^{-1}$, where E_i is the energy of the state. The contribution of each diagram thus has for the form

$$\mathfrak{L}(n) = -t^{2n+2} \prod_{i=1}^{2n+1} \frac{1}{E_i - E_0} = -t^{2n+2} \exp\left(\sum_{i=1}^{2n+1} \ln(E_i - E_0) \right), \tag{3.1}$$

where n is the number of intermediate sites, and E_0 and E_i are functions of random variables, the single-site energies. Since in the asymptotic region n is large, we have sampling of a large number of denominators in $\mathfrak{L}$. Therefore, the leading behavior of $\mathfrak{L}$ for large n can be calculated by the use of the central-limit theorem which gives

$$\mathfrak{L}(n) \simeq -t^{2n+2} \exp\left(- \sum_{i=1}^{2n+1} \langle \ln(E_i - E_0) \rangle \right). \tag{3.2}$$

E_j and E_0 have the form

$$E = \sum_{j=1}^{n+2} n_j \epsilon_j + kU, \tag{3.3}$$

with ϵ_j being the single-site energies, n_j the occupation of the j site, and k the number of doubly occupied sites. Sites 1 and $n+2$ are sites whose energies belong to the region $(-\frac{1}{2}U, \frac{1}{2}U)$ while sites $2, \ldots, n+1$ have energies belonging in one of the regions $(-\infty, -\frac{1}{2}U)$ or $(\frac{1}{2}U, \infty)$.

To avoid analytical difficulties, we approximate the Gaussian probability distribution of single site energies given by Fig. 1 by the probability distribution

$$P(\epsilon) = \begin{cases} \dfrac{1}{(2\pi s^2)^{1/2} + U} \exp\left(- \dfrac{(|\epsilon| - \frac{1}{2}U)^2}{2s^2} \right) & \text{for } |\epsilon| > \tfrac{1}{2}U, \\ \dfrac{1}{U + (2\pi s^2)^{1/2}} & \text{for } |\epsilon| \leq \tfrac{1}{2}U. \end{cases} \tag{3.4}$$

For $U/s \to 0$ this distribution approaches a Gaussian. We require that distribution (3.4) has the same rms as the original Gaussian distribution. This requirement gives a relation that connects s with σ (the rms of the Gaussian distribution)

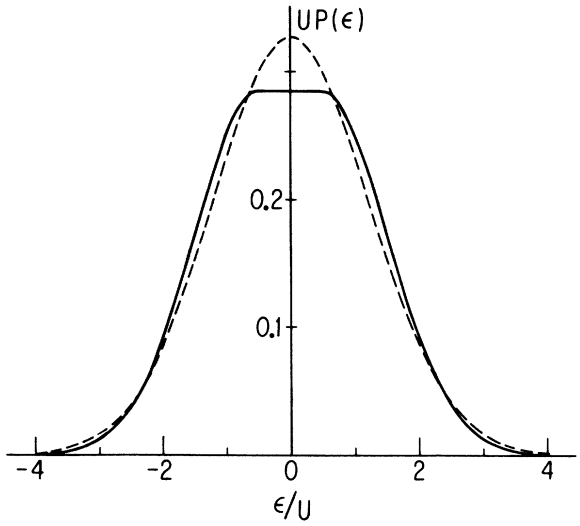

FIG. 6. Gaussian distribution (broken curve) of the single-site energies and an approximate distribution, as given by (3.4), with the same rms (solid curve) are plotted for the case $U = s$.

$$\sigma^2 = \{U^2/[1 + (2\pi)^{1/2} s/U]\} \times [\tfrac{1}{12} + \tfrac{1}{4}(2\pi)^{1/2} s/U + 2(s/U)^2 + (2\pi)^{1/2}(s/U)^3]. \tag{3.5}$$

Figure 6 gives the probability distribution (3.4) and a Gaussian with the same rms for the case of $U = s$. Figure 7 is a plot of σ/U as a function of s/U as given by Eq. (3.5). This figure indicates that it is a good approximation to write

$$\sigma = s + 0.217U. \tag{3.6}$$

We can now calculate the average $\langle \ln(E_i - E_0) \rangle$. We find in the Appendix

$$\langle \ln(E_i - E_0) \rangle \simeq \ln(a_i \sigma + b_i U). \tag{3.7}$$

We expect $\mathfrak{L}$ overall to have the behavior

$$\mathfrak{L}(n) = tf'(n)[t/(a'\sigma + b'U)]^{2n+1}, \tag{3.8}$$

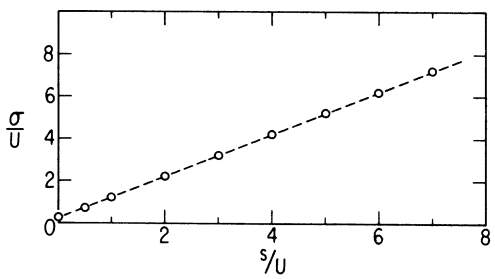

FIG. 7. σ/U as a function of s/U. The crosses represent relation (3.5) and the broken curve Eq. (3.6).

and that the coupling constant J, which comes from the summation of all possible diagrams, will eventually have the same behavior, that is,

$$J(n) = tf(n)[t/(a\sigma + bU)]^{2n+1}. \tag{3.9}$$

We now outline the calculations which we have carried out and give our results. The evaluation of the diagrams was performed on the IBM370 computer of The University of Chicago Computation Center. The values of a and b, as well as the form of $f(n)$ were then deduced by fitting the calculated values for $J(n)$ with a function of the form of Eq. (3.9).

A. Case 1: $t \ll U \ll \sigma$

In this case Eq. (3.9) becomes $J(n) = tf(n)(bt/\sigma)^{2n+1}$. Calculating $J(n)$ for $n = 1, 2, 3, \ldots, 6$ and doing the fitting, we found that J is given by

$$J(n) = n(0.82\sigma^2/U + 1.95\sigma)(1.4t/\sigma)^{2n+2}. \tag{3.10}$$

B. Case 2: $t \ll U \sim \sigma$

Here J can be written

$$J(n) = U(t/\sigma)^{2n+2} f(n)[(a\sigma/U + b)^{-1}]^{2n+1}. \tag{3.11}$$

We calculated $J(n)$ for $n = 1, 2, 3, 4$ and for different values of σ/U. The result of the fitting gives the form

$$J(n) = 7.77t^2\left[1 - \tanh\left(\frac{U}{\sigma}\right)\right] n^{1.35 - 2.17U/\sigma + 0.23U^3/\sigma^3} \left(\frac{t}{0.92\sigma - 0.26U}\right)^{2n} \left(\frac{1}{U} + \frac{(0.8)^{1.91 - 2.42U/\sigma + 0.18U^3/\sigma^3}}{1.82U + 0.02\sigma}\right). \tag{3.12}$$

Formula (3.12) for $U \ll \sigma$ reduces to

$$J(n) = n^{1.35}(6.4\sigma^2/U + 210\sigma)(1.1t/\sigma)^{2n+2}. \tag{3.13}$$

Result (3.13) has some differences from (3.10). The differences in $f(n)$ are not very important since the behavior of J is dominated by the power term. We attribute these differences to the form of $f(n)$ we chose. We expect a better choice of $f(n)$ to remove these disagreements. We also notice that there is a difference in the coefficient of the power term. However, taking into account the fact that Eq. (3.13) was deduced by doing a perturbation expansion in the region $U \sim \sigma$ while Eq. (3.10) is the result of a perturbation expansion in the region $U \ll \sigma$, the agreement between the coefficients of the power term can be considered as good enough.

Summarizing the expansion results we conclude that in both cases J has the behavior

$$J(n) = Dn^{\alpha}\beta^{2n}, \tag{3.14}$$

where n is the number of intermediate sites. Thus a necessary condition for the perturbation expansion to exist is $\beta < 1$.

IV. PROBABILITY DISTRIBUTION OF J

Equation (3.14) gives us the dependence of J on n. The distance, n, between two singly occupied sites is a random variable. The random character of n mades J also a random variable. The probability for a site to be singly occupied is given by Eq. (2.1). The probability that between a given singly occupied site and the next singly occupied site exist n empty or doubly occupied sites is

$$P(n) = (1-p)^n p. \tag{4.1}$$

We assume that p is sufficiently smaller than unity that $\ln(1-p) \simeq -p$. In that case Eq. (4.1) becomes

$$P(n) \simeq pe^{-np}. \tag{4.2}$$

The probability distribution of J is equal to

$$P(J) = \frac{1}{J} P(n)\left|\frac{d\ln J}{dn}\right|^{-1}. \tag{4.3}$$

Using Eq. (3.14) we can obtain the following relations:

$$\frac{d\ln J}{dn} = \frac{\alpha}{n} + 2\ln\beta \underset{n\to\infty}{\simeq} 2\ln\beta, \tag{4.4}$$

$$n = \frac{\ln(J/D)}{2\ln\beta} - \frac{\alpha \ln n}{2\ln\beta}. \tag{4.5}$$

Inserting Eq. (4.5) into Eq. (4.2) we get

$$P(n) = p(J/D)^c 1/n^{\alpha c}, \tag{4.6}$$

where $c = p/2|\ln\beta|$. For large n Eq. (3.14) gives

$$\ln(J/D) \simeq 2n\ln\beta. \tag{4.7}$$

Combining Eqs. (4.3), (4.4), (4.6), and (4.7) we obtain

$$P(J) = \frac{p}{2D|\ln\beta|} \frac{1}{(J/D)^{1-c}} \frac{(2|\ln\beta|)^{\alpha c}}{[|\ln(J/D)|]^{\alpha c}}. \tag{4.8}$$

Then the probability distribution of J/σ is given by

$$P_a(J/\sigma) = \frac{p\sigma}{2D|\ln\beta|} \frac{1}{(J/D)^{1-c}} \frac{(2|\ln\beta|)^{\alpha c}}{[|\ln(J/D)|]^{\alpha c}}. \tag{4.9}$$

The main characteristic of Eq. (4.9) is that for $c < 1$, $P_a(J/\sigma)$ has a singularity at $J = 0$.

Equation (4.9) gives $P(J/\sigma)$ in the asymptotic region, that is for $J \ll \sigma$. We are interested in finding $P(J/\sigma)$ not only in the asymptotic region, but also for every J/σ. Before going on with the general case we shall consider some special cases.

FIG. 8. Nearest-neighbor configuration.

A. Nearest neighbors

The configuration for this case is shown in Fig. 8. We treat the nearest-neighbor interaction exactly. From conservation of total spin we have that the Hamiltonian does not mix singlet and triplet states. Also the hopping matrix element does not couple the spins in the triplet state. The singlet states of the system are the following:

$$\psi_1 = a_{1\uparrow}^{\dagger} a_{1\downarrow}^{\dagger} |0\rangle ,$$
$$\psi_2 = (1/\sqrt{2})(a_{1\uparrow}^{\dagger} a_{2\downarrow}^{\dagger} - a_{1\downarrow}^{\dagger} a_{2\uparrow}^{\dagger})|0\rangle , \qquad (4.10)$$
$$\psi_3 = a_{2\uparrow}^{\dagger} a_{2\downarrow}^{\dagger} |0\rangle ,$$

with $a_{i\sigma}^{\dagger}$ the creation operator at site i. In this representation, the Hamiltonian has the form

$$H = \begin{pmatrix} 2\epsilon_1 + U & \sqrt{2}\,t & 0 \\ \sqrt{2}\,t & \epsilon_1 + \epsilon_2 & \sqrt{2}\,t \\ 0 & \sqrt{2}\,t & 2\epsilon_2 + U \end{pmatrix} , \qquad (4.11)$$

with ϵ_1, ϵ_2 the single-site energies. Because we require that the unperturbed ground state corresponds to both levels ϵ_1 and ϵ_2 singly occupied, the maximum difference between ϵ_1 and ϵ_2 is U. The energy of two singly occupied levels $\epsilon_1 + \epsilon_2$ is therefore less than the energy of either of the two doubly occupied levels $2\epsilon_1 + U$ or $2\epsilon_2 + U$ except

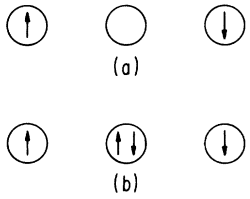

FIG. 9. Next-nearest-neighbor configuration. (a) Empty intermediate site; (b) doubly occupied intermediate site.

when $|\epsilon_1 - \epsilon_2| = U$, when it coincides with one of them. Apart from that limiting case $E_{\min}$ the smallest eigenvalue of the Hamiltonian corresponds to a singlet state consisting predominantly of two singly occupied sites. The coupling constant J, equal to the difference between singlet and triplet state, is then given by $J = \epsilon_1 + \epsilon_2 - E_{\min}$. We find $E_{\min}$ numerically, and the calculation of the probability distribution of J is done by the Monte Carlo method. In order to apply this method, we must know the values at t, U, σ, and p. We have used $t = 0.055$ eV, $U = 0.13$ eV, $\sigma = 0.136$ eV, and $p = 0.367$ from Ref. 9. The nearest-neighbor probability distribution, normalized to p, for these values is given in Fig. 10.

B. Next nearest neighbors

We have two possible configurations which are shown in Fig. 9. The diagrams that contribute to the coupling constant for the configuration of Fig. 9(b) are shown in Fig. 5. Evaluation of these diagrams gives that the coupling constant is equal to

$$J = 2\left[\frac{t^4}{(\epsilon_1 - \epsilon_2)^2(\epsilon_1 + U - \epsilon_3)} + \frac{t^4}{(\epsilon_3 - \epsilon_2)^2(\epsilon_3 + U - \epsilon_1)} + \frac{t^4}{-\epsilon_2 + U + \epsilon_1}\left(\frac{1}{\epsilon_1 - \epsilon_2} + \frac{1}{\epsilon_3 - \epsilon_2}\right)^2\right] . \qquad (4.12)$$

The coupling constant for the configuration of Fig. 9(a) can be found in the same way. The result of this calculation is

$$J = 2\left[\frac{t^4}{(\epsilon_3 - \epsilon_1)^2(\epsilon_3 + U - \epsilon_1)} + \frac{t^4}{(\epsilon_2 - \epsilon_3)^2(\epsilon_1 + U - \epsilon_3)} + \frac{t^4}{\epsilon_2 + U - \epsilon_1}\left(\frac{1}{\epsilon_2 - \epsilon_3} + \frac{1}{\epsilon_2 - \epsilon_1}\right)^2\right] . \qquad (4.13)$$

To attempt to find the probability distribution of J/σ analytically is a rather complicated process. Instead, we found the probability distribution $P(J/\sigma)$ by Monte Carlo techniques, using the previous values of t, U, and σ. The probability distribution $P_{nnn}(J/\sigma)$, normalized to $p(1-p)$, is shown in Fig. 10.

C. Total probability distribution

From Fig. 10 we see that the P_{nn} distribution is more or less separated from the rest of the distribution. Therefore, we write the total probability distribution in the form

$$P_t(J/\sigma) = P_1(J/\sigma) + P_{nn}(J/\sigma) . \qquad (4.14)$$

Since

$$\int_0^{\infty} P_t\left(\frac{J}{\sigma}\right) d\left(\frac{J}{\sigma}\right) = 1$$

and

$$\int_0^{\infty} P_{nn}\left(\frac{J}{\sigma}\right) d\left(\frac{J}{\sigma}\right) = p ,$$

we have

$$\int_0^{\infty} P_1\left(\frac{J}{\sigma}\right) d\left(\frac{J}{\sigma}\right) = 1 - p . \qquad (4.15)$$

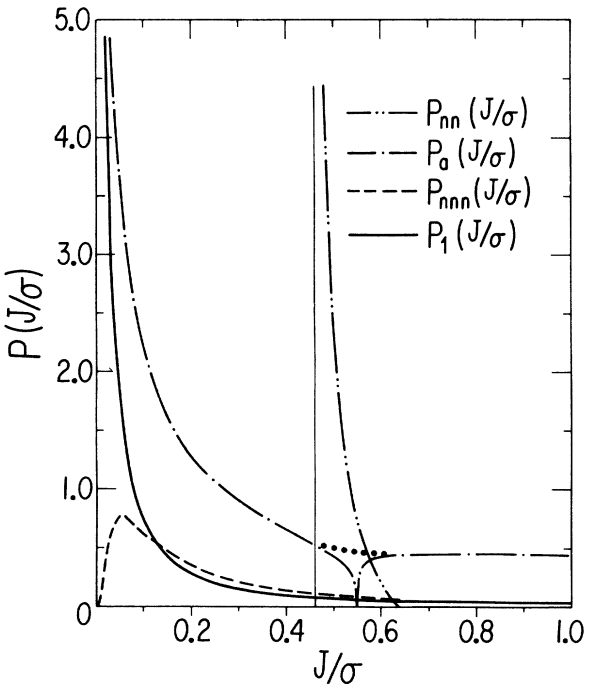

FIG. 10. Probability distribution of J/σ as a function of J/σ for $t=0.055$ eV, $U=0.130$ eV, and $\sigma=0.136$ eV.

$P_1(J/\sigma)$ must coincide with $P_a(J/\sigma)$ for $J/\sigma \ll 1$. Furthermore, $P_1(J/\sigma)$ must coincide with P_{nnn} in the tail region, because the contribution from more isolated spins will go to zero faster than the next-nearest-neighbor configuration. The distribution $P_a(J/\sigma)$ does not satisfy Eq. (4.15) and does not coincide with P_{nnn} in the tail region, as is apparent from Fig. 10. We cannot use $P_1 = P_a(J/\sigma)$ as is and are forced to modify it as follows:

$$P_1\left(\frac{J}{\sigma}\right) = P_a\left(\frac{J}{\sigma}\right)\left(A + Be^{-C_1 J/\sigma}\right)^{-1} . \tag{4.16}$$

Since $P_1(J/\sigma)$ must coincide with $P_a(J/\sigma)$ for $J/\sigma \ll 1$ we obtain

$$A + B = 1 . \tag{4.17}$$

Another condition can be obtained by requiring that $P_1(J/\sigma)$ coincide with $P_{nnn}(J/\sigma)$ in the tail region. Choosing J' to be a point of coincidence we have

$$P_a\left(\frac{J'}{\sigma}\right)\left(A + Be^{-C_1 J'/\sigma}\right)^{-1} = P_{nnn}\left(\frac{J'}{\sigma}\right) . \tag{4.18}$$

Furthermore Eq. (4.15) must also be satisfied. The integral from zero to infinity of (4.16) is infinite. In order to avoid the difficulty we introduce a cutoff to the probability distribution at $J=\sigma$, which we expect to be higher than temperatures of interest. Therefore condition (4.15) should be replaced by

$$\int_0^1 P_1\left(\frac{J}{\sigma}\right) d\left(\frac{J}{\sigma}\right) = 1 - p . \tag{4.19}$$

Conditions (4.17)–(4.19) determine parameters A, B, C_1. The values of these parameters for the choice $J' = 0.8\sigma$ and for $t=0.055$ eV, $U=0.130$ eV, and $\sigma=0.136$ eV are given by: $A=10.37$, $B=-9.37$, and $C_1=2.4$. Plot of $P_1(J/\sigma)$ as a function of J/σ is given in Fig. 10.

From the above analysis it is apparent that the probability distribution $P_1(J/\sigma)$ is found by making an interpolation between the probability distributions in the asymptotic region and in the tail region of $P_{nnn}(J/\sigma)$. Figure 10 also includes plots of $P_a(J/\sigma)$ as a function of J/σ. The parameter a which is defined by Eq. (3.14) is negative, therefore from Eq. (4.9) we obtain that $P_a(J/\sigma)$ goes to zero logarithmically as $J \to D$. This zero is extraneous because formula (4.9) is correct only for $J \ll D$. Thus we must correct the probability distribution $P_a(J/\sigma)$ in the region where the dip to zero occurs. The correction is indicated in Fig. 10 by a dotted line.

V. SUMMARY AND CONCLUSIONS

For low temperatures ($T \lesssim U/4k$), treating the hopping part of the Hubbard Hamiltonian as a perturbation, we have been able to transform the Hubbard Hamiltonian into an equivalent Heisenberg antiferromagnetic Hamiltonian with random coupling constant. In evaluating the coupling constant from all the diagrams that contribute to the coupling of localized spins, we took into account only the lowest-order diagrams. Additionally the perturbation expansion was carried out only up to the 14th order for the case $t \ll U \ll \sigma$, and up to the 10th order for $t \ll U \sim \sigma$. From the expansion we obtained that the coupling constant is given by the relation $J = Dn^{\alpha}\beta^{2n}$, with $\beta < 1$ and n equal to the number of intermediate sites between localized spins and gave numerical estimates for D, α, and β. Thus the coupling constant decays according to a power law. More accurate calculations, in which diagrams of higher order are included, as well as configurations with more intermediate sites, will modify the numerical values of the coefficients D, α, and β, but will leave the form of the coupling constant unchanged since the biggest contribution comes from the $2n+2$ order diagrams, which we have considered. We also note that the coupling $J_i \vec{S} \cdot \vec{S}_{i+1}$ between localized spins reduces the required energy for an electron to be excited from a doubly occupied site to an empty one. The modification is unimportant for $t \ll U, \sigma$ but for large t it will have considerable reduction of excitation energy, and renormalization effects will become important. One of the effects of renormalization is to change the probability p for a site to be singly

occupied.

Furthermore, we calculated the probability distribution of the coupling constant and found that it has an integrable singularity at the origin, for $p/2|\ln\beta| < 1$. The effect of this singularity on the magnetic properties of one-dimensional systems will be the subject of further papers. We should point out that $P(J) \propto 1/J^{1-c}$ is more general than the half-filled band Hubbard model used to obtain it explicitly. Only two features are necessary: (i) random distribution of localized spins along a line, and (ii) an exponential decay of the exchange coupling with separation. Whatever additional interactions are present, (i) follows from disorder if the net electron-electron interaction is repulsive and (ii) then follows automatically from localization. Since the exponent $1-c = 1 - p/2|\ln\beta|$ which is an important feature of our theory, was obtained by making use of the approximate formula $P(n) \simeq e^{-np}$ instead of the exact one $P(n) = e^{n\ln(1-p)}$, we note that use of the latter would give

$$1 - c = 1 + \ln(1-p)/2|\ln\beta| \ .$$

The difference between the two expressions for $1-c$ is unimportant for the case we have examined, that is for p sufficiently smaller than unity. All the previous analysis can be carried out equally well for the case of an arbitrarily filled band. The only modifications are that the chemical potential will no longer be equal to $\frac{1}{2}U$ and the probability for a site to be empty will differ from that of being doubly occupied.

ACKNOWLEDGMENTS

I am deeply indebted to Professor M. H. Cohen for suggesting this problem to me and for his constant guidance and encouragement. I am also grateful to Professor J. A. Hertz for many helpful discussions.

APPENDIX

We are interested in calculating the average $\langle \ln(E_i - E_0)\rangle$. Using the fact that E_i and E_0 have the form (3.3) and $E_i > E_0$ we get that

$$E_i - E_0 = m_1\epsilon_1 + m_{n+2}\epsilon_{n+2} + \sum_{j=2}^{n+1} m_j|\epsilon_j| + kU \ , \qquad \text{(A1)}$$

with m_1, $m_{n+2} = 0, \pm 1$ and $m_j = 0, 1, 2$ for $j = 2, \ldots, n+1$ and k integer. Making the transformations

$$\begin{aligned} |\epsilon_j| &= (\tfrac{1}{2} + y_j)U, \quad j = 2, 3, \ldots, n+1 \ , \\ |\epsilon_j| &= x_j U \ , \quad j = 1, n+2 \ , \end{aligned} \qquad \text{(A2)}$$

we obtain that $\langle \ln(E_i - E_0)\rangle$ is given by the expression

$$\langle \ln(E_i - E_0)\rangle = \ln U + \left\langle \ln\left(m_1 x_1 + m_{n+2}x_{n+2} + \sum_{j=2}^{n+1} m_j y_j + k_1 \right)\right\rangle . \qquad \text{(A3)}$$

We now define the function

$$F(\alpha) = \left\langle \ln\left(\alpha + m_1 x_1 + m_{n+2}x_{n+2} + \sum_{j=2}^{n+1} m_j y_j + k_1 \right)\right\rangle , \qquad \text{(A4)}$$

which has the behavior

$$F(\alpha) \underset{\alpha\to\infty}{\simeq} \ln\alpha \ . \qquad \text{(A5)}$$

Then

$$\langle \ln(E_i - E_0)\rangle = \ln U + F(0) \ . \qquad \text{(A6)}$$

Differentiation of (A4) gives

$$\frac{dF(\alpha)}{d\alpha} = \int_0^\infty du\, e^{-u(\alpha+k_1)} \langle e^{-um_1x_1}\rangle \langle e^{-um_{n+2}x_{n+2}}\rangle \prod_{j=2}^{n+1} \langle e^{-um_jy_j}\rangle \ . \qquad \text{(A7)}$$

From Eq. (A5) we derive that $F(0)$ is given by

$$F(0) = \lim_{A\to\infty}\left(\ln A - \int_0^A \frac{dF}{d\alpha} d\alpha \right) ,$$

and making use of Eq. (A7) $F(0)$ becomes

$$F(0) = \lim_{A\to\infty}\left(\ln A - \int_0^\infty du \frac{i - e^{-uA}}{u} e^{-uk_1} \langle e^{-um_1x_1}\rangle \langle e^{-um_{n+2}x_{n+2}}\rangle \prod_{j=2}^{n+1} \langle e^{-um_jy_j}\rangle \right) . \qquad \text{(A8)}$$

In order to be able to calculate the averages contained in Eq. (A8) we need to know the probability distribution of x_j and y_j. Combination of (A2) and (3.4) gives

$$P(x_j) = \Theta(\tfrac{1}{4} - x_j^2) \ , \quad j = 1, n+2 \ , \qquad P(y_j) = \Theta(y_j) \frac{U}{(2\pi s^2)^{1/2}} \exp\left(-\frac{U^2 y_j^2}{2s^2} \right) , \quad j = 2, \ldots, n+1 \ , \qquad \text{(A9)}$$

with $\Theta(x)$ the Heaviside step function, being zero for negative argument and unity for positive argument. The averages can then be calculated trivially and we get

$$\langle e^{-um_j x_j}\rangle = \sinh(\tfrac{1}{2}m_j u)/\tfrac{1}{2}m_j u \ , \quad j=1,\ n+2 \ , \tag{A10}$$

$$\langle e^{-um_j y_j}\rangle = \exp\left[-\left(\frac{sum_j}{\sqrt{2}\,U}\right)^2\right]\operatorname{erfc}\left(\frac{sum_j}{\sqrt{2}\,U}\right) \ , \quad j=2,\ \ldots,n+1 \ , \tag{A11}$$

with erfc the complementary error function. Using (A10) and (A11), $F(0)$ becomes

$$F(0) = \lim_{A\to\infty}\left(\ln A - \int_0^\infty du\,\frac{1-e^{-uA}}{u}f(u)\right) \ , \tag{A12}$$

where

$$f(u) = e^{-uk_1}\frac{\sinh(\frac{1}{2}m_1 u)}{\frac{1}{2}m_1 u}\,\frac{\sinh(\frac{1}{2}m_{n+2}u)}{\frac{1}{2}m_{n+2}u}\prod_{j=2}^{n+1}\left\{\exp\left[-\left(\frac{sum_j}{\sqrt{2}\,U}\right)^2\right]\operatorname{erfc}\left(\frac{sum_j}{\sqrt{2}\,U}\right)\right\} \ , \tag{A13}$$

and has the property $f(0)=1$. Thus our task is to calculate the integral in Eq. (A12). Using ξ such that $\xi \gg 1$ but $\xi/A \ll 1$ we obtain

$$\int_0^\infty du\,\frac{1-e^{-uA}}{u}f(u) = \gamma + \ln\xi + \int_{\xi/A}^\infty du\,\frac{1-e^{-uA}}{u}f(u), \tag{A14}$$

with γ the Euler's constant. The major contribution to the integral

$$\int_{\xi/A}^\infty du\,\frac{1-e^{-uA}}{u}f(u)$$

comes from $u \ll 1$. In that region $f(u)$ can be approximated by

$$f(u) \simeq e^{-uk_1}\exp\left(-\frac{us\sqrt{2}}{(\pi)^{1/2}U}\sum_{j=2}^{n+1}n_j\right). \tag{A15}$$

Also for $\xi \gg 1$ we have

$$(1-e^{-uA}/u) \simeq 1/u. \tag{A16}$$

Evaluating the integral of the right-hand side of (A14) with the use of approximations (A15) and (A16) we finally obtain

$$\langle \ln(E_i - E_0)\rangle \simeq \ln[k_1 U + sm\sqrt{2}/(\pi)^{1/2}], \tag{A17}$$

with

$$m = \sum_{i=2}^{m+1} m_i .$$

Using Eq. (3.5) we can express $\langle \ln(E_i - E_0)\rangle$ as a function of U and σ

$$\langle \ln(E_i - E_0)\rangle \simeq \ln\{[k_1 - 0.217\,m\sqrt{2}/(\pi)^{1/2}]U + \sigma m\sqrt{2}/(\pi)^{1/2}\}. \tag{A18}$$

*Submitted in partial fulfillment of the requirements for a Ph.D. degree in the Department of Physics, The University of Chicago.

†Supported by the Louis Block Fund, by NSF grant No. DMR75-13343, and by the Materials Research Laboratory of the NSF at The University of Chicago.

[1]See the review article by I. F. Shchegolev, Phys. Status Solidi 12, 9 (1972).

[2]K. Krogmann, Angew. Chem. (Int. Ed. Engl.) 8, 35 (1969), and references contained therein.

[3]L. R. Melby, Can. J. Chem. 43, 1448 (1965).

[4]A. N. Bloch, R. B. Weisman, and C. M. Varma, Phys. Rev. Lett. 28, 753 (1972).

[5]C. J. Fritchie, Acta Crystallogr. 20, 892 (1966).

[6]H. Kobayashi, F. Marumo, and Y. Saito, Acta Crystallogr. B 27, 373 (1971).

[7]J. Hubbard, Proc. R. Soc. A 276, 238 (1963); 281, 401 (1964).

[8]J. H. Van Vleck, in *Quantum Theory of Atoms, Molecules and the Solid State*, edited by P. O. Löwdin (Academic, New York, 1966), p. 475.

[9]G. Theodorou and Morrel H. Cohen, Bull. Am. Phys. Soc. 20, 415 (1975); and Phys. Rev. Lett. 37, 1014 (1976).

[10]N. F. Mott and W. D. Twose, Adv. Phys. 10, 107 (1961).

[11]R. Borland, Proc. R. Soc. A 274, 529 (1963).

[12]E. N. Economou and Morrel H. Cohen, Phys. Rev. B 4, 396 (1971).

[13]E. N. Economou and Morrel H. Cohen, Phys. Rev. B 5, 2931 (1972).

[14]T. A. Kaplan, S. D. Mahanti, and W. M. Hartmann, Phys. Rev. Lett. 27, 1796 (1971).

[15]D. J. Klein and W. A. Seitz, Phys. Rev. B 8, 2236 (1973).