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Hopping conductivity of the extended-hard-core cubic lattice gas

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The uniform cubic lattice gas with infinite repulsion between particles on nearest-neighbor sites is considered. The conductivity is calculated in the stationary state in the presence of a uniform electric field. The necessary equilibrium averages are estimated within the Bethe-Peierls approximation. The correlation factor is derived, and numerical values are presented for concentrations below the critical one. Comparison with Monte Carlo results of Murch shows good agreement.

I. INTRODUCTION

A remarkable interest in atomic motion in condensed matter has been observed for the past 20 years, in connection with superionic conductors[1] and metal hydrides.[2] An essential aspect of transport in such highly defective solids is the interaction between particles. While inclusion of nearest-neighbor (NN) interactions in the treatment of hopping in lattice gases proves a simple enough task, often with exact results, in one dimension,[3–5] for two- and especially for three-dimensional systems calculations become tedious and somehow discouraging. The honeycomb lattice was intensively studied in connection with β- and β''-alumina.[6,7] A series of results was obtained by Monte Carlo simulations.[8]

In two previous papers we calculated the conductivity of the square-lattice gas with infinite nearest-neighbor (NN) repulsions[9] (to be referred to hereafter as I) and the honeycomb lattice gas with arbitrary NN repulsions.[10]

In the present paper we deal with the three-dimensional version of the model in I, namely, in cubic lattice in which the only interaction prevents simultaneous occupation of NN sites. A former study of the model was made by Murch with computer experiments.[11] To our knowledge, the only previous analytical approach to NN interacting hopping in three dimensions was that of Richards[12] who also considered the cubic lattice but with a different type of repulsion. The difference was that the interaction did not affect equilibrium properties but it only restricted the possibility of jumping between sites.

In Sec. II we use the Bethe-Peierls approximation (BPA) to calculate equilibrium correlation functions. The chemical potential and the vacancy availability factor are obtained and compared with Monte Carlo results of Ref. 11. The concentration dependence of some correlators is also given.

In Sec. III we use a steady-state formalism devised by Richards[13] (see also Refs. 9 and 10) to calculate the conductivity in one degree of approximation beyond mean field. This is done by a self-consistent calculation of the two most important third-order dynamical correlation functions. The other correlators are expressed in terms of these two by a decoupling scheme which was successfully used in I. The correlation factor of the conductivity is obtained and its concentration dependence is presented along with the Monte Carlo results of Murch.

Some final remarks are given in Sec. IV.

II. STATIC CORRELATIONS

We consider a system of N_p identical particles on a cubic lattice with N equivalent sites. The particles interact with an infinite repulsion at NN distance. The configurations of the system are described in terms of the set of occupation numbers $\{n_i\}_i$, n_i being 0 or 1 when the site i is empty or occupied, respectively. In the equilibrium state without external fields, all average quantities are translationally invariant. The mean value of n_i is equal to the concentration of particles,

$$\langle n_i \rangle_0 = c = \frac{N_p}{N} , \tag{2.1}$$

where the subscript 0 indicates an equilibrium average.

The extended-hard-core interaction restricts the concentration values to the interval below 0.5. In fact, there is a further limitation due to the appearance of an ordered state at concentrations above some critical value which was estimated at $c_{\text{cr}} \simeq 0.213$.[14] Equation (2.1) is correct only up to c_{cr}. For higher concentrations, translational invariance is broken, so that one of the two sublattices made up of next-nearest-neighbor sites is preferentially occupied. In the following, although we shall do the calculations for the whole interval $0 \le c \le 0.5$, we must say that only results up to c_{cr} will be relevant. In the ordered state, transport is drastically hindered, and in fact it stops at a concentration higher than, but close to c_{cr}.[11] Also, we did not aim at handling the additional complications implied by describing the state above c_{cr}.

We shall follow the steps in I for calculating the equilibrium correlation functions. In a paper by Froböse and Jäckle[15] it was shown that the best analytical method for this purpose is the BPA. In I we considered a 4×4 cluster on the square lattice, which was ideal for that system since it incorporated all correlators necessary for the calculation of conductivity. In three dimensions the same property would be held by the 4×4×3 cluster, but from the first attempts to calculate its partition function the task proved too cumbersome and so we had to be content with the 3×3×3 cluster shown in Fig. 1. The central site has the bulk fugacity z, while sites on the frontier have different fugacities z_1, z_2, z_3 in order to account for the influence of the rest of the lattice.

In order to calculate the sum over states, we found that the shortest way to count the configurations of particles on the cluster begins by making a bisection as in Fig. 1. All sites of the hexagonal section are of the same symmetry, i.e., they have the same fugacity z_2. We shall denote by S_k, $k=0,1,\ldots,6$, the sum over those states with k particles on the hexagon. S_k is easy to compute since the configurations on the two pyramids are independent. With the short-hand notations

$$\begin{aligned} u &= z_1+1 , \\ t &= z_3+1 , \end{aligned} \tag{2.2}$$

we have

$$\begin{aligned} S_0 &= (u^3t^4+3z_2ut^2+3z_2^2t+z_2^3)^2 , \\ S_1 &= 6z_2[u^2t^3+z_2(ut^2+ut+t)+z_2^2(2t+1)+z_2^3]^2 , \\ S_2 &= 3z_2^2(P_{21}^2+2P_{22}^2+2P_{23}P_{24}) , \\ S_3 &= 2z_2^3(P_{31}^2+3P_{22}^2+6P_{33}P_{34}) , \\ S_4 &= 3z_2^4(3P_{31}^2+2P_{33}P_{34}) , \\ S_5 &= 6z_2^5P_{31}^2 , \\ S_6 &= z_2^6P_{31}^2 , \end{aligned} \tag{2.3}$$

where

$$\begin{aligned} P_{21} &= ut^2+z_2(u+2t)+z_2^2(t+2)+z_2^3 , \\ P_{22} &= ut^2+z_2(ut+t+1)+z_2^2(t+2)+z_2^3 , \\ P_{23} &= u^2t^2+z_2(ut+t+1)+z_2^2(t+2)+z_2^3 , \\ P_{24} &= ut^3+z_2(ut^2+2t)+z_2^2(2t+1)+z_2^3 , \\ P_{31} &= z_3+(z_2+1)^3 , \\ P_{33} &= z_3u+z_1+(z_2+1)^3 , \\ P_{34} &= t^2-1+(z_2+1)^3 . \end{aligned} \tag{2.4}$$

The partition function of the cluster is given by

$$Z_{\mathrm{cl}} = \sum_{k=0}^{6} S_k . \tag{2.5}$$

The fugacities are calculated by imposing the same value of the average occupation number on each site of the cluster, i.e., by applying Eq. (2.1),

$$\begin{aligned} c &= z\frac{\partial Z_{\mathrm{cl}}}{\partial z} , \\ c &= \frac{z_1}{6}\frac{\partial Z_{\mathrm{cl}}}{\partial z_1} , \\ c &= \frac{z_2}{12}\frac{\partial Z_{\mathrm{cl}}}{\partial z_2} , \\ c &= \frac{z_3}{8}\frac{\partial Z_{\mathrm{cl}}}{\partial z_3} . \end{aligned} \tag{2.6}$$

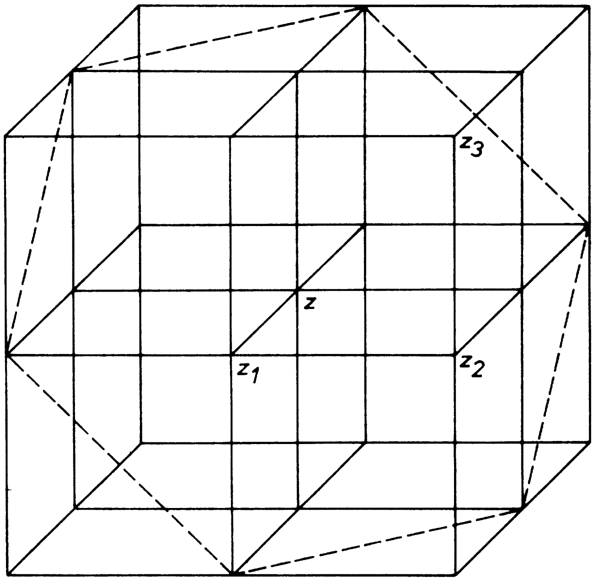

FIG. 1. The $3\times3\times3$ cluster representing the lattice in the Bethe-Peierls approximation. The values of the fugacity are indicated. The hexagonal section necessary for the calculation of Z_{cl} is shown.

Rather than writing down Eqs. (2.6) explicitly and solving them numerically, we observe that this is equivalent to finding a minimum for the function

$$F = -\frac{1}{Z_{\mathrm{cl}}}(zz_1^6z_2^{12}z_3^8)^c . \tag{2.7}$$

A powerful minimization subroutine was used to determine the fugacities for several values of the concentration. In Ref. 11, Murch presented the Monte Carlo measurements of the chemical potential divided by temperature, i.e.,

$$\frac{\mu}{kT} = \ln z . \tag{2.8}$$

For comparison, we illustrate the same quantity in Fig. 2. So far, the $3\times3\times3$ BPA seems good enough.

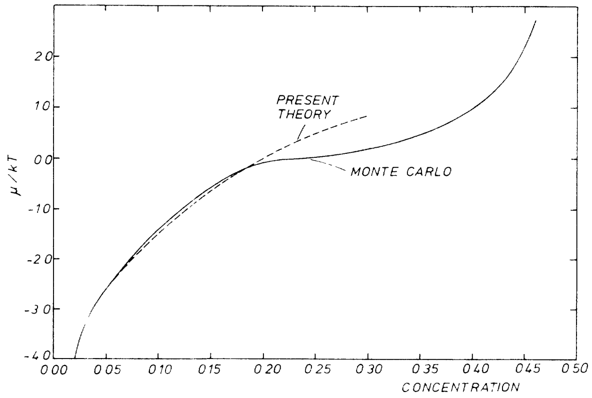

FIG. 2. The chemical potential divided by temperature vs concentration in the BPA compared with Monte Carlo results of Murch.

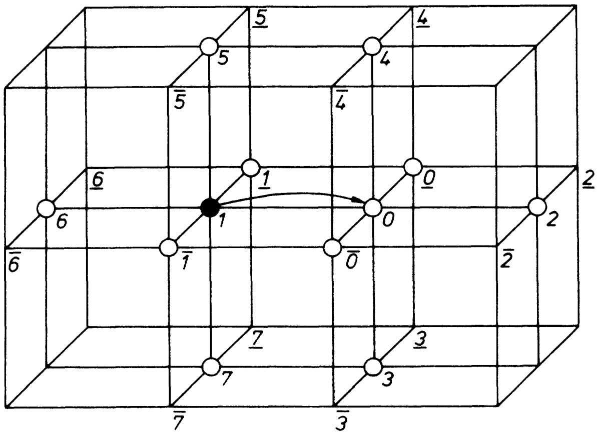

FIG. 3. The jump of a particle to a vacancy.

This impression is strengthened after the examination of the vacancy availability factor. In order to define it we shall anticipate notations of Sec. III by introducing the jump rate of a particle to an empty NN site. This jump is allowed only if the vacancy is "available" from the point of view of the interaction, i.e., if all its NN's are also empty. Thus, the average rate for the jump in Fig. 3 is given by

$$\langle W_{10} \rangle = W \langle n_1 (1-n_{\bar{0}})(1-n_{\underline{0}})(1-n_2)(1-n_3)(1-n_4) \rangle \ , \tag{2.9}$$

where W is the jump rate for free particles. The factor $1-n_0$ is unnecessary because $n_0=0$ whenever $n_1=1$. The brackets in Eq. (2.9) indicate an average in an arbitrary time-dependent or stationary ensemble. The vacancy availability factor is an equilibrium quantity defined by

$$V = \frac{1}{c} \langle n_1 (1-n_{\bar{0}})(1-n_{\underline{0}})(1-n_2)(1-n_3)(1-n_4) \rangle_0 \ . \tag{2.10}$$

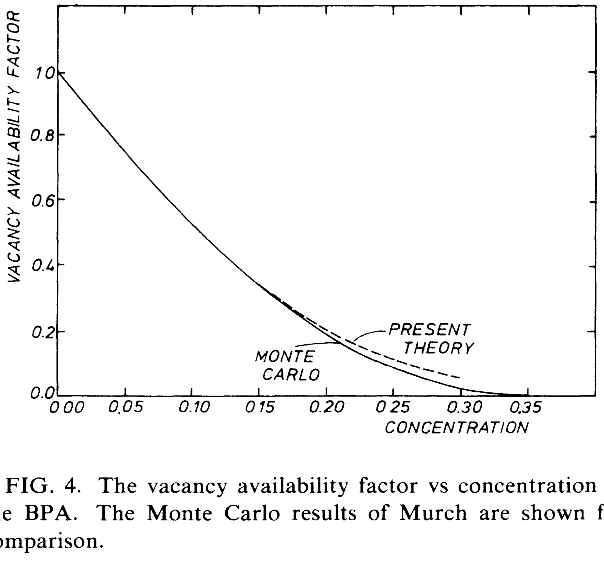

FIG. 4. The vacancy availability factor vs concentration in the BPA. The Monte Carlo results of Murch are shown for comparison.

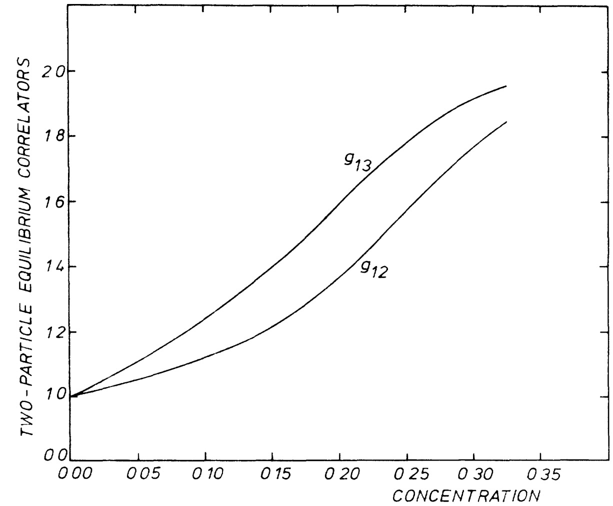

FIG. 5. Two of the second-order equilibrium correlation functions in the BPA.

This was called the jump probability[11,16] and also the effective jump frequency factor[17] in previous papers. The present name was chosen in analogy with I and Ref. 15. In Fig. 4 we present the BPA values of V, in comparison with the Monte Carlo experimental results of Murch.[11]

We also present for illustration the normalized correlation functions of two particles (Fig. 5) and of three particles (Fig. 6) which enter Eq. (2.10) and which are given by

$$g_{13} = \langle n_1 n_3 \rangle / c^2 \ , \tag{2.11a}$$

$$g_{12} = \langle n_1 n_2 \rangle / c^2 \ , \tag{2.11b}$$

$$g_{1\bar{0}4} = \langle n_1 n_{\bar{0}} n_4 \rangle / c^3 \ , \tag{2.12a}$$

$$g_{134} = \langle n_1 n_3 n_4 \rangle / c^3 \ . \tag{2.12b}$$

At $c=0.5$, all averages of products of occupation numbers on sites of the same sublattice are equal to 0.5 and all

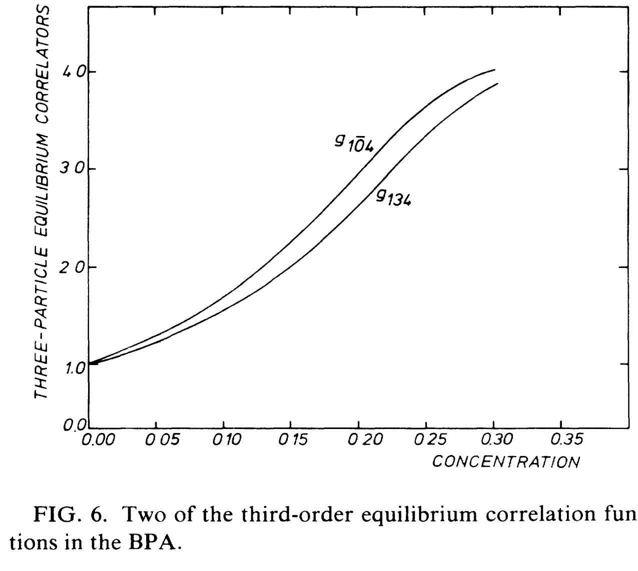

FIG. 6. Two of the third-order equilibrium correlation functions in the BPA.

other correlators vanish. Therefore, the normalized correlators of Eqs. (2.11) and (2.12) approach the values 2 and 4 as $c \to 0.5$.

III. STATIONARY FLOW

We shall use a steady-state formalism developed by Richards for a one-dimensional system.[13] The lattice is considered at $l \times m \times n = N$ parallelepiped periodically repeated to cover the whole space, so that a stationary flow is possible without sources of particles. The particles having the electrical charge e can jump to a NN site with the jump rate given by Eq. (2.9). In the presence of an electric field E parallel to bond 10 in Fig. 3, the difference in energy between two NN sites in the direction of the field is eEa, a being the NN distance. Detailed balance is satisfied by modifying the jump rates symmetrically as follows:

$$\begin{aligned} W^E_{10} &= W_{10}(1+\Delta) , \\ W^E_{01} &= W_{01}(1-\Delta) , \end{aligned} \tag{3.1}$$

with

$$\Delta = \frac{eEa}{2kT} . \tag{3.2}$$

Equations (3.1) are written only up to first order in E which is sufficient for the calculation of conductivity. The higher-order terms in Δ will be systematically discarded. If $\Omega = a^3$ denotes the volume per site, the charge current density is given by

$$j = \frac{N_p}{N\Omega} ev = \frac{cev}{\Omega} , \tag{3.3}$$

where v is the stationary flow mean velocity of the particles in the field direction. As in I, due to the translational invariance of steady-state correlators, the velocity is given by

$$v = aN(\langle W^E_{10} \rangle - \langle W^E_{01} \rangle) . \tag{3.4}$$

By using the labeling of sites as in Fig. 3, Eq. (3.4) becomes

$$v = v_{\text{corr}} + v_\infty , \tag{3.5}$$

where

$$v_{\text{corr}} = NW[\langle n_1(1-n_{\bar 0})(1-n_{\underline 0})(1-n_2)(1-n_3)(1-n_4) \rangle - \langle n_0(1-n_{\bar 1})(1-n_{\underline 1})(1-n_5)(1-n_6)(1-n_7) \rangle] \tag{3.6}$$

and

$$v_\infty = 2NW\Delta \langle n_1(1-n_{\bar 0})(1-n_{\underline 0})(1-n_2)(1-n_3)(1-n_4) \rangle_0 = 2NW\Delta cV . \tag{3.7}$$

In Eq. (3.7), the average is taken in the equilibrium ensemble, which is order zero in the field, due to the Δ prefactor. The quantity v_∞, which is seen to be proportional to V, leads to the infinite frequency conductivity

$$\sigma_\infty = \frac{j_\infty}{E} = \frac{N_p e^2 a^2}{\Omega kT} WV . \tag{3.8}$$

The dynamical effects of the interaction, which make the dc conductivity σ lower than σ_∞ are all contained in the first term in Eq. (3.5), v_{corr}. Due to the invariance of the steady-state correlators under reflection with respect to any plane containing the field direction, some terms in Eq. (3.6) cancel and we get

$$\begin{aligned} v_{\text{corr}} = NW(& 2\langle\langle n_1 n_3 n_4 \rangle\rangle + 4\langle\langle n_1 n_{\bar 0} n_4 \rangle\rangle \\ & - 4\langle\langle n_1 n_{\bar 0} n_3 n_4 \rangle\rangle + \langle\langle n_1 n_{\bar 0} n_{\underline 0} n_3 n_4 \rangle\rangle) , \end{aligned} \tag{3.9}$$

where we have introduced the notation $\langle\langle f(n) \rangle\rangle$ for a symmetrized correlator which is the difference between $\langle f(n) \rangle$ and its reflection with respect to the plane perpendicular to the field. We illustrate the notation with the three-particle correlators of Eq. (3.9), denoted by ζ and ξ,

$$\zeta = \langle\langle n_1 n_3 n_4 \rangle\rangle \equiv \langle n_1 n_3 n_4 \rangle - \langle n_0 n_5 n_7 \rangle , \tag{3.10}$$

$$\xi = \langle\langle n_1 n_{\bar 0} n_4 \rangle\rangle \equiv \langle n_1 n_{\bar 0} n_4 \rangle - \langle n_0 n_{\underline 1} n_5 \rangle . \tag{3.11}$$

So far, Eq. (3.5) together with Eqs. (3.7) and (3.9) are exact formulas. However, approximations are needed for the evaluation of the dynamic correlation functions in Eq. (3.9). We shall apply the same method as in I. We make the notation

$$\delta_i = n_i - c . \tag{3.12}$$

A correlator of n_i's can be expressed in terms of the deviations δ_i's. For illustration consider a four-particle one:

$$\begin{aligned} \langle\langle n_a n_b n_c n_d \rangle\rangle = {} & c^3 \sum_i \langle\langle \delta_i \rangle\rangle + c^2 \sum_{i,j} \langle\langle \delta_i \delta_j \rangle\rangle \\ & + c \sum_{i,j,k} \langle\langle \delta_i \delta_j \delta_k \rangle\rangle + \langle\langle \delta_a \delta_b \delta_c \delta_d \rangle\rangle . \end{aligned} \tag{3.13}$$

By symmetry, we have for all i,j

$$\langle\langle \delta_i \rangle\rangle = \langle\langle \delta_i \delta_j \rangle\rangle = 0 . \tag{3.14}$$

The trivial approximation is to neglect all δ correlators which leads to $\sigma \sim \sigma_\infty$ with no dynamical effect accounted for. The first nontrivial approximation is to keep only the third-order δ correlators which enter Eq. (3.9), for which we can write the following exact formulas:

$$\zeta = \langle\langle \delta_1 \delta_3 \delta_4 \rangle\rangle , \tag{3.15}$$

$$\xi = \langle\langle \delta_1 \delta_{\bar 0} \delta_4 \rangle\rangle . \tag{3.16}$$

In I, we kept only one third-order correlator, which was the analog of ζ. The arguments presented there are also suitable in three dimensions with the important modification that there are now two correlators of the same magnitude which have to be considered in calculations. Both involve sites of the same sublattice, and it was argued in I that correlators with sites on both sublattices are less important. Furthermore, ζ and ξ are of essentially the same close-spacing and from this point of view, also more important than other three-particle correlators.

By keeping only ζ and ξ of all δ correlators, the other three-particle n correlators vanish and higher-order ones can be expressed in terms of ζ and ξ. For illustration for those in Eq. (3.9) we have

$$\langle\langle n_1 n_{\bar{0}} n_3 n_4 \rangle\rangle = c(\zeta + 2\xi) , \tag{3.17}$$

$$\langle\langle n_1 n_{\bar{0}} n_{\underline{0}} n_3 n_4 \rangle\rangle = 2c^2(\zeta + 2\xi) , \tag{3.18}$$

and so Eq. (3.9) becomes

$$v_{\text{corr}} = 2NW(1-c)^2(\zeta + 2\xi) . \tag{3.19}$$

We are left with the task of evaluating ζ and ξ. We start with the rate equation describing the time evolution of $\langle n_1 n_3 n_4 \rangle$. The jumps which contribute to its decrease are illustrated in Fig. 7, while its increase is achieved by the reverse jumps. Thus we have

$$\begin{aligned} \frac{d}{dt}\langle n_1 n_3 n_4 \rangle = &-\langle 2[W_{4A}(1+\Delta) + W_{4B} + 2W_{4\bar{4}}]n_1 n_3 \\ &+ [W_{16}(1-\Delta) + 2W_{1\bar{1}}]n_3 n_4 \rangle \\ &+ \langle 2[W_{A4}(1-\Delta) + W_{B4} + 2W_{\bar{4}4}]n_1 n_3 \\ &+ [W_{61}(1+\Delta) + 2W_{\bar{1}1}]n_3 n_4 \rangle . \end{aligned} \tag{3.20}$$

The right-hand side (rhs) of Eq. (3.20) is now treated in the same manner as the rhs of Eq. (3.4) and in the stationary state we get

$$\begin{aligned} 0 = {} & 2\langle n_1 n_3 [(W_{A4} - W_{4A}) + (W_{B4} - W_{4B}) + 2(W_{\bar{4}4} - W_{4\bar{4}})] + n_3 n_4 [(W_{61} - W_{16}) + 2(W_{\bar{1}1} - W_{1\bar{1}})] \rangle \\ & - \Delta \langle 2n_1 n_3 (W_{A4} + W_{4A}) - n_3 n_4 (W_{61} + W_{16}) \rangle_0 . \end{aligned} \tag{3.21}$$

The first term of the rhs of Eq. (3.21) contains correlators of the $\langle\langle\ \rangle\rangle$ type and they will be expressed in terms of ζ and ξ through the δ decomposition. The second term involves equilibrium correlators which are evaluated in the BPA.

A second equation is obtained in an analogous manner from the time-dependent $\langle n_1 n_{\bar{0}} n_4 \rangle$. The details of this will be omitted.

By using the labeling of sites as in Fig. 7, the two coupled linear equations are

$$\begin{aligned} & A_{11}\zeta + A_{12}\xi = B_1 , \\ & A_{21}\zeta + A_{22}\xi = B_2 , \end{aligned} \tag{3.22}$$

where

$$\begin{aligned} & A_{11} = -4(1-c)^4 - 7(1-c)^5 - c^2(5 - 12c + 2c^2) , \\ & A_{12} = 4c(1-c)^4 - 4c^2(2 - 2c - c^2) , \\ & A_{21} = 2c(1-c)^2(1 - 3c + c^2) , \\ & A_{22} = -3c^2 + 4c^2(1-c)^2 + 2c^2(1-c)^3 + 4c(1-c)^4 - 9(1-c)^5 , \end{aligned} \tag{3.23}$$

and

$$\begin{aligned} B_1 = \Delta W [& 2\langle n_1 n_3 n_A (1 - n_{\bar{4}})(1 - n_{\underline{4}})(1 - n_B) \rangle_0 + 2\langle n_1 n_3 n_4 (1 - n_{\bar{A}})(1 - n_{\underline{A}})(1 - n_2)(1 - n_E)(1 - n_F) \rangle_0 \\ & - \langle n_3 n_4 n_6 (1 - n_{\bar{1}})(1 - n_{\underline{1}}) \rangle_0 - \langle n_1 n_3 n_4 (1 - n_{\bar{6}})(1 - n_{\underline{6}})(1 - n_K)(1 - n_L)(1 - n_M) \rangle_0] , \end{aligned} \tag{3.24}$$

$$\begin{aligned} B_2 = \Delta W [& 2\langle n_1 n_{\bar{0}} n_A (1 - n_{\underline{4}})(1 - n_B) \rangle_0 + 2\langle n_1 n_{\bar{0}} n_4 (1 - n_{\bar{A}})(1 - n_{\underline{A}})(1 - n_2)(1 - n_E)(1 - n_F) \rangle_0 \\ & - \langle n_{\bar{0}} n_4 n_6 (1 - n_{\underline{1}})(1 - n_7) \rangle_0 - \langle n_1 n_{\bar{0}} n_4 (1 - n_{\bar{6}})(1 - n_{\underline{6}})(1 - n_K)(1 - n_L)(1 - n_M) \rangle_0] . \end{aligned} \tag{3.25}$$

TABLE I. Results for dimensionless quantities ζ/Δ and ξ/Δ.

c	0.05	0.10	0.15	0.20	0.25
$\frac{\zeta}{\Delta}\times 10^3$	-0.0271	-0.2424	-0.8265	-1.7255	-2.5007
$\frac{\xi}{\Delta}\times 10^3$	-0.0338	-0.3035	-1.0601	-2.7664	-8.2728

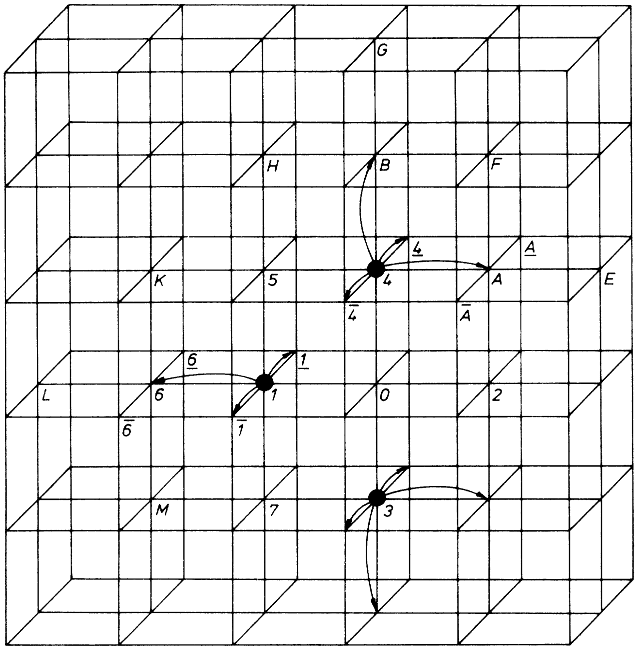

FIG. 7. Jumps contributing to the decrease of the time-dependent correlator $\langle n_1 n_3 n_4 \rangle$.

The calculation of B_1 and B_2 in the BPA involves one further approximation concerning those correlators which involve sites situated farther apart than in the $3\times3\times3$ cube. These are evaluated by a factorization formula suitably chosen so that it retains most of the information about the configuration of sites in the initial correlator.

This is done as follows: a cluster which does not enter the $3\times3\times3$ cube is considered as a reunion of two clusters which do have this property. The two smaller configurations are chosen so that their intersection is maximal with the same restriction of going in the BPA cube. We shall illustrate this with an eight-particle correlator in Eq. (3.24):

$$\langle n_1 n_3 n_4 n_{\bar{A}} n_{\underline{A}} n_2 n_E n_F \rangle_0 \simeq \frac{\langle n_1 n_3 n_4 n_{\bar{A}} n_{\underline{A}} n_2 \rangle_0 \langle n_4 n_{\bar{A}} n_{\underline{A}} n_2 n_E n_F \rangle_0}{\langle n_4 n_{\bar{A}} n_{\underline{A}} n_2 \rangle_0} . \quad (3.26)$$

Now it is only a matter of patience and computer time before we get numerical values for ζ and ξ. Some results for the dimensionless quantities ζ/Δ and ξ/Δ are presented in Table I.

It is seen that the two correlators are indeed of the same order of magnitude, that they have negative values, and that ξ, which is more close-spaced, has larger absolute values.

The correlation factor of the conductivity, defined by

$$f=\frac{\sigma}{\sigma_\infty} \quad (3.27)$$

is now readily expressed as follows:

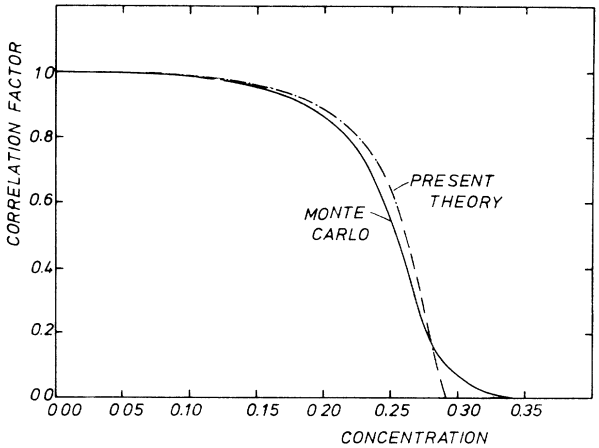

FIG. 8. The correlation factor of the conductivity vs concentration compared with the Monte Carlo results of Murch.

$$f=\frac{v}{v_\infty}=1+\frac{v_{\text{corr}}}{v_\infty}=1+\frac{(1-c)^2(\zeta+2\xi)}{cV\Delta} . \quad (3.28)$$

The values obtained for f are illustrated in Fig. 8. A satisfactory agreement with the Monte Carlo results of Murch[11] is found. We note again that only results up to $c_{\text{cr}} \simeq 0.213$ are relevant, as mentioned in Sec. I.

IV. SUMMARY AND CONCLUSIONS

A study of the extended-hard-core cubic-lattice gas was presented. The main purpose of the paper was the calculation of the correlation factor of the conductivity. A steady-state approach due to Richards[13] was used to obtain a formula for the dc conductivity which involves static as well as dynamic correlators. The evaluation of these correlation functions was possible only by using three types of approximations, one for the steady-state averages and two for the equilibrium ones.

As in I, we pushed the calculation of conductivity one step beyond the trivial approximation $\sigma \sim \sigma_\infty$. The novelty of the three-dimensional case was the necessity of keeping not one but two third-order dynamic correlators, ζ and ξ, defined by Eqs. (3.10) and (3.11), judged to be of the same order of magnitude, which was confirmed by the results. By neglecting all δ correlators except ζ and ξ and by expressing all n correlators in terms of these two, the correlation factor was obtained in terms of static averages.

The two approximations used for the evaluation of equilibrium correlators were the BPA and the factorization scheme illustrated by Eq. (3.26). The $3\times3\times3$ cluster used for carrying out the BPA recipe seems to be the largest cluster for which calculations are reasonably feasible. The results obtained within this approximation were judged by comparing them with the Monte Carlo experiments on two quantities: the chemical potential divided by temperature and the vacancy availability factor. The verdict was favorable, which can also be said about the final results on the correlation factor in spite of the mentioned three successive approximations.

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