Static Correlations of Higher Order and Diffusion in an Interacting Lattice Gas[1]

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For a lattice gas with extended hard core interaction on a square lattice the static correlation functions of higher order, which determine the average jump rate in the diffusion process, are calculated both by the Monte Carlo method and by analytic, approximations. It is found that the superposition approximation is very inaccurate for the correlation functions of third and fourth order, but gives better results for the average jump rate. Up to concentrations of $c = 0.3$ better consistency with the Monte Carlo data for both quantities is obtained by treating the site occupation numbers as Gaussian random variables and accordingly expressing the correlation functions of higher order by products of averages of two particle correlations. For concentrations $c > 0.3$, however, a Bethe–Peierls cluster approximation is superior to the superposition approximation.

1. INTRODUCTION

It is well known that the transport properties of dense fluids depend sensitively on their structural properties. The variation of transport coefficients, like the self-diffusion coefficient, with temperature and pressure is strongly affected by structural changes occurring as a function of these parameters. The relevant structural properties are determined by static (i.e., equal-time) correlation functions of higher order in addition to the pair

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correlation function. For example, as is intuitively obvious, the self-diffusion coefficient of a liquid depends not only on the average coordination number of the molecules, which is determined by the pair correlation function, but also on the mean-square fluctuation of the coordination number, which can be expressed by the three-particle correlation function. The calculation of static correlation functions of higher order is not a trivial matter. Usually, for this purpose approximation schemes like the superposition approximation (SA) are used, by means of which the correlation functions of higher order are reduced to products of the pair correlation function. In the present paper the question of the reducibility of the static correlation functions of higher order which enter the self-diffusion coefficient is examined for an interacting lattice gas model.

2. MODEL

The model describes particles on a two-dimensional square lattice, with an extended hard core which forbids both the multiple occupation of sites and the simultaneous occupation of nearest-neighbor sites. A Monte Carlo study of diffusion in the same model for three dimensions has been reported by Murch.[1,2] This extended hard core model may be interpreted as the zero-temperature limit of a lattice gas with a finite repulsive potential U between nearest neighbors. (The case of finite repulsive potential and finite temperatures will be treated in a subsequent paper. For a three-dimensional fcc lattice see Kutner, Binder, and Kehr.[3]) For our model a second-order phase transition occurs at a critical concentration $c_{\rm crit} = 0.37$.[4,5] In the ordered phase one of the two sublattices is preferentially occupied. Since we consider the interacting lattice gas as a simplified model of a liquid, we are interested only in the disordered phase ($c < 0.37$). For the usual dynamics of lattice gases,[6] the transition rate $p(l \to l')$ of a particle from site l to a nearest-neighbor site l' is given by the jump frequency $1/\tau_s$ unless the transition is impeded by the presence of other particles; in this case the transition rate is zero.[3] Using the notation of Figure 1, the transition rate $p(1 \to 0)$ can be written in terms of occupation numbers $n_i = 0, 1$ as

$$p(1 \to 0) = \frac{1}{\tau_s} w(1, 0) \qquad (2.1)$$

with

$$w(1, 0) = n_1(1 - n_2)(1 - n_3)(1 - n_4)$$

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[3] In a Monte Carlo simulation of the diffusion process during one time step a chosen particle attempts to jump only in one direction which is selected at random.
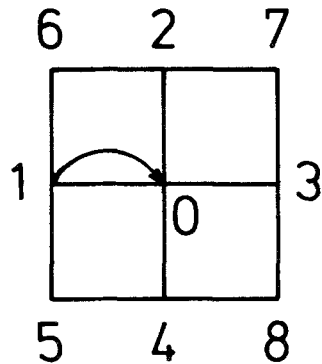
Fig. 1. A particle at site 1 jumps to site 0.
The indicated notation is used throughout
the paper.

The average transition rate of a particle originally at site 1 to the nearest-neighbor site 0 is given by $(1/\tau_s)V$, where

$$V = \langle n_1(1 - n_2)(1 - n_3)(1 - n_4) \rangle/c \qquad (2.2)$$

is the conditional probability that the sites 2, 3, and 4 are vacant if the site 1 is occupied. The vacancy of site 0 is guaranteed by the extended hard core of the particle at 1. In the expression for V, the brackets denote the average over an equilibrium ensemble, and $c = \langle n_i \rangle$ is the concentration. V may be called the "vacancy availability factor" for the extended hard-core model. In terms of τ_s and V, the mean residence time of a particle on a lattice site is given by

$$1/\tau = (4/\tau_s)V \qquad (2.3)$$

For a charged lattice gas, the vacancy availability factor V together with τ_s also determines the high-frequency limit of the electrical conductivity:

$$\sigma(\infty) = \frac{q^2 \cdot V}{\tau_s a k_B T} \qquad (2.4)$$

where q is the electric charge of a particle and a is the lattice constant. In the static conductivity $\sigma(0)$ as well as in the self-diffusion coefficient, in addition to V a correlation factor enters which expresses dynamic correlations.[7-10]

According to formula (2.2), the vacancy availability factor V depends on correlations between the occupation of four neighboring sites. The significance of correlations of any order for V may be assessed by compar-

ing with the value $(1 - c)^3$ which is obtained if correlations are entirely neglected. The correlated part $V - (1 - c)^3$ is a measure of the influence of correlations. The vacancy availability factor V can be expressed in terms of correlation functions up to fourth order, which are defined for general n by

$$g_n(l_1, l_2,..., l_n) = \langle n_{l_1} n_{l_2} \cdots n_{l_n} \rangle / c^n \qquad (2.5)$$

From formula (2.2) one obtains

$$V = 1 - c[2g_2(1, 2) + g_2(1, 3)] + 3c^2 g_3(1, 2, 3) - c^3 g_4(1, 2, 3, 4) \quad (2.6)$$

Since the correlation functions of higher than second order are more difficult to calculate than the pair correlation function and cannot, in real systems, be measured directly, it is of considerable interest to what extent they can be approximated by combinations of the pair correlation function. As mentioned above, Kirkwood's superposition approximation (SA) for the triplet correlation function[11] and its generalization to correlation functions of arbitrary order[12,13] is commonly used for this purpose. In the present paper the validity of the SA for g_3, g_4, and V is tested by comparing with the results of a Monte Carlo calculation. As an alternative reduction scheme for higher-order correlation functions the Gaussian factorization is also examined. In addition, it is shown that these quantities can be obtained with good accuracy from a Bethe–Peierls cluster approximation.

3. MONTE CARLO SIMULATION

The Monte Carlo calculations were performed for a square lattice of 256×256 sites with periodic boundary conditions. The equilibrium states of the system were generated at a given temperature and chemical potential using Glauber dynamics.[14] At each Monte Carlo step a lattice site was chosen randomly. The cost of ΔF of free energy $F = E - \mu N$ of changing the occupation of the chosen site was calculated. In case of negative ΔF the occupation of the site was changed immediately (i.e., a particle was removed or added to the site if it was occupied or empty originally). For positive ΔF, the occupation was changed only with the probability $\exp(-\Delta F/k_B T)$.[15] In all computer experiments reported in this paper the extended hard core lattice gas was actually treated as the low-temperature limit of a lattice gas with finite repulsive potential U of a pair of nearest neighbors. The temperature was kept fixed at a value of 0.1 in units of U, at which the number of pairs of particles occupying nearest-neighbor sites is negligible. The simulation was started with an empty lattice and a value of the chemical potential of -0.3, which led to an equilibrium concentration

$c = 0.04$. After a period of thermalization of 100 Monte Carlo steps per site (MCS), the configurations were recorded at intervals of 10 MCS. After sampling 50 configurations the chemical potential was raised to the next higher value and the procedure was repeated, using the last configuration of the preceding run as the starting configuration. After ten steps the critical concentration was reached and the procedure was stopped. As the critical concentration was approached (for $c > 0.34$, say) the equilibration time of the system increased considerably. Therefore in this range of concentrations the period of thermalization was extended to 300 MCS. With this precaution, even at the highest concentrations no significant time dependence of the concentratio and the vacancy availability factor could be detected in the Monte Carlo runs following the thermalization period. The correlation functions were evaluated by scanning the recorded configurations. All results were compared with an independent simulation for smaller systems of up to 128×128 sites, for which a simpler program could be used. Within the statistical errors no deviations were found.

4. TEST OF THE SUPERPOSITION APPROXIMATION

Kirkwood's superposition approximation[11] for the triplet correlation function g_3 reads

$$g_3(l_1, l_2, l_3) = g_2(l_1, l_2)\, g_2(l_2, l_3)\, g_2(l_3, l_1) \tag{4.1}$$

The value of g_3 which enters V is given by (see Figure 1)

$$g_3(1, 2, 3) = [g_2(1, 2)]^2\, g_2(1, 3) \tag{4.1'}$$

The superposition approximation can be extended to correlation functions g_n of arbitrary order n by expanding the "potential of mean force"

$$\psi_n = -k_B T \ln g_n \tag{4.2}$$

in terms of "correlation potentials" for pairs and larger groups of up to n particles.[12,13] The approximation is defined by neglecting multiparticle potentials beyond a certain order. Kirkwood's approximation (4.1) is obtained by taking only the correlation pair potential into account. Neglecting the correlation potentials beyond the three-particle potential, the following expression for g_4 is derived:

$$g_4(l_1, l_2, l_3, l_4) = \frac{g_3(l_1, l_2, l_3)\, g_3(l_2, l_3, l_4)\, g_3(l_3, l_4, l_1)\, g_3(l_4, l_1, l_2)}{g_2(l_1, l_2)\, g_2(l_1, l_3)\, g_2(l_1, l_4)\, g_2(l_2, l_3)\, g_2(l_2, l_4)\, g_2(l_3, l_4)} \tag{4.3}$$

Replacing g_3 by approximation (4.1) yields

$$g_4(l_1, l_2, l_3, l_4) = g_2(l_1, l_2)\, g_2(l_2, l_3)\, g_2(l_3, l_4)\, g_2(l_4, l_1)$$
$$\times\ g_2(l_1, l_3)\, g_2(l_2, l_4) \tag{4.4}$$

In this approximation (4.4), g_4 is factorized into the product of two-particle correlation functions g_2 for all pairs of sites. For the ring configuration of sites 1, 2, 3, and 4 (see Figure 1) the approximations (4.3) and (4.4) become

$$g_4(1, 2, 3, 4) = \frac{[g_3(1, 2, 3)]^4}{[g_2(1, 2)]^4 \cdot [g_2(1, 3)]^2} \tag{4.3'}$$

and

$$g_4(1, 2, 3, 4) = [g_2(1, 2)]^4 \cdot [g_2(1, 3)]^2 \tag{4.4'}$$

respectively.

We have tested the accuracy of the SA by comparing with the results of the Monte Carlo calculation, both for the correlation functions $g_3(1, 2, 3)$ and $g_4(1, 2, 3, 4)$ of third and fourth order and for the vacancy availability factor V. Monte Carlo data for the pair and triplet correlation function g_2 and g_3 were also used to evaluate the expressions obtained in the SA. As shown in Figure 2, the error of the SA for $g_3(1, 2, 3)$ is more
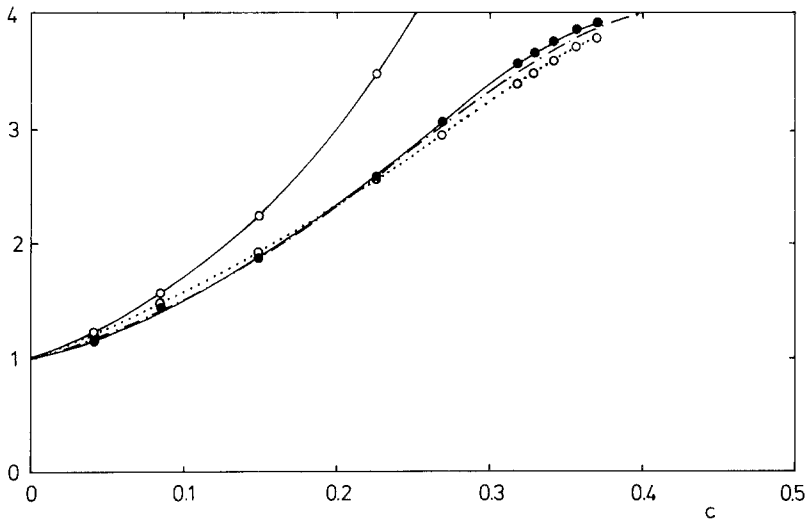

Fig. 2. Triplet correlation function $g_3(1, 2, 3)$ in the SA (——○——) and in the Gaussian factorization (··○··) compared with the result of Monte Carlo calculation (——●——). The lines are guides to the eye. The dash-dotted line is the result of the Bethe–Peierls approximation.
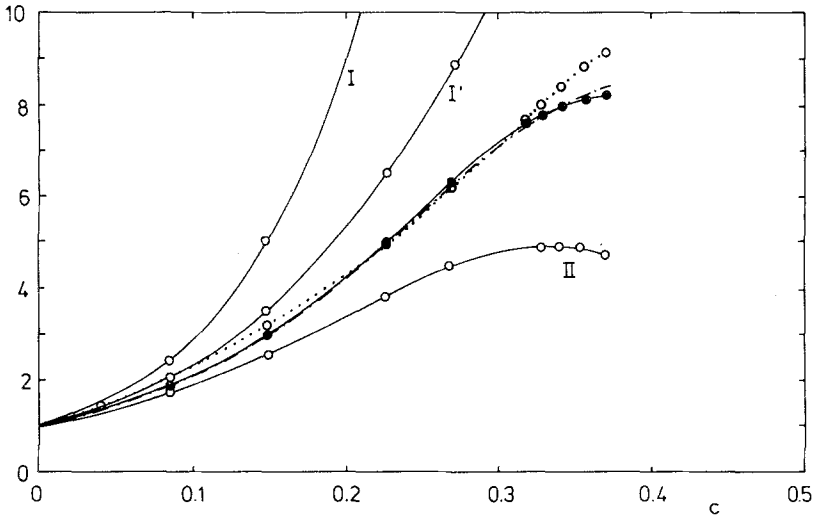
Fig. 3.   Fourth-order correlation function $g_4(1, 2, 3, 4)$ (see text) in various versions of the SA (—○—) and in the Gaussian factorization (··○··) compared with the result of the Monte Carlo calculation (—●—). The lines are guides to the eyes. The dash-dotted line is the result of the Bethe–Peierls approximation.

than 50% at concentrations $\geqslant 0.2$. In Figure 3 the approximations (4.3′) and (4.4′) of the fourth-order correlation function $g_4(1, 2, 3, 4)$ are marked as (II) and (I), respectively. The error of approximation (II) is close to 50% only at the highest concentrations, but the error of approximation (I) exceeds 50% already at rather low concentrations $c \geqslant 0.12$. The low accuracy of approximation I for $g_4(1, 2, 3, 4)$ may be guessed from the very large error obtained in the limit $c \to 0.5$. In this limit the approximation yields a value of 64, which is eight times the correct value. In view of these large discrepancies, tentatively a modified approximation (I′) is introduced, in which the pair correlations across the ring of sites 1, 2, 3, and 4 (Figure 1) are dropped; the modified approximation for $g_4(1, 2, 3, 4)$ reads

$$g_4(1, 2, 3, 4) = [g_2(1, 2)]^4 \tag{4.5}$$

As is to be expected from the smaller limiting value of 8 for $c \to 0.5$, approximation (I′) is in better agreement with the Monte Carlo result, with an error exceeding 50% only at concentrations $c \geqslant 0.3$. It should be noted, however, that approximation (4.5) is not derived in a systematic way. Figure 4 shows the various approximate results for the reduced vacancy availability factor $V/(1 - c)^3$ together with the Monte Carlo data. Surprisingly, for concentrations up to $c = 0.3$, the approximation (I) is now
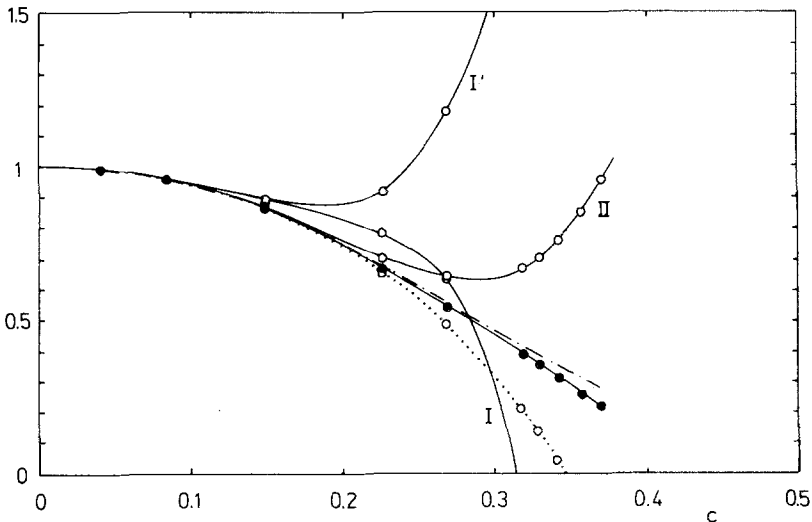
Fig. 4.   Vacancy availability factor in units of the uncorrelated part $(1-c)^3$ in various versions of the SA (—○—) (see text) and in the Gaussian factorization (··○··) compared with the results of the Monte Carlo calculation (—•—). The lines are guides to the eye. The dash-dotted line is the result of the Bethe–Peierls approximation.

about as accurate as approximation (II), with a 30% error at $c = 0.3$ in both cases. Only at higher concentrations $c > 0.3$ the result of approximation (I) deteriorates rapidly, leading to very small and finally negative values of V. Obviously, the error in the approximation for g_4 is largely compensated by the error involved in the approximation for g_3. The modified approximation (I′), on the other hand, is now very inaccurate, with an error exceeding 50% already at $c = 0.24$ and growing rapidly at higher concentrations.

5. TEST OF GAUSSIAN FACTORIZATION

An alternative approximation scheme for reducing higher-order correlation functions is obtained by treating the site-occupation numbers n_i as Gaussian variables, as is done in the mean spherical approximation (MSA). Using the factorization of averages of products of Gaussian random variables, the following expression for the three- and four-site correlation function and the vacancy-availability factor are derived:

$$g_3(1, 2, 3) = 2g_2(1, 2) + g_2(1, 3) - 2 \tag{5.1}$$

$$g_4(1, 2, 3, 4) = 1 + 4[g_2(1, 2) - 1]$$
$$+ 2[g_2(1, 3) - 1]$$
$$+ 2[g_2(1, 2) - 1]^2 + [g_2(1, 3) - 1]^2 \qquad (5.2)$$
$$V = (1 - c)^3$$
$$- c(1 - c)(1 - 2c)\{2[g_2(1, 2) - 1] + g_2(1, 3) - 1\}$$
$$- c^3\{2[g_2(1, 2) - 1]^2 + [g_2(1, 3) - 1]^2\} \qquad (5.3)$$

The validity of these formulas is tested using Monte Carlo data for the pair-correlation function. The results for $g_3(1, 2, 3)$, $g_4(1, 2, 3, 4)$ and for V are included in Figures 2, 3, and 4, respectively. It can be seen that the results for the three- and four-site correlation function are much more accurate than those obtained in the superposition approximation, whereas for the vacancy availability factor for concentrations higher than 0.3 the Gaussian factorization fails equally.

6. BETHE–PEIERLS CLUSTER APPROXIMATION

Since only short-range correlations enter the vacancy availability factor, a Bethe–Peierls cluster approximation is appropriate. (As an alternative, Kikuchi's cluster variation method could also be used.[17,18]) It is found that the cluster of nine sites shown in Figure 1 is large enough to produce satisfactory results. It would not be sufficient to consider the cluster of the five inner sites only, since the correlations between the first and second coordination shell are important. (The results do not change, however, if the four sites of the third coordination shell are added to the cluster.) In the Bethe–Peierls approximation the effect of the medium surrounding the cluster is taken into account by allowing the chemical potential of the surface sites to differ from the bulk chemical potential μ which exists at the central site. The values of the surface chemical potentials

$$\mu_1 = \mu_2 = \mu_3 = \mu_4$$

and

$$\mu_5 = \mu_6 = \mu_7 = \mu_8$$

are determined by the condition that all sites of the cluster are equally populated on the average. The conditions for μ_1 and μ_5 therefore read

$$\langle n_0 \rangle = \langle n_1 \rangle = \langle n_5 \rangle \qquad (6.1)$$

In terms of the fugacities

$$z = \exp(\beta\mu), \qquad z_1 = \exp(\beta\mu_1), \qquad z_5 = \exp(\beta\mu_5) \tag{6.2}$$

the grand canonical partition function Z_{cl} of the cluster is given by

$$Z_{cl} = (z + 1)(1 + z_5)^4 + 4z_1(1 + z_5)^2$$
$$+ z_1^2(4z_5 + 6 + 4z_1 + z_1^2) \tag{6.3}$$

Differentiating with respect to μ, μ_1, and μ_5 one obtains

$$\langle n_0 \rangle = z(1 + z_5)^4/Z_{cl} \tag{6.4a}$$

$$\langle n_1 \rangle = z_1\{(1 + 2z_1 + z_5)(1 + z_5)$$
$$+ [(z_1 + 3)z_1 + 1]z_1\}/Z_{cl} \tag{6.4b}$$

$$\langle n_5 \rangle = z_5\{[(1 + z_5)^2(z + 1) + 2z_1](1 + z_5) + z_1^2\}/Z_{cl} \tag{6.4c}$$

With these expressions, the equations (6.1) have to be solved numerically for μ_1 and μ_5 at given $\beta = (k_B T)^{-1}$ and μ. The result for the concentration $c = \langle n \rangle$ as a function of the fugacity z is shown in Figure 5.

Although we are not interested in the properties of the ordered phase existing above the critical concentration, it is of interest to know at which
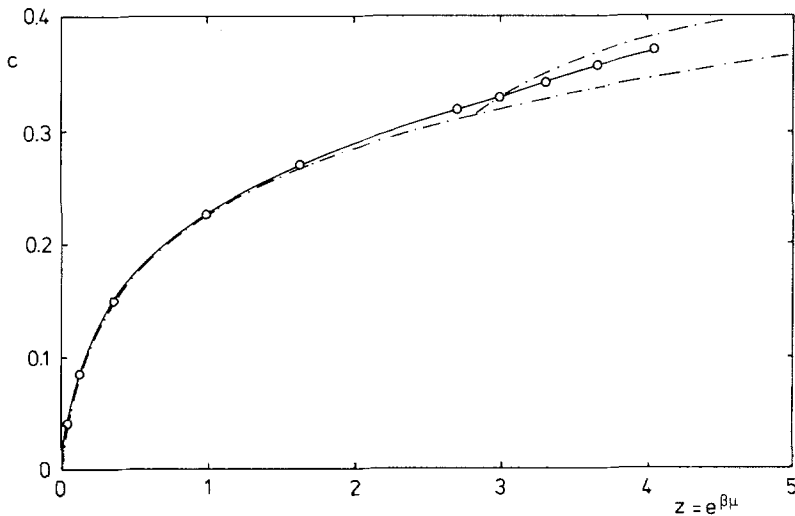

Fig. 5. Concentration c in dependence of the fugacity $z = e^{\beta\mu}$ from the Monte Carlo calculation compared with the result of the Bethe–Peierls approximation (—·—·—). The upper curve describes the ordered phase. The full line is a guide to the eye.

concentration the phase transition occurs in the approximation. To extend the cluster approximation to the ordered phase, one must take the broken symmetry between the two sublattices A and B into account.[19,20] Because of the asymmetry, there are two inequivalent ways of selecting a cluster from the lattice, in which the central site belongs either to sublattice A or B. The two different clusters of type A and B have to be considered simultaneously. The four chemical potentials $\mu_1^{(A)}$, $\mu_5^{(A)}$, $\mu_1^{(B)}$, and $\mu_5^{(B)}$ at the surfaces of the two types of clusters are determined by the four equations

$$\langle n_0^{(A)} \rangle = \langle n_1^{(B)} \rangle = \langle n_5^{(A)} \rangle \tag{6.5a}$$

and

$$\langle n_0^{(B)} \rangle = \langle n_1^{(A)} \rangle = \langle n_5^{(B)} \rangle \tag{6.5b}$$

which express the condition that equivalent lattice sites in both clusters should be equally populated. Below a critical value z^* of the fugacity, the equations (6.5) have a unique solution with $\langle n^{(A)} \rangle = \langle n^{(B)} \rangle$, corresponding to the symmetric disordered phase. Above z^* two asymmetric solutions for the ordered phase with an order parameter

$$\langle n^{(A)} \rangle - \langle n^{(B)} \rangle \neq 0$$

are obtained in addition. The two asymmetric solutions are mirror images of one another. A calculation of the free energy shows that the asymmetric solution is thermodynamically stable. For z values above the critical value z^*, Figure 5 shows both the concentration in the unstable symmetric phase and the average concentration

$$\langle n \rangle = (\langle n^{(A)} \rangle + \langle n^{(B)} \rangle)/2$$

for the stable asymmetric phase. At the branching point z^*, the critical concentration has the value $c^* = 0.32$, which has to be compared with the correct value $c_{crit} = 0.37$. In the concentration range $0.32 \leqslant c \leqslant 0.37$, consistency would require to calculate correlation functions and vacancy availability factor for the asymmetric solution corresponding to the ordered phase. In the figures, however, the results for the disordered phase are drawn up to the critical concentration of 0.37.

With the chemical potentials μ_1 and μ_5 calculated from Eqs. (6.1), the correlation functions $g_n(l_1, l_2, ..., l_n)$ are calculated in the usual way by differentiating the partition function with respect to suitable auxiliary potentials. For the pair correlation function $g_2(1, 2)$, for example, the following formula in terms of the fugacities z, z_1, and z_5 is derived:

$$g_2(1, 2) = z_1^2[4(1 + z_5) + 8z_1 + z_1^2]/(Z_{cl} c^2) \tag{6.6}$$

Comparing the correlation functions obtained from a Bethe–Peierls cluster approximation with Monte Carlo data, one must remember that translational invariance is broken by the selection of a particular cluster. Therefore, in the approximation correlation functions may have different values for groups of sites which are equivalent in the infinite system, but not equivalent on the cluster. For example, the approximate $g_2(1, 2)$ differs from $g_2(0, 5)$. (Translational invariance would be maintained if Kikuchi's cluster variation method[21,22] were used.) The ambiguity, which occurs in the approximate calculation of the two- and three-site correlation function, does not arise, however, for $g_4(1, 2, 3, 4)$ nor for V. Figure 6 shows the results of the Bethe–Peierls cluster approximation for the pair correlation functions $g_2(1, 2)$ and $g_2(0, 5)$, and for $g_2(1, 3)$ and $g_2(5, 6)$ in comparison with Monte Carlo data. The violation of translational invariance is very noticeable, but is not dramatic. The results of the approximation for the three- and four-site correlation function and for the vacancy availability factor are included in the Figures 2, 3, and 4, where they are shown by the dashed-dotted lines. In all three cases, the result of the Bethe–Peierls approximation is in much better agreement with the Monte Carlo results than any version of the SA. Despite its relative simplicity, the Bethe–Peierls approximation is well suited for the description of higher-order correlations which determine the average jump rate in our lattice gas model.
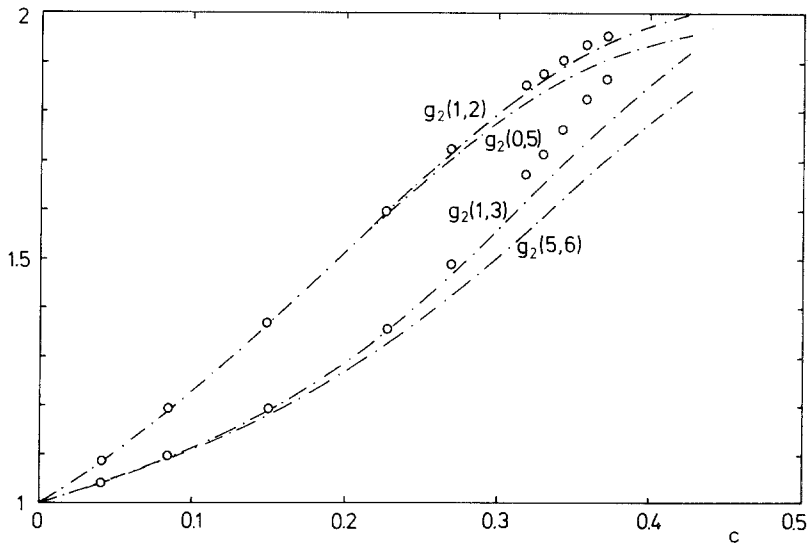

Fig. 6. Pair correlation functions for next-nearest neighbors from the Monte Carlo calculation (— ○ —) compared with the results of the Bethe–Peierls approximation (–·–·–). Because of broken translational invariance $g_2(1, 2)$ and $g_2(0, 5)$ are different.

Finally it is shown that for the particular cluster chosen, the Bethe–Peierls approximation leads to some factorizations of correlation functions of higher order, which can be compared with the SA. Because of the greater accuracy of the Bethe–Peierls approximation, these factorizations are much more accurate than similar factorizations obtained from the SA. The factorizations can be derived directly by considering situations in which the occupation of some sites in the cluster leads to statistical independence of the occupation of some remaining sites. For example, if site 0 in the cluster of Figure 1 is occupied, the populations of sites 5, 6, 7, and 8 are mutually unrelated, since the extended hard core of the particle on site 0 forbids the occupation of sites 1, 2, 3, and 4. As a result of this, the following relations hold in our cluster approximation:

$$g_3(0, 5, 6) = [g_2(0, 5)]^2 = g_3(0, 5, 7) \tag{6.7}$$

$$g_4(0, 5, 6, 7) = [g_2(0, 5)]^3 \tag{6.8}$$

$$g_5(0, 5, 6, 7, 8) = [g_2(0, 5)]^4 \tag{6.9}$$

Equation (6.7), for example, is a better approximation than the equation

$$g_3(0, 5, 6) = [g_2(0, 5)]^2 g_2(5, 6) \tag{6.10}$$

which is a special case of the SA [Eq. (4.1)]. [Under conditions of translational invariance (6.10) is, of course, equivalent to (4.1′).] Similarly, if sites 1 and 3 are occupied, the populations of sites 2 and 4 are mutually uncorrelated. This leads to the relation

$$g_4(1, 2, 3, 4) = \frac{[g_3(1, 2, 3)]^2}{g_2(1, 3)} \tag{6.11}$$

which should be compared with Eq. (4.3′). O'Keeffe[23] used a similar relation in an approximate calculation of the vacancy availability factor for a simple cubic lattice. The projection on the square lattice of the cluster considered by him is shown in Figure 7. If the central site (1) of this cluster is occupied, the populations of all surface sites, in particular of sites 2, 3, and 4, are mutually uncorrelated. The vacancy availability factor is then obtained as

$$V = [1 - cg_2(1, 2)]^2 \cdot [1 - cg_2(1, 3)] \tag{6.12}$$

This approximation is, however, not very accurate because it corresponds to neglecting the sites of the second coordination shell in the cluster of Figure 1. [With Monte Carlo functions $g_2(1, 2)$ and $g_2(1, 3)$, the result (6.12) is by more than 30% too low at concentrations of 0.3 and higher.]
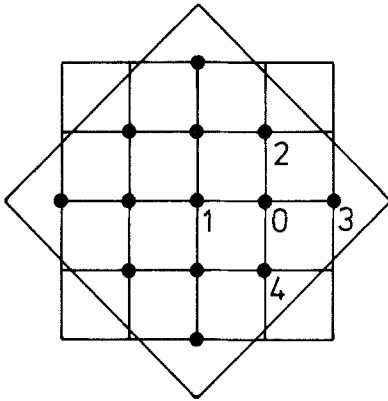
Fig. 7. The cluster which would correspond to O'Keefe's approximation in two dimensions (black dots) compared with the cluster considered in this paper.

7. FREE-VOLUME FORMULA

In the phenomenological theory of molecular transport in dense fluids, the concept of the "free molecular volume"[24-26] is widely used. The idea is that a certain amount of free volume, which corresponds to a sufficiently large hole, is necessary for a molecular rearrangement. The free-volume model is expected to apply only at higher densities at which the number of holes is small. It is worth trying to extend these considerations to our lattice gas model.

Under the assumption that the total number N_f of "free sites" in the lattice is distributed among the N particles in a statistically independent way one finds for the probability distribution for the number n_f of free sites assigned to a particular molecule

$$p(n_f) = \frac{1}{1 + \bar{n}_f} \left(\frac{\bar{n}_f}{1 + \bar{n}_f} \right)^{n_f}, \qquad n_f = 0, 1, 2,... \tag{7.1}$$

where the average $\bar{n}_f$ is given by N_f/N. Assuming the relation between $\bar{n}_f$ and the inverse c^{-1} of the concentration to be linear, one obtains

$$\bar{n}_f = 1/c - 2 \tag{7.2}$$

since at $c = 0.5$ all sites are blocked in the close-packed structure. The third assumption is that a particle can jump to some other site only if its free volume exceeds a certain critical value corresponding to n_c free sites. This assumption leads to the following free-volume expression for the analog of the vacancy-availability factor:

$$V_{\text{f.v.}} = \sum_{n_f = n_c}^{\infty} p(n_f) = \left(1 + \frac{1}{\bar{n}_f} \right)^{-n_c} \tag{7.3}$$
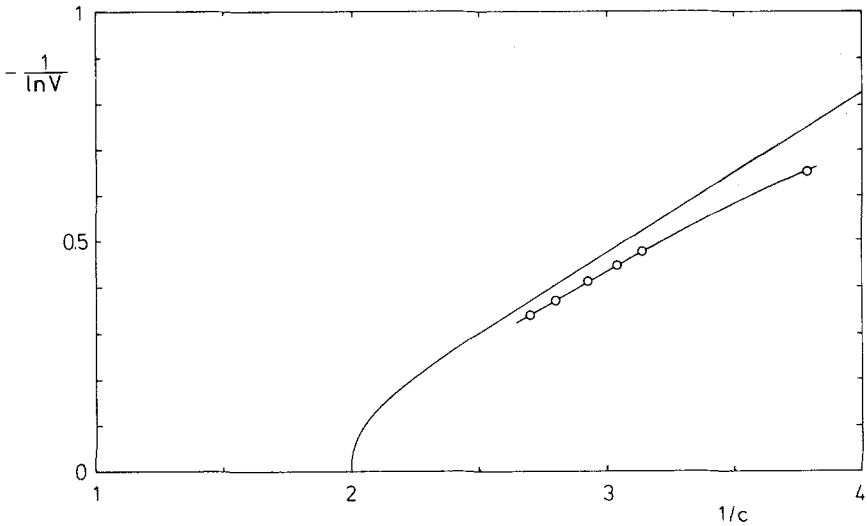
Fig. 8.   Vacancy availability factor V from the Monte Carlo calculation ($— \circ —$) compared
to the result of the free-volume theory (7.3) with $n_c = 3$.

Since the jump of a particle to a nearest-neighbor site requires at least three
vacancies on neighboring sites, it is reasonable to put $n_c = 3$. For this value
of n_c, the result of Eqs. (7.2) and (7.3) is shown in Figure 8 together with
the Monte Carlo data at higher concentrations $0.25 < c < 0.37$. In view of
the simplifying assumptions made, the agreement is gratifying. Unfor-
tunately, these assumptions cannot be justified by a more detailed analysis.
First, it is easy to see that the free volumes of neighboring particles are not
independent. Second, a proper geometrical definition of free volume by the
Wigner–Seitz construction leads to fractional values which are not mul-
tiples of some unit of free volume. A detailed analysis of the distribution of
free volume so defined would not be any simpler than the original problem
of calculating the vacancy availability factor.

8. CONCLUSION

For the lattice gas model investigated, it has been shown that the use
of the SA in the calculation of correlation functions of higher order may
lead to substantial errors. For the three- and four-site correlation function
the SA proves to be unreliable, except at low concentration ($c < 0.1$). Sur-
prisingly, the results of the SA for the vacancy availability factor are in
much better agreement with the Monte Carlo data due to partial can-
cellation of errors. At higher concentrations ($0.3 < c < 0.37$), however,

serious discrepancies remain. The Gaussian factorization of the correlation functions and the vacancy availability factor agree remarkably well with the Monte Carlo data but they also fail beyond $c = 0.3$. Much better results for the correlation functions and for the vacancy availability factor are obtained with a Bethe–Peierls cluster approximation. The cluster approximation also suggests more accurate factorizations of the correlation functions of higher order as an alternative to the SA. Our results confirm that static correlations, as they affect diffusion processes in interacting lattice gases, are by no means trivial and deserve being studied further.

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