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

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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.

KEY WORDS: Diffusion; square lattice gas; repulsive interaction; static correlation function; Monte Carlo simulation; superposition approximation; Bethe–Peierls approximation; free-volume theory.

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 \(c_{\text{crit}} = 0.37\).\(^{(4,5)}\) 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 \(p(l \rightarrow l')\) 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 \(p(1 \rightarrow 0)\) can be written in terms of occupation numbers \(n_i = 0, 1\) as

\[
p(1 \rightarrow 0) = \frac{1}{\tau_s} w(1, 0)
\]

with

\[
w(1, 0) = n_1(1 - n_2)(1 - n_3)(1 - n_4)
\]

\(^3\) 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.