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Effective medium theory of collective diffusion of lattice gases in lattices with site energy disorder

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Abstract. Collective diffusion of lattice gases of arbitrary concentrations is investigated in lattices of dimensions $d \geqslant 2$ with randomly distributed site energies. The Gaussian, exponential and dichotomic distributions of site energies are employed. An effective medium theory of the coefficient of collective diffusion is given using symmetrized single-particle transition rates. A previous phenomenological theory is rederived in the limit $d \to \infty$. The effective medium theory gives good agreement with simulation data at smaller particle concentrations, and rough agreement at large particle concentrations.

1. Introduction

Diffusion of lattice gases in disordered lattices is an important problem in view of the various applications of this model. Lattice gas particles occupy the sites of lattices; multiple occupancy of the sites is excluded. Disorder is usually introduced in the form of random, quenched transition rates for the particles between neighbouring sites. Examples for lattice gases in disordered lattices are provided by hydrogen in random alloys [1, 2], charge carriers in mixed oxides [3], and particles on disordered surfaces [4]. Also hydrogen in metglasses has been modelled as a lattice gas in disordered lattices, with appropriate distributions of the site energies [5]. Further, superionic conductors with random immobile constituents belong to this class [6]. Thus there is much practical need to comprehend diffusion of lattice gases in disordered systems. The difficult theoretical problem is the proper treatment of the correlations between the occupancies of different sites by the particles in non-equilibrium situations. This problem has been addressed in several papers that were devoted to one-dimensional chains [7, 8, 9, 10], but no complete solution at arbitrary particle concentrations has been found for the disordered chains.

Our aim in this paper is somewhat different. We will present an effective medium theory for collective diffusion in disordered lattices of dimensions $d \geqslant 2$. This approximate theory will be based on effective single-particle transition rates, in which the correlation effects mentioned above are neglected. Hence we employ two approximations together, yet the results constitute an improvement over previous phenomenological theories. Diffusion of many particles in lattices with random traps that can be saturated by the diffusing particles has been of continuing interest to metal physicists [1, 11, 12, 13] as well as to surface physicists [14, 15]. Hence they have developed phenomenological theories which are based on the decomposition of the diffusion coefficient into a kinetic factor and a thermodynamic factor. The thermodynamic factor can be calculated from equilibrium statistical mechanics,

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but the kinetic factor requires additional assumptions. A minimal requirement for any theory is that it should give the correct low-concentration limit. This requirement was not met by the early theories [11, 12]. A satisfactory phenomenological formula was finally given by Brouwer *et al* [2]; see also Salomons [16].

It was pointed out in previous work [17, 18] that the phenomenological theory fails generally in the limit of large particle concentration. This will also be discussed in some detail in this paper. Here it may suffice to mention that percolation effects are not properly included in the phenomenological kinetic factor. The effective medium theory to be developed here does somewhat better in this respect, although complete agreement between theory and simulations is not obtained. This theory also allows us to elucidate the nature of the approximation of the phenomenological theory.

In the following section we will introduce the site energy model and give the single-particle transition rates that are used later. The phenomenological theory is described in the third section, and the effective medium theory is developed in the fourth section. Results of computer simulations are compared with the theories in section 5, for three different distributions of the site energies. Section 6 then contains concluding remarks. A preliminary account of this work is contained in the conference contribution [19].

2. Model

We study the customary lattice-gas model where particles occupy the vertices of d-dimensional hypercubic lattices. The vertices or 'sites' are labelled by integers l. Multiple occupancy of the sites is not allowed. Apart from the exclusion of multiple occupancy, no further interactions between the particles are taken into account. The overall concentration c of the particles is defined as $c = N_p/N$ where N_p is the number of particles and N the number of lattice sites. The particles may perform transitions to empty neighbour sites with prescribed transition rates. Random transition rates are assigned to pairs of neighbouring sites of the lattices, hence we have quenched disorder.

In the random site energy model the set of random transition rates is introduced by the assignment of random site energies E_l ($E_l \leqslant 0$) to the lattice sites. The energies are taken from a common distribution $v(E)$ and the distribution may be dichotomic, Gaussian or exponential. The transition rate originating from site l is given by the Arrhenius law

$$\Gamma(E_l) = \Gamma_0 \exp(\beta E_l) \tag{1}$$

and it does not depend on the energies of the final sites. The coefficient β is the inverse temperature and Γ_0 is a frequency constant which will be taken as unity. The introduction of the Arrhenius law provides a physical motivation for the model. Abstractly it is defined by the specification of a set of random transition rates $\{\Gamma_l\}$ where the rates depend on the initial sites but not on the final ones. The random site energy model is a prototype model for diffusion of particles in the presence of temporary trapping centres. It has been used, e.g., for diffusion in metals with a dilute concentration of traps [11, 12], but also for hydrogen diffusion on metglasses [13]. More complicated models take the energy differences between the initial and final sites into account [22], or also modifications of the saddle point energies between the sites [1].

Collective diffusion of the lattice gas where the identity of the particles is disregarded is completely described by the set of probabilities $P(l, t)$ of finding a particle at site l at time t. Appropriate initial conditions have to be specified. The quantity $P(l, t)$ obeys a

master equation

$$\frac{\mathrm{d}}{\mathrm{d}t}P(l,t) = \sum_{\langle l'\rangle_l}\left[\Gamma_{l'\to l}P(l',\bar{l},t) - \Gamma_{l\to l'}P(\bar{l}',l,t)\right]. \tag{2}$$

The notation $\langle l'\rangle_l$ designates the summation over all neighbouring sites l' of l. $P(l',\bar{l},t)$ is the joint probability that at time t site l' is occupied by a particle and site l is unoccupied, indicated by the overbar. The quantity $\Gamma_{l\to l'}$ is the transition rate from site l to l'. In the random site energy model the rate $\Gamma_{l\to l'}$ only depends on the starting site l of a particle transition, hence we can set

$$\Gamma_l := \Gamma_{l\to l'}. \tag{3}$$

The equilibrium occupation of a lattice site with energy E_l by a particle is given by the Fermi function, $P(l) = f(E_l)$, where

$$f(E) = \frac{1}{1+\exp[\beta(E-\mu)]} \tag{4}$$

and $\mu = \mu(c)$, the chemical potential for a given particle concentration c. It is determined from

$$c = \int_{-\infty}^{0} \mathrm{d}E\, \nu(E) f(E). \tag{5}$$

A stationary solution of the master equation is obtained when the condition of detailed balance is fulfilled,

$$\Gamma_l P(l)[1-P(l')] = \Gamma_{l'} P(l')[1-P(l)]. \tag{6}$$

The difficulty in solving the master equation (2) arises from the joint probabilities. The joint probabilities that appear in (2) may be related to the joint probability $P(l',l,t)$ of finding a particle at site l' and another particle at site l at time t by

$$P(l',\bar{l},t) + P(l',l,t) = P(l',t). \tag{7}$$

This equation follows from the fact that non-occupancy and occupancy of site l are mutually exclusive events. The analogous relation holds with the unoccupied site $\bar{l}'$. If the transition rates between the sites are symmetric, $\Gamma_{l\to l'} = \Gamma_{l'\to l}$, then the joint probabilities $P(l,l',t)$ cancel each other in the master equation (2). In this case the problem is reduced to a single-site problem, which is formally equivalent to a single-particle problem [20, 21].

The random site energy model where the rates depend on the initial sites, but do not exhibit a symmetry between neighbouring sites, cf. (3), is the simplest non-trivial case where the joint probabilities have to be taken into account. The joint probability $P(l,l',t)$ factorizes in equilibrium, but not in the general, time-dependent case.

A reduction to a single-site problem is achieved by factorization of the joint probability $P(l,l',t)$ and linearization near equilibrium. This direct factorization yields asymmetric transition rates [10] which are useful for the treatment of the one-dimensional problem. Miller and Abrahams [22] considered the hopping conductivity of electrons between sites of different energies and reduced the problem to a random network problem with symmetric impedances between the sites. The factorization of the joint probabilities is implicit in their work. Gartner and Pitis introduced symmetrized rates in their treatment of the disordered chain [9]. We will utilize later such symmetrized rates, and they read for the random site energy model after a suitable normalization

$$\Gamma_{\mathrm{sym}} = \Gamma_l P(l)(1-P(l'))\beta\frac{\partial\mu}{\partial c}. \tag{8}$$

The symmetry of these rates is obvious from the condition of detailed balance (6). The normalization factor is given by

$$\beta\frac{\partial\mu}{\partial c} = \{P(l)(1 - P(l))\}^{-1}. \tag{9}$$

The curly brackets indicate the average over the distribution $\rho(\Gamma)$ of the transition rates.

3. Previous approaches

Gartner and Pitis [9] have published a mean field theory of collective diffusion on linear chains and given a recursion method for calculating decreasing upper bounds of the collective diffusion coefficient D_{coll}. The coefficient of collective diffusion is defined by the diffusion equation (i.e., Fick's second law) describing the decay of density deviations on a mesoscopic scale,

$$\frac{\mathrm{d}}{\mathrm{d}t}P(l,t) = D_{\text{coll}}\Delta P(l,t). \tag{10}$$

The mean field result for D_{coll} is identified by restricting the resolvent of the master-evolution operator to a single-particle subspace. Their result is

$$D_{\text{coll}}^{\text{MF}} = \left\{\Gamma_{\text{sym}}^{-1}\right\}^{-1}. \tag{11}$$

An equivalent result was obtained in [10] from the asymmetric mean field transition rates by using first-passage time methods.

The result (11) gives the correct low-concentration limit. In this limit the diffusion coefficient reduces to the diffusion coefficient of single, independent particles in the random site energy model, which is exactly known [23],

$$D_{\text{sp}} = \left\{\Gamma^{-1}\right\}^{-1}. \tag{12}$$

The diffusion coefficient of single particles is defined by the diffusion equation for the probability density of a single particle. Note that (12) is valid in all dimensions d, while (11) or the equivalent result in [10] is only valid in $d = 1$. Since (12) is an exact result, it can serve as a criterion for the correctness of the low-concentration limit of further approximate results.

In the large-concentration limit diffusion is effected by single, independent vacancies, and $D_{\text{coll}} = D_{\text{sv}}$. The diffusion coefficient D_{sv} of single vacancies in the site energy model is given for linear chains by [10]

$$D_{\text{sv}} = \{\Gamma\}^{-1}\{\Gamma^{-1}\}^{-2}. \tag{13}$$

Also (11) approaches this expression in the limit $c \to 1$. From elementary probability theory we obtain, assuming that the pertinent moments exist,

$$\{\Gamma^{-1}\}^{-1} \leqslant \{\Gamma\}. \tag{14}$$

This equation leads to

$$D_{\text{sv}} \leqslant D_{\text{sp}} \tag{15}$$

for arbitrary energy distributions in the one-dimensional random site energy model.

In higher dimensions further approximations are necessary. In the next section we will formulate an effective medium theory in arbitrary dimensions. In the remainder of

this section we describe the phenomenological theories that were given in the past. The phenomenological theories are essentially based on the Nernst–Einstein relation

$$D_{\text{coll}} = Bc\frac{\partial \mu}{\partial c}. \tag{16}$$

This relation gives a decomposition of the diffusion coefficient into a kinetic factor B and a thermodynamic factor $c\partial\mu/\partial c$. The calculation of the thermodynamic factor poses no problem since it follows from equilibrium statistical mechanics. The concentration can also be represented as $c = \{P(l)\}$ and $\partial\mu/\partial c$ has been given in (9). This equation is easily evaluated, e.g., for the dichotomic model. The situation is quite different for the kinetic factor or mobility B where assumptions have to be made. One has $B = \beta\Gamma(1-c)$ for the lattice gas on lattices with uniform transition rates Γ. The phenomenological theory, if correctly formulated, replaces Bc by the average

$$\beta\{\Gamma_l P(l)[1 - P(l')]\}. \tag{17}$$

Now the curly brackets indicate an average over the two sites involved. The result of the phenomenological theory is then

$$D_{\text{coll}}^{\text{phen}} = \{\Gamma_{\text{sym}}\} = \{\Gamma_l P(l)[1 - P(l')]\}\,\beta\frac{\partial \mu}{\partial c}. \tag{18}$$

An explicit result for n trap levels was given by Salomons [16],

$$D_{\text{coll}}^{\text{phen}} = \left(\sum_{i=1}^{n} \nu_i \Gamma_i c_i\right)(1-c)/\sum_{i=1}^{n} \nu_i c_i (1 - c_i) \tag{19}$$

where ν_i is the fraction of lattice sites with transition rates Γ_i and c_i are the particle concentrations at these sites. The particle concentrations c_i on the sites of type i can be calculated from the total concentration c and the discrete distribution of site energies E_i using (4) and (5). Hence the diffusion coefficient (19) is completely determined by the input data of the model. The phenomenological result (19) reduces to the correct single-particle limit (12) in the limit $c \to 0$. As will be discussed in section 5, the phenomenological theory does not give the correct result for $c \to 1$ for finite dimensions, hence an improvement is necessary.

4. Effective medium theory

In the effective medium theory (EMT), the problem of particle diffusion in a disordered lattice is replaced by a diffusion problem on an ordered lattice with effective transition rates. These effective transition rates are frequency dependent for the hopping problem on disordered lattices. The effective medium theory for this problem was developed by several authors [24, 25, 26, 27]. In the long-time or zero-frequency limit the hopping problem becomes equivalent to the random-resistor problem. The effective medium theory for that problem was already given by Kirkpatrick [28] in the context of the percolation problem. The self-consistency condition of the problem with random transition rates reads in the zero-frequency limit

$$\left\{\frac{\Gamma^{\text{EMT}} - \Gamma}{(d-1)\Gamma^{\text{EMT}} + \Gamma}\right\} = 0. \tag{20}$$

Here Γ is a random but fixed transition rate that is taken from a distribution $\rho(\Gamma)$, and the curly brackets indicate the average over this distribution. In this formulation of the effective medium theory, the transition rates have to be symmetric. Symmetric transition

rates were introduced in the preceding section; we utilize Γ_{sym} from (8) to determine Γ^{EMT} from the self-consistency condition (20). The coefficient of collective diffusion is then $D_{coll}^{EMT} = \Gamma^{EMT}$. One can show with the help of the Fermi function (4) and the detailed balance relation (6) that the EMT approach leads to the right single-particle limit (12) in all dimensions.

At this point we have to mention a problem in our effective medium approach. In the self-consistency condition (20) an average is made over a distribution $\rho(\Gamma)$ of symmetric transition rates Γ. The symmetrized transition rates utilized in this paper depend on two site indices, l and l', cf. (8). This leads to an average over two random site energies in the self-consistency condition (20). Moreover, different bonds are not statistically independent. This may decrease the accuracy of our effective medium approximation, in particular for larger particle concentrations. For smaller concentrations, the factor $(1 - P(l'))$ in Γ_{sym} is less important and Γ_{sym} mainly depends on one random site energy.

For the linear chain, $d = 1$, the result of the self-consistency condition is

$$D_{coll} = \{\Gamma_{sym}^{-1}\}^{-1}. \tag{21}$$

Hence the result of the effective medium theory coincides with the correct solution of the disordered hopping problem, where the *approximate* single-particle or mean field transition rates are used.

In arbitrary, finite dimensions a numerical solution of the self-consistency condition is necessary for general distributions, which is easily feasible. The results will be presented in the next section, together with the simulation results.

We obtain from the self-consistency condition (20) in the limit $d \to \infty$

$$D_{coll}^{EMT} = \{\Gamma_{sym}\} \equiv D_{coll}^{phen}. \tag{22}$$

It is reasonable that we regain the result of the phenomenological theory in this limit. The problem is the correct determination of the kinetic coefficient B, which is strongly influenced by the backward correlations of particles when they meet particles that are immobilized in deep trap sites. When the dimension, and consequently the coordination number of the lattice sites, becomes large, the influence of these backward correlations is diminished, and it is absent in the limit $d \to \infty$. Then the phenomenological considerations lead to the correct result.

In the large-concentration limit, $c \to 1$, (22) gives

$$D_{sv} = \{\Gamma\}. \tag{23}$$

With the inequality (14) we obtain for infinite dimensions and arbitrary energy distributions

$$D_{sv} \geqslant D_{sp}. \tag{24}$$

This relation is opposite to the equivalent one (15) for one-dimensional lattices. We will see later that the ratio D_{sv}/D_{sp} increases with increasing dimensions, between the limits given by (15) and (24).

5. Comparison with computer simulations

To examine the validity of the effective medium theory at finite dimensions we compare its results with Monte Carlo simulations for several energy distributions and various particle concentrations. We obtain collective diffusion coefficients by observing the decay of a concentration profile which follows from Fick's second law (10). The system is initially prepared with a cosine profile in the x-direction

$$c(x) = c + \delta c(t = 0)\cos(kx) \tag{25}$$

where $k = 2\pi/\lambda$ and λ is the wavelength of the density disturbance. The quantity c is the mean particle concentration of the lattice gas and $\delta c(t = 0)$ the amplitude of the initial disturbance. The amplitude should be small and the wavelength large to avoid non-linear and k-dependent effects. We use hypercubic lattices with two or more dimensions; results for linear chains have already been given in [10]. We introduce helical boundary conditions instead of periodic ones for computational reasons [29]. For large lattices the diffusion results should be independent of the choice of the boundary conditions. The lattices have 202×200 ($d = 2$), $44 \times 44 \times 42$ ($d = 3$), $20^3 \times 18$ ($d = 4$) and $13^4 \times 11$ ($d = 5$) sites. The special values of the edge lengths are advantageous for the vectorized computer code that has been used by us. Energies are selected randomly from the chosen energy distribution and assigned to the lattice sites. Then particles are put randomly but according to (25) onto the lattice. For equilibration we let the particles make transitions perpendicular to the density profile before starting the simulation of the profile decay. The customary lattice gas dynamics is used with transition rates defined in (1). We employ the fast vectorized algorithm described in [29]. From Fick's second law (10) we obtain a decay of the amplitude $\delta c(t)$ as $\exp(-D_{\text{coll}}k^2t)$. In the case of very large disorder in the energy distribution we observe deviations from the expected exponential decay for small times. This means we have deviations from the ideal diffusional behaviour of the lattice gas at smaller times and the diffusion coefficient has to be determined from data at larger times.

In the following subsections we will present simulation data for the different energy distributions.

5.1. Dichotomic distribution

This distribution is characterized by two different energy levels, leading to two different transition rates, Γ and $\Gamma^<$, with $\Gamma^< < \Gamma$. Lattice sites with transition rate Γ are called free sites and those with $\Gamma^<$ trap sites; they have concentrations $1 - c_t$ and c_t, respectively. We normalize the energy scale to have $\Gamma = 1$. Then the smaller transition rate $\Gamma^<$ is measured in units of Γ. In this simple case one can calculate the equilibrium distribution of the particles analytically and one knows the particle concentrations c_1 and c_2 on free and trap sites explicitly [17]. Apart from its simplicity, the advantage of the dichotomic distribution is that concepts such as saturation of traps are clearly defined. In the computer simulations the systems are initialized in the equilibrium state and no equilibration process is necessary.

For the dichotomic distribution we have to distinguish two different cases, namely $c_t < 1 - p_c$ and $c_t > 1 - p_c$, where p_c is the percolation threshold of the free sites [30]. First we will treat the case of small trap concentrations c_t. This means that clusters of free sites with an infinite extension exist and long-range diffusion of particles is possible even if $\Gamma^< \to 0$. If $\Gamma^<$ vanishes, occupied trap sites become static blocking sites and thus hinder the diffusion of other particles.

The diffusion coefficient of single particles in a lattice with randomly blocked sites of concentration $c_t < 1 - p_c$ is approximately given by

$$D_{\text{sp}} = D_0\left(1 - \frac{c_t}{f} + \ldots\right) \tag{26}$$

where the diffusion coefficient in an ideal lattice $D_0 = 1$ in our normalization. Equation (26) was derived by approximate methods in [31]; the exactness of the term linear in c_t was established in [32, 33] for $d = 2$. The quantity f is the correlation factor for tagged particle diffusion in ideal lattice gases in the limit $c \to 1$. The correlation factor is exactly known for all lattices of interest [34], e.g., $f = 0.466\,942$ for the simple square lattice and

$f = 0.653\,109$ for the simple cubic lattice. For $d > 3$ the factor f can taken from the estimate $f = 1 - 2/z$ with z the coordination number of the lattice [34]. The collective diffusion coefficient coincides with the single-particle diffusion coefficient in lattices with randomly blocked sites, as has been analytically shown in [21] and verified for the simple cubic lattice by numerical simulations in [35].

It has been pointed out repeatedly that (26) applies to diffusion of lattice gas particles in lattices with the dichotomic site energy distribution when $c_t < 1 - p_c$ and $\Gamma^< \ll \Gamma$ [17, 18]. We also utilize (26) as a reference point. Note that the expression (26) takes the value $D_0(1 - c_t)$ when $f \to 1$, whence it agrees with the phenomenological result. The correlation factor for tagged particle diffusion is one in the limit $d \to \infty$; in this limit also the EMT agrees with the phenomenological approach.

Figure 1(a)–(c) presents the results of computer simulations for $d = 2$, 3, 4 and 5, at a trap concentration $c_t = 0.2$ and three different values of $\Gamma^<$, together with the results of the effective medium theory and the phenomenological expression for D_{coll}.

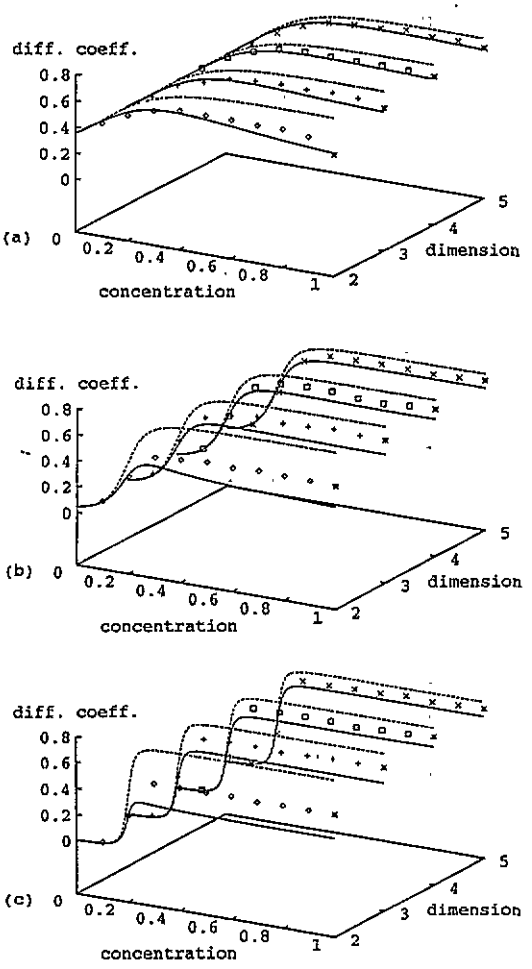

Figure 1. Coefficient of collective diffusion as a function of particle concentration and lattice dimension for $\Gamma^< = 0.1$ (a), 0.01 (b), and 0.001 (c) and $c_t = 0.2$. The different symbols represent simulation results except (*) indicating the limit (26) for $d \geqslant 3$. For $d = 2$ a second-order correction is included [32, 33]. The full curves represent the EMT results and the dashed curves the phenomenological expression.

The simulation data show a strongly increasing diffusion coefficient for $\Gamma^< \ll 1$ up to a particle concentration $c \approx c_t$. The strong increase of the diffusivity is due to a saturation

effect, i.e., when additional particles are put onto the lattice, more trap sites are occupied by them and the probability for free particles to be trapped decreases. The occupied trap sites impede diffusion only slightly, because c_t is small and moving particles can easily bypass occupied trap sites. If $c > c_t$ and $\Gamma^< \to 0$ occupied trap sites become permanent blocking sites and the collective diffusion coefficient is given by (26). In the data of figure 1(a)–(c) the transition rate out of traps is not really zero and no completely static percolation lattice exists, but values of $\Gamma^< = 0.01$ or $\Gamma^< = 0.001$ are already sufficient that (26) can be applied with good accuracy.

Figure 1(a)–(c) demonstrates that the EMT agrees somewhat better with the numerical data for $c < c_t$ than the phenomenological expression. For $c > c_t$ the EMT underestimates the diffusivity while the phenomenological expression is an overestimate. Since the effective medium theory consists of two approximations, it no longer constitutes an upper bound to the diffusion coefficient, contrary to the mean field expression in $d = 1$ [9]. Generally, as we expected in section 4, the EMT is more accurate for smaller than for larger particle concentrations.

If the particle concentration is smaller than 0.1 and $d > 1$ the collective diffusion coefficient is independent of the lattice dimension for the studied transition rates $\Gamma^<$, in agreement with (12). In the region of higher concentrations the different percolation thresholds of the simulated lattices become more important and the diffusion coefficient depends on the lattice dimensionality. Comparing the simulation results with the effective medium theory in different dimensions we observe that the effective medium theory becomes more accurate with increasing d. At the same time, the differences between the EMT and the phenomenological expression become smaller, and they vanish in the limit $d \to \infty$, as pointed out in section 4. Now we will discuss collective diffusion in lattices with

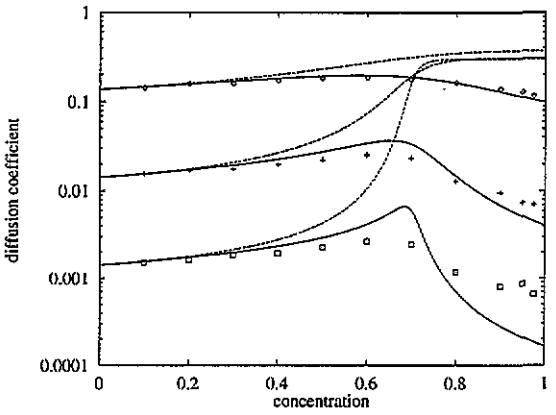

Figure 2. Coefficient of collective diffusion as a function of the concentration of the lattice gas for $d = 2$ and $c_t = 0.7$. The different symbols represent simulation results with $\Gamma^< = 0.1$ (◇), 0.01 (+), and 0.001 (□). The full curves represent the EMT results and the dashed curves the phenomenological expression.

large trap concentrations $c_t > 1 - p_c$, where no normal diffusion is possible for $\Gamma^< = 0$. Simulations were made at $c_t = 0.7$ in two dimensions (figure 2) and $c_t = 0.75$ in three dimensions (figure 3). The simulation results show very different behaviour from that for small trap concentrations. As in the case of small trap concentrations we observe an increasing collective diffusion coefficient for particle concentrations $c \lesssim c_t$, but the rise near c_t is not as strong as for smaller trap concentrations. There is a peak in the diffusion coefficient at $c \approx c_t$ which seems to become more pronounced for decreasing $\Gamma^<$.

In the region of larger particle concentrations we can no longer invoke diffusion in the presence of randomly blocked sites for $\Gamma^< \ll 1$. Now it is important that we have no real static occupation of the trap sites. For all concentrations collective diffusion is governed

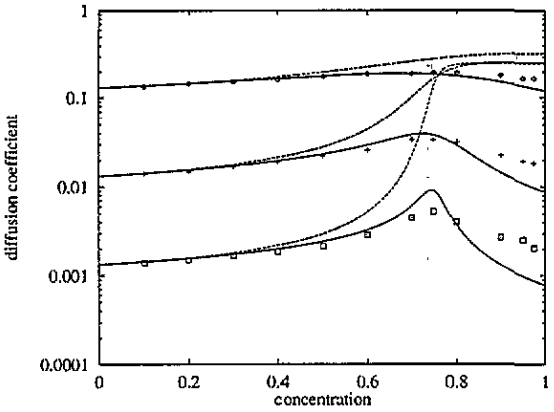

Figure 3. Coefficient of collective diffusion as a function of the concentration of the lattice gas for $d = 3$ and $c_t = 0.75$. The different symbols and curves have the same meaning as in figure 2.

by transitions in and out of trap sites, because there exists no infinite cluster of free sites in the lattice and particles have to enter and leave trap sites to let the density profile decay. For this reason the collective diffusion coefficient is always of the order of $\Gamma^<$.

Figures 2 and 3 show that the effective medium theory gives a better description of the simulation data for $c < c_t$ than the phenomenological theory. When $c > c_t$ the phenomenological theory fails completely in that it predicts a diffusion coefficient proportional to Γ. There are discrepancies between the results of the effective medium theory and the simulation data in this region, but the EMT reproduces at least the trend of the data. Contrary to the case of the linear chain, no exact results are available for the limit $c \to 1$, $\Gamma^< \to 0$ and finite c_t. It is interesting to note that the diffusion coefficient for $c \to 1$ is apparently smaller than the single-particle value in $d = 2$ while it seems to be larger than it is in $d = 3$. We have shown in section 3 that $D_{sv} \leqslant D_{s,p}$ in $d = 1$ and in section 4 that $D_{sv} \geqslant D_{sp}$ in the limit $d = \infty$. Hence our data indicate a gradual change from one to the other limit with increasing dimension.

5.2. *Gaussian distribution*

In this section we will discuss computer simulations of the diffusion problem for a Gaussian distribution of site energies,

$$\nu(E) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left(\frac{(E-\bar{E})^2}{2\sigma^2}\right) \tag{27}$$

where σ is the standard deviation and $\bar{E}$ the mean value of the Gaussian distribution. Gaussian distributions of site energies are of experimental relevance. For instance, Kirchheim [13] considered such distributions to describe the diffusivity of hydrogen in amorphous metals. It is also of general interest to study other distributions than the dichotomic one. In the case of a Gaussian distribution of site energies no well defined trap concentration exists.

The technical problem is now that the Gaussian distribution (27) gives energy values extending from $-\infty$ to $+\infty$, however, no positive site energies are allowed in the random site energy model. To resolve this problem we have to alter the distribution. We cut off 1% of the positive tail and set the corresponding energy values to zero. In this way we get a modified Gaussian distribution

$$\dot{\nu}(E) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left(\frac{(E-\bar{E})^2}{2\sigma^2}\right) + (1-q)\delta(E) \tag{28}$$

with $\bar{E} = -\sigma \mathrm{erf}^{-1}(q)$ where $\delta()$ is Dirac's δ function, erf() the error function and $q = 0.99$. Apart from q, the other free parameter of the distribution is the standard deviation. The combination with the Arrhenius law (1) introduces the temperature as a third parameter. In this subsection we will express σ in units of the temperature. The quantity $\bar{E}$ can be considered as a displacement of the energy scale, which means that all transition rates (1) or the diffusion coefficients are effectively multiplied by a factor. Figures 4 and 5 show the simulation results of the collective diffusion coefficient in two and three dimensions as a function of the particle concentration. If the standard deviation is small ($\sigma = 0.1$ or

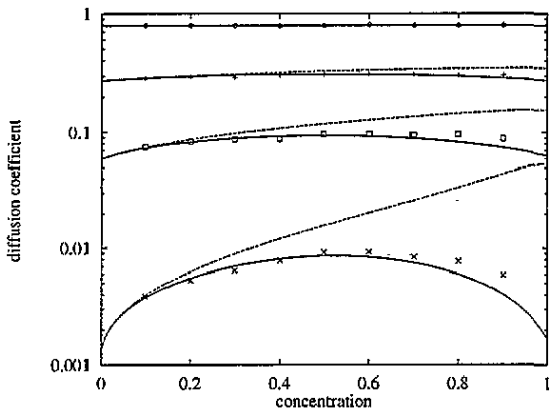

Figure 4. Coefficient of collective diffusion as a function of the concentration of the lattice gas for $d = 2$. The different symbols represent simulation results with $\sigma = 0.1$ (◈), 0.5 (+), 1 (⊡), and 2 (×). The full curves represent the EMT results and the dashed curves the phenomenological expression.

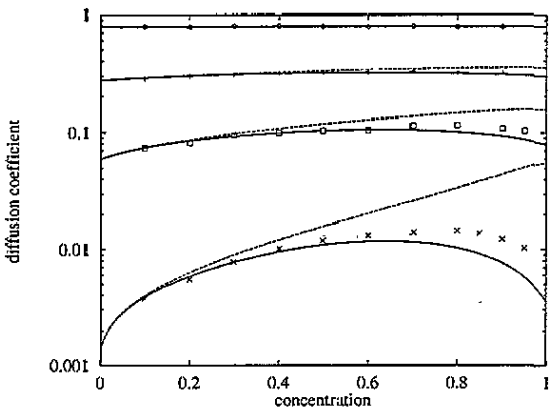

Figure 5. Coefficient of collective diffusion as a function of the concentration of the lattice gas for $d = 3$. The different symbols and curves have the same meaning as in figure 4.

0.5), the diffusion coefficient is approximately independent of the concentration and we get $D_{\mathrm{coll}} \approx D_{\mathrm{sp}}$. For small standard deviations the Gaussian distribution becomes sharp and we get a system that is very similar to a lattice with a uniform transition rate of lattice sites with energy $\bar{E}$, where collective diffusion becomes independent of particle concentration. For large parameters σ the situation is different. The diffusion coefficient increases for small concentrations due to saturation effects, reaches a maximum at a particular concentration, and decreases at larger concentrations because of blocking effects. In $d = 3$ the maximum is at a larger concentration than in $d = 2$, because blocking effects become less important for higher dimensions. Up to a particle concentration $c \approx 0.1$ the diffusion coefficient is independent of the lattice dimension for $d > 1$ and $\sigma \leqslant 2$. If σ becomes larger we also will get a d dependence at smaller concentrations. Generally the d dependence increases with increasing σ.

The effective medium theory agrees with the simulation data for smaller particle concentrations, roughly up to $c = 0.5$. For larger concentrations the theoretical values lie below the numerical ones. The phenomenological approach agrees with the data at low particle concentrations only. At larger concentrations it predicts larger diffusion coefficients than observed, and the differences become considerable for large σ.

5.3. Exponential distribution

Finally we consider the exponential distribution of site energies,

$$\nu(E) = \frac{1}{\sigma} \exp\left(\frac{E}{\sigma}\right) \quad \text{with} \qquad E \leqslant 0. \tag{29}$$

This distribution is very interesting because there exists no coefficient of single-particle diffusion for larger values of the width parameter σ and/or for low temperatures. Introducing the parameter $\alpha = k_B T/\sigma$ one finds from (12) for $\alpha \geqslant 1$

$$D_{sp} = \Gamma_0(1 - 1/\alpha) \tag{30}$$

and $D_{sp} \equiv 0$ for $\alpha < 1$. It was demonstrated in [36] that collective diffusion still exists in the situation where the single-particle diffusion coefficient is zero. One may occupy the sites with an equilibrium concentration of particles, and superimpose a small density disturbance. The density deviation decays via Fick's law (10), and a coefficient of collective diffusion can be deduced. The effect is apparently due to the saturation of the very deep traps by particles. In figure 6 data for two-dimensional lattices are presented; data for $d = 3$ have

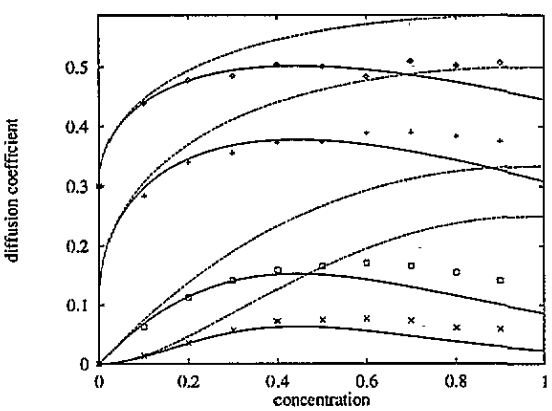

Figure 6. Coefficient of collective diffusion as a function of the concentration of the lattice gas for $d = 2$. The different symbols represent simulation results with $\Gamma_0 = 1$ and $\alpha = 10/7$ (◇), 1 (+), 1/2 (□), and 1/3 (×). The symbols (∗) indicate the exactly known small-concentration limit (30). The full curves represent the EMT results and the dashed curves the phenomenological expression.

already been published in [36]. The behaviour is essentially the same in both dimensions. We observe stronger blocking effects in $d = 2$ than in $d = 3$, resulting in smaller diffusion coefficients for larger c. For the parameters α studied we again find no dependence of the diffusion coefficient on the lattice dimensionality up to roughly $c \approx 0.1$.

There is good agreement between the simulation data and the results of the effective medium theory, which are also presented in figure 6, at lower particle concentrations. At larger concentrations the agreement is only qualitative. An argument put forward in [36] predicts $D_{coll} \sim c^1/\alpha - 1$ for small c in arbitrary dimensions, in agreement with the data, the EMT and the phenomenological theory. The numerical data are consistent with this behaviour. At larger particle concentrations, the EMT underestimates the diffusion coefficient, while the phenomenological expression gives values which are considerably larger.

6. Conclusion

We have presented an effective medium theory of collective diffusion of lattice gases in the random site energy model and compared it with computer simulations for the dichotomic, Gaussian and exponential site energy distributions, at various particle concentrations. We regained a previous phenomenological expression in the limit of infinite lattice dimensionality. Before we discuss the relative merits of the effective medium theory we summarize the physical picture that emerges from the comparison of simulations with theory.

In the region of small concentrations of the lattice gas particles collective diffusion is governed by the saturation of deep traps with particles. When more particles are put on the lattice, additional traps of low energy are occupied and the collective diffusion coefficient increases with increasing particle concentration. In this region the thermostatistical properties are more important for the diffusional behaviour than the kinetic ones. Therefore the phenomenological result, which approximates the kinetic factor in a qualitative, thermostatistical way, is found to be in good agreement with the simulations. For larger concentrations kinetic properties such as correlations between successive particle transitions in the presence of occupied lattice sites, blocking effects, etc become more important and the diffusion coefficient ceases to increase. The correlation effects are more pronounced for small lattice dimensions.

For the dichotomic distribution of site energies we can distinguish the cases where the trap concentration is so small that the free sites are above the percolation threshold, and where it is so large that the free sites do no longer percolate. In the first case we find a constant collective diffusion coefficient for large particle concentration, because the occupied trap sites act as blocking sites in an infinite lattice. In the limit $c \to 1$ and $\Gamma^{<} \to 0$ we find agreement with known approximations of the diffusion coefficient for lattices with blocked sites. In the second case, when we have a large trap concentration, dynamical processes of capture into and release from traps govern the diffusion process and the diffusion coefficient reaches a maximum at $c \approx c_t$.

The results of the effective medium theory are in good agreement with the simulation results for smaller particle concentration and in rough qualitative agreement at larger concentration, for all distributions that were studied. One may say that the effective medium theory is a theory which describes percolative aspects at least in a qualitative way. The discrepancy between the EMT and the data may be due to the fact that two approximations are involved in the theory (approximate single-particle transition rates in addition to the effective medium). Moreover, the transition rates at different bonds are not statistically independent; this should be more detrimental at larger particle concentrations. The phenomenological approach predicts generally too large diffusion coefficients; this is most pronounced at large particle concentrations. It becomes completely wrong in situations where a large fraction of trap sites is more or less permanently blocked.

For small particle concentrations and $d > 1$ the diffusion coefficient is nearly independent of the lattice dimension. Hence the phenomenological expression may be used by experimentalists in this region. The agreement between simulations and the EMT is improved with increasing dimension of the lattice. In the limit of $d \to \infty$ the effective medium theory becomes equivalent to the phenomenological approximation. We believe that the effective medium result, or the equivalent phenomenological expression, is exact in the limit $d \to \infty$.

In this paper we have not treated frequency dependence of the diffusion coefficient. It would be easy to extend the effective medium approach to include this dependence. The frequency dependence is of considerable interest for the interpretation of neutron scattering

experiments on metglasses [37], and for the frequency dependence of the conductivity of many-particle systems, i.e., for the problem of the so called 'universal response' [38].

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