

18 Diffusion of Particles on Lattices

Klaus W. Kehr[†], Kioresch Mussawisade, Gunter M. Schütz, and Thomas Wichmann

18.1 Introduction

Diffusion processes take place almost everywhere in the material world; they are ubiquitous in condensed matter. Diffusion occurs in the different forms of condensed matter: in fluids, complex fluids, and solids. This chapter is concerned with the description of diffusion of particles in *lattices*. The theoretical description refers to diffusion in crystalline but also amorphous solids. Experimental facts on diffusion processes in solids are given in Chaps. 1-6, in particular. Empirical information gives the motivation and the basis for the theoretical description. Two important special cases of diffusion processes in crystalline solids are the tracer diffusion, where the displacement of marked atoms (radioactive isotopes) is determined, and interstitial diffusion, where atoms move on interstitial sites within the solid (see Chap. 1).

Diffusion processes appear in two distinct forms, namely

- Relaxation of density disturbances, or particle currents induced by density gradients or external forces. These phenomena are usually described by Fick's laws.
- Displacements of individual entities (particles, aggregates of particles) within condensed matter systems. The first description of these phenomena was provided by Einstein [1].

The treatment of diffusion of particles on lattices is theoretically advantageous for the following reasons: Lattice problems are generally easier to treat than continuum problems. The most important point, however, is the *separation of time scales* that exists between the elementary transition processes of the particles between lattice sites, and the succession of steps that lead to the observed diffusion phenomena. The elementary step of diffusion of a particle on a lattice, for instance exchange of a vacancy with a tracer atom, or motion of an interstitial atom, is generally rapid compared to the time between two elementary steps. Hence the problem of a theory of diffusion in lattices can be separated into two different tasks:

[†] Klaus W. Kehr died in 2000. He was the leading author of the corresponding chapter of the first edition on which the present chapter is based.

– *Theory for rate of the individual step*

This topic is usually not treated in detail in books on diffusion in solids. An exception is the monograph of Flynn [2]. A more general review on activated processes is given in [3]. Diffusion processes in solids are promoted by thermal activation. Usually an Arrhenius law is assumed for the transition rate Γ

$$\Gamma = \Gamma_0 \exp(-\Delta E/k_{\text{B}}T). \quad (18.1)$$

The prefactor Γ_0 is sometimes interpreted as an attempt frequency. ΔE is the activation energy; it is actually a free energy, or a free enthalpy. Further details may be found in Chap. 1, where different factorizations of Γ into prefactor and exponential factor are made. The theory of the transition rate Γ is especially interesting for light particles (hydrogen, muons), where possible quantum effects are discussed.

– *Combination of several/many individual steps to diffusion in lattices*

This is the topic addressed in this chapter.

Let us begin with a few general remarks on the correlation between theoretical models and experimental systems. Experimental systems of current interest are very complicated. Examples are polycrystalline systems, amorphous metals, glasses, etc. Theoretical modeling of particle diffusion in such systems has evolved in different ways and one may distinguish between several classes of models:

– *Models that are extensions of models for regular lattices with uniform transition rates*

Examples are two-state models for diffusion and trapping, and lattice models with correlated walks. These models are often useful for the interpretation of experiments. One may also subsume the effective-medium approximation under this class, for it relates a disordered system to an ordered, effective medium [4].

– *Models with disordered transition rates*

There are various idealized models, for instance random barriers or random traps, and realistic models that try to incorporate as much as possible the complexities of real substances. The idealized models are treated by exact or approximate analytical methods, supported by numerical simulations. The realistic models are typically investigated by numerical simulations (e.g. [5]).

– *Models that realize new paradigms for disordered systems*

Examples are percolation models, fractal structures, and Sinai models. These models are rarely realized in ideal form in nature, however, they capture essential properties of disordered systems; for instance, the appearance of scaling laws with different exponents.

In this chapter lattice models with uniform and disordered transition rates will be considered (“idealized models” in the above sense). Models that contain the new paradigms of fractality and percolation are treated in Chaps. 10, 19 and 22. Realistic models for particle transport in ionic conductors are described in Chaps. 20 and 21.

This chapter consists of four sections:

- *One particle on uniform lattices*
Diffusion of one particle is well understood for regular lattices with uniform transition rates. The treatment is basic for many extensions, as exemplified in Chaps. 1, 3, 9 and 10.
- *One particle on disordered lattices*
The problem of diffusion of one particle on a regular lattice with disordered transition rates is now relatively well understood. It will be one major focus of this chapter.
- *Many particles on uniform lattices*
The problem of diffusion of many identical particles on regular lattices with uniform transition rates is also quite well understood, provided that exclusion of double occupancy is taken into account. Here the distinction between collective or Fickian and tracer diffusion is essential. A particularly interesting topic is tracer diffusion in one dimension.
- *Many particles on disordered lattices*
The theory of diffusion of many particles on disordered lattices is a difficult problem, except for collective diffusion on lattices with symmetric barriers. In this chapter collective diffusion of particles on lattices with site-energy disorder will be included.

Finally, some remarks on the general literature will be made. Monographs on the topics of random walks have been represented by Barber and Ninham [6], and Weiss [7]. Somewhat more mathematical are the books of van Kampen [8], Spitzer [9], Spohn [10], and Liggett [11]. Monographs that are more focused on diffusion in metals are cited in Chap. 1. A survey on the fields of fractals, percolation, and other disordered systems is given in the book of Bunde and Havlin [12]. Several reviews on the topics addressed in this chapter have appeared, with quite different emphasis, namely Alexander et al. [13], Weiss and Rubin [14], Haus and Kehr [15], Havlin and ben-Avraham [16], Bouchaud and Georges [17] and Schütz [18].

18.2 One Particle on Uniform Lattices

18.2.1 The Master Equation

In this section the diffusion of one particle, or of an ensemble of independent particles on regular lattices with uniform transition rates, is considered. Examples are

- One, or few independent interstitial particle(s) (muon, low concentration of hydrogen). The particles diffuse on the lattice of interstitial sites that is schematically represented in Fig. 18.1 (a). Actual lattices of interstitial sites may have a more complicated structure.
- One vacancy, or small concentration of vacancies. This diffusion process is important for diffusion in metals. Figure 18.1 (b) gives a schematic representation of this process.

These two processes are the simplest ones for a theoretical description. There are other important diffusion processes in metals that are described in the monographs, for instance by Manning [19] and Philibert [20]. These mechanisms are also addressed in Chaps. 1 and 2.

The theoretical description of the lattice diffusion process is provided by the *master equation*. It is an equation for $P(\mathbf{l}t|\mathbf{0}0)$, the conditional probability of finding a particle at site \mathbf{l} at time t when it was at site $\mathbf{0}$ at time 0. The quantity P is generally referred to as the propagator (see Chaps. 10, 19, 23). The sites are designated by d -dimensional integer vectors \mathbf{l} . The master equation reads

$$\frac{d}{dt}P(\mathbf{l}t|\mathbf{0}0) = \Gamma \sum_{\langle \mathbf{l}', \mathbf{l} \rangle} [P(\mathbf{l}'t|\mathbf{0}0) - P(\mathbf{l}t|\mathbf{0}0)]. \quad (18.2)$$

The sum in (18.2) runs over the nearest-neighbour sites \mathbf{l}' of \mathbf{l} . This equation is essentially a balance equation for the increase/decrease of $P(\mathbf{l}t|\mathbf{0}0)$. It consists of a gain term, describing the jumps from nearest neighbours \mathbf{l}' to \mathbf{l} , and a loss term describing the jumps off site \mathbf{l} to nearest neighbour sites. Γ is the

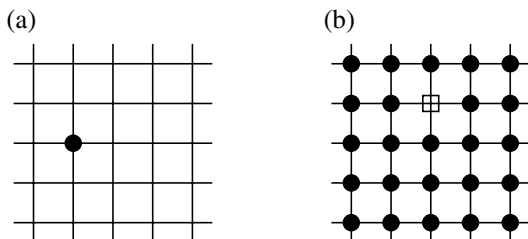


Fig. 18.1. (a) Single particle on uniform lattice; (b) single vacancy in occupied lattice.

transition rate between two nearest-neighbour sites. The last term can also be written as $-z\Gamma P(\mathbf{l}t|\mathbf{00})$, where z is the number of nearest neighbours. The master equation is intuitively obvious.

Theoretically, the master equation follows from the assumption of a Markovian process for the lattice diffusion problem. In a Markovian process, the present state is determined by the past state at one time, rather than by a more complicated history such as states at two different times, etc. More details about these types of processes including the derivations of the most essential relations may be found in van Kampen's monograph [8].

18.2.2 Solution of the Master Equation

The solution of the master equation is obtained by Fourier transformation. This is a general method for lattice-translation invariant problems (connected with the validity of Bloch's theorem). The spatial Fourier transform is defined by

$$P(\mathbf{k}, t) = \sum_{\mathbf{l}} e^{-i\mathbf{k}\cdot\mathbf{R}_l} P_{\mathbf{l}}(t). \tag{18.3}$$

It is in fact this spatial Fourier transform of the propagator which is directly experimentally accessible by quasielastic neutron scattering (in particular by the neutron spin echo method - see Chaps. 3 and 13) and by pulsed field gradient NMR (Chap. 10).

The initial condition will not be written explicitly henceforth.

For simplicity, a restriction to the hypercubic lattices (chain, square lattice, simple-cubic lattice, etc.) will be made. A cube with $N = L^d$ sites will be introduced, and periodic boundary conditions are assumed. The sum over \mathbf{l} in (18.3) then runs over N sites, whose position vectors are given by

$$\mathbf{R}_l = (al_1, \dots, al_d) \tag{18.4}$$

with the lattice constant a . The periodic boundary conditions imply for the wavevector \mathbf{k}

$$\mathbf{k} = \frac{2\pi}{La} \boldsymbol{\nu}, \tag{18.5}$$

where $\boldsymbol{\nu}$ is an integer vector, restricted to values between $-L/2$ and $L/2$ (first Brillouin zone).

The master equation (18.2) can be written in a more compact form as

$$\frac{d}{dt} P(\mathbf{l}t|\mathbf{00}) = - \sum_{\mathbf{l}'} A_{\mathbf{l},\mathbf{l}'} P(\mathbf{l}'t|\mathbf{00}) \tag{18.6}$$

$$A_{\mathbf{l},\mathbf{l}'} \sim \begin{cases} z\Gamma & \mathbf{l} = \mathbf{l}' \\ -\Gamma & \mathbf{l}, \mathbf{l}' \text{ nearest neighbours} \\ 0 & \text{otherwise} . \end{cases} \tag{18.7}$$

Note that for uniform lattices, the matrix $A_{\mathbf{l},\mathbf{l}'}$ only depends on $|\mathbf{l} - \mathbf{l}'|$.

The above equation has a convolution form. It is well-known that convolution in direct space becomes a product in Fourier space,

$$\frac{d}{dt}P(\mathbf{k}, t) = -\Lambda(\mathbf{k})P(\mathbf{k}, t), \quad (18.8)$$

with the Fourier transform of the transition rate matrix

$$\Lambda(\mathbf{k}) = \Gamma \sum_{\mathbf{l}-\mathbf{l}'} e^{-i\mathbf{k}\cdot(\mathbf{R}_l - \mathbf{R}_{l'})}. \quad (18.9)$$

(One can derive (18.8) directly by multiplying (18.6) for fixed \mathbf{l} with $\exp(-i\mathbf{k}\cdot\mathbf{R}_l)$ and summing over \mathbf{l}). For hypercubic lattices is

$$\Lambda(\mathbf{k}) = \Gamma \left[z - 2 \sum_{j=1}^d \cos(k_j a) \right]. \quad (18.10)$$

The main point is that a diagonalization of the master equation (18.6) has been accomplished through Fourier transformation. Now the solution of the master equation is possible

$$P(\mathbf{k}, t) = P(\mathbf{k}, 0) \exp[-\Lambda(\mathbf{k})t] \quad t \geq 0. \quad (18.11)$$

The initial condition is

$$P(\mathbf{k}, 0) = \sum_{\mathbf{l}} e^{-i\mathbf{k}\cdot\mathbf{R}_l} P(\mathbf{l}0|\mathbf{0}0) = 1. \quad (18.12)$$

There are experimental methods that also allow a determination of the Fourier transforms of the conditional probability $P(\mathbf{l}t|\mathbf{0}0)$ from time to the frequency domain. It is defined by

$$P(\mathbf{k}, \omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} P(\mathbf{k}, t). \quad (18.13)$$

The quantity $P(\mathbf{k}, t)$ is also required for negative times. It can be obtained by symmetric continuation,

$$P(\mathbf{k}, -t) = P(\mathbf{k}, t). \quad (18.14)$$

Performing the Fourier integral (18.13) one obtains

$$P(\mathbf{k}, \omega) = \frac{2\Lambda(\mathbf{k})}{\omega^2 + \Lambda^2(\mathbf{k})}. \quad (18.15)$$

This is a Lorentzian, whose width $\Lambda(\mathbf{k})$ can be measured, e. g. by quasielastic Mößbauer spectroscopy and quasielastic incoherent neutron scattering. Details may be found in Chaps. 2 and 3. Also the NMR relaxation times are determined by Fourier transforms of (different) correlation functions. This topic is considered in Sects. 9.2 and 9.9 of Chap. 9.

18.2.3 Diffusion Coefficient

In this section the diffusion coefficient of a particle that performs random walk on a regular lattice with uniform transition rate will be calculated. For this purpose, the mean square displacement of the particle is derived from the solution of the master equation. Consider the definition of the Fourier transform which was given in (18.3), and differentiate it with respect to a component of the wavevector \mathbf{k} ,

$$\frac{\partial}{\partial k_j} P(\mathbf{k}, t) = \sum_l (-iR_{lj}) e^{-i\mathbf{k}\cdot\mathbf{R}_l} P(lt|\mathbf{0}\mathbf{0}) . \tag{18.16}$$

Differentiate the expression again and sum over all components,

$$\sum_{j=1}^d \frac{\partial^2}{\partial k_j \partial k_j} P(\mathbf{k}, t) = - \sum_l \left(\sum_{j=1}^d R_{lj}^2 \right) e^{-i\mathbf{k}\cdot\mathbf{R}_l} P(lt|\mathbf{0}\mathbf{0}) . \tag{18.17}$$

The expression on the right-hand side, evaluated at $\mathbf{k} = 0$, is the mean square displacement of the particle at time t , when it started at site $\mathbf{0}$ at time 0,

$$\langle \mathbf{R}^2 \rangle(t) = - \sum_{j=1}^d \frac{\partial^2}{\partial k_j \partial k_j} P(\mathbf{k}, t) \Big|_{\mathbf{k}=0} . \tag{18.18}$$

From the explicit solution of the master equation (18.11) one obtains

$$\langle \mathbf{R}^2 \rangle(t) = \sum_{j=1}^d \frac{\partial^2 \Lambda(\mathbf{k})}{\partial k_j \partial k_j} \Big|_{\mathbf{k}=0} t . \tag{18.19}$$

For hypercubic lattices one finds from (18.10)

$$\sum_{j=1}^d \frac{\partial^2 \Lambda(\mathbf{k})}{\partial k_j \partial k_j} \Big|_{\mathbf{k}=0} = 2d\Gamma a^2 . \tag{18.20}$$

Hence one has

$$\langle \mathbf{R}^2 \rangle(t) = 2dDt, \tag{18.21}$$

with the diffusion coefficient

$$D = \Gamma a^2 . \tag{18.22}$$

In this derivation, the diffusion coefficient has been derived from the mean squared spreading of the conditional probability with time. This is Einstein's description of particle diffusion [1].

It is possible to derive the diffusion equation (see Chandrasekhar [21]) from the master equation in the long-wavelength limit $\mathbf{k} \rightarrow 0$. For this purpose one has to replace the discrete conditional probability by a continuous probability density,

$$P(\mathbf{l}, t) \longrightarrow p(\mathbf{r}, t), \quad (18.23)$$

where $p(\mathbf{r}, t)d^d r$ is the probability density of finding the particle in the volume element $d^d r$ at location \mathbf{r} and time t (initial conditions omitted). The probability density obeys the diffusion equation (Fick's 2nd law)

$$\frac{\partial}{\partial t} p(\mathbf{r}, t) = D \nabla \cdot \nabla p(\mathbf{r}, t), \quad (18.24)$$

where $\nabla \cdot \nabla$ is the Laplace operator in d dimensions.

18.2.4 Extensions

There are important extensions of the master-equation description of diffusion of a single particle on a regular lattice with uniform transition rates.

– *More complicated lattices*

Examples are lattices with a basis, e.g. the lattice of tetrahedral sites of hydrogen in bcc metals. This extension is trivial from the theoretical point of view, however, the derivation of $P(\mathbf{k}, t)$ may require considerable labour. References are given in [15].

– *Lattices with inequivalent sites*

Inequivalent sites can occur in lattices with a basis, when some sites in the unit cell are energetically lower than the others. This leads to a larger thermal occupation of these sites. The problem of taking the different thermal occupation factors into account was solved in principle in [22] and [23], for a review, see [15]. Applications were made by Anderson et al. [24].

– *Two-state models for diffusion and trapping*

These models provide a very simple description of trapping processes. The basis is the decomposition of the conditional probability into a part corresponding to a free state and a part corresponding to a trapped state,

$$P_{\mathbf{l}}(t) = P_{\mathbf{l}}^{\text{free}}(t) + P_{\mathbf{l}}^{\text{trapped}}(t). \quad (18.25)$$

A particle may be alternatively in a free or a trapped state, with mean times of stay τ_1 , or τ_0 , respectively. The two-state model can be treated by differential equations (Schroeder [25]), or by integral equations (Richter and Springer [26]), with equivalent results. The differential equations are somewhat more compact and they read

$$\begin{aligned} \frac{d}{dt} P_{\mathbf{l}}^f(t) &= \Gamma \sum_{\langle \mathbf{l}', \mathbf{l} \rangle} [P_{\mathbf{l}'}^f(t) - P_{\mathbf{l}}^f(t)] \\ &\quad - \Gamma_{\mathbf{l}} P_{\mathbf{l}}^f(t) + \Gamma_{\mathbf{r}} P_{\mathbf{l}}^t(t) \\ \frac{d}{dt} P_{\mathbf{l}}^t(t) &= -\Gamma_{\mathbf{r}} P_{\mathbf{l}}^t(t) + \Gamma_{\mathbf{l}} P_{\mathbf{l}}^f(t), \end{aligned} \quad (18.26)$$

with the trapping rate $\Gamma_t = 1/\tau_1$ and the release rate $\Gamma_r = 1/\tau_0$. The first equation in (18.26) is the usual master equation, augmented by a loss and gain term, corresponding to transitions into and out of the trapped state. The second equation describes the temporal development of the trap state. An application of the two-state model has been given in Sect. 3.6 of Chap. 3.

All models mentioned above, and some additional models, for instance correlated-walk models, have in common that they are lattice-translation invariant. Hence they are solved by similar techniques as described above. Spatial Fourier transformation leads to a partial diagonalization, the rest is the solution of coupled ordinary first-order differential equations. As already said, this may require considerable effort in complicated cases, but in principle the solution of these models is understood.

18.3 One Particle on Disordered Lattices

18.3.1 Models of Disorder

In this section the random walk of a single particle, or of independent particles, on lattices with disordered transition rates will be considered. The main emphasis of this chapter will be on the derivation of asymptotic diffusion coefficients, but also the time dependence of the mean square displacement, or the frequency dependence of the conductivity will be considered. The models of disorder will be defined on regular lattices, and topological disorder will not be included. This is a popular approach for modeling diffusion in disordered materials, even if many materials of interest do not have crystalline structure. It means that the disorder is put completely into the transition rates,

$$\Gamma \longrightarrow \Gamma_{fi}, \quad (18.27)$$

which depend on the initial (i) and final (f) sites. The rates are assumed to be fixed, i.e. the case of quenched disorder is treated. In principle, one could include transitions between arbitrary sites, in practice only nearest-neighbour transitions are taken into account, as is appropriate for diffusion of atoms.

Various models of disorder have been introduced in different contexts. Here some idealized models of disorder will be considered:

– *Random barriers (RB)*

In this model the transition rates between neighbour sites have the symmetry

$$\Gamma_{ji} = \Gamma_{ij}. \quad (18.28)$$

It is usually assumed that the rates are given by an Arrhenius law,

$$\Gamma_{ji} = \Gamma_0 \exp\left(-\frac{E_{ji}}{k_B T}\right) \quad E_{ji} \geq 0. \quad (18.29)$$

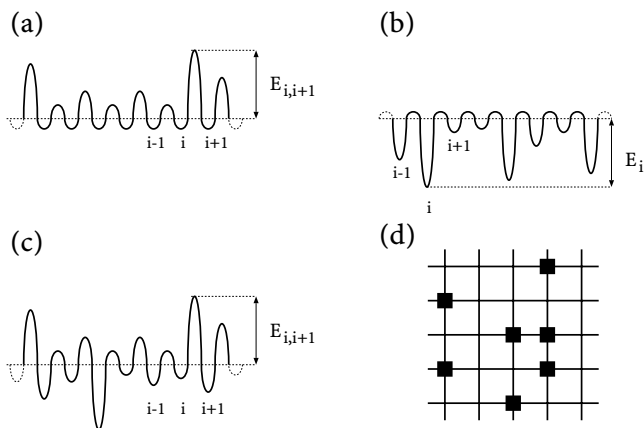


Fig. 18.2. Models of disorder.

The disorder then originates from random barrier energies E_{ji} , which are taken from a distribution $\nu_B(E)$. A pictorial representation of the RB model is given in Fig. 18.2(a).

– *Random site energies (RT)*

Another important model is the random site-energy model, which is also called random-trap model. One should keep in mind that the traps do not capture the particles permanently. The model is defined by transition rates that depend on the initial sites, but not on the final sites,

$$\Gamma_{ji} = \Gamma_0 \exp\left(\frac{E_i}{k_B T}\right) \quad E_i \leq 0. \quad (18.30)$$

The site energies E_i are counted negative and they are taken from a distribution $\nu_T(E)$. A pictorial representation of the RT model is given in Fig. 18.2(b).

– *Combination of RB and RT*

In this chapter also a combination of random barriers and random site energies will be studied. The rates of the combined RB and RT model shall be given by

$$\Gamma_{ji} = \Gamma_0 \exp\left(-\frac{E_{ji} - E_i}{k_B T}\right). \quad (18.31)$$

The random-barrier energies E_{ji} and the random-site energies E_i are taken independently from the distributions $\nu_B(E)$ and $\nu_T(E)$. A pictorial representation of the model is given in Fig. 18.2(c). Note that all energies refer to a common origin $E = 0$.

– *Randomly blocked sites (RBS)*

Finally, the model of randomly blocked sites will be included in this list of models of disorder. Sites of a lattice are randomly blocked with probability $1 - p$ and not accessible to the particle that performs random walk. The transition rates of this model are defined by

$$\Gamma_{ji} = \begin{cases} \Gamma & \text{if } j \text{ is "open"} \\ 0 & \text{if } j \text{ is blocked.} \end{cases} \quad (18.32)$$

The pictorial representation of the model is included in Fig. 18.2(d). Of course, this model is nothing else than the site percolation model, which is exclusively treated in Chap. 22. In the present chapter, however, the RBS model will only be considered for concentrations p of open sites above the percolation threshold, where long-range diffusion of a particle is possible.

There are other models with disordered transition rates which are not included in the list above. One example is the Miller-Abrahams model, where transitions that lead to sites with lower energies have rates that do not depend on the energy difference, while the transitions to sites with higher energies require thermal activation. For a treatment of this model with similar methods as applied here the reader is referred to [29].

18.3.2 Exact Expression for the Diffusion Coefficient in $d = 1$

It is possible to give an exact expression for the diffusion coefficient of a particle in a linear chain for rather general disordered rates. Some restrictions on the disorder have to be made, which will be explained below. Linear chains with sites at a distance a will be considered and one may view Fig. 18.2(c) as a graphical representation of such a model. The task is to derive the asymptotic, long-time diffusion coefficient of a particle, averaged over the disorder.

The expression to be given below was derived independently by Dieterich [27] and Kutner [28], and by Wichmann [29]. Dieterich and Kutner calculated the mobility of a particle from the linear response to a force while Wichmann used a mean first-passage time method. Here a derivation will be given which utilizes Fick's first law. Of course, there are relations between the different derivations.

Consider a finite chain of length Na , as schematically displayed in Fig. 18.3. A particle current I (precisely: probability current) into site 0 is assumed such that P_0 is fixed. The same particle (probability) current is then taken out at site N and a stationary situation is maintained.

The derivation for general disorder is somewhat tedious and hence put into the appendix. A much simpler derivation can be made for the random-barrier model with $\Gamma_{i+1,i} = \Gamma_{i,i+1}$ and it should convey the idea of the derivation.

Consider Kirchhoff's node equation for site 0 which expresses the fact that the sum of all currents into the site must be zero:

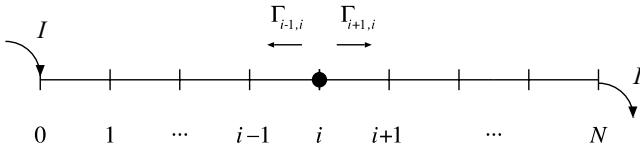


Fig. 18.3. Linear chain with constant current I .

$$I + \Gamma_{10}(P_1 - P_0) = 0. \tag{18.33}$$

The master equation at site 1 reads

$$\frac{d}{dt}P_1 = \Gamma_{10}(P_0 - P_1) + \Gamma_{21}(P_2 - P_1). \tag{18.34}$$

One finds in the stationary situation

$$\Gamma_{21}(P_1 - P_2) = \Gamma_{10}(P_0 - P_1) = I, \tag{18.35}$$

where also (18.33) was used. The same consideration yields for all sites $0 \leq i < N$

$$\Gamma_{i+1,i}(P_i - P_{i+1}) = I. \tag{18.36}$$

One can now play the following trick: Write

$$\begin{aligned} P_0 - P_N &= P_0 - P_1 + P_1 - P_2 + P_2 - \dots \\ &\quad - P_{N-1} + P_{N-1} - P_N. \end{aligned} \tag{18.37}$$

Introduce the current I into the differences by using (18.36),

$$P_0 - P_N = I \left(\sum_{i=0}^{N-1} \frac{1}{\Gamma_{i+1,i}} \right). \tag{18.38}$$

This expression is already Fick's first law. To recognize this, rewrite (18.38) as

$$\frac{P_0 - P_N}{N} = I \left\{ \frac{1}{\Gamma} \right\}, \tag{18.39}$$

where the sum has been replaced by the disorder average (valid for large N)

$$\left\{ \frac{1}{\Gamma} \right\} = \frac{1}{N} \sum_{i=0}^{N-1} \frac{1}{\Gamma_{i+1,i}}. \tag{18.40}$$

The length of the chain is Na and the probability density at site i is P_i/a . Hence one can identify the gradient of the probability density,

$$\frac{P_0 - P_N}{Na^2} = -\nabla n. \tag{18.41}$$

Fick's first law reads $I = -D\nabla n$. Comparison with the above expressions yields

$$D = \left\{ \frac{1}{\Gamma} \right\}^{-1} a^2. \quad (18.42)$$

The expression (18.42) is the exact result for the diffusion coefficient of the RB model in $d = 1$, which is known since a long time [13].

The physical significance of the result is that the highest barriers dominate diffusion in $d = 1$. This is evident: particles have to overcome all barriers in the course of long-range diffusion, and it takes long times to overcome the high barriers.

The generalization of the result to arbitrarily disordered transition rates is

$$D = \left\{ \frac{1}{\Gamma_{i+1,i}\rho_i} \right\}^{-1} a^2, \quad (18.43)$$

with the thermal occupation factors

$$\rho_i = \frac{\exp(-\beta E_i)}{\frac{1}{N} \sum_{j=0}^{N-1} \exp(-\beta E_j)}, \quad (18.44)$$

where $\beta = 1/(k_B T)$. The existence of the thermal occupation factors ρ_i is required in the proof, which is given in the appendix. The ρ_i exist when one can introduce a reference energy E_0 and the sum in the denominator of (18.44) remains finite for arbitrary N . A counterexample, where the ρ_i do not exist in the limit $N \rightarrow \infty$ will be given in Sect. 18.3.7.

The expression (18.43) for the diffusion coefficient of a particle on a linear chain with general disorder means that one has to use transition rates that are weighted by the mean thermal occupation of the sites. This is an exact result in $d = 1$ (see [27–29]).

18.3.3 Applications of the Exact Result

The expression (18.43) for the diffusion coefficient in $d = 1$ will now be examined for the models that have been introduced in Sect. 18.3.1. Henceforth the lattice constant will be set $a = 1$.

For the random barrier model, where $\Gamma_{i,i+1} = \Gamma_{i+1,i}$ one has $\rho_i = 1$. The result (18.42) is then immediately obtained from (18.43) and it is the correct result in $d = 1$.

In the random site-energy model, where $\Gamma_{ji} = \Gamma_0 \exp(\beta E_i)$, the product is

$$\Gamma_{ji}\rho_i = \Gamma_0 \left[\frac{1}{N} \sum_j \exp(-\beta E_j) \right]^{-1}. \quad (18.45)$$

Hence the diffusion coefficient is given by

$$D = \frac{\Gamma_0}{\frac{1}{N} \sum_j \exp(-\beta E_j)}. \quad (18.46)$$

This is the exact result in $d = 1$; it is also valid in *all* dimensions [15, 30]. Normally it is written in the form $D = \{\frac{1}{T}\}^{-1}$ which is equivalent to (18.46). Equation (18.46) signifies that the diffusion coefficient of the RT model is solely determined by the inverse of a partition function, which becomes large for strong site-energy disorder and/or low temperatures.

An immediate consequence of the exact expression (18.46) for the diffusion coefficient of the RT model is its downward curvature in an Arrhenius plot, where $\ln D$ is displayed as a function of $\beta = 1/k_B T$. Differentiating $\ln D$ according to (18.46) with respect to β one obtains

$$\frac{\partial \ln D}{\partial \beta} = \frac{\sum_j E_j \exp(-\beta E_j)}{\sum_j \exp(-\beta E_j)} = \langle E \rangle. \quad (18.47)$$

Thus the slope of the Arrhenius plot of D is the mean thermal energy of a particle in the RT model. The mean thermal energy decreases with increasing β in the case of energetic disorder, hence one has convex (downward) curvature of $D(\beta)$ in the Arrhenius plot. This is the generic cause for downward curvature of $D(\beta)$ in the Arrhenius plot.

Finally the combined RB and RT model will be considered. The rates of this model were given in (18.31). The weighted rates are then

$$\Gamma_{ji}\rho_i = \Gamma_0 \left[\frac{1}{N} \sum_j \exp(-\beta E_j) \right]^{-1} \exp(-\beta E_{ji}). \quad (18.48)$$

One obtains for independent distributions of barrier and site energies [31]

$$D_{\text{comb}} = \frac{1}{\Gamma_0} D_{\text{RB}} D_{\text{RT}}. \quad (18.49)$$

Thus the diffusion coefficient of this model factorizes into two independent contributions in $d = 1$. A numerical verification of the result is given in Fig. 18.4.

18.3.4 Frequency Dependence in $d = 1$: Effective-Medium Approximation

Not only the asymptotic behaviour of the mean square displacement is of interest, but also the behaviour at finite times. It corresponds to the frequency dependence of the mobility. Asymptotic expansions of the time-dependent mean square displacement were made for the RB and RT models; they yield exact results in $d = 1$ for the RB model and all d for the RT model [32, 33]. Here an approximate treatment will be introduced for several reasons:

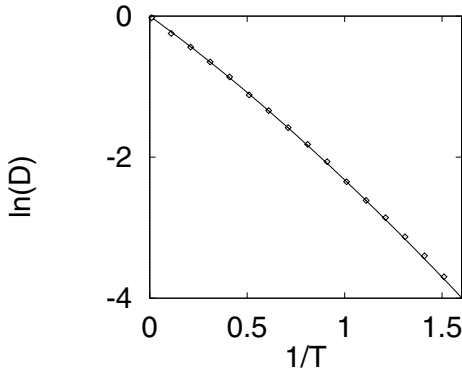


Fig. 18.4. Diffusion coefficient in combined RB and RT model. Uniform distributions of barriers and site energies of width $E_c = 2$. Line: Equation (18.48); symbols: Monte Carlo (MC) simulations.

- i) The technique is rather simple and intuitive.
- ii) The approximation yields an overall description of the frequency-dependent mobility.
- iii) It is easily generalized to higher dimensions.

To formulate the effective-medium approximation (EMA), the random barrier model will be considered in $d = 1$. The master equation reads

$$\begin{aligned} \frac{d}{dt}P_i(t) = & \Gamma_{i,i+1}[P_{i+1}(t) - P_i(t)] \\ & + \Gamma_{i,i-1}[P_{i-1}(t) - P_i(t)]. \end{aligned} \quad (18.50)$$

The rates $\Gamma_{i,i\pm 1}$ are taken from a common distribution $\rho(\Gamma)$ (or, equivalently, are determined from the distribution of barrier energies).

The frequency-dependent formulation of the EMA was developed by several authors around 1980 (Alexander and Orbach [34], Summerfield [35], Odagaki and Lax [36], Webman [37]). Here a derivation by an embedding procedure will be given, following Haus et al. [38]. One systematic, random transition rate Γ_{01} is embedded in a linear chain, which consists of time-dependent, effective transition rates. A graphical representation is given by Fig. 18.5 (bottom).

The systematic rate is taken from the distribution $\rho(\Gamma)$ and, once selected, considered as fixed.

The master equations for the conditional probabilities $P_i(t)$ for sites that do not involve sites 0 and 1 are

$$\frac{d}{dt}P_i(t) = \int_0^t dt' \Gamma_{\text{eff}}(t-t')[P_{i+1}(t') + P_{i-1}(t') - 2P_i(t')]. \quad (18.51)$$

The master equation for the conditional probabilities P_0 and P_1 is then

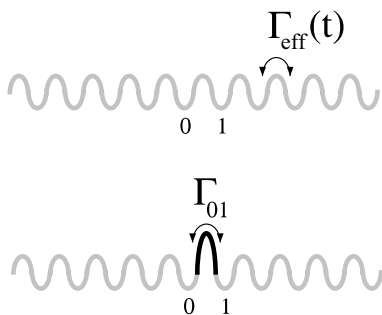


Fig. 18.5. Embedding procedure for effective-medium approximation.

$$\begin{aligned}
 \frac{d}{dt}P_0 &= \int_0^t dt' \Gamma_{\text{eff}}(t-t')[P_{-1}(t') - P_0(t')] \\
 &\quad + \Gamma_{01}[P_1(t) - P_0(t)], \\
 \frac{d}{dt}P_1 &= \Gamma_{01}[P_0(t) - P_1(t)] \\
 &\quad + \int_0^t dt' \Gamma_{\text{eff}}(t-t')[P_2(t') - P_1(t')]. \tag{18.52}
 \end{aligned}$$

This set of master equations will be compared with the master equation for the effective medium only, where the conditional probability will be called $E_i(t)$ (see also Fig. 18.5 (top))

$$\frac{d}{dt}E_i(t) = \int_0^t dt' \Gamma_{\text{eff}}(t-t')[E_{i+1}(t') + E_{i-1}(t') - 2E_i(t')]. \tag{18.53}$$

Now a Fourier and Laplace transformation of both equations will be made. The Laplace transform of a function $f(t)$ is defined by

$$\tilde{f}(s) = \int_0^\infty dt E^{-st} f(t). \tag{18.54}$$

The advantage of the Laplace transformation is that the initial condition of the master equations appears explicitly, because

$$\begin{aligned}
 \int_0^\infty dt e^{-st} \frac{df(t)}{dt} &= e^{-st} f(t) \Big|_0^\infty + s \int_0^\infty dt e^{-st} f(t) \\
 &= s\tilde{f}(s) - f(t=0). \tag{18.55}
 \end{aligned}$$

The master equation for the effective medium reads after the transformations

$$[s + 2\Gamma_{\text{eff}}(s)(1 - \cos ka)]\tilde{E}(k, s) = 1. \tag{18.56}$$

The 1 on the right-hand side of the equation comes from the initial condition $E_i(t=0) = \delta_{i,0}$.

It is possible to solve the equations for $\tilde{P}_0(s)$ and $\tilde{P}_1(s)$, as explicitly shown in the appendix. The requirement will be made that the average over the different realizations of the embedded bond will reproduce the effective medium. Hence the requirement is

$$\{\tilde{P}_0(s)\}_{\rho(\Gamma)} = \tilde{E}_0(s). \quad (18.57)$$

Equation (18.57) is a self-consistency condition for $\tilde{\Gamma}_{\text{eff}}(s)$. In the appendix the following explicit form of the self-consistency condition is derived,

$$\left\{ \frac{\tilde{\Gamma}_{\text{eff}}(s) - \Gamma_{10}}{\Gamma_{1,0} + s\tilde{E}_0(s)[\tilde{\Gamma}_{\text{eff}}(s) - \Gamma_{10}]} \right\}_{\rho(\Gamma_{10})} = 0. \quad (18.58)$$

The conditional probability of the effective medium at site 0 can be given explicitly in $d = 1$,

$$\tilde{E}_0(s) = [s(s + 4\tilde{\Gamma}_{\text{eff}}(s))]^{-1/2}. \quad (18.59)$$

The self-consistency condition (18.58) corresponds to a fourth-order equation whose general solution is of no practical use. Hence an ansatz is made to determine $\Gamma_{\text{eff}}(s)$ for small s , corresponding to long times,

$$\Gamma_{\text{eff}}(s) = \Gamma_{\text{eff}}(1 + \vartheta_1(s/\Gamma_{\text{eff}})^{1/2} + \dots) \quad s \longrightarrow 0. \quad (18.60)$$

The self-consistency condition yields

$$\Gamma_{\text{eff}} = \left\{ \frac{1}{\Gamma} \right\}^{-1} \quad (18.61)$$

and

$$\vartheta_1 = \frac{1}{2}\Gamma_{\text{eff}}^2 \left\{ \left(\frac{1}{\Gamma} - \frac{1}{\Gamma_{\text{eff}}} \right)^2 \right\}. \quad (18.62)$$

The results for Γ_{eff} and ϑ_1 are exact [32]; note that ϑ_1 is specific for the presence of disorder.

Having obtained the effective transition rate for small s , one can deduce the asymptotic mean square displacement of a particle by an extension of the procedure of Sect. 18.2.3. The result for the disorder-averaged mean square displacement is

$$\{\langle \delta x^2 \rangle\}(t) = 2\Gamma_{\text{eff}}a^2 \left(t + 2\vartheta_1(t/\pi\Gamma_{\text{eff}})^{1/2} + \dots \right). \quad (18.63)$$

There appears a ‘‘long-time tail’’ correction to the asymptotic mean square displacement. Note that (18.63) together with (18.61) reproduces the exact result (18.42) of the RB model, which was derived earlier.

The result for the s -dependence of the effective transition rate gives also information on the frequency dependence of the mobility. The frequency-dependent mobility of a particle is obtained from the linear response to a

periodic force. Equivalently, one may define a frequency-dependent diffusion coefficient as the Fourier transform of the velocity autocorrelation function of the particle. The connection with the s -dependent effective rate is ($a = 1$)

$$D(\omega) = \text{Re}[\tilde{\Gamma}_{\text{eff}}(s = i\omega)] \quad (18.64)$$

and comparison with (18.60) shows that

$$D(\omega) = \Gamma_{\text{eff}}(1 + \vartheta_1(\omega/\Gamma_{\text{eff}})^{1/2} + \dots) \quad \omega \longrightarrow 0. \quad (18.65)$$

Hence one finds a strong increase of the diffusion coefficient and the mobility with frequency, for small frequencies.

18.3.5 Higher-Dimensional Lattices: Approximations

Approximations are generally necessary when one treats diffusion of single particles on higher-dimensional lattices. An exception is the random site-energy model, where the diffusion coefficient is known exactly in all dimensions [15, 30]. First the effective-medium approximation (EMA) will be discussed; this is an approximation that includes frequency dependence. As already said in the introduction, the EMA replaces the disordered medium by an effective ordered medium. A candid criticism of the philosophy of the EMA from the point of view of a theorist has been given by Anderson [4]. Nonetheless, EMA provides an adequate overall description of various disordered systems.

Effective-Medium Approximation

The embedding procedure for one random bond described in the previous section can be extended to higher dimensions. The result is the self-consistency condition [37]

$$\left\{ \frac{\tilde{\Gamma}_{\text{eff}}(s) - \Gamma}{\frac{z-2}{2}\tilde{\Gamma}_{\text{eff}}(s) + \Gamma + s\tilde{E}_0(s)[\tilde{\Gamma}_{\text{eff}}(s) - \Gamma]} \right\}_{\rho(\Gamma)} = 0. \quad (18.66)$$

The relevant parameter is z , the coordination number; $z = 2d$ for hypercubic lattices. The conditional probability for the effective medium $\tilde{E}_0(s)$ is more complicated for $d > 1$ than in $d = 1$. To obtain the static, long-time diffusion coefficient one has to set $s = 0$. The product $s\tilde{E}_0(s)$ vanishes for $s = 0$ in all d and the self-consistency condition reduces to

$$\left\{ \frac{\Gamma_{\text{eff}} - \Gamma}{\frac{z-2}{2}\Gamma_{\text{eff}} + \Gamma} \right\}_{\rho(\Gamma)} = 0. \quad (18.67)$$

This self-consistency condition was already established by Kirkpatrick [39] who considered the equivalent problem of random resistor networks. If the

effective transition rate has been determined, the diffusion coefficient is given by $D = \Gamma_{\text{eff}} a^2$ in hypercubic lattices.

The average in (18.67) can be evaluated explicitly for a uniform distribution of activation energies [40],

$$\nu_{\text{B}}(E) = \begin{cases} \frac{1}{E_c} & 0 \leq E \leq E_c \\ 0 & \text{otherwise.} \end{cases} \quad (18.68)$$

One finds for $E_c \gg k_{\text{B}}T$ and $z > 2$

$$\Gamma_{\text{eff}} \longrightarrow \frac{2\Gamma_0}{z-2} \exp\left(-\frac{2E_c}{zk_{\text{B}}T}\right). \quad (18.69)$$

The EMA result for the simple-square lattice is then

$$\Gamma_{\text{eff}} \longrightarrow \Gamma_0 \exp\left(-\frac{E_c}{2k_{\text{B}}T}\right), \quad (18.70)$$

and the one for the simple-cubic lattice

$$\Gamma_{\text{eff}} \longrightarrow \frac{\Gamma_0}{2} \exp\left(-\frac{E_c}{3k_{\text{B}}T}\right). \quad (18.71)$$

Good agreement with numerical simulations has been found [41, 42]. Figure 18.6 shows simulation results [42] for the mean square displacement of particles on a simple-square lattice with random barriers. One observes pronounced transient behaviour for stronger disorder at intermediate times, until the asymptotic behaviour is reached. Good agreement with the predicted asymptotic behaviour (18.70) is recognized.

Critical-Path Approach

For very large disorder or very low temperatures, the diffusion coefficient of the RB model can be estimated by the critical-path approach. This intuitive method was proposed by Shklovskii and Efros [43] and by Ambegaokar, Halperin, and Langer [44]. Consider a large but finite d -dimensional lattice and decorate the bonds with random hopping rates. Identify the largest hopping rate on the lattice, then the second largest rate, etc. (see Fig. 18.7).

Continue until a connection between two opposite sides of the (large) lattice is obtained. In the limit $N \longrightarrow \infty$ the possibility of connection defines the bond percolation threshold [45], see also Chap. 22. The smallest rate in the set of all selected rates represents an estimate for the diffusion coefficient.

The activation energy for the smallest rate will be determined for the uniform distribution of activation energies. Evidently (cf. Fig. 18.8)

$$\int_0^{E^*} dE \nu_{\text{B}}(E) = p_c. \quad (18.72)$$

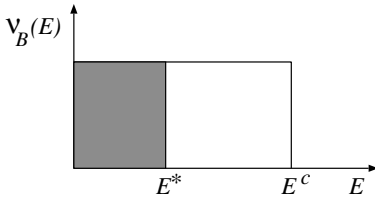


Fig. 18.8. Determination of the barrier E^* from density of states.

In $d = 2$ the bond percolation threshold is $p_c = 0.5$ and one has

$$D \cong \Gamma_0 \exp\left(-\frac{E_c}{2k_B T}\right). \quad (18.75)$$

This result is identical to the EMA result (18.70). In fact, it is an exact result, as was shown by Bernasconi et al. using the self-duality of the square lattice [46]. In $d = 3$, where $p_c \approx 0.244$ one obtains

$$D \cong \Gamma_0 \exp\left(-\frac{0.244E_c}{k_B T}\right), \quad (18.76)$$

i. e. a result that is different from the EMA result. As said above it gives the dominant behaviour for very low temperatures or very strong disorder, but there are important corrections to it [47, 48].

Single Particles in the RBS Model

The diffusion of single particles in lattices with randomly blocked sites belongs to the same category of problems as other diffusion models on disordered lattices. However, the methods of treatment are somewhat different. As already said, only low concentrations p of blocked sites will be considered, such that long-range diffusion of test particles is always possible. An approximate derivation of the diffusion coefficient was made by Tahir-Kheli [49] and his result is ($a = 1$)

$$D = \Gamma_0 \left(1 - \frac{1-p}{f} + \dots\right). \quad (18.77)$$

In the formula the correlation factor f for tracer diffusion in lattice gases appears, which will be discussed in Sect. 18.4.3. Ernst et al. [50] could establish (18.77) by performing a perturbation expansion with respect to $1 - p$.

The validity of (18.77) was investigated by numerical simulations in simple-cubic lattices [51] and it was found that it is a good approximation for small and moderate concentrations of blocked sites, see Fig. 18.9.

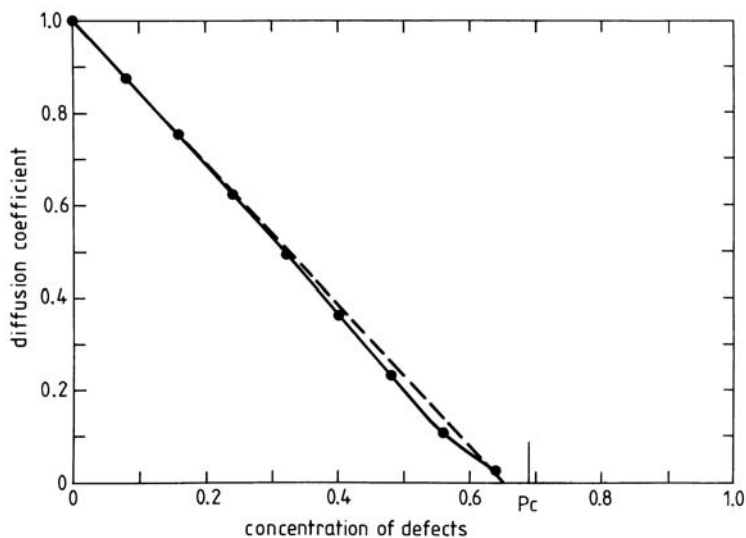


Fig. 18.9. Diffusion coefficient of single particles in the RBS model, as a function of the concentration of blocked sites. Symbols: MC simulations; continuous line: spline fit to the MC results; dashed line: (18.77). From [51].

18.3.6 Higher-Dimensional Lattices: Applications

Vanishing of D for Exponentially Distributed Site Energies

An interesting application of the exact result (18.46) for the RT model in arbitrary dimensions can be made for the exponential energy distribution. This distribution is given by

$$\nu_T(E) = \frac{1}{E_c} \exp\left(\frac{E}{E_c}\right) \quad E \leq 0. \tag{18.78}$$

Combining this expression with the Arrhenius law (18.30) for the transition rates of the RT model, one can calculate the distribution of transition rates $\rho(\Gamma)$ (this is equivalent to a change of the integration variable from E to Γ),

$$\rho(\Gamma) = \frac{\alpha}{\Gamma_0} \left(\frac{\Gamma}{\Gamma_0}\right)^{\alpha-1}, \quad \Gamma \leq \Gamma_0, \tag{18.79}$$

where $\alpha = k_B T / E_c$. The inverse of the diffusion coefficient is then given by ($a = 1$)

$$D^{-1} = \int_0^{\Gamma_0} d\Gamma \rho(\Gamma) \frac{1}{\Gamma}. \tag{18.80}$$

D^{-1} diverges for $\alpha < 1$, and consequently

$$D \equiv 0 \quad \text{for } \alpha < 1. \quad (18.81)$$

Hence the diffusion coefficient vanishes for random site energies with an exponential distribution, for temperatures $k_B T \leq E_c$, in arbitrary dimensions.

The mean square displacement of particles does no longer exhibit linear behaviour at long times for $\alpha < 1$. Instead one finds subdiffusive behaviour, as was derived by Havlin, Trus, and Weiss [52]:

$$\langle \mathbf{R}^2 \rangle(t) \sim \begin{cases} t^{\frac{2\alpha}{\alpha+1}} & d = 1 \\ t^\alpha & d \geq 2. \end{cases} \quad (18.82)$$

Combined RB and RT Model for $d > 1$

How can one treat more general models with disorder by approximations in higher dimensions? The EMA as formulated above with one systematic bond requires symmetric rates. A hint can be obtained from the exact result (18.43) for generally disordered rates in $d = 1$. The message of this result is: Use thermally weighted transition rates $\Gamma_{ji}\rho_i$ for the general models. Invoking the relation of detailed balance,

$$\Gamma_{ji}\rho_i = \Gamma_{ij}\rho_j, \quad (18.83)$$

one observes that the thermally weighted rates are symmetric, hence they can be employed in the EMA as formulated above.

The utilization of thermally weighted transition rates will be illustrated for the combined RB and RT model. Its rates were given in (18.31) and the weighted rates were already given in (18.48). From the self-consistency condition (18.67) follows for independent barriers and site-energies in arbitrary dimensions [31]

$$D_{\text{comb}}^{\text{EMT}} = \frac{1}{\Gamma_0} D_{\text{RB}}^{\text{EMT}} D_{\text{RT}}. \quad (18.84)$$

Since D_{RT} is known exactly, cf. (18.46), only the application of the EMA for the random barriers is necessary [31].

The interest in the combined RB and RT model originates from experiments on diffusion in amorphous metallic alloys. The diffusion coefficient in these substances exhibits typically linear behaviour in an Arrhenius plot of $\ln D$ vs. $\ln 1/T$. This is not expected from the simple models for diffusion in disordered lattices.

As was discussed in Sect. 18.3.3, the RT model exhibits downward curvature in an Arrhenius plot of $\ln D$ versus $\ln 1/T$ (i. e. the deepest trap sites dominate at low temperatures). In contrast, the RB model exhibits upward curvature in an Arrhenius plot of $\ln D$ vs. $\ln 1/T$ for $z > 4$. One can give the following argument for the origin of this upward curvature: The critical path dominates the behaviour of the diffusion coefficient at the lowest temperature; additional paths contribute at higher temperatures and they comprise higher activation energies.

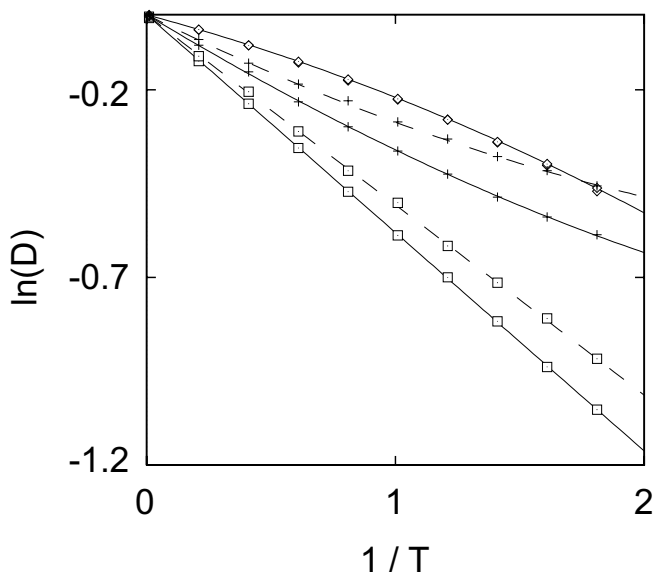


Fig. 18.10. Arrhenius plot of the diffusion coefficient for two-level models. Continuous lines: EMA, $d = 3$; dashed lines: EMA, $d = 5$. Symbols: MC results (+: RB model, \diamond : RT model, \square : combined model).

Limoge and Bocquet suggested a possible compensation of the effects of random barriers and of random traps [53]. The original derivations given in [53] were only partially satisfactory. We investigated the problem by the analytic approach outlined above and by numerical simulations [54]. This reference also contains a more detailed discussion of the previous work. It was found that compensation is possible in finite temperature intervals if the relative strengths of RB and RT are properly adjusted. Fig. 18.10 shows this compensation for uniform distributions of barrier and trap energies in $d = 3$ when $|E_c^T| \approx 3/5 E_c^B$. Complete compensation of the curvature is only possible for $d \rightarrow \infty$, as was shown by Wichmann [29].

Frequency Dependence

Only some remarks on the frequency dependence of the mobility or the diffusion coefficient will be made. There are many observations of frequency-dependent conductivities in disordered substances with typically

$$\sigma(\omega) \sim \omega^\beta \quad 0 < \beta < 1. \quad (18.85)$$

The question is whether this behaviour can be understood in the framework of single-particle theories, for instance by EMA. So far, asymptotic results were derived for the frequency-dependent conductivity in the limit $\omega \rightarrow 0$ [33], for

a review, see [15]. They seem to be not really useful in the frequency ranges of interest. Numerical evaluations of the self-consistency condition for finite ω were made by Wagener and Schirmacher [55] and Hoerner et al. [56]. The authors found a frequency dependence in qualitative accord with (18.85). In the opinion of the authors, no simple physical picture of the origin of anomalous frequency dependence has been established so far (see however Chap. 21).

It should also be pointed out that the problem of the frequency-dependent mobility is truly a many-particle problem, in addition, the particles can have interactions. Work has been done on this problem mainly by numerical simulations [57–59], see also Chap. 20.

18.3.7 Remarks on Other Models

In this section some comments will be made concerning several models that are not treated in this chapter. The first three are addressed in other chapters of this textbook, hence some cursory remarks will suffice.

Fractals

These objects are considered in Chaps. 10 and 19. If they are regularly constructed objects, often an explicit solution of recursion relations is possible, and the mean square displacement of diffusing particles can be calculated.

Percolation lattice

This model is treated in Chap. 22, together with experimental realizations. It can be viewed as the RBS model, where the concentration of blocked sites is adjusted at the threshold value where the diffusion coefficient vanishes. Diffusion of particles on fractals and on percolation lattices exhibits an interesting behaviour including scaling laws that are different from ordinary diffusion.

Extended defects

Also extended defects are not included in this chapter. An example are grain boundaries, which are of great practical importance. They are treated in Chap. 8.

Sinai model

Also here no detailed treatment will be given, only some introductory considerations concerning the one-dimensional model will be presented.

In the Sinai model (see the references in [60]) the transition rates to the right, $\Gamma_{i+1,i}$, and to the left, $\Gamma_{i-1,i}$, are independent random variables with the restriction

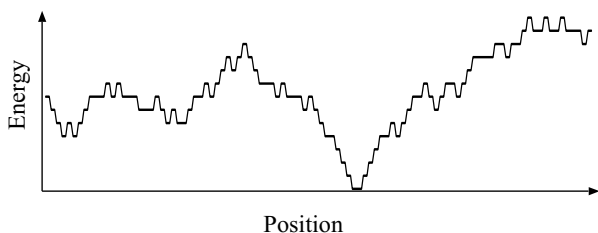


Fig. 18.11. Pictorial representation of the Sinai model on a larger scale.

$$\left\{ \ln \frac{\Gamma_{i+1,i}}{\Gamma_{i-1,i}} \right\} = 0. \quad (18.86)$$

The potential that would yield such transition rates from the Arrhenius law can be imagined as representing a random walk by itself, cf. Fig. 18.11. The Sinai condition can be interpreted as the requirement that the potential does not contain additional systematic forces that would induce drift of the particle in either direction.

An estimate of the behaviour of the mean square displacement can be given in the following way [60]: Since the potential displayed in Fig. 18.11 represents a random walk, the typical height difference over a length L is described by

$$V \sim \sqrt{L}. \quad (18.87)$$

The motion of the particle requires thermal activation, hence the typical time for a particle to move the length L is

$$t \sim \exp(V/k_B T). \quad (18.88)$$

Using (18.87) one finds $\sqrt{L} \sim \ln t$. Hence the typical mean square displacement in this model is given by

$$\langle \delta x^2 \rangle \sim (\ln t)^4. \quad (18.89)$$

Diffusion of a particle in the Sinai model cannot be treated by the methods of Sect. 18.3.2, because the condition of existence of the ρ_i is violated. If one increases the length of the chain, deeper and deeper valleys appear, in which the ρ_i are concentrated. Thus the limit $L \rightarrow \infty$ does not exist for the ρ_i . In summary, the Sinai model is theoretically extremely interesting. Its practical relevance, however, is limited: unbounded variations of the potential are not physical for real substances.

18.4 Many Particles on Uniform Lattices

18.4.1 Lattice Gas (Site Exclusion) Model

In the lattice-gas model, sites of a lattice are occupied by particles. Each site can be occupied by at most one particle. A pictorial representation is given in Fig. 18.12.

There are many applications of lattice-gas models. Two prominent examples are hydrogen in metals (see Sect. 3.5 in Chap. 3), where the atoms occupy interstitial sites of the metal lattice, and impurity atoms on surfaces of crystals.

The concentration of the lattice gas is defined as

$$c = \frac{\text{number of particles } N_p}{\text{number of available sites } N}. \quad (18.90)$$

The simplest lattice-gas model is the site-exclusion model, where multiple occupancy of the sites is excluded, and no further interactions of the particles are taken into account. Of course, real particles have interactions, but many important properties of lattice gases can already be studied in this model. In this section uniform lattices will be considered, where the transition rate of a particle to an *empty* site is Γ everywhere.

Two different diffusion coefficients have to be defined for lattice gases:

- *Coefficient of collective diffusion, D_{coll}*
This diffusion coefficient is defined through Fick's law (1st or 2nd law), and it describes the decay of density disturbances. Alternative expressions are chemical or transport diffusivity.
- *Coefficient of tagged-particle diffusion, D_t*
This coefficient is defined through the mean square displacement of tagged particles. It is commonly called tracer diffusion coefficient or self-diffusion coefficient.

The single-particle diffusion coefficient, which was discussed in the preceding sections, is obtained either from the collective diffusion coefficient, or from the tagged-particle diffusion coefficient, in the limit of small particle concentrations, $c \rightarrow 0$. Both definitions lead to the single-particle diffusion coefficient in this limit.

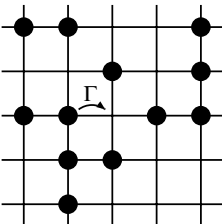


Fig. 18.12. Site-exclusion lattice gas.

In all lattice-gas models the physical properties depend crucially on whether a net bias in the hopping rates leads to a mean drift in the motion of the particles (and hence to a finite density-dependent current) or not. The intrinsic non-equilibrium behavior of driven diffusive systems is reviewed in detail in [18, 61]. Besides the existence of novel and unusual non-equilibrium phase transitions, the most remarkable features are the occurrence of shocks [62–64] and the importance of the physical boundaries of the system [65–69]. In this section we consider only symmetric hopping models where the rate of hopping does not depend on the direction of hopping across the bond between the two sites.

18.4.2 Collective Diffusion

Consider the most basic site exclusion model where particles hop between nearest neighbor sites with a constant rate Γ . This model is known as the simple symmetric exclusion process, introduced by Spitzer [70]. Many exact results are known, see [18, 71].

The basic quantity for the description of collective diffusion is $P(\mathbf{l}, t)$, the probability that site \mathbf{l} is occupied by a particle at time t . The important point is that the identity of the particles is disregarded in its definition. The quantity $P(\mathbf{l}, t)$ has a different meaning than the conditional quantity $P_{\mathbf{l}}(t)$ in the single-particle case. It is a member of a set of probabilities, defined on the lattice sites \mathbf{l} which gives the mean occupation number and hence the mean density on site \mathbf{l} at time t . Let $P(\bar{\mathbf{l}}, t)$ be the probability that site \mathbf{l} is empty. Obviously the following normalization condition holds:

$$P(\mathbf{l}, t) + P(\bar{\mathbf{l}}, t) = 1. \quad (18.91)$$

The master equation for $P(\mathbf{l}, t)$ in the site-exclusion model is:

$$\frac{d}{dt}P(\mathbf{l}, t) = \Gamma \sum_{\langle \mathbf{l}', \mathbf{l} \rangle} [P(\mathbf{l}', \bar{\mathbf{l}}, t) - P(\mathbf{l}, \bar{\mathbf{l}}, t)]. \quad (18.92)$$

Here $P(\mathbf{l}', \bar{\mathbf{l}}, t)$ is the joint probability that site \mathbf{l}' is occupied and site \mathbf{l} is empty at time t . The joint probabilities fulfil the relations

$$\begin{aligned} P(\mathbf{l}', \bar{\mathbf{l}}, t) + P(\mathbf{l}', \mathbf{l}, t) &= P(\mathbf{l}', t) \\ P(\mathbf{l}, \bar{\mathbf{l}}, t) + P(\mathbf{l}, \mathbf{l}', t) &= P(\mathbf{l}, t). \end{aligned} \quad (18.93)$$

Since $P(\mathbf{l}, \mathbf{l}', t) = P(\mathbf{l}', \mathbf{l}, t)$, insertion of (18.93) into (18.92) yields

$$\frac{d}{dt}P(\mathbf{l}, t) = \Gamma \sum_{\langle \mathbf{l}', \mathbf{l} \rangle} [P(\mathbf{l}', t) - P(\mathbf{l}, t)]. \quad (18.94)$$

This equation is identical to the master equation for the single-particle case. The initial conditions, however, are different. The derivation presented above

including that of the coherent dynamical structure function has been proposed by Kutner [72].

As a consequence of the master equation (18.94), the coefficient of collective diffusion results to be

$$D_{\text{coll}} = \Gamma a^2, \quad (18.95)$$

which is identical to the diffusion coefficient of a single particle on a uniform lattice (The numerical factor applies to hypercubic lattices in *all* dimensions). The important feature of (18.95) is that the collective diffusion coefficient does not depend on the concentration of the site-exclusion lattice gas.

The mathematical reason for the absence of the concentration dependence in the symmetric exclusion process is an underlying SU(2) symmetry of the generator of this Markov process. In the quantum Hamiltonian formalism for the master equation the Markov generator turns out to be the SU(2)-symmetric quantum Hamiltonian of the Heisenberg ferromagnet [73, 74]. In this correspondence the (many-particle) dynamics of the local density $P(\mathbf{l}, t)$ is related in a simple fashion to the (single-particle) spin-wave dynamics of the ferromagnet. This accounts for the identity of the dynamical equation (18.94) for the local density with the single-particle diffusion equation.

18.4.3 Tracer Diffusion for $d > 1$

The diffusion coefficient of a tagged particle, D_t , is defined from the asymptotic behaviour of its mean square displacement for $t \rightarrow \infty$

$$\langle \mathbf{R}^2 \rangle(t) \rightarrow 2dD_t t. \quad (18.96)$$

In this chapter only a cursory treatment of tagged-particle diffusion in the site-exclusion model for $d > 1$ will be given.

Consider a tagged particle. Its mean transition rate is $(1 - c)\Gamma$, where $1 - c$ is the blocking factor, i. e. the probability of finding an unoccupied site in the site-exclusion model. A mean field estimate of the tagged-particle diffusion coefficient is

$$D_t^{\text{MF}} = (1 - c)\Gamma a^2, \quad (18.97)$$

hence D_t is smaller than D_{coll} . Bardeen and Herring [75] pointed out that (in the limit $c \rightarrow 1$) there exists a backward correlation in the random walk of a tagged atom. To understand its origin, regard Fig. 18.13, where a tagged particle has made an exchange with an empty site.

Immediately after the transition there is an increased probability for a backward transition of the tagged particle, due to the presence of a vacancy, with certainty, at the initial particle position. This can be accounted for by introducing a correlation factor $f(c)$, with generally $f(c) \leq 1$,

$$D_t = (1 - c)\Gamma a^2 f(c). \quad (18.98)$$

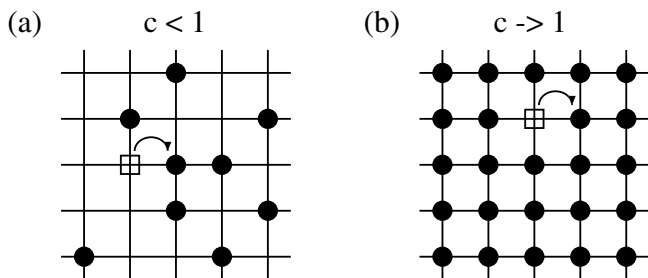


Fig. 18.13. Illustration of origin of backward correlation; (a) lattice gas of arbitrary concentration; (b) limit relevant to metal physics.

In metal physics the factor $1 - c$ is the concentration c_V of thermally activated vacancies and $c_V \ll 1$. The correlation factor $f = f(c \rightarrow 1)$ can be calculated from the random walk of a single vacancy. Its walk is uncorrelated and can be described by the methods of Sect. 18.2.1. The tagged atom, however, performs correlated random walk. In the limit $c \rightarrow 1$ only consecutive jumps of the tagged particle are correlated. Then [76]

$$f = \frac{1 + \langle \cos \vartheta \rangle}{1 - \langle \cos \vartheta \rangle}, \quad (18.99)$$

where $\langle \cos \vartheta \rangle$ is the average angle between two consecutive transitions of the tagged particle. This quantity can be calculated exactly from the random walk of a single vacancy [77]. Values of $\langle \cos \vartheta \rangle$ and f for various lattices are given in [78]. An example is the value $f = 0.727 \dots$ for the bcc lattice.

Extensions to arbitrary concentrations of the lattice gas were made by Nakazato and Kitahara [79] and Tahir-Kheli and Elliott [80]. They derived

$$f = \frac{1 + \langle \cos \vartheta \rangle}{1 + [(2 - 3c)/(2 - c)] \langle \cos \vartheta \rangle}, \quad (18.100)$$

where $\langle \cos \vartheta \rangle$ has the same meaning as above. Equation (18.100) is an approximate expression, but simulations show that the deviations are less than 1-2 % of the correct value (see Fig. 18.14). Of course, $f(c = 0) = 1$, and $f(c \rightarrow 1)$ reproduces (18.99). More details about the correlation factor, in particular about its relevance for experimental studies, have been presented in Chap. 1.

18.4.4 Tagged-Particle Diffusion on a Linear Chain

Tagged-particle diffusion on a linear chain is completely different from tagged-particle diffusion in higher dimensions ($d \geq 2$). The reason is that the tagged particle cannot pass the other particles, as schematically illustrated by Fig. 18.15.

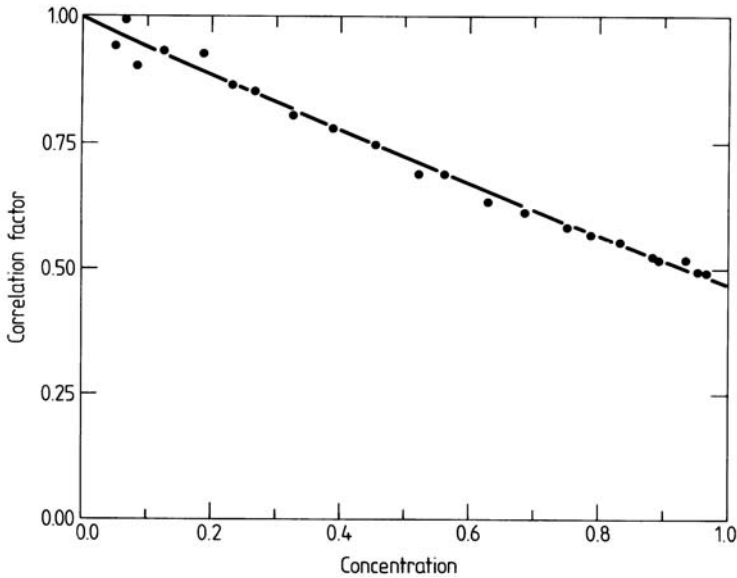


Fig. 18.14. Correlation factor for site-exclusion lattice gas on a square lattice as a function of concentration. Line: (18.100); symbols: MC simulations. From [81].

As a consequence, the mean square displacement of the tagged particle, $\langle \delta x^2 \rangle(t)$, is no longer proportional to t . It turns out that the mean square displacement of a tracer particle under the single-file constraint is asymptotically proportional to \sqrt{t} . This phenomenon is called single-file diffusion and it was first described in the physical literature by Richards [82]. There exist formal derivations of this behaviour (see [83] and references therein). However, the analytical derivations are rather difficult. Therefore, a derivation of the asymptotic behaviour from a physical consideration will be presented that is due to Alexander and Pincus [84]. The main idea is that the relative displacements of two tagged particles are caused by density fluctuations of the other particles. These density fluctuations are governed by collective diffusion.

For the derivation a continuum description will be adopted. In Fig. 18.16 the equilibrium positions and the displacements of two tagged particles are indicated.

A relation between the displacement difference and the change of density $\delta n(x, t)$ in between the two particles is required. This relation is derived in

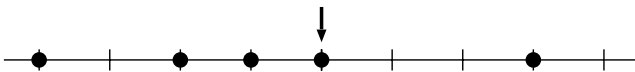


Fig. 18.15. Tagged-particle diffusion on a linear chain.

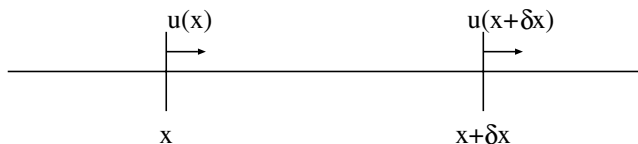


Fig. 18.16. Coordinates for the derivation of the mean square displacement in single-file diffusion, following [84].

the appendix (Sect. 18.7.3) and it reads in Fourier space

$$\frac{1}{n}\delta n(k, t) = ik u(k, t), \quad (18.101)$$

where $u(k, t)$ is the Fourier transform of the displacement $u(x, t)$ of the tagged particle. It follows

$$u(x, t) - u(x, 0) = \frac{1}{n} \int \frac{dk}{2\pi} e^{ikx} \frac{1}{ik} [\delta n(k, t) - \delta n(k, 0)]. \quad (18.102)$$

The square of this expression will be taken. One is interested in the random-walk average of the square. Instead of performing this average, one can take the ensemble average over many tagged particles, with the result

$$\begin{aligned} \langle [u(x, t) - u(x, 0)]^2 \rangle &= \frac{1}{N} \int dx [u(x, t) - u(x, 0)]^2 \\ &= \frac{1}{Nn^2} \int \frac{dk}{2\pi} \frac{2}{k^2} [\langle \delta n(k, 0) \delta n(-k, 0) \rangle \\ &\quad - \langle \delta n(k, t) \delta n(-k, 0) \rangle]. \end{aligned} \quad (18.103)$$

Here the density fluctuations are averaged over the stochastic dynamics of the lattice gas. The decay of density fluctuations is governed by collective diffusion; in the limit of long wavelengths $k \rightarrow 0$, i.e., for long times, one has

$$\langle \delta n(k, t) \delta n(-k, 0) \rangle \longrightarrow Nc(1-c) \exp(-D_{\text{coll}} k^2 t). \quad (18.104)$$

Insertion of this relation into (18.103) and transcription of the right-hand side into a lattice formulation gives ($a = 1$)

$$\langle [u(t) - u(0)]^2 \rangle = \frac{2(1-c)}{c} \int_{-\infty}^{\infty} \frac{dk}{2\pi} \frac{1 - \exp(-Dk^2 t)}{k^2}. \quad (18.105)$$

The integral is

$$\int_0^{\infty} dx \frac{1 - e^{-\lambda^2 x^2}}{x^2} = \lambda \sqrt{\pi}. \quad (18.106)$$

Hence one obtains using the result (18.95) for D_{coll}

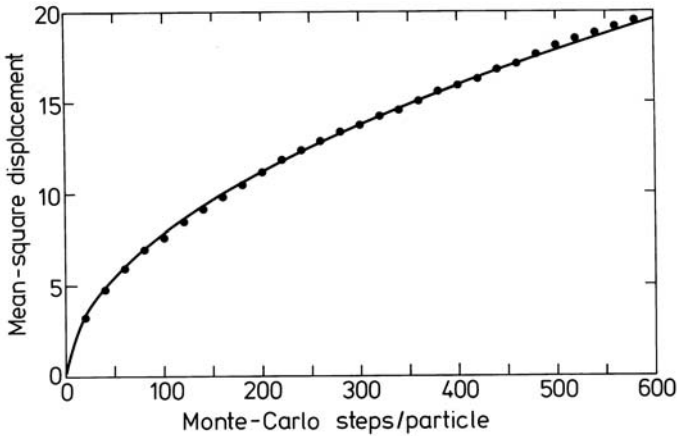


Fig. 18.17. Mean square displacement of tagged particles on a linear chain at concentration $c \approx 0.5$ as a function of time. Lines: theory; symbols: MC simulations. From [83].

$$\langle [u(t) - u(0)]^2 \rangle = \frac{2(1-c)}{c} \sqrt{\frac{\Gamma t}{\pi}}. \quad (18.107)$$

This is the characteristic behaviour of the mean square displacement of tagged particles under the single-file constraint. Experimental evidence for single-file diffusion is reported in Chap. 10.

Expression (18.107) is valid for long times. For short times $(1-c)\Gamma t \ll 1$ one has

$$\langle \delta x^2 \rangle(t) = 2(1-c)\Gamma a^2 t. \quad (18.108)$$

In this time regime one recovers the mean-field result (18.97) for the tracer diffusion coefficient. In [83], an approximate expression was derived that covers the complete time region. Figure 18.17 shows numerical simulation results for the mean square displacement of tagged particles, together with the theoretical curve of [83]. One recognizes the proportionality of $\langle \delta x^2 \rangle(t)$ with \sqrt{t} for longer times.

It is instructive to consider two coupled lines between which the particles can make transitions with rate Γ_{\perp} , under the condition that the target sites on the other chain are not occupied, cf. Fig. 18.18. The single-file constraint is now relieved and one expects that a tagged particle makes asymptotically normal diffusion,

$$\langle \delta x^2 \rangle(t) = 2D_t t. \quad (18.109)$$

A heuristic derivation of the diffusion coefficient D_t in this situation can be given by putting together single-file mean square displacements of the particle according to (18.107) at time intervals $1/\Gamma_{\perp}(1-c)$, see Fig. 18.19.

This is the mean time, where a tagged particle makes a transition to the other chain and starts a new displacement. The slope of the dashed line

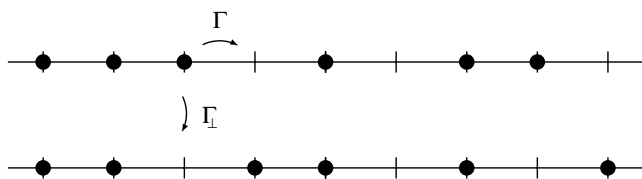


Fig. 18.18. Particle diffusion on two coupled lines.

in Fig. 18.19 can be determined in the following way: Take $\langle \delta x^2 \rangle$ at time $t = 1/\Gamma_{\perp}(1 - c)$ and divide by this time. This gives as an estimate for the diffusion coefficient

$$D_t \cong \frac{(1 - c)^{3/2}}{c} \Gamma \sqrt{\frac{\Gamma_{\perp}}{\Gamma}}. \tag{18.110}$$

An approximate theory which is valid at all times, was given in [85]. Figure 18.20 presents the results of numerical simulations together with the theoretical results of this paper. One recognizes how the asymptotic behaviour $\sim t$ is reached for $\Gamma_{\perp}/\Gamma \neq 0$ after a crossover region.

18.5 Many Particles on Disordered Lattices

18.5.1 Models with Symmetric Rates

In this final section of this chapter, diffusion of many particles on regular lattices with disordered transition rates will be treated. The disordered rates are assumed to be fixed, i.e. quenched disorder is assumed. The considerations will be restricted to the site exclusion model, where double occupancy of the sites is forbidden, and no further interactions of the particles are present. Only the coefficient of collective diffusion will be studied. Even with all

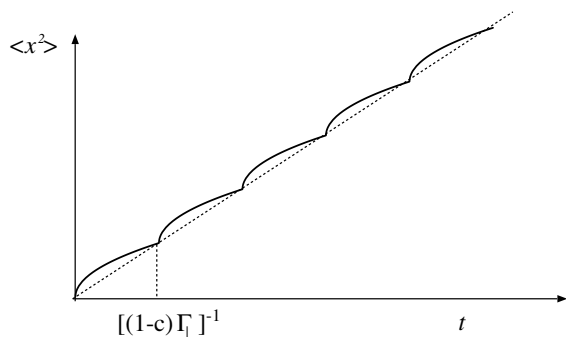


Fig. 18.19. Heuristic derivation of the diffusion coefficient of a tagged particle on two coupled lines.

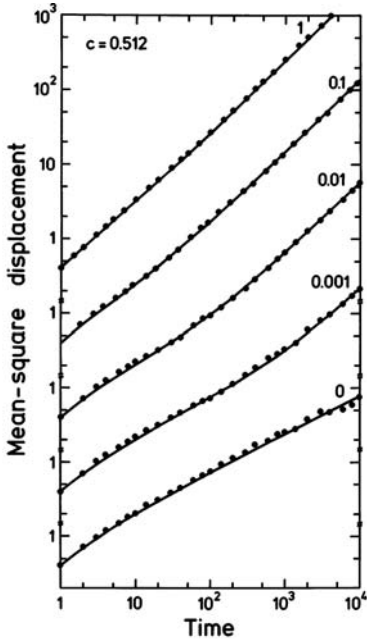


Fig. 18.20. Mean square displacement of tagged particles on two coupled lines as a function of time. Lines: theory; symbols: MC simulations. The ratio Γ_{\perp}/Γ is indicated on the curves. From [85].

these restrictions, the problem is very difficult, with one important exception. Namely, for symmetric transition rates, the problem can be reduced to the independent-particle problem. This case will be treated in this section.

The cancelation of the joint probabilities in the master equation for $P(\mathbf{l}, t)$ that has been shown in Sect. 18.4.2 for lattices with uniform transition rates is also valid for disordered lattices as long as $\Gamma_{ij} = \Gamma_{ji}$. In this case the hierarchy of many-particle equations reduces to the single-particle equation with disordered, symmetric rates. Consequently [86]

$$\text{if } \Gamma_{ij} = \Gamma_{ji} \text{ then } D_{\text{coll}} = D_{\text{s.p.}} . \tag{18.111}$$

The index s.p. means single, independent particles. The origin of this cancelation is the symmetry under the Lie algebra for the special unitary group $SU(2)$ of the generator of the process which holds on any type of lattice with arbitrary bond-symmetric disorder [74]. Also symmetric processes with partial exclusion of up to M_i particles on lattice site i have this property [18]. A result equivalent to (18.111) was obtained for the conductivity by Harder et al. [87].

The models of interest are the random barrier model and the model with randomly blocked sites.

18.5.2 Selected Results for the Coefficient of Collective Diffusion in the Random Site-Energy Model

The nontrivial case for collective diffusion of site-exclusion lattice gases in disordered lattices is the case of site-energy disorder. No cancelation of the joint probabilities $P(\mathbf{l}, \mathbf{l}', t)$ occurs in the master equation and one has to resort to approximations, with two exceptions. The first exception is the site-exclusion lattice gas on a linear chain with random site energies (RT model) in the limit of very small vacancy concentrations, $c_V \rightarrow 0$. The diffusion problem of single vacancies can then be solved, for instance by the methods of Sect. 18.3.2, and the exact result for the corresponding diffusion coefficient $D_{s.v.}$ was given in [88]. In the limit $c \rightarrow 1$ $D_{s.v.}$ agrees with D_{coll} . Second, an *exact* expression for the collective diffusion coefficient can be given for the RT model in the limit of infinite dimensions. Apart from these two cases, no further exact results for the collective diffusion coefficient are known. Hence approximate treatments are necessary.

An effective medium approximation for collective diffusion of site-exclusion lattice gases can be formulated in the following way. First the problem has to be reduced to an effective one-particle problem. This can be achieved by an obvious extension of the results for the single-particle case, where weighted transition rates were used. The following effective or mean field single-particle transition rates will be introduced

$$\Gamma_{ji}^{Sym} = \frac{P_i(1 - P_j)\Gamma_{ji}}{\{P_i(1 - P_i)\}}. \quad (18.112)$$

The quantity P_i is the thermal equilibrium occupation of site i . It is normalized differently from ρ_i , hence a normalization factor in the denominator of Γ_{Sym} is required. The symmetry of the rates Γ_{Sym} follows from detailed balance. The rate equations (18.112) were already introduced in [89] in the context of lattice-gas diffusion on linear chains.

The second step is the use of Γ_{Sym} in an effective-medium approximation. Since the rate equations (18.112) are symmetric, the formulation of the EMA of Sect. 18.3.5 can be used. From the EMA the limit of infinite dimensions (infinite coordination number) is easily obtained [90]. The result is

$$D_{coll}^{phen} = \{\Gamma_{ji}^{Sym}\} = \frac{P_i(1 - P_j)\Gamma_{ji}}{\{P_i(1 - P_i)\}} \quad (18.113)$$

and it represents a phenomenological expression for the collective diffusion coefficient that was derived in the context of metal physics [91] and surface physics [92]. It is not surprising that a phenomenological theory is obtained in the limit of infinite coordination number. The main problem in treating collective diffusion of lattice gases in disordered lattices are the correlations that are caused by particles which occupy sites with low energies and act as blocking sites. The effects of these correlations become irrelevant in the limit of infinite coordination number.

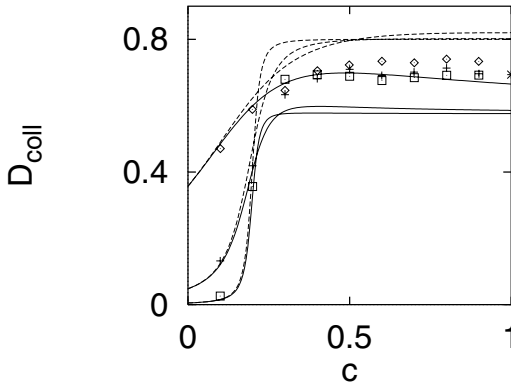


Fig. 18.21. Collective diffusion coefficient of site-exclusion lattice gas in a two-level RT model in $d = 3$, as a function of concentration. 20 % of the sites are trap sites. Continuous lines: EMA; dashed lines: phenomenological theory; symbols: MC results for $\Gamma^</\Gamma = 0.1$ (\diamond), 0.01 ($+$) and 0.001 (\square). Limiting value $c \rightarrow 1$: $*$.

Fig. 18.21 shows results for a two-level RT model in $d = 3$ which consists of free sites with concentration $1 - c_t$ and transition rates Γ , and trap sites with concentration c_t and rates $\Gamma^<$. The results of numerical simulations are compared with the EMA and the phenomenological expression (18.113).

The main feature of the results is that D_{coll} is determined by the saturation of deep trap sites by particles. This was first pointed out by Kirchheim who modelled hydrogen diffusion in metglasses [93]. The saturation effect is a rather general feature of collective diffusion in systems with site-energy disorder and is not restricted to a particular realization of the disorder.

The figure also shows that the single-particle result is approached for $c \rightarrow 0$. Also the limit $c \rightarrow 1$ and $\Gamma^</\Gamma \ll 1$ can be understood for the two-level RT model. In this limit D_{coll} is given by the single-particle result for the RBS model. Namely, the deep trap sites are saturated by particles and act as blocking sites. It was discussed in Sect. 18.5.1 that for the RBS model $D_{\text{coll}} \equiv D_{\text{s.p.}}$. Additional EMA and numerical results are given in [90].

It has been shown in Sect. 18.3.6 that the diffusion coefficient of single, independent particles vanishes in the RT model for an exponential distribution of site energies, at low temperatures. The relevant parameter is $\alpha = k_B T / E_c$, where E_c characterizes the width of the distribution. The result was $D_{\text{s.p.}} \equiv 0$ for $\alpha < 1$ (cf. (18.81)).

What happens when a finite concentration of particles is filled into the lattice? The particles tend to occupy the sites with low site-energies, saturating thereby the low-lying levels. If now a density disturbance is set up in the lattice gas, the disturbance should decay by collective diffusion. This was indeed observed in the numerical simulations of [94], and D_{coll} was obtained by monitoring the decay of cosine density profiles.

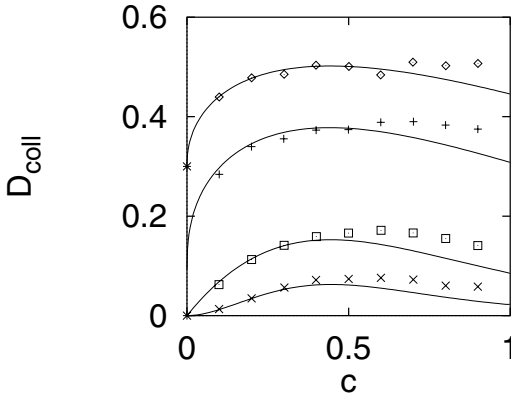


Fig. 18.22. Collective diffusion coefficient in the RT model in $d = 3$ with exponential distribution of site energies. Continuous lines: EMA; symbols: MC results for $\alpha = 1.43$ (\diamond), 1.0 ($+$), 0.5 (\square), and 0.333 (\times). Limit $c \rightarrow 1$ (*).

Fig. 18.22 shows numerical results for the RT model in $d = 3$ together with EMA results. It is evident that $D_{\text{coll}}(c \rightarrow 0) \rightarrow D_{\text{s.p.}}$, also for $\alpha < 1$, where $D_{\text{s.p.}} = 0$. There is qualitative agreement between the simulations and the EMA, particularly at lower particle concentrations.

The behaviour of D_{coll} for $c \ll 1$ can be understood from the following qualitative consideration: Since only one particle can occupy a given site, the equilibrium occupancy of a site is given by the Fermi-Dirac distribution. In the limit of low temperatures, all levels are occupied up to a pseudo Fermi level E^* (see Fig. 18.23). For the exponential distribution

$$\int_{-\infty}^{E^*} dE \frac{1}{E_c} \exp\left(\frac{E}{E_c}\right) = c, \tag{18.114}$$

from which follows

$$E^* = E_c \ln(c). \tag{18.115}$$

At small concentrations and low T , diffusion is mainly carried by particles at or above the Fermi level, and the coefficient of collective diffusion is approximately given by the single-particle diffusion expression,

$$D_{\text{coll}}^{-1} \approx \int_{E^*}^0 dE \nu_T(E) \frac{1}{\Gamma(E)}. \tag{18.116}$$

The result for small c is (note that $\alpha < 1$)

$$D_{\text{coll}} \approx \Gamma_0 \left(\frac{1}{\alpha} - 1\right) c^{(\frac{1}{\alpha}-1)}. \tag{18.117}$$

That is, D_{coll} exhibits a power-law dependence on the concentration.

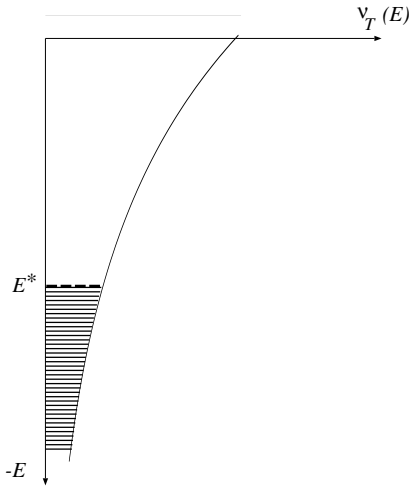


Fig. 18.23. Exponential density of site energies; the levels are filled up to the “Fermi” level E^* .

Power-law dependence of the conductivity on the concentration has been observed in ionic conductors, see, e. g., [95]. Of course, the actual systems are much more complex than described by the site-exclusion lattice gas in the RT model. Indeed, power-law dependence of the mobility was obtained in numerical simulations of models that were designed to describe superionic conductors [96, 97]. Nonetheless, it is interesting to note that already rather simple models exhibit these effects.

18.6 Conclusion

This chapter was concerned with the theoretical description of diffusion of particles on lattices. Two different dimensions of difficulties were encountered: Diffusion of single versus many particles and diffusion in ordered versus disordered lattices. The diffusion of a single particle on a uniform lattice is a well-understood textbook problem. Of practical interest are extensions of this problem, for example two-state models for diffusion and trapping of single particles. The problem of diffusion of a single particle in disordered lattices is now well understood with respect to the asymptotic properties, if local (site and/or bond) disorder is present. One remaining topic for future work is diffusion in the presence of extended defects. Also the frequency dependence seems to be not completely understood.

Various aspects of the diffusion of many particles on uniform lattices have been clarified in the past, in particular the differences between collective and tracer diffusion, the inherent correlation effects in tracer diffusion, and the anomalous diffusion of tagged particles on linear chains (single-file diffusion). Open problems can be found in the consideration of various forms of the interactions of the particles.

Least well understood is, of course, the problem of diffusion of many particles in lattices with quenched, disordered transition rates. Since this is a problem of current interest, the corresponding remarks will be more detailed than those concerning the previous sections. In the preceding section diffusion of site-exclusion lattice gases in disordered lattices was considered. There exist now reasonable approximate descriptions for the coefficient of collective diffusion in form of the phenomenological theory and the EMA. The approximations are rather accurate for two-level models of site energies if the lattice-gas concentration c is smaller than the trap concentration c_t . However, one should be aware of the limitations of the approximations. Simulation results in $d = 3$ show that there are large discrepancies between the approximations and the numerical results when $c \approx c_t$. Hence an exact theory for collective diffusion for the site-exclusion model in disordered linear chains is desired.

The following important aspects of diffusion of lattice gases in disordered lattices were omitted in this chapter:

- *Tracer diffusion*
The theory of tracer diffusion is more complicated than that of collective diffusion, in view of the inherent backward correlations for tracer diffusion. The inclusion of backward correlations in the presence of quenched disorder appears to be very difficult.
- *Effects of interactions*
Even for lattices with uniform transition rates, interactions can only be treated by approximations like mean field. If disorder is present, and the particles have interactions, one has to resort to numerical simulations, see [57–59, 96, 97] and Chap. 20.
- *Frequency dependence*
Although frequency dependence was investigated in numerical works (see the references given in the preceding item), many of the observed features are not yet understood in a qualitative way (see however Chap. 21).

One could easily add more points to this list of partially understood problems. The main message perhaps should be that the field of diffusion of particles in condensed matter systems is still an open field with many unsolved problems.

18.7 Appendix

18.7.1 Derivation of the Result for the Diffusion Coefficient for Arbitrarily Disordered Transition Rates

Consider a segment of a linear chain with general (nonsymmetric) transition rates, as indicated in Fig. 18.3 of Sect. 18.3.2. A constant current I is fed into site 0 and extracted at site N . Kirchhoff's node equation for site 0 is

$$\Gamma_{10}P_0 - \Gamma_{01}P_1 = I. \quad (18.118)$$

It expresses the fact that the sum of all currents into site 0 is zero. The master equation for site 1 is

$$\frac{d}{dt}P_1(t) = \Gamma_{10}P_0(t) + \Gamma_{12}P_2(t) - (\Gamma_{01} + \Gamma_{21})P_1(t). \quad (18.119)$$

One has in the stationary situation

$$-\Gamma_{10}P_0 + (\Gamma_{01} + \Gamma_{21})P_1 - \Gamma_{12}P_2 = 0. \quad (18.120)$$

Add this equation to the node equation (18.118) to obtain

$$\Gamma_{21}P_1 - \Gamma_{12}P_2 = I. \quad (18.121)$$

This procedure is continued and the equation for site i is

$$\Gamma_{i+1,i}P_i - \Gamma_{i,i+1}P_{i+1} = I. \quad (18.122)$$

The last equation is Kirchhoff's node equation at site N ,

$$\Gamma_{N,N-1}P_{N-1} - \Gamma_{N-1,N}P_N = I. \quad (18.123)$$

The aim is to relate I to the difference $P_0 - P_N$. This can be achieved by first expressing P_{N-1} through P_N , I , using (18.123),

$$P_{N-1} = \frac{\Gamma_{N-1,N}}{\Gamma_{N,N-1}}P_N + \frac{I}{\Gamma_{N,N-1}}. \quad (18.124)$$

The quantity P_{N-2} can be expressed through P_{N-1} and I ,

$$P_{N-2} = \frac{\Gamma_{N-2,N-1}}{\Gamma_{N-1,N-2}}P_{N-1} + \frac{I}{\Gamma_{N-1,N-2}}. \quad (18.125)$$

Insert P_{N-1} to obtain a relation between P_{N-2} , P_N , and I ,

$$P_{N-2} = \frac{\Gamma_{N-2,N-1}}{\Gamma_{N-1,N-2}} \frac{\Gamma_{N-1,N}}{\Gamma_{N,N-1}} P_N + \left(\frac{\Gamma_{N-2,N-1}}{\Gamma_{N-1,N-2}} \frac{1}{\Gamma_{N,N-1}} + \frac{1}{\Gamma_{N-1,N-2}} \right) I. \quad (18.126)$$

Continue this procedure with P_{N-3} , etc. The final result is

$$P_0 = \frac{\Gamma_{01}\Gamma_{12} \times \cdots \times \Gamma_{N-1,N}}{\Gamma_{10}\Gamma_{21} \times \cdots \times \Gamma_{N,N-1}} P_N + \left(\frac{\Gamma_{01} \times \cdots \times \Gamma_{N-2,N-1}}{\Gamma_{10} \times \cdots \times \Gamma_{N-1,N-2}} \frac{1}{\Gamma_{N,N-1}} + \frac{\Gamma_{01} \times \cdots \times \Gamma_{N-3,N-2}}{\Gamma_{10} \times \cdots \times \Gamma_{N-2,N-3}} \frac{1}{\Gamma_{N-1,N-2}} + \cdots + \frac{\Gamma_{01}}{\Gamma_{10}} \frac{1}{\Gamma_{21}} + \frac{1}{\Gamma_{10}} \right) I. \quad (18.127)$$

The expression (18.127) can be further simplified by introducing the relation of detailed balance which holds in thermal equilibrium. It is clear that a non-equilibrium situation is maintained in the segment of the chain. The relation of detailed balance will be used to express the ratio of two rates by equilibrium occupation factors. An implicit assumption is the validity of the Arrhenius law. The equilibrium occupation probabilities are proportional to

$$\rho_i \sim \exp(-\beta E_i); \quad (18.128)$$

note that $E_i \leq 0$. The condition of detailed balance is

$$\Gamma_{01}\rho_1 = \Gamma_{10}\rho_0 \quad (18.129)$$

or

$$\frac{\Gamma_{01}}{\Gamma_{10}} = \frac{\rho_0}{\rho_1} = \exp[-\beta(E_0 - E_1)]. \quad (18.130)$$

The product of two factors is

$$\frac{\Gamma_{12}\Gamma_{01}}{\Gamma_{21}\Gamma_{10}} = \exp[-\beta(E_1 - E_2)] \exp[-\beta(E_0 - E_1)] = \exp[-\beta(E_0 - E_2)] \quad (18.131)$$

and the product

$$\prod_{i=0}^{N-1} \frac{\Gamma_{i,i+1}}{\Gamma_{i+1,i}} = \exp[-\beta(E_0 - E_N)]. \quad (18.132)$$

Equation (18.127) can then be written as

$$\begin{aligned} P_0 - \exp[-\beta(E_0 - E_N)]P_N = \\ = \left(\frac{1}{\exp[-\beta(E_{N-1} - E_0)]\Gamma_{N,N-1}} + \frac{1}{\exp[-\beta(E_{N-2} - E_0)]\Gamma_{N-1,N-2}} \right. \\ \left. + \dots + \frac{1}{\exp[-\beta(E_1 - E_0)]\Gamma_{21}} + \frac{1}{\Gamma_{10}} \right) I. \end{aligned} \quad (18.133)$$

It will be required that $P_0 = P_N$ if $I = 0$, and $P_0 \neq P_N$ only through maintaining a current through the chain. This requirement will be satisfied if $E_0 = E_N$, i. e., if the initial and final site energies are equal. It is henceforth assumed that always $E_0 = E_N$, which is a reasonable assumption.

The disorder average of (18.133) will now be taken. Each term on the right-hand side of this equation can be averaged independently and the pertinent quantities are taken from common distributions. The result is then

$$P_0 - P_N = N \left\{ \frac{1}{\Gamma_{i+1,i} \exp[-\beta(E_i - E_0)]} \right\} I, \quad (18.134)$$

where the dummy indices have been kept to indicate the direction of the transition rate. The curly brackets represent the average over the different realizations of the disorder.

The further requirement will be made that the initial site is a typical site with respect to the disorder average. Hence it is assumed that

$$\{\exp(-\beta E)\} = \exp(-\beta E_0). \quad (18.135)$$

This means that the thermal occupation of the initial (and final) site is equal to the average occupation. Large segments will be considered, where the disorder average is approximated by the sum over all sites,

$$\{\exp(-\beta E)\} = \frac{1}{N} \sum_{j=0}^N \exp(-\beta E_j). \quad (18.136)$$

Thermal occupation factors will be defined by

$$\rho_i = \frac{\exp(-\beta E_i)}{\{\exp(-\beta E)\}} = \frac{\exp(-\beta E_i)}{\frac{1}{N} \sum_{j=0}^{N-1} \exp(-\beta E_j)}. \quad (18.137)$$

Relation (18.134) between $P_0 - P_N$ and the current I can then be written as

$$P_0 - P_N = IN \left\{ \frac{1}{\Gamma_{i+1,i} \rho_i} \right\}. \quad (18.138)$$

This relation represents Fick's first law. The following identification can be made (lattice constant $a = 1$)

$$\frac{P_0 - P_N}{N} \cong -\nabla n \quad d = 1. \quad (18.139)$$

Fick's first law reads

$$I = -D\nabla n. \quad (18.140)$$

Hence one finds

$$D = \left\{ \frac{1}{\Gamma_{i+1,i} \rho_i} \right\}^{-1}. \quad (18.141)$$

18.7.2 Derivation of the Self-Consistency Condition for the Effective-Medium Approximation

The Fourier-Laplace transformation of the conditional probability $P_l(t)$ is defined by

$$\tilde{P}(k, s) = \int_0^\infty dt \exp(-st) \sum_l \exp(-ika) P_l(t). \quad (18.142)$$

The equation for $\tilde{P}(k, s)$ is obtained by multiplying (18.51) and (18.52) with $\exp(-ikal)$, summing over l , and integrating:

$$\begin{aligned}
 & [s + 2\tilde{\Gamma}_{\text{eff}}(s)(1 - \cos ka)]\tilde{P}(ks,) \\
 & = 1 + (e^{-ika} - 1)[\tilde{\Gamma}_{\text{eff}}(s) - \Gamma_{10}] [\tilde{P}_1(s) - \tilde{P}_0(s)]. \quad (18.143)
 \end{aligned}$$

Combining this equation with the master equation (18.56) for the effective medium one finds

$$\begin{aligned}
 \tilde{P}(k, s) & = \tilde{E}(k, s) + \tilde{E}(k, s)(e^{-ika} - 1) \\
 & \quad \times [\tilde{\Gamma}_{\text{eff}}(s) - \Gamma_{10}][\tilde{P}_1(s) - \tilde{P}_0(s)]. \quad (18.144)
 \end{aligned}$$

The inverse Fourier transform of $\tilde{E}(k, s)$ is

$$\tilde{E}_l(s) = \int_{-\pi}^{\pi} \frac{dk}{2\pi} \frac{\exp(ikal)}{s + 2\tilde{\Gamma}_{\text{eff}}(s)(1 - \cos ka)}. \quad (18.145)$$

Note that $\tilde{E}_l(s) = \tilde{E}_{-l}(s)$. Multiplying (18.144) with $1/2\pi$ and integrating over k one obtains

$$\tilde{P}_0(s) = \tilde{E}_0(s) + [\tilde{E}_1(s) - \tilde{E}_0(s)][\tilde{\Gamma}_{\text{eff}}(s) - \Gamma_{10}] [\tilde{P}_1(s) - \tilde{P}_0(s)]. \quad (18.146)$$

Multiplying (18.144) with $\exp(ika)/2\pi$ and integrating one obtains

$$\tilde{P}_1(s) = \tilde{E}_1(s) + [\tilde{E}_1(s) - \tilde{E}_0(s)][\tilde{\Gamma}_{\text{eff}}(s) - \Gamma_{10}] [\tilde{P}_1(s) - \tilde{P}_0(s)]. \quad (18.147)$$

The difference of the two equations is

$$\tilde{P}_1(s) - \tilde{P}_0(s) = \frac{\tilde{E}_1(s) - \tilde{E}_0(s)}{1 + 2[\tilde{E}_1(s) - \tilde{E}_0(s)][\tilde{\Gamma}_{\text{eff}}(s) - \Gamma_{10}]} \quad (18.148)$$

and thus

$$\tilde{P}_0(s) = \tilde{E}_0(s) + \frac{[\tilde{E}_1(s) - \tilde{E}_0(s)]^2[\tilde{\Gamma}_{\text{eff}}(s) - \Gamma_{10}]}{1 + 2[\tilde{E}_1(s) - \tilde{E}_0(s)][\tilde{\Gamma}_{\text{eff}}(s) - \Gamma_{10}]} \quad (18.149)$$

The self-consistency requirement $\{\tilde{P}_0(s)\} = \tilde{E}_0(s)$ (cf. (18.57)) leads to

$$\left\{ \frac{[\tilde{E}_1(s) - \tilde{E}_0(s)]^2[\tilde{\Gamma}_{\text{eff}}(s) - \Gamma_{10}]}{1 + 2[\tilde{E}_1(s) - \tilde{E}_0(s)][\tilde{\Gamma}_{\text{eff}}(s) - \Gamma_{10}]} \right\} = 0. \quad (18.150)$$

The difference squared in the numerator is systematic and can be factored out. From the master equation for the effective medium in $d = 1$ follows

$$\tilde{E}_1(s) - \tilde{E}_0(s) = \frac{s\tilde{E}_0(s) - 1}{2\Gamma_{\text{eff}}(s)}. \quad (18.151)$$

The self-consistency condition can now be brought into the form that has been given in the main text.

18.7.3 Relation Between the Relative Displacement and the Density Change

The displacements of two tagged particles from their equilibrium positions x and $x + \delta x$ are considered. The notation is explained in Fig. 18.16. The initial distance changes into the actual distance

$$\delta x \longrightarrow \delta x + u(x + \delta x) - u(x) . \quad (18.152)$$

Because the number of particles in the interval between the two tagged particles is conserved, the local density change induced by the difference in the displacements of the two particles is

$$\delta n = \frac{n\delta x}{\delta x + u(x + \delta x) - u(x)} - n . \quad (18.153)$$

Here n is the (spatially constant) equilibrium particle density. A Taylor expansion for small δx is made, together with the assumption of small gradients, $\partial u / \partial x \ll 1$. From (18.153) follows in linear approximation

$$\frac{1}{n} \delta n = - \frac{\partial u}{\partial x} . \quad (18.154)$$

The inverse Fourier transformation is defined by

$$f(x, t) = \int \frac{dk}{2\pi} e^{ikx} f(k, t) . \quad (18.155)$$

The relation between density change and displacement gradient reads in Fourier space

$$\frac{1}{n} \delta n(k, t) = iku(k, t) . \quad (18.156)$$

This is the relation used in the main text.

Notation

$D = D_{\text{s.p.}}$	Diffusion coefficient of single, independent particles
D_{coll}	Collective (Fick's) diffusion coefficient
D_{t}	Tagged particle (tracer) diffusion coefficient
E_i	Energy level of site i
E_{ij}	Activation energy of barrier between sites i and j
$f(c)$	Correlation factor for tagged-particle diffusion in lattice gas
$f = f(c \rightarrow 1)$	Correlation factor for metal physics
$P(\mathbf{l}t \mathbf{00})$	Conditional probability of finding a particle on site \mathbf{l} at time t when it was at site $\mathbf{0}$ at $t = 0$.
$P_{\mathbf{l}}(t)$	Abbreviated form of $P(\mathbf{l}t \mathbf{00})$

$P(\mathbf{l}, t)$	Probability of finding a particle at site \mathbf{l} at time t (applies to lattice gases)
$P(\mathbf{k}, t)$	Fourier transform of $P_{\mathbf{l}}(t)$
$\tilde{P}(\mathbf{l}, s)$	Fourier-Laplace transform of $P_{\mathbf{l}}(t)$
Γ	Transition rate between two neighbour sites in uniform lattice
Γ_{ji}	Transition rate from site i to neighbour site j in disordered lattice
$\Gamma_{\text{eff}}(t)$	Time-dependent transition rate in effective medium
$\Lambda_{\mathbf{l}, \mathbf{l}'}$	Transition-rate matrix between two neighbour sites
$\Lambda(\mathbf{k})$	Fourier transform of transition rate matrix
$\nu_{\text{B}}(E)$	Density of activation energies of random barriers
$\nu_{\text{T}}(E)$	Density of random site energies
$\rho(\Gamma)$	Probability density of random transition rates
$\langle \quad \rangle$	Random walk and/or thermal average
$\{ \quad \}$	Average over (quenched) disordered rates.

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