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Correlation factor, velocity autocorrelation function and frequency-dependent tracer diffusion coefficient

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Abstract. The correlation factor, defined as the ratio between the tracer diffusion coefficient in lattice gases and the diffusion coefficient for a corresponding uncorrelated random walk, is known to assume a very simple form under certain conditions. A simple derivation of this is given with the aid of the Green–Kubo formula for the tracer diffusion coefficient and it is generalised to a frequency-dependent correlation factor. The application to lattice gases with nearly vanishing vacancy concentration is critically discussed. The derivation is also extended to more complex hopping processes where the correlation factor is a tensor. The velocity autocorrelation function of the tracer particle is demonstrated to exhibit a $t^{-(d/2-1)}$ long-time tail, in agreement with mode-coupling predictions.

1. Introduction

The correlation factor was introduced into the theory of hopping diffusion by Bardeen and Herring (1952). They pointed out that in the process of self-diffusion in metals successive jumps of tracer atoms are correlated. The correlation factor is then defined as the ratio between the actual tracer diffusion coefficient and the one that would result from an uncorrelated random walk with the same jump frequency. A very simple expression for the correlation factor is obtained under the assumption that only consecutive jumps of the tracer particle are correlated, and under some simplifying assumptions concerning the types and symmetries of the jumps of the particles in the underlying lattice. The expression reads (Compaan and Haven 1956, LeClaire 1970):

$$f = \frac{1 + \langle \cos \theta \rangle}{1 - \langle \cos \theta \rangle} \tag{1}$$

where $\langle \cos \theta \rangle$ is the *average* angle between two successive jumps of the tracer particle. The customary application of equation (1) is to self-diffusion in metals, where the assumptions leading to (1) are fulfilled for small vacancy concentrations and for most of the common lattice types. Also the generalisations necessary to include anisotropic lattices have been worked out (Howard 1966).

The derivation of equation (1) is usually performed by considering the mean-square displacement of the tracer particle (see, e.g., any of the references given above). A

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completely equivalent derivation, which to our taste has the attraction of extreme simplicity, employs the Green–Kubo expression for the tracer diffusion coefficient in terms of the velocity autocorrelation function. We will present this derivation in § 2. An additional advantage is the possibility of immediate generalisation to a frequency-dependent diffusion coefficient. In § 3 we apply our formulation to tracer diffusion in lattice gases with nearly vanishing vacancy concentration in one, two, and three dimensions. In two dimensions, we express $\langle\cos\theta\rangle$ in terms of lattice Green functions, regaining the results of Benoist *et al* (1977). We show that the interpretation of the tracer diffusion process as a continuous-time random walk with a one-step memory leads to apparent inconsistencies, which can be resolved by careful considerations. In three dimensions the possibility of escape of the vacancies to infinity is most naturally included in our derivation of (1), again leading back to the results of the standard formulation. In an Appendix we extend our formulation to the case of lattices with inequivalent jumps, where the correlation factor becomes a tensor.

Finally we direct our attention to the long-time behaviour of the velocity autocorrelation function, corresponding to the low-frequency behaviour of the tracer diffusion coefficient. We show in § 4 by simple stochastic considerations that there appears a 'long-time tail behaviour' $t^{-(d/2+1)}$ in the velocity autocorrelation function of a tracer particle in a lattice gas in the limit of $c \to 1$.

2. The correlation factor

Before proceeding to derive (1) from the velocity autocorrelation function we list the assumptions on the diffusion process that we will employ in the derivation. Suppose the hopping model for the tagged particle is characterised by jump vectors $\boldsymbol{\Delta}_i(l)$ where l designates the starting site, with $|\boldsymbol{\Delta}_i(l)| = a$ for all directions, and with

$$\sum_{i=1}^{z} \boldsymbol{\Delta}_i(l) = 0$$

where z is the coordination number. The allowed jump directions are then characterised by unit vectors

$$\hat{\boldsymbol{n}}_i(l) = \boldsymbol{\Delta}_i(l)/a.$$

Suppose further that the number $n(\theta)$ of allowed directions $\hat{\boldsymbol{m}}$ for a jump following a jump in the direction $\hat{\boldsymbol{n}}$ and satisfying $\hat{\boldsymbol{m}} \cdot \hat{\boldsymbol{n}} = \cos\theta$ is independent of $\hat{\boldsymbol{n}}$, and the average value of these directions is parallel to $\hat{\boldsymbol{n}}$. The above conditions are satisfied for nearest-neighbour jumps on various lattices, in particular for the quadratic, triangular, and honeycomb lattices in two dimensions, and the simple cubic BCC, FCC and diamond lattices in three dimensions. Let $R(\hat{\boldsymbol{m}} \cdot \hat{\boldsymbol{n}}, \tau)$ be the probability density that a jump in direction $\hat{\boldsymbol{n}}$ at time t_0 is followed by a jump in direction $\hat{\boldsymbol{m}}$ at time $t_0 + \tau$ where we want to impose the restriction that the resulting random-walk process is ergodic (Feller 1967). Hopping processes characterised by transition kernels of this type are commonly referred to as processes with a one-step memory. They are a generalisation of the 'persistent' random walk introduced by Fuerth (1920) and Taylor (1922). A natural condition on the waiting-time distributions $R(\hat{\boldsymbol{m}} \cdot \hat{\boldsymbol{n}}, \tau)$ is their normalisation. For fixed $\hat{\boldsymbol{n}}$ one has

$$\sum_{\hat{\boldsymbol{m}}} \int_0^\infty R(\hat{\boldsymbol{m}} \cdot \hat{\boldsymbol{n}}, \tau)\, \mathrm{d}\tau = 1. \tag{2}$$

In addition, we require the average waiting time τ_0 to be finite, that is

$$\tau_0 = \sum_{\hat{m}} \int_0^\infty \tau R(\hat{m} \cdot \hat{n}, \tau)\, d\tau < \infty. \tag{3}$$

This condition is necessary for the existence of a stationary state of the hopping process under consideration (Tunaley 1974). The assumptions made above are sufficient to derive equation (1) and the average $\langle \cos \theta \rangle$ is given by

$$\langle \cos \theta \rangle = \sum_\theta n(\theta) \cos \theta \int_0^\infty R(\hat{m} \cdot \hat{n}, \tau)\, d\tau \tag{4}$$

where the sum goes over all angles between consecutive jumps.

The frequency-dependent tracer diffusion tensor is defined in the Green–Kubo formalism as

$$\mathbf{D}_t(\omega) = \mathrm{Re}\left(\int_0^\infty \langle \boldsymbol{v}(0)\boldsymbol{v}(t)\rangle\, e^{-i\omega t}\, dt\right) \tag{5}$$

where Re denotes the real part, $\boldsymbol{v}(t)$ is the velocity of a given tracer particle at time t, and $\langle \ldots \rangle$ denotes an average over all realisations of the hopping process with the proper probability measure. In the limit $\omega \to 0$ the equivalence of (5) to the usual Einstein relation

$$\mathbf{D}_t = \lim_{t\to\infty}\left(\frac{1}{2t}\langle [\boldsymbol{r}(t) - \boldsymbol{r}(0)][\boldsymbol{r}(t) - \boldsymbol{r}(0)]\rangle\right) \tag{6}$$

with $\mathbf{D}_t = \mathbf{D}_t(0)$ is easily shown (McQuarrie 1976). If the tracer particle makes jumps $\boldsymbol{\Delta}_i$ at times t_i, where we will assume $t_0 < t_1 < t_2 < \ldots$, its generalised velocity is defined as (Van Beijeren 1982)

$$\boldsymbol{v}(t) = \sum_i \Delta_i \delta(t - t_i). \tag{7}$$

This can be substituted into (5). Then, for $\boldsymbol{v}(0)$ to be non-vanishing one must require $t_0 = 0$. Hence (5) can be rewritten as

$$\mathbf{D}_t(\omega) = \mathrm{Re}\left(\int_0^\infty \left\langle \sum_{i=0}^\infty \boldsymbol{\Delta}_0 \boldsymbol{\Delta}_i \delta(t_0)\delta(t - t_i)\right\rangle e^{-i\omega t}\, dt\right)$$
$$\equiv \sum_{i=1}^\infty \mathbf{D}_t^{(i)}(\omega). \tag{8}$$

Let us first consider the terms in the sum with $i > 0$. We evaluate them by using the assumptions on the stochastic hopping process given above. In particular, the jump vector $\boldsymbol{\Delta}_0$ is not directly correlated with $\boldsymbol{\Delta}_i$, but indirectly through the correlations between $\boldsymbol{\Delta}_0$ and $\boldsymbol{\Delta}_1$, for the first jump at t_1, between $\boldsymbol{\Delta}_1$ and $\boldsymbol{\Delta}_2$, for the second jump at t_2, etc. Hence the average implied by the angular brackets is given for the ith term by the following convolution:

$$\mathbf{D}_t^{(i)}(\omega) = \mathrm{Re}\left(\frac{\nu}{n}\sum_{\hat{n}_0} \boldsymbol{\Delta}_0 \sum_{\hat{n}_1} \ldots \sum_{\hat{n}_i} \int_0^\infty dt \int_0^t dt_{i-1} \ldots\right.$$
$$\times \int_0^{t_2} dt_1 R(\hat{\boldsymbol{n}}_0 \cdot \hat{\boldsymbol{n}}_1, t_1) R(\hat{\boldsymbol{n}}_1 \cdot \hat{\boldsymbol{n}}_2, t_2 - t_1)$$
$$\left.\times \ldots \times R(\hat{\boldsymbol{n}}_{i-1} \cdot \boldsymbol{n}_i, t - t_i)\boldsymbol{\Delta}_i\, e^{-i\omega t}\right). \tag{9}$$

Here ν is the average jump frequency and n is the total number of allowed jump directions (which need not be the same as the coordination number z, cf. the honeycomb or diamond lattice). Next we introduce the quantity

$$r(\omega) = \sum_{\theta} n(\theta) \cos\theta \int_0^\infty R(\cos\theta, \tau)\, \mathrm{e}^{-\mathrm{i}\omega\tau}\, \mathrm{d}\tau. \tag{10}$$

The $(i-1)$-fold convolution in (9) is a product in the Fourier domain. Also the sum over $\hat{\boldsymbol{n}}_i$ can be simplified with the aid of the conditions formulated above, namely

$$\sum_{\hat{\boldsymbol{n}}_i} \int_0^\infty R(\hat{\boldsymbol{n}}_{i-1} \cdot \hat{\boldsymbol{n}}_i, \tau)\, \mathrm{e}^{-\mathrm{i}\omega\tau}\, \mathrm{d}\tau \boldsymbol{\Delta}_i = r(\omega)\boldsymbol{\Delta}_{i-1}. \tag{11}$$

After this the sums over $\hat{\boldsymbol{n}}_{i-1}$, $\hat{\boldsymbol{n}}_{i-2}$, etc can be performed successively, and finally $\mathbf{D}_t^{(i)}$ is reduced to $(i > 0)$:

$$\begin{aligned}\mathbf{D}_t^{(i)}(\omega) &= \operatorname{Re}\left(r^i(\omega) \frac{\nu}{n} \sum_{\hat{\boldsymbol{n}}_0} \boldsymbol{\Delta}_0 \boldsymbol{\Delta}_0\right) \\ &= \operatorname{Re}\left(r^i(\omega) \frac{\nu a^2}{d} \mathbf{E}\right)\end{aligned} \tag{12}$$

where d is the dimensionality of the system and $\mathbf{E}$ is the unit tensor in $\mathbf{R}^d$.

The term in (8) with $i = 0$ requires some special attention. It is understood most easily by defining the δ-function as the limit of a step function:

$$\delta(t) = \lim_{\varepsilon \to 0} \left[\frac{1}{\varepsilon} \theta\left(\frac{\varepsilon}{2} - |t|\right)\right]$$

with $\theta(x) = 1$ for $x \geqslant 0$ and $\theta(x) = 0$ for $x < 0$. Inserting this into (8) and interchanging the limit $\varepsilon \to 0$ with the time integral, one obtains

$$\begin{aligned}\mathbf{D}_t^{(0)}(\omega) &= \sum_{\hat{\boldsymbol{n}}_0} \int_0^\infty \langle \boldsymbol{\Delta}_0 \boldsymbol{\Delta}_0 \delta(t_0) \delta(t - t_0)\rangle\, \mathrm{d}t \\ &= \frac{\nu}{2n} \sum_{\hat{\boldsymbol{n}}_0} \boldsymbol{\Delta}_0 \boldsymbol{\Delta}_0 = \frac{\nu}{2d} a^2 \mathbf{E}.\end{aligned} \tag{13}$$

Substitution of (12) and (13) into (8) yields the result

$$\mathbf{D}_t(\omega) = \operatorname{Re}\left(\frac{\nu a^2}{2d} \frac{1 + r(\omega)}{1 - r(\omega)} \mathbf{E}\right). \tag{14}$$

For the uncorrelated random walk only the contribution (13) would be different from zero and one would have

$$\mathbf{D}_t^{\mathrm{unc}}(\omega) = \frac{\nu a^2}{2d} \mathbf{E} \tag{15}$$

independently of the form of the waiting-time distribution $R(\tau)$ (which may not depend on θ in this case), as is well known (Tunaley 1974). The frequency-dependent correlation factor can now be defined as the ratio between $\mathbf{D}_t(\omega)$ and $\mathbf{D}_t^{unc}(\omega)$. It has the form

$$f(\omega) = \mathrm{Re}\left(\frac{1 + r(\omega)}{1 - r(\omega)}\right). \tag{16}$$

Indeed, for $\omega = 0$ this reduces to (1), as can be seen by comparing (4) and (10).

In this section we have derived the correlation factor f, equation (1), and its frequency-dependent generalisation $f(\omega)$, equation (16), by considering the velocity autocorrelation function. We point out that there exists already a much more general description of the hopping process under consideration. The conditional probabilities of finding the tracer particle at site l at time t for given initial conditions were derived from the waiting-time distribution for jumps of the tracer particle where a memory to the preceding step was retained (Kehr *et al* 1981). This formulation yields the frequency- and wave-vector dependent response, and in the limit of long wavelengths again equations (1) or (16). However, the calculations involved are rather lengthy, whereas the derivation presented above leads quite directly to these expressions.

3. Application to self-diffusion in lattice gases with small vacancy concentrations

Lattice gases with very small concentrations of empty sites are the prototype examples for the application of this theory. On the one hand, the assumption that a one-step memory is sufficient to describe the random walk of a tagged particle becomes correct in the limit of infinitesimal vacancy concentration. On the other hand, since the motion of the tracer particle is generated by the vacancies, which form a very dilute gas, the pertinent quantities can be deduced from the (uncorrelated) random walk of these vacancies.

The simplest example to illustrate the result of the last section is the one-dimensional infinite chain in the limit of infinitesimal vacancy concentration. A tagged particle jumps only when it exchanges with a vacancy. It is usual to designate by Γ the hopping rate of the vacancy. The average jump rate ν which appears e.g. in equation (14) must then be identified with $2\Gamma c_v$ where c_v is the vacancy concentration and $c_v \ll 1$ is assumed. The waiting-time distribution for the next exchange of the tagged particle with this vacancy is identical with the probability density of the first return of the vacancy to its position before the first jump took place. The quantity $r(\omega)$ is then minus one (jump in reverse direction) times the one-sided Fourier transform of the waiting-time distribution. Its form is well known (Van Beijeren *et al* 1983), and $r(\omega)$ reads

$$r(\omega) = \frac{(\mathrm{i}\omega/2\Gamma)^{1/2} - (2 + \mathrm{i}\omega/2\Gamma)^{1/2}}{(\mathrm{i}\omega/2\Gamma)^{1/2} + (2 + \mathrm{i}\omega/2\Gamma)^{1/2}}. \tag{17}$$

Hence the correlation factor assumes the form

$$f(\omega) = \mathrm{Re}\left(\frac{\mathrm{i}\omega}{4\Gamma + \mathrm{i}\omega}\right)^{1/2}. \tag{18}$$

It vanishes in the limit $\omega \to 0$, corresponding to the fact that the tracer diffusion coefficient vanishes for the one-dimensional chain. It is easy to deduce the asymptotic $t^{1/2}$ behaviour of the mean-square displacement from the expression given above (Van Beijeren *et al* 1983). We return to the long-time behaviour of the velocity autocorrelation function in the next section.

One of the difficulties we referred to above becomes immediately apparent in this case: the average waiting time, which is identical to the average time of first return of the vacancy to its position before the initial jump, is divergent, hence the condition (3) is violated. The same holds true in two dimensions. This problem can be resolved as follows: if c_v is the concentration of vacancies (one must require $c_v \ll$) 1 and Γ is the average jump frequency of a single vacancy, then on the timescale $(c_v\Gamma)^{-1}$ exchanges of a given particle with a different vacancy than the one that performed the initial jump become likely. So on this timescale the waiting-time distribution becomes damped and especially the average waiting time between exchanges with *arbitrary* vacancies assumes the value $(2c_v\Gamma)^{-1}$. However, the directions of jumps of the tagged particle due to exchanges with other vacancies are completely uncorrelated to the direction of the initial jump (at least to leading order in c_v), hence these jumps do not contribute to the velocity autocorrelation function. They do, however, put in jeopardy our condition that all correlations between jumps can be specified by giving the correlations between subsequent jumps (the one-step memory assumption), because jumps that are due to exchanges with *the same* vacancy do remain correlated to each other, no matter how many exchanges of the tagged particle with other vacancies have occurred in the mean time. Yet this interference of other vacancies after long times causes no real problem, as on the relevant timescale $(c_v\Gamma)^{-1}$ the resulting displacement of the tagged particle leaves the first return probabilities of the initial vacancy unchanged, again to leading order in c_v. Hence we can still treat the chain of *correlated jumps*, which are due to exchanges with the same vacancy with which the initial jump took place, as though the tagged particle would never jump at intermediate instants of time. Although the resulting distribution for the waiting times between *subsequent correlated jumps* has a divergent average waiting time, yet the jump frequency for the initial jump derives from the stationary distribution of vacancies and has the obvious value $2c_v\Gamma$.

In two or more dimensions we require the waiting-time distribution $R(\hat{\boldsymbol{m}} \cdot \hat{\boldsymbol{n}}, t)$ for a jump of the tagged particle at time t in direction $\hat{\boldsymbol{m}}$ when it performed the first jump at time 0 in direction $\hat{\boldsymbol{n}}$. This quantity is identical to the probability density $R(0, t, -\hat{\boldsymbol{m}}|0, 0, -\hat{\boldsymbol{n}})$ for the event that the first passage to the origin of a vacancy, starting at $-\hat{\boldsymbol{n}}a$ at time 0, occurs at time t through a jump from the site $\hat{\boldsymbol{m}}a$ to the origin. It is given by the following expression:

$$R(0, t, -\hat{\boldsymbol{m}}|0, 0, -\hat{\boldsymbol{n}}) = \Gamma\left[G(\hat{\boldsymbol{m}}a, t|-\hat{\boldsymbol{n}}a, 0) - \int_0^t G(\hat{\boldsymbol{m}}a, t|0, t')F(0, t'|-\hat{\boldsymbol{n}}, 0)\,\mathrm{d}t'\right]. \tag{19}$$

The quantity $G(\hat{\boldsymbol{m}}a, t|-\hat{\boldsymbol{n}}a, 0)$ is the Green function for diffusion of the vacancy on the lattice, i.e. the probability of finding it at the site $\hat{\boldsymbol{m}}a$ at time t, when it was at site $-\hat{\boldsymbol{n}}a$ at $t = 0$. The second term on the right-hand side of (19) subtracts the contributions to $G(\hat{\boldsymbol{m}}a, t|-\hat{\boldsymbol{n}}a, 0)$ from random walks passing through the origin at some intermediate time t'. The probability density $F(0, t'|-\hat{\boldsymbol{n}}, 0)$ for first passage to the origin at time t' when the vacancy was at $-\hat{\boldsymbol{n}}a$ at $t = 0$ can be expressed in terms of the Green functions. In the Fourier domain, and for different start and final sites, the following well known relation holds:

$$F(0, \mathrm{i}\omega|-\hat{\boldsymbol{n}}) = \frac{G(0, \mathrm{i}\omega|-\hat{\boldsymbol{n}}a)}{G(0, \mathrm{i}\omega|0)}. \tag{20}$$

Using this relation in (19) we obtain

$$R(\hat{\boldsymbol{m}} \cdot \hat{\boldsymbol{n}}, \mathrm{i}\omega) = G(\hat{\boldsymbol{m}}a, \mathrm{i}\omega|-\hat{\boldsymbol{n}}a) - \frac{G(\hat{\boldsymbol{m}}a, \mathrm{i}\omega|0)G(0, \mathrm{i}\omega|-\hat{\boldsymbol{n}}a)}{G(0, \mathrm{i}\omega|0)}. \tag{21}$$

In the standard treatment (Montet 1973, Koiwa and Ishioka 1983) only the first term on the right-hand side of (21) is used. The static Green functions diverge for $d = 1$ and 2, corresponding to the infinite number of visits to any site. It is easy to see that the subtraction terms in (21) eliminate these divergences. They also cancel each other in the combination in which they enter into $\langle\cos\theta\rangle$, cf. (4). Hence the standard treatment is justified in the case of dimensionalities one and two.

A correct treatment was given by Benoist *et al* (1977). They set up a master equation for the motion of the vacancy on the lattice, together with a sink term at the origin. Since the sink term does not allow a second escape of the vacancy from the origin, the solution represents the first return to the origin. The final expressions for the time integrals over these waiting-time distributions agree with (21) including the subtraction terms. Also Sholl (1981) derived the subtraction terms by pointing out their necessity and by requiring proper normalisation of the sum of the weights.

Another type of difficulty becomes manifest in three dimensions. It is connected with the finite probability of a vacancy to escape to infinity in infinite crystals. One vacancy promotes a tracer atom only a few times (e.g. only about 1.345 times on the average in the FCC lattice (Koiwa 1978) and then disappears. Hence other vacancies have to effect the diffusion process, but the motion of the tracer induced by different vacancies can not be correlated in the limit $c_v \ll 1$. Bardeen and Herring (1952) were aware of this problem in their pioneering work on the correlation factor. Explicit analyses have been given by Kidson (1978) and Koiwa (1978). We will show that our derivation of the correlation factor from the velocity autocorrelation function allows the above complication to be included in a simple way. We want to substitute the waiting-time distribution $R(\hat{\boldsymbol{m}}\,.\,\hat{\boldsymbol{n}}, t)$ by the probability density for first return of the vacancy to the origin, $R(0, t, -\hat{\boldsymbol{m}}|0, 0, -\hat{\boldsymbol{n}})$, with specified initial $(-\hat{\boldsymbol{n}})$ and final $(-\hat{\boldsymbol{m}})$ jump directions. The sum over $\hat{\boldsymbol{m}}$ of these probability densities for first return is no longer normalised to unity, due to the possibility for escape to infinity. Let P be the probability of return to the origin. We write

$$R(0, t, -\hat{\boldsymbol{m}}|0, 0, -\hat{\boldsymbol{n}}) = PR_r(0, t, -\hat{\boldsymbol{m}}|0, 0, -\hat{\boldsymbol{n}}; R) \tag{22}$$

where R_r is the probability density of return under the condition that a return actually occurs. As in the one- and two-dimensional cases the $D_t^{(i)}$ in (9) count the contributions to the velocity autocorrelation function resulting from i subsequent exchanges between the tracer particle and the *same* vacancy, disregarding possible exchanges with other vacancies at intermediate times, hence in each term R may be replaced by PR_r. The result (12) will then contain a factor P^i, and the resummation of the whole series gives

$$f(\omega) = \mathrm{Re}\left(\frac{1 + Pr(\omega|R)}{1 - Pr(\omega|R)}\right) \tag{23}$$

where $r(\omega|R)$ is defined similar to (10) with $R_r(0, t, -\hat{\boldsymbol{m}}|0, 0, -\hat{\boldsymbol{n}}; R)$ to be used instead. The analogous result in the static limit was found by Kidson (1978) and Koiwa (1978),

$$f = \frac{1 + P\langle\cos\theta\rangle_R}{1 - P\langle\cos\theta\rangle_R} \tag{24}$$

where $\langle\cos\theta\rangle_R$ is the average angle between two jumps under the condition that the same vacancy returned. Evidently

$$P\langle\cos\theta\rangle_R = \langle\cos\theta\rangle$$

or, in the frequency-dependent generalisation, $Pr(\omega|R) = r(\omega)$ where $\langle\cos\theta\rangle$ or $r(\omega)$ are calculated with weights whose sum is P. As we have done in connection with the two-dimensional case, one can relate $R(0, t, -\hat{m}|0, 0, -\hat{n})$ to the Green function $G(\hat{m}a, t|-\hat{n}a, 0)$, including the proper subtraction term (20). In the static limit, the weights are then normalised to P. The subtraction terms in (21) can be omitted again in the calculation of $\langle\cos\theta\rangle$ since they yield vanishing contributions.

In the case that not all jump directions are equivalent, for example for an anisotropic lattice, or in the case that jumps to further neighbours may occur, the correlation factor has to be generalised to a tensor. This is worked out in an Appendix.

4. Long-time tails

In the one-dimensional lattice gas with small vacancy concentration, the velocity autocorrelation function of tracer particles decays in proportion to $t^{-3/2}$, as has been shown in the last section. One expects on general grounds that the velocity autocorrelation function of a tagged particle in the type of hopping models discussed above decays as $t^{-(d/2+1)}$ for large time in an infinite d-dimensional system. This result follows for instance from mode-coupling theory (Van Beijeren 1984) and it can also be illustrated by the theory developed above.

To explain this we consider the hopping model at infinitesimal vacancy concentration on a d-dimensional simple cubic lattice and concentrate on the quantity $r(\omega)$. Without loss of generality we may restrict ourselves to the case that $\boldsymbol{\Delta}_0$ is directed in the positive x-direction and choose the origin of our coordinate system at the position of the tracer particle just after the first jump. From (10) it follows that the only non-vanishing contributions to $r(\omega)$ come from walks where the vacancy returns to the tracer particle from the x-direction, since otherwise $\cos\theta = 0$. For a first return from the positive x-direction, however, it is required that the walk passes through the hyperplane $x = 0$. But, as soon as the vacancy enters this hyperplane before finishing its first return, it has the same probability to finish its first return from the positive as from the negative x-direction, because of reflection symmetry. Hence all non-vanishing contributions to $r(\omega)$ result from returns from the negative x-direction in which the vacancy has never entered the plane $x = 0$ before (Aizenman 1983). Further, observe that a random walk with a time-independent jump rate Γ on a simple cubic lattice may be considered as a superposition of d independent one-dimensional random walks in the main lattice directions with the same jump rate. Hence the only non-vanishing contributions to $R(\cos\theta, \tau)$ require $\cos\theta = -1$ and are found as the product of minus the first return probability in the x-direction and the $(d-1)$th power of the probability that a one-dimensional random walk starting at the origin at $t = 0$ will be at the origin again at time t. The first return probability for large t is of the form (Feller 1967)

$$F(t) \sim 4\pi\Gamma(4\pi\Gamma t)^{-3/2} \tag{25}$$

whereas the probability of a one-dimensional random walk for being at the origin at time t is given by (Feller 1967)

$$G(t) \sim (4\pi\Gamma t)^{-1/2}. \tag{26}$$

Hence it follows that the small-ω behaviour of $r(\omega)$ is of the form

$$r(\omega) = r_0 - \frac{(-\mathrm{i}\omega/4\pi\Gamma)^{d/2} p(d, \omega)}{\Gamma(d/2+1)} \tag{27}$$

where $p(d, \omega)$ equals $i\pi$ for d odd and is given as

$$p(d, \omega) = \log(i\omega/\Gamma)$$

for d even. The quantity r_0 is an as yet undetermined constant. Equation (14) allows one to relate it to the coefficient of tracer diffusion, with the result

$$r_0 = -\frac{\Gamma a^2/2d - D_t}{\Gamma a^2/2d + D_t} = -\frac{1-f}{1+f}. \tag{28}$$

Combining (27), (28) and (14) and performing an inverse Fourier transform one finds an asymptotic long-time behaviour for the velocity autocorrelation function of the tracer particle in the form

$$\langle v(0)v(t)\rangle \sim -(1-c)\frac{\Gamma a^2}{2t}(4\pi\Gamma t)^{-d/2}(1+f)^2\mathbf{E} \tag{29}$$

where again c is the concentration of the lattice gas. This result agrees with that of mode-coupling theory (Van Beijeren 1984).

Appendix. Inequivalent jumps

The generalisation of the correlation factor to anisotropic models can be done in the following way. Let ν_μ be the frequency with which jumps $\mathbf{\Delta}_\mu$ occur and suppose one can define a tensorial matrix $\mathbf{R}$ with components

$$\mathbf{R}_{\lambda\mu}(\omega) = \int_0^\infty R(\mathbf{\Delta}_\mu, t_0 + \tau|\mathbf{\Delta}_\lambda, t_0)\hat{\boldsymbol{n}}_\lambda\hat{\boldsymbol{n}}_\mu\, e^{-i\omega\tau}\, d\tau \tag{A1}$$

where $R(\mathbf{\Delta}_\mu, t_0 + \tau|\mathbf{\Delta}_\lambda, t_0)$ is the probability density that a jump with jump vector $\mathbf{\Delta}_\lambda$ at time t_0 is followed by a jump with jump vector $\mathbf{\Delta}_\mu$ at time $t_0 + \tau$, and we assumed again that this quantity is independent of t_0. Define a matrix multiplication through $(\mathbf{A}\cdot\mathbf{B})_{\lambda\mu} = \Sigma_\nu \mathbf{A}_{\lambda\nu} . \mathbf{B}_{\nu\mu}$, where the dot, as usual, denotes a contraction in $\mathbf{R}^d$. Then the tracer diffusion tensor is given by

$$\mathbf{D}_t(\omega) = \mathrm{Re}\left(\sum_\lambda \frac{\nu_\lambda}{2}\mathbf{\Delta}_\lambda \sum_\mu \{(\mathbf{E} + \mathbf{R}(\omega))\cdot(\mathbf{E} - \mathbf{R}(\omega))^{-1}\}\cdot\mathbf{\Delta}_\mu\right) \tag{A2}$$

where the unit matrix $\mathbf{E}$ is defined through $\mathbf{E}_{\lambda\mu} = \delta_{\lambda\mu}\mathbf{E}$. The derivation of (A2) is completely analogous to that of (14). The tensor $(\mathbf{E} + \mathbf{R}(\omega))\cdot(\mathbf{E} - \mathbf{R}(\omega))^{-1}$ may be interpreted as a frequency-dependent correlation factor; for $\mathbf{R}(\omega) = 0$ one recovers the result for an uncorrelated random walk. For isotropic systems the rank nd of the tensor $\mathbf{R}$ can be reduced immediately to n. Depending on the symmetries among jump directions it may be possible to reduce its rank in the $\lambda\mu$ variables to the number of inequivalent types of jump. In the limit $\omega \to 0$ (A2) encompasses the results of Howard (1966).

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