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# Energy transfer as a random walk on regular lattices

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In this paper we study the incoherent energy transfer in molecular crystals, where the intermolecular interactions are due to electrostatic forces. We analyze the random walk of the excitation both analytically and numerically and we take into account the occurence of long-range transfer steps. For five lattices (simple-cubic, body-centered-cubic, face-centered-cubic, diamond, and a sparse-cubic lattice) we present the average number $M_n$ of returns to the origin and the mean number $S_n$ of distinct sites visited on an $n$-step walk, where the steps are due to different multipolar interactions. The computations are carried out using both simulation and matrix inversion methods and they are checked against analytical asymptotic forms. We give the coefficients of these analytical expressions obtained from the first four terms in the expansion of the generating functions for nearest-neighbor walks. The results obtained behave smoothly with respect to changes in the range of the interaction and in the coordination number of the lattice (number of nearest neighbors). This allows us to use the continuous description of the random walk in terms of a diffusion model to obtain convenient semiquantitative expressions for $M_n$ and $S_n$ for different lattices. Since the methods presented vary greatly in their degree of sophistication, we are also able to demonstrate the advantages and drawbacks of the different approaches under realistic conditions.

## I. INTRODUCTION

Problems involving random-walk models arise in many fields which range from solid state physics to chemistry and to biology.[1] An important area of applications is the incoherent energy transfer in ordered and in disordered materials; here migration concepts have been proven to be useful in the description of the dynamics of the electronic and vibronic energy transfer in molecular crystals and among rare ions.[2-21] Particularly noteworthy in this respect is the energy trapping in the photosynthetic unit; starting with Förster,[22,23] photosynthesis was repeatedly mentioned as a central field of interest.[24-30]

A prevailing feature of the microscopic energy transfer from site to site is that in many cases electrostatic forces are involved. As shown by Förster[22] and by Dexter[31] these mechanisms lead to power law dependences on the distance between the sites which take part in the individual transfer steps. Due to the long range of the electrostatic potentials long range transfer steps are also possible. A realistic description of the microscopic situation has to consider also random walks with longer range than nearest-neighbor steps.[10,32,33] In this article we analyze the influence of these interactions on basic quantities which characterize the random walk: The probability of returns to the origin and the mean number of distinct sites visited in $n$-step walks.

A major advance in the study of the analytical properties of these basic quantities was the systematic use of the generating-functions formalism by Montroll and Weiss[26,34,35] and Joyce.[36-39] Using this approach the connection between the nearest-neighbor random walks on cubic lattices and the Watson integrals[40] was established. Also the average number of different sites visited and the mean number of returns to the origin are readily expressed in terms of the generating functions for these random walks.

The generating functions, however, are given as relatively complex integrals. This renders their use awkward when more realistic situations must be accounted for. As emphasized already, the transfer steps are not necessarily restricted to nearest neighbors[32,33] and the systems encountered in applications seldom have cubic symmetry. For these situations the generating functions become increasingly complex. Also the results which may be extracted from them by analytical methods depend on their specific form in each particular case.[36-39] We recall that each of the three Watson integrals was determined by a mathematically different procedure (they correspond to random walks on the simple-cubic, body-centered-cubic, and face-centered-cubic lattices).[1,40]

A unified, general way to proceed is to use numerical methods, either to determine the generating functions, or to establish *directly* the values of the quantities of interest for the random walks. Especially, direct numerical procedures (simulation or matrix methods) have the major advantage of being very flexible with respect to changes in the underlying lattice structure and in the interaction laws. In this paper we will present results obtained applying numerical methods to a series of random walks on different lattice types (sc, bcc, fcc, diamond, and a sparse cubic-type lattice), and for transfers due to dipolar and quadrupolar forces, i.e., to interactions which show a power-law dependence on distance.

The purpose of this work is fourfold: First, we present the data calculated numerically for the average number of returns to the origin and for the mean number of distinct sites visited in an $n$-step random walk on the above-mentioned lattices, when steps which are not necessarily restricted to nearest neighbors are also taken

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into account. Next, we assess the accuracy of the numerical procedures by determining the corresponding values for nearest-neighbor walks and by comparing these with results from generating functions.[32-41] The latter are given as asymptotic expansions in (broken) powers of the number of steps. This leads us to consider the higher-order terms in these expansions, since we compare with results obtained using a relatively small number (~100) of steps. For all lattices we present the first few coefficients in the pertinent expansions of the corresponding generating functions; we also establish the relations between functions belonging to different types of lattices. Finally we show the connection between the random walk and diffusion models by obtaining approximate quantitative expressions from the latter.

The paper is structured as follows: In Sec. II we present the generating functions for nearest-neighbor random walks in the diamond (d) and sparse-cubic or edge (e) lattices, and we reformulate them in terms of the generating functions for the face-centered-cubic (fcc) and simple-cubic (sc) lattices. For all five lattice types considered (e, d, sc, bcc, fcc) we give the analytical expressions for the first few terms in the asymptotic expansions of the average number of returns to the origin, $M_n$, and of distinct sites visited, $S_n$, in an $n$-step nearest-neighbor walk. These results are smooth functions of the coordination number (number of nearest neighbors) of each lattice, and they corroborate the approximate, semiquantitative equations which we obtain from a diffusion model of the random walk.

In Sec. III we numerically evaluate the pertinent quantities ($M_n$ and $S_n$) for random walks whose steps are not restricted to nearest-neighbors only, but where the jumping probabilities show power-law dependences on distance; this corresponds to steps mediated by multipolar interactions. We use (a) a simulation routine and (b) a matrix method. We analyze the data in terms of the expansions of Sec. II and we determine the leading coefficients. By evaluating these coefficients also for nearest-neighbor random walks we are able to assess the precision of the numerical procedures employed. Since the matrix method implicitly assumes an absorbing external boundary we derive the dependence of $M_n$ on $n^{-1/2}$ from a diffusion equation with an absorbing boundary. This equation offers an additional check on the accuracy of the numerical data. We conclude this article with a summary of results in Sec. IV.

## II. NEAREST-NEIGHBOR RANDOM WALKS

The technique of the generating functions in the treatment of random walks on Bravais lattices has been applied by Montroll and Weiss[34,35] and explicit results have been obtained by Joyce.[36-39] In Sec. II A we summarize some of the theoretical results and in Sec. II B we compare them with those obtained from a continuous diffusion model.

In doing so we will consider five types of lattices: the simple-cubic (sc), face-centered cubic (fcc), and body-centered-cubic (bcc), the diamond lattice (d), and the lattice obtained from a simple cubic one by adding the median points of the bonds connecting nearest-neighbor lattice sites (Fig. 1). We call the latter an edge lattice and denote it with "e." Evidently the d and e lattices are non-Bravais.

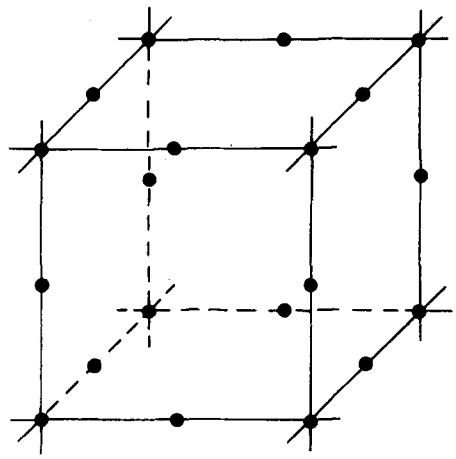

FIG. 1. The edge (edge-centered-cubic) lattice.

In our choice of lattices we were lead by the consideration that many previous results on random walks were obtained for the three cubic lattices[2-4,10,26,32-39]; it is therefore advisable to consider them in order to facilitate the comparison with earlier work. The diamond lattice was included both because many materials crystallize in this form and because its coordination number (i.e., number of nearest neighbors), $Z^d=4$, is lower than those of the cubic lattices: $Z^{sc}=6$, $Z^{bcc}=8$, $Z^{fcc}=12$. As is intuitively evident and as will be quantified in the following, many properties of the random walk are very sensitive to the coordination number. The edge lattice was considered because it represents a more complex structure and it allows to appreciate the ease with which the numerical simulations may be adapted to handle complex problems. Since sites on corners and edges see different environments, the e lattice reflects in part the properties of disordered lattices, where the environments vary from site to site. The e lattice belongs to the sparsely periodic lattices[42,43] and it has an average coordination number of three: $\bar{Z}^e=3$.

### A. Generating functions

Of particular interest are the average number of returns to the origin, $M_n$, and the mean number of different sites, $S_n$, visited during a random walk of $n$ steps. It is convenient to consider the generating functions $S(z)$ and $M(z)$ of $S_n$ and of $M_n$, respectively:

$$S(z)\equiv\sum_{n=0}^{\infty}S_n z^n\,, \tag{2.1}$$

$$M(z)\equiv\sum_{n=0}^{\infty}M_n z^n\,. \tag{2.2}$$

As shown in Ref. 35 for the three cubic lattices, $S(z)$ and $M(z)$ are connected with the generating function $P(\mathbf{r};z)$ of the random walk (see also Refs. 44 and 45)

$$P(\mathbf{r};z)=\frac{1}{(2\pi)^3}\iiint_{-\pi}^{\pi}\frac{\exp(-i\mathbf{r}\cdot\mathbf{k})d^3\mathbf{k}}{1-z\lambda(\mathbf{k})}\,, \tag{2.3}$$

through

$$S(z)=[(1-z)^2P(\mathbf{0};z)]^{-1} \tag{2.4}$$

and

$$M(z)=(1-z)^{-1}P(\mathbf{0};z)\ . \tag{2.5}$$

In Eq. (2.3), $\lambda(\mathbf{k})$ is the structure function of the walk. It is given through

$$\lambda(\mathbf{k})=\sum_{\mathbf{r}}p(\mathbf{r})\,e^{i\mathbf{r}\cdot\mathbf{k}}\ , \tag{2.6}$$

where the $p(\mathbf{r})$ are the normalized probabilities of steps with displacement $\mathbf{r}$, and the sum extends over all lattice sites. For simplicity one has assumed each of the lattices considered here to be derived by deleting sites in an sc lattice with lattice constant of unity. For nearest-neighbor walks on the cubic lattices one therefore has

$$\lambda^{\mathrm{sc}}(\mathbf{k})=(c_1+c_2+c_3)/3\ , \tag{2.7a}$$

$$\lambda^{\mathrm{bcc}}(\mathbf{k})=c_1c_2c_3\ , \tag{2.7b}$$

$$\lambda^{\mathrm{fcc}}(\mathbf{k})=(c_1c_2+c_2c_3+c_3c_1)/3\ , \tag{2.7c}$$

with $c_i=\cos k_i$.

The evaluation of $P(\mathbf{0};z)$ for the three cubic lattices in terms of standard higher functions has been achieved by Joyce.[36–39] He found

$$P^{\mathrm{sc}}(\mathbf{0};z)=f_1K(f_2)K(f_3)\ , \tag{2.8a}$$

$$P^{\mathrm{bcc}}(\mathbf{0};z)=(4/\pi^2)[K(f_4)]^2\ , \tag{2.8b}$$

$$P^{\mathrm{fcc}}(\mathbf{0};z)=f_5K(f_6)K(f_7)\ , \tag{2.8c}$$

where $K$ is the elliptic integral of the first kind[46] and $f_i$ are algebraic functions of $z$. For their explicit form the reader is referred to Refs. 36–39.

For non-Bravais lattices the random walk is described by several generating functions and the situation becomes more complex. For the diamond lattice, with two lattice points per unit cell one has two generating functions $P(\mathbf{r};z)$ and $Q(\mathbf{r};z)$. For nearest-neighbor random walks they have the form[47]

$$P^d(\mathbf{r};z)=\frac{1}{(2\pi)^3}\iiint_{-\pi}^{\pi}\frac{\exp(-i\mathbf{r}\cdot\mathbf{k})d^3\mathbf{k}}{1-z^2|\lambda^d(\mathbf{k})|^2}\ , \tag{2.9}$$

$$Q^d(\mathbf{r};z)=\frac{1}{(2\pi)^3}\iiint_{-\pi}^{\pi}\frac{z\lambda^d(\mathbf{k})\exp(-i\mathbf{r}\cdot\mathbf{k})d^3\mathbf{k}}{1-z^2|\lambda^d(\mathbf{k})|^2}\ , \tag{2.10}$$

[see Eqs. (A6a) and (A6b) of Appendix A], with $\lambda^d(\mathbf{k})$ given by the following expression, analogous to Eq. (2.6):

$$\lambda^d(\mathbf{k})=\tfrac{1}{2}[\cos(k_1+k_2)\,e^{ik_3}+\cos(k_1-k_2)\,e^{-ik_3}]\ . \tag{2.11}$$

As shown in Appendix A, the average number of returns to the origin $M_n$ and the average number of distinct sites visited $S_n$, again follow from Eqs. (2.4) and (2.5). Thus we will only be concerned with $P^d(\mathbf{r};z)$, Eq. (2.9), and not with $Q^d(\mathbf{r};z)$, Eq. (2.10). One verifies readily that $\lambda^d(\mathbf{k})$ is given by

$$|\lambda^d(\mathbf{k})|^2=\tfrac{1}{4}[1+3\lambda^{\mathrm{fcc}}(2\mathbf{k})]\ , \tag{2.12}$$

either from Eq. (2.11) or by observing that every second nearest-neighbor step on a diamond lattice is a step on an fcc lattice. Therefore,

$$P^d(\mathbf{0};z)=\frac{1}{(2\pi)^3}\iiint_{-\pi}^{\pi}\frac{d^3\mathbf{k}}{1-(z^2/4)[1+3\lambda^{\mathrm{fcc}}(2\mathbf{k})]}$$

$$=P^{\mathrm{fcc}}\left(\mathbf{0};\frac{3z^2}{4-z^2}\right)/(1-z^2/4)\ , \tag{2.13}$$

where we have used the periodicity of the integrand to revert from $\lambda^{\mathrm{fcc}}(2\mathbf{k})$ to $\lambda^{\mathrm{fcc}}(\mathbf{k})$. Thus $M_n^d$ and $S_n^d$ are obtainable from $P^{\mathrm{fcc}}(\mathbf{0};z)$.

For the edge lattice the generating function $P^{\mathrm{e}}(\mathbf{r};z)$ for nearest-neighbor walks which start at the origin is [see Eq. (A33)]

$$P^{\mathrm{e}}(\mathbf{r};z)=\frac{1}{(2\pi)^3}\iiint_{-\pi}^{\pi}\frac{e^{-i\mathbf{k}\cdot\mathbf{r}}d^3\mathbf{k}}{[1-(z^2/3)(\cos^2k_1+\cos^2k_2+\cos^2k_3)]}\ , \tag{2.14}$$

and thus, by remarking that

$$\tfrac{1}{3}(\cos^2k_1+\cos^2k_2+\cos^2k_3)=\tfrac{1}{2}[1+\lambda^{\mathrm{sc}}(2\mathbf{k})]\ , \tag{2.15}$$

one obtains

$$P^{\mathrm{e}}(\mathbf{0};z)=\frac{1}{(2\pi)^3}\iiint_{-\pi}^{\pi}\frac{d^3\mathbf{k}}{\left(1-\frac{z^2}{2}\right)-\frac{z^2}{2}\lambda^{\mathrm{sc}}(2\mathbf{k})}$$

$$=P^{\mathrm{sc}}\left(\mathbf{0};\frac{z^2}{2-z^2}\right)/(1-z^2/2)\ . \tag{2.16}$$

The last relation permits the straightforward evaluation of $P^{\mathrm{e}}(\mathbf{0};z)$ from $P^{\mathrm{sc}}(\mathbf{0};z)$.

We now turn our attention to the determination of $M_n$ and $S_n$ from the known properties of the generating functions $P(\mathbf{0};z)$. Of central interest are the following expansions of $P(\mathbf{0};z)$ around the main singularity $z=1$[36–39]:

$$P(\mathbf{0};z)=u_0-u_1(1-z)^{1/2}$$

$$+u_2(1-z)-u_3(1-z)^{3/2}+\cdots\ . \tag{2.17}$$

For $M(z)$, given by Eq. (2.5) or by Eq. (A25), one has therefore,

$$M(z)=u_0(1-z)^{-1}$$

$$-u_1(1-z)^{-1/2}+u_2-u_3(1-z)^{1/2}+\cdots\ . \tag{2.18}$$

From this equation one obtains asymptotically for large $n$,

$$M_n=u_0-(u_1/\sqrt{\pi})n^{-1/2}+O(n^{-3/2})\ , \tag{2.19}$$

since the other singularities on the unit circle do not influence $M_n$ to this order.

Consider now the case of the e lattice and of random walks which start from a site on an edge. According to Eq. (A39b), $M(z)$ is given by

$$M(z)=\tfrac{2}{3}(1-z)^{-1}+\tfrac{1}{3}(1-z)^{-1}P(\mathbf{0};z)\ , \tag{2.20}$$

and $M_n$ by

$$M_n=(2+u_0)/3-(u_1/3\sqrt{\pi})n^{-1/2}+O(n^{-3/2})\ . \tag{2.21}$$

We proceed to discuss the average number of distinct lattice sites visited in a random walk of $n$ steps $S_n$ as derived from the generating function $S(z)$. For random walks on the sc, bcc, fcc, and d lattices [Eqs. (2.4) and (A22)] the expansion of Eq. (2.17) to order $n^{-1/2}$ yields[35]

$$S_n = u_0^{-1} n + (2u_1 u_0^{-2}/\sqrt{\pi})n^{1/2} + (u_0^2 - u_2 u_0 + u_1^2)u_0^{-3} + O(n^{-1/2}) \ . \tag{2.22}$$

For the e lattice and for random walks starting on the main sc sublattice one has [Eq. (A47)]

$$S(z) = (1-z)^{-2}(1+z)^{-1}\left[\frac{1}{P(0;z)} + \frac{3z}{2+P(0;z)}\right] \ . \tag{2.23}$$

We take note of the following two relationships,

$$(1+z)P(0;z) = [2-(1-z)]P(0;z) = 2u_0 - 2u_1(1-z)^{1/2} + (2u_2 - u_0)(1-z) - (2u_3 - u_1)(1-z)^{3/2} + \cdots \ , \tag{2.24a}$$

$$(1+z)[2+P(0;z)]/3z = \tfrac{1}{3}[2u_0 + 4 - 2u_1(1-z)^{1/2} + (2u_2 + u_0 + 2)(1-z) - (2u_3 + u_1)(1-z)^{3/2} + \cdots] \ , \tag{2.24b}$$

and we obtain $S_n$ using Eqs. (2.22) and (2.24),

$$S_n = \left(\frac{1}{2u_0} + \frac{3}{2u_0+4}\right)n + \left[\frac{u_1}{2u_0^2} + \frac{6u_1}{(2u_0+4)^2}\right]2\sqrt{\frac{n}{\pi}} + O(1) \ . \tag{2.25}$$

For random walks starting on an edge site of the e lattice one similarly obtains $S_n$ from $\tilde{S}(z)$ given by Eq. (A54). This alternate $S_n$ agrees with Eq. (2.25) to order unity; evidently, for large $n$ the number of sites visited does not depend much on the starting point.

For nearest-neighbor random walks on the lattices considered here (sc, bcc, fcc, d, and e) it is thus sufficient to know the coefficients $u_i$ $(i=0, 1, 2)$ in the expansion of $P(0;z)$ in order to be able to calculate $M_n$ to order $n^{-3/2}$ and $S_n$ to order unity. Indeed, since random walks on the diamond and on the edge lattice are directly connected to the generating functions for random walks on the fcc and the sc lattices, respectively, [Eqs. (2.13) and (2.16) together with Eq. (A38b)] the coefficients $u_i$ for only the three cubic lattices are needed.

According to the development of Joyce, one has for the expansion of $P(0;z)$ for the cubic lattices,[36-39]

$$P^{sc}(0;z) = u_0^{sc} - (3\sqrt{3}/\sqrt{2}\pi)(1-z)^{1/2} + (9/16)(u_0^{sc} + 6/\pi^2 u_0^{sc})(1-z) - (9\sqrt{3}/4\sqrt{2}\pi)(1-z)^{3/2} \ , \tag{2.26a}$$

$$P^{bcc}(0;z) = u_0^{bcc} - (2\sqrt{2}/\pi)(1-z)^{1/2} + (u_0^{bcc}/2 + 2/\pi^2 u_0^{bcc})(1-z) - (3/\sqrt{2}\pi)(1-z)^{3/2} \ , \tag{2.26b}$$

$$P^{fcc}(0;z) = u_0^{fcc} - (3\sqrt{3}/2\pi)(1-z)^{1/2} + (u_0^{fcc}/2 + 27/16\pi^2 u_0^{fcc})(1-z) - (9\sqrt{3}/8\pi)(1-z)^{3/2} \ . \tag{2.26c}$$

For the diamond and e lattices one derives from Eqs. (2.13) and (2.16),

$$P^{d}(0;z) = u_0^{d} - (4\sqrt{2}/\pi)(1-z)^{1/2} + (2u_0^{d}/3 + 8/\pi^2 u_0^{d})(1-z) - (3\sqrt{2}/\pi)(1-z)^{3/2} \ , \tag{2.26d}$$

$$P^{e}(0;z) = u_0^{e} - (6\sqrt{6}/\pi)(1-z)^{1/2} + (u_0^{e}/4 + 54/\pi^2 u_0^{e})(1-z) + (3\sqrt{3}/\sqrt{2}\pi)(1-z)^{3/2} \ . \tag{2.26e}$$

For the cubic lattices the values of $u_0$ have been established by Watson[40]:

$$u_0^{sc} = 1.516\,386 \ , \tag{2.27a}$$

$$u_0^{bcc} = 1.393\,204 \ , \tag{2.27b}$$

$$u_0^{fcc} = 1.344\,661 \ , \tag{2.27c}$$

whereas for the diamond and e lattices one obtains with the aid of Eqs. (2.13) and (2.16):

$$u_0^{d} = \tfrac{4}{3}u_0^{fcc} \ , \tag{2.28a}$$

$$u_0^{e} = 2u_0^{sc} \ . \tag{2.28b}$$

In Table I the numerical values of the $u_i$ are summarized for all lattice types considered. Using the values of Table I, the expressions for $M_n$ follow from Eqs. (2.19) and (2.21):

$$\begin{aligned} M_n^{e} &= 3.032\,772 - 2.639\,381\, n^{-1/2} + O(n^{-3/2}) \ , \\ &\quad [= 1.677\,591 - 0.879\,793\, n^{-1/2} + O(n^{-3/2}), ] \\ M_n^{d} &= 1.792\,881 - 1.015\,898\, n^{-1/2} + O(n^{-3/2}) \ , \\ M_n^{sc} &= 1.516\,386 - 0.659\,845\, n^{-1/2} + O(n^{-3/2}) \ , \\ M_n^{bcc} &= 1.393\,204 - 0.507\,949\, n^{-1/2} + O(n^{-3/2}) \ , \\ M_n^{fcc} &= 1.344\,661 - 0.466\,581\, n^{-1/2} + O(n^{-3/2}) \ . \end{aligned} \tag{2.29}$$

TABLE I. The first four coefficients $u_i$ in the expansion of the generating function $P(0;z) = \sum_{i=0}^{\infty}(-1)^i u_i (1-z)^{i/2}$, Eq. (2.17), for nearest-neighbor random walks. Presented are the values for five different lattices: edge (e, see text), diamond (d), simple-cubic (sc), body-centered-cubic (bcc), and face-centered-cubic (fcc). The results in parentheses hold for random walks starting at an edge site of the e lattice.

| | $u_0$ | $u_1$ | $u_2$ | $u_3$ |
|---|---|---|---|---|
| e | 3.032 772 | 4.678 180 | 2.562 267 | −1.169 545 |
| | (1.677 591) | (1.559 393) | (0.854 089) | (−0.389 848) |
| d | 1.792 881 | 1.800 632 | 1.647 359 | 1.350 474 |
| sc | 1.516 386 | 1.169 545 | 1.078 476 | 0.877 158 |
| bcc | 1.393 204 | 0.900 316 | 0.842 053 | 0.675 237 |
| fcc | 1.344 661 | 0.826 993 | 0.799 485 | 0.620 245 |

Comparing these expressions for different lattice types it is evident that the coefficients vary smoothly with the coordination number. The same behavior turns out to hold for $S_n$, the average number of different sites visited on a random walk over nearest neighbors. The values of $S_n$ are readily computed using Table I and Eqs. (2.22) and (2.25):

$$\begin{aligned} S_n^{e} &= 0.462\,912\, n + 0.599\,574\, n^{1/2} + O(1)\,, \\ S_n^{d} &= 0.557\,762\, n + 0.632\,087\, n^{1/2} + 0.607\,87\,, \\ S_n^{sc} &= 0.659\,463\, n + 0.573\,921\, n^{1/2} + 0.582\,73\,, \\ S_n^{bcc} &= 0.717\,770\, n + 0.523\,384\, n^{1/2} + 0.583\,69\,, \\ S_n^{fcc} &= 0.743\,682\, n + 0.516\,097\, n^{1/2} + 0.582\,81\,. \end{aligned} \tag{2.30}$$

### B. Continuous diffusion model

It may be of interest to realize that many of the qualitative features of the results for the average number of returns to the origin, Eqs. (2.29) may be obtained from a diffusion model of the random walk. Intuitively there is an appealing connection between random walks on discrete lattices and diffusion in continuous media; in fact many properties of the two approaches are equivalent if one is interested in large distances compared to the nearest-neighbor distance and in long times compared to the hopping time.[48,49] However, as has been stressed repeatedly,[19–21,30,50–52] such a correspondence does not necessarily hold if the quantities of interest depend on distances comparable to the lattice constant; in such cases caution is required.

The problem of repeated visits to the *origin* arises evidently from a question formulated for a discrete lattice. We now proceed to show that viewing $M_n$ as the average *time* spent at the origin (instead of the average number of visits) allows us to derive approximate quantitative expressions for $M_n$ from a continuous diffusion model. The diffusion equation in three dimensions is

$$\frac{\partial \Psi}{\partial t} = D\left[\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2}\right]. \tag{2.31}$$

The solution of Eq. (2.31) for an instantaneous source of unit strength at the origin for $t=0$ is[53]

$$\Psi(\mathbf{r}; t) = \Psi(r; t) = e^{-r^2/4Dt}/[8(\pi D t)^{3/2}]\,. \tag{2.32}$$

The connection between a random-walk model and Eq. (2.31) is made by determining the value of the diffusion constant $D$. The mean-squared displacement from the origin $\langle r^2 \rangle$, is obtained from Eq. (2.32),

$$\begin{aligned} \langle r^2 \rangle &= \int_0^\infty 4\pi r^4 \Psi(r; t)\, dr \\ &= \frac{16Dt}{\sqrt{\pi}} \int_0^\infty x^4 e^{-x^2}\, dx = 6Dt\,, \end{aligned} \tag{2.33}$$

hence $D$ is given by $D = \langle r^2 \rangle / 6t$, or $D = \frac{1}{6}(\partial \langle r^2 \rangle / \partial t)$, in the diffusion model. For a nearest-neighbor random walk one verifies readily that after each step of time $\tilde{\tau}$ the mean squared displacement increases with the square of the step length. Since we use as a reference a simple cubic lattice from which sites are deleted, we obtain $D$ in units of the squared lattice constant of the sc lattice: $D^{fcc} = 1/3\tilde{\tau}$; $D^{bcc} = 1/2\tilde{\tau}$; $D^{sc} = 1/6\tilde{\tau}$; $D^{d} = 1/2\tilde{\tau}$; $D^{e} = 1/6\tilde{\tau}$, where $\tilde{\tau}$ is the hopping time.

Consider now the average time spent by the excitation at $\mathbf{r}$, $T(\mathbf{r})$, calculated according to the diffusion model. If we are interested in the average time spent at $\mathbf{r}$ between 0 and $t$, the quantity to be evaluated is

$$T(\mathbf{r}; t) = \int_0^t d\tilde{t}\, \Psi(\mathbf{r}; \tilde{t})\,. \tag{2.34}$$

Thus,

$$\begin{aligned} T(\mathbf{r}; t) &= \frac{1}{(4\pi D)^{3/2}} \int_0^t d\tilde{t}\, e^{-r^2/4D\tilde{t}}\, \tilde{t}^{-3/2} \\ &= \frac{1}{4\pi D r} - \frac{1}{4\pi D r \sqrt{\pi}} \int_0^{r^2/4Dt} e^{-x} x^{-1/2}\, dx\,. \end{aligned} \tag{2.35}$$

For large $t$ we expand the exponential in Eq. (2.35) and obtain

$$\begin{aligned} T(\mathbf{r}; t) &= \frac{1}{4\pi D r} - \frac{1}{4(\pi D)^{3/2}} \sum_{i=0}^{\infty} \frac{(-1)^i}{i!\,(2i+1)} (r^2/4D)^i\, t^{-i-1/2} \\ &= \frac{1}{4\pi D r} - \frac{1}{4(\pi D)^{3/2}} \left( t^{-1/2} - \frac{r^2}{12D} t^{-3/2} + \cdots \right)\,, \end{aligned} \tag{2.36}$$

where in the large parentheses on the right-hand side of Eq. (2.36) only half-integer negative powers of $t$ appear. This agrees with the form of Eq. (2.19) in which only negative half-integer exponents of $n$ contribute to $M_n$ because of the form of $M(z)$ in Eq. (2.18). Consider now the average time $M(t)$ spent in a spherical region of radius $R$ around the origin between the times 0 and $t$:

$$\begin{aligned} M(t) &= \int_0^R 4\pi r^2\, T(r; t)\, dr \\ &= \frac{R^2}{2D} - \frac{R^3}{\sqrt{\pi} D^{3/2}} \sum_{i=0}^{\infty} \frac{(-1)^i (R^2/4D)^i}{i!\,(2i+1)(2i+3)}\, t^{-i-1/2} \\ &= \frac{R^2}{2D} - \frac{R^3}{3\sqrt{\pi} D^{3/2}} t^{-1/2} + \frac{R^5}{60\sqrt{\pi} D^{5/2}} t^{-3/2} - \cdots\,. \end{aligned} \tag{2.37}$$

The right-hand side of Eq. (2.37) is parametrized with respect to $R^2/D$. Setting $R^2/2D$ in each case equal to $u_0$ we obtain the following approximate expressions for $M_n$ from the diffusion model

$$\begin{aligned} M_n^{e} &= 3.032\,772 - 2.81\, n^{-1/2} + 0.85\, n^{-3/2}\,, \\ M_n^{d} &= 1.792\,881 - 1.28\, n^{-1/2} + 0.23\, n^{-3/2}\,, \\ M_n^{sc} &= 1.516\,386 - 0.99\, n^{-1/2} + 0.15\, n^{-3/2}\,, \\ M_n^{bcc} &= 1.393\,204 - 0.87\, n^{-1/2} + 0.12\, n^{-3/2}\,, \\ M_n^{fcc} &= 1.343\,661 - 0.83\, n^{-1/2} + 0.11\, n^{-3/2}\,. \end{aligned} \tag{2.38}$$

Comparing Eqs. (2.29) and (2.38) we see that the quantitative agreement is not accurate but that the expression (2.37) correctly reproduces the qualitative behavior of the correction terms to $u_0$.

From the relation $u_0 = R^2/2D$ we obtain $R$ for the various lattices as $R^{fcc} = 0.669d$; $R^{bcc} = 0.681d$; $R^{sc} = 0.711d$; $R^{d} = 0.773d$; and $R^{e} = 1.005d$ (or $R^{e} = 0.748d$) where $d$ is the nearest-neighbor distance in each lattice. Evidently these values are consistent with our notion that $R$ is the radius of a sphere which defines the "domain" of the origin in the continuum model. Instead of defining $R$ through $u_0$ we might even set $(4\pi/3)R^3$ equal to $\rho^{-1}$, the

reciprocal density of lattice points. The first correction term in (2.37) then becomes equal to

$$-\frac{R^3}{3\sqrt{\pi}D^{3/2}}t^{-1/2}=-\frac{\rho^{-1}}{4\pi\sqrt{\pi}D^{3/2}}t^{-1/2}, \tag{2.39}$$

and this formula reproduces the corresponding terms in Eq. (2.29) *exactly*.

In the next section we will use the exact results Eqs. (2.29) and (2.30) for nearest-neighbor random walks in order to check the accuracy of the different numerical ways to compute $S_n$ and $M_n$, without having to resort to generating functions. This is of importance in view of the fact that numerical methods must be employed in evaluating the $S_n$ and $M_n$ values for random walks whose steps are not restricted to nearest neighbors only. In these cases the use of generating functions turns out to be exceedingly cumbersome, whereas simulation and matrix methods prove to be feasible in the determination of the pertinent quantities.

## III. RANDOM WALKS WITH VARIABLE STEP LENGTH

The use of generating functions in the description of random walks is complex and depends strongly on the detailed analysis of the particular functions. As shown in Sec. II one can express $P(\mathbf{0};z)$ for walks with nearest-neighbor steps in the cubic lattices in terms of elliptic integrals; however, the corresponding information for random walks which are not restricted to nearest-neighbor steps is lacking.

In this section we consider random walks with variable step length. A random-walk problem is characterized by specifying the underlying lattice and the set of probabilities $p(\mathbf{r})$ that the next step of the walk will involve a displacement of $\mathbf{r}$ from the actually occupied position.

The transition rate $w_{mn}$ of an excitation from site $m$ to site $n$ depends on the distance $R_{mn}$ between the sites. For dipolar interactions (these are assumed to govern the energy transfer in photosynthesis[28,29]) $w_{mn}$ is proportional to $R_{mn}^{-6}$ and may be expressed (assuming the rate to be isotropic) as $w_{mn}=(1/\tau)(d/R_{mn})^6$, where $\tau^{-1}$ is the energy transfer rate to a nearest neighbor at distance $d$ (see Ref. 52 for a discussion of the approximations involved). In this case the probabilities $p(\mathbf{r})$ depend on the step length via $p(\mathbf{r})\propto r^{-6}$. If the dipolar interactions are weak other interactions may play an important role. For multipolar interactions one generally has $w_{mn}=1/\tau\times(d/R_{mn})^s$, where $s$ is specified by the microscopic transition law; thus for dipole–quadrupole interactions one has $s=8$ and $p(\mathbf{r})\propto r^{-8}$; for quadrupole–quadrupole interactions $s=10$ and thus $p(\mathbf{r})\propto r^{-10}$.[31]

In the following we set $p(\mathbf{r})\propto r^{-s}$, where $s$ is a measure of the interaction range. The normalized $p(\mathbf{r})$ are

$$p(\mathbf{r})=r^{-s}\Big/\sum_{\mathbf{r}}{}' r^{-s}, \tag{3.1}$$

where the sum extends over all lattice sites $\mathbf{r}$ with the exclusion of the origin. In the limit $s\to\infty$ the probabilities $p(\mathbf{r})$ in Eq. (3.1) revert to those of random walks over nearest neighbors. In this case one has $w_{mn}=\tau^{-1}$ for $R_{mn}=d$, and $w_{mn}=0$ for $R_{mn}\neq d$.

Because of the relatively large values for $s$, $s\geq 6$, the sum in Eq. (3.1) converges rapidly and the variance of the random walk remains finite. Gillis and Weiss have extensively studied random walks with infinite variances.[32] The problem is of extreme interest in one and two dimensions since with an infinite variance one is led to a qualitatively different asymptotic behavior of $S_n$. In three dimensions, however, the qualitative behavior does not change since nearest-neighbor random walks are transient and $S_n\sim n$.[32] In this work we concentrate on the determination of the exact values in the asymptotic expansion of $S_n$ and restrict ourselves to the above mentioned cases of physical interest.

In the preceding section we have employed the generating function formalism. Here we make use of numerical methods. We have the choice either to directly simulate a number of random walks or to perform a matrix inversion of the pertinent master equation.[3,4,25,30,41,54,55] Both methods lead to the determination of coefficients which appear in the expressions for the average number of returns to the origin $M_n$ and for the mean number $S_n$ of different sites visited in a walk of $n$ steps. The advantage of these methods is: firstly, that they are more direct, in that the quantities $M_n$ and $S_n$ are evaluated in a straightforward manner, without having recourse to transformations to and from auxiliary functions; secondly, that they are more flexible so that we can readily exhibit values for $S_n$ and $M_n$ which obtain for more complex (and more realistic) situations like the transfer with variable step length.

Let us consider first the simulation procedure. This technique allows the direct determination of $S_n$ and $M_n$ for each lattice type and for each microscopic transfer law [e.g., Eq. (3.1)]. We have simulated a number of distinct walks (in the order of 5000) on the five lattice types discussed in Sec. II and have determined for each value of $n$ the average number of sites visited during the walk. For $s$ in Eq. (3.1) we have chosen the values 6, 8, and 10, but as a check on the accuracy of our simulation results we have also considered nearest-neighbor random walks ($s=\infty$). These simulations are very rapid and do not consume much computer time: Less than 150 sec CPU were used on the CDC 174 computer for a given lattice type and $s$ value. We applied two different random-number generators, without any significant change in the results. For walks with variable step length we included neighbors up to the 50th shell.

In Fig. 2 we present the results of such a series of random walks on different lattices when the probability of a jump of length $r$ is proportional to $r^{-6}$ (dipole–dipole interaction); this exemplifies the procedure and gives a feeling for the scatter of the data in such computer experiments. Plotted is the average number of different sites $S_n$ visited during the first $n$ steps of the walk. The continuous curve through the computed points is the best fit (least squares) to the expression

$$S_n=a_1n+a_2n^{1/2}+a_3, \tag{3.2}$$

where we adjusted the three parameters $a_1$, $a_2$, and $a_3$. Another representation of these data is given in Fig. 3 where we plotted $dS_n/dn$ for the fcc, sc, d, and e lat-

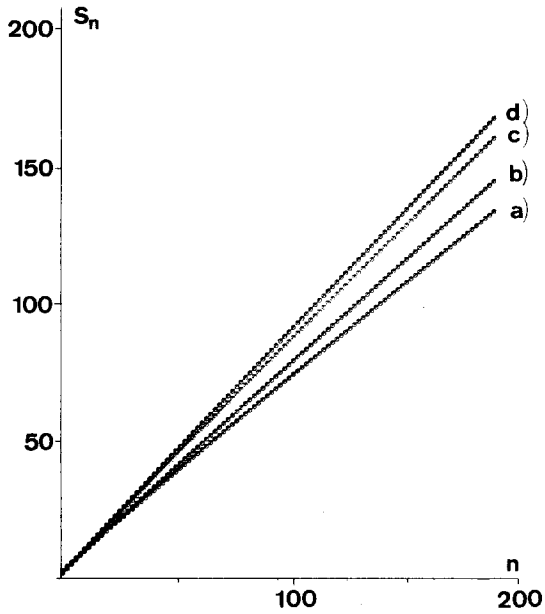


FIG. 2. Average number $S_n$ of different sites visited during a walk of $n$ steps, when the probability of a jump of length $r$ is proportional to $r^{-6}$: (a) edge; (b) diamond; (c) sc; and (d) fcc lattices. The continuous curves correspond to Eq. (3.2).

tices. Again the continuous curve through the data points corresponds to Eq. (3.2).

In Table II we summarize the simulation results, using the parameters $a_i$ $(i=1,2,3)$, for nearest-neighbor random walks $(s=\infty)$ and for random walks mediated by dipolar interactions $(s=6)$. The results for $s=\infty$ may be directly compared to the exact expressions Eqs. (2.30). Whereas $a_1$ agrees with the exact results within two significant digits, the agreement of $a_2$ and $a_3$ is poorer—mostly within the first significant digit only. For $s=6$ we expect the values of $a_1$ to be as accurate as for $s=\infty$. Here we are aware only of the results of Ref. 10 for the sc lattice, where the value 0.795 46 is reported from an approximate evaluation of the integral (2.3); our corresponding $a_1$ value is slightly lower.

We now turn our attention to the second numerical

TABLE II. The average number $S_n$ of different sites visited in a random walk of $n$ steps, as obtained from a simulation procedure. Here $S_n$ is given through $S_n = a_1 n + a_2 n^{1/2} + a_3$. The results correspond to steps mediated by dipolar interactions $(s=6)$ and to nearest-neighbor steps $(s=\infty)$.

| | | $a_1$ | $a_2$ | $a_3$ |
|---|---|---|---|---|
| $s=6$ | e | 0.630 | 0.553 | 0.658 |
| | d | 0.704 | 0.322 | 1.153 |
| | sc | 0.785 | 0.363 | 0.803 |
| | bcc | 0.819 | 0.347 | 0.738 |
| | fcc | 0.824 | 0.290 | 0.953 |
| $s=\infty$ | e | 0.462 | 0.618 | 0.617 |
| | d | 0.560 | 0.607 | 0.734 |
| | sc | 0.662 | 0.525 | 0.501 |
| | bcc | 0.716 | 0.537 | 0.509 |
| | fcc | 0.749 | 0.426 | 0.661 |

method at our disposal, the matrix inversion. This method yields higher accuracy than the simulation. The procedure starts from the following system of master equations,[9,23,25,29,54]

$$\frac{d}{dt}P_n(t) = \sum_m{}' w_{mn} P_m(t) - \left(\sum_m{}' w_{nm}\right) P_n(t) \ , \qquad (3.3)$$

which describe the time evolution of the probability $P_n(t)$ to find the excitation on site $n$. As before, the $w_{mn}$ are the transition rates of the excitation from site $m$ to site $n$ and the sums extend over all sites (with the exclusion of $n$). The first term on the right-hand side of (3.3) describes the gain due to the energy transfer from other lattice sites, whereas the second term accounts for the losses due to the transfer from site $n$.

For an infinite lattice the (infinite) system of equations (3.3) is exact and corresponds to the original problem. Numerically, however, only a finite number of equations can explicitly be considered. For each numerical inversion we denote with $\zeta$ the set of sites $n$ whose time evolution, $dP_n(t)/dt$, is explicitly accounted for. The gain and loss terms on the right-hand side of Eq. (3.3) are then asymmetrical. Through an exact evaluation of the second sum we can, following Koiwa's approach,[54] take all loss terms into account. On the other hand, only gain terms from sites $m \in \zeta$ enter. The physical interpretation is that sites outside $\zeta$ act as absorbers.

One now readily calculates the average time $t$ (lifetime) spent by the excitation on the set $\zeta$. We define $\mathbf{V}$ to be the following finite transfer matrix:

$$V_{mn} \equiv (1-\delta_{m,n}) w_{mn} - \delta_{m,n} \sum_q{}' w_{nq} \quad (m,n \in \zeta) \ . \qquad (3.4)$$

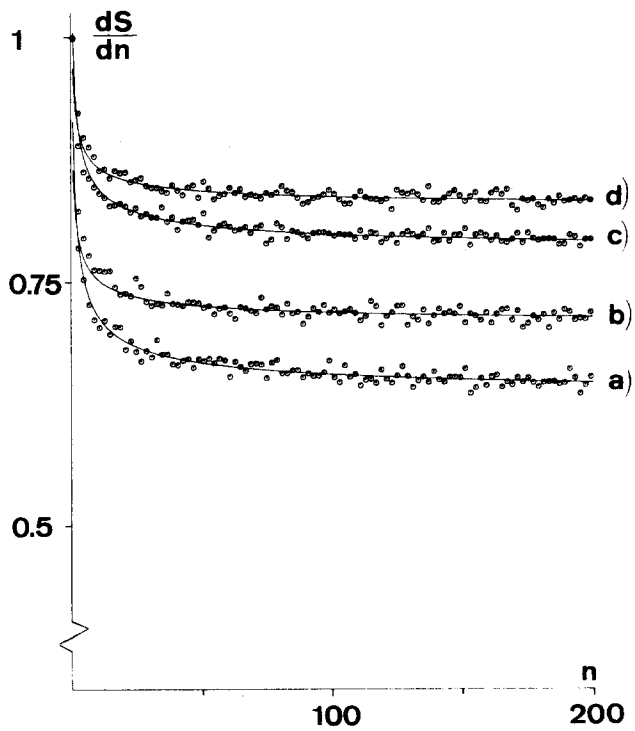


FIG. 3. Results for $dS_n/dn$ for the (a) edge; (b) diamond; (c) sc; and (d) fcc lattices. The continuous curves correspond to Eq. (3.2).

In Eq. (3.4), $m$ and $n$ belong to the set $\zeta$, whereas the sum over $q$ is restricted only by the condition $q \neq n$. Equation (3.3) now takes the form $\dot{\mathbf{P}} = \mathbf{V} \cdot \mathbf{P}$. Assuming the excitation to be located at the origin at time $t = 0$, $P_n(t) = \delta_{n,0}$, we are led to the solution

$$P_n(t) = [\exp(t\mathbf{V})]_{n0} \,. \tag{3.5}$$

The probability that the excitation is still in $\zeta$ at time $t$ is given by $\sum_{n\in\zeta} P_n(t)$. Thus the mean lifetime $\bar{t}$ is[30,54]

$$\bar{t} = -\int_0^\infty dt\, t \frac{d}{dt}\left[\sum_{n\in\zeta} P_n(t)\right] = \sum_{n\in\zeta}\int_0^\infty dt\, P_n(t)$$

$$= \sum_{n\in\zeta} [\mathbf{V}^{-1} \exp(t\mathbf{V})]_{n0}\Big|_0^\infty = -\sum_{n\in\zeta} (\mathbf{V}^{-1})_{n0} \,. \tag{3.6}$$

As is evident from Eq. (3.6), the lifetime of the excitation inside $\zeta$ is the sum over the average time spent on each site of $\zeta$ separately. As an example, the average time spent at the origin is

$$\bar{t}_0 = -\int_0^\infty dt\, t \frac{d}{dt} P_0(t) = \int_0^\infty dt\, P_0(t) = -(\mathbf{V}^{-1})_{00} \,. \tag{3.7}$$

So far the discussion of the matrix method has centered on absorption *times*, whereas the considerations of Sec. II were formulated in terms of distinct *steps*. For lattices in which the sites have identical surroundings the two formulations are easily interchangeable; the mean stepping time is $(\sum_q' w_{nq})^{-1}$, independent of $n$. Therefore, the mean lifetime $\bar{t}$ is connected with $n_{ab}$, the average number of steps until absorption occurs, through

$$n_{ab} = \bar{t} \sum_q' w_{0q} \,. \tag{3.8}$$

As a special case, one has for nearest-neighbor random walks $n_{ab} = \bar{t} Z \tau^{-1}$, where $Z$ is the coordination number [Eq. (7) of Ref. 54].

An argument analogous to the one which led to Eq. (3.8) gives the connection between $\bar{t}_0$ in Eq. (3.7) and the average number of steps from the origin during the time $\bar{t}$:

$$n_0 = \bar{t}_0 \sum_q' w_{0q} \,. \tag{3.9}$$

For the infinite lattices discussed in Sec. II the time spent at the origin is given by $P(0;1)$ multiplied by the same factor $\sum_q' w_{0q}$ as in Eq. (3.9); thus $n_0$ and $P(0;1)$ are related. In order to obtain $P(0;1)$ one must, in principle, only determine $n_0$ for increasingly larger systems of lattice points $\zeta$ and perform an adequate limiting treatment. According to Eq. (2.17) $u_0$ is also determined in this way.

By comparison with the results for nearest-neighbor random walks on Bravais lattices one finds (vide infra and Ref. 54) that the representation

$$n_0 = b_1 - b_2 n_{ab}^{-1/2} \tag{3.10}$$

leads to very accurate $u_0$ values, $u_0 \simeq b_1$. In Eq. (3.10) the constants $b_1$ and $b_2$ are least-squares fitted to the values for $n_0$ and $n_{ab}$ obtained for different choices of the sets $\zeta$. We have found it convenient to use the determination scheme (3.10) also for non-Bravais lattices, although here (due to potentially different surroundings of different sites) $n_{ab}$ in Eq. (3.8) does not necessarily represent the total number of steps until absorption. Before presenting the results, however, we give more details about the numerical procedure.

TABLE III. The number $n_0$ of steps from the origin as a function of the absorption parameter $n_{ab}$, $n_0 = b_1 - b_2 n_{ab}^{-1/2}$. The values are obtained by the matrix method for steps due to multipolar interactions on the five lattices considered. The parameter $u_1$ has the same meaning as in Table I and was evaluated following the prescriptions of Appendix B.

| | | $b_1$ | $b_2$ | $u_1$ | $(u_1/b_2\sqrt{\pi})$ |
|---|---|---|---|---|---|
| $s=6$ | e | 1.895 | 0.746 | | |
| | d | 1.424 | 0.301 | | |
| | sc | 1.266 | 0.195 | 0.423 73 | 1.23 |
| | bcc | 1.214 | 0.166 | 0.358 52 | 1.22 |
| | fcc | 1.211 | 0.164 | 0.356 30 | 1.23 |
| $s=8$ | e | 2.4751 | 1.7248 | | |
| | d | 1.6564 | 0.5788 | | |
| | sc | 1.4039 | 0.3615 | 0.879 09 | 1.372 |
| | bcc | 1.3071 | 0.2882 | 0.699 44 | 1.369 |
| | fcc | 1.2994 | 0.2838 | 0.689 35 | 1.370 |
| $s=10$ | e | 2.7563 | 2.2186 | | |
| | d | 1.7450 | 0.6829 | | |
| | sc | 1.4637 | 0.4267 | 1.040 73 | 1.376 |
| | bcc | 1.3418 | 0.3284 | 0.799 16 | 1.373 |
| | fcc | 1.3281 | 0.3203 | 0.779 76 | 1.374 |
| $s=\infty$ | e | 3.0332 | 2.7116 | 6.615 94[a] | 1.376 |
| | d | 1.7931 | 0.7377 | 1.800 63 | 1.377 |
| | sc | 1.5165 | 0.4792 | 1.169 55 | 1.377 |
| | bcc | 1.3934 | 0.3696 | 0.900 32 | 1.374 |
| | fcc | 1.3448 | 0.3394 | 0.826 99 | 1.375 |

[a] $\sqrt{2}\, u_1$ is given, to account for the different occupancy times of the edge- and of the sc-sublattice points.

According to Eq. (3.10) both $n_0$ and $n_{ab}$ have to be evaluated. As mentioned, $\bar{t}$ given by Eq. (3.6) is the sum of the average times spent at each site of $\zeta$. Hence, for Bravais lattices $n_{ab}$ may be interpreted [Eq. (9) of Ref. 54] as the sum of the steps from the origin, $n_0$, and of all other steps from sites in $\zeta$. Koiwa achieved the separation of $n_0$ from $n_{ab}$ by "tagging" the origin (multiplying its rate by an additional factor $\alpha$). From Eqs. (3.6) and (3.7) we see that only matrix elements $(\mathbf{V}^{-1})_{n0}$ are involved; from these $n_0$ may be obtained directly and the tagging is superfluous.

Furthermore, instead of inverting the matrix $\mathbf{V}$ we proceed in a numerically more convenient fashion: We determine $\mathbf{x}$, the root of the equation

$$\mathbf{V} \cdot \mathbf{x} = \mathbf{b} \,, \quad \text{with } b_n = \delta_{n,0} \,, \tag{3.11}$$

because $x_n$ equals then $(\mathbf{V}^{-1})_{n0}$. The advantage resides in the fact that to solve a linear system of equations requires less time than to invert a matrix.

Finally, it is convenient to enlarge $\zeta$ radially from the origin. For highly symmetrical crystals this allows a substantial reduction of the order of the matrix $\mathbf{V}$. This is achieved by grouping together all lattice points which are equidistant to the origin and equivalent owing to the symmetry of the system. Calling these groups "shells" one rewrites Eq. (3.3) for the different shells rather than for the individual sites, see Ref. 54.

In Table III we have summarized the results for the

five lattices and for the different interaction types ($s = 6$, 8, 10, and $\infty$). In the first two columns we present the values of $b_1$ and of $b_2$, obtained according to Eq. (3.10). In these calculations 100 shells of lattice points were taken into account. The parameters $b_1$ and $b_2$ were determined from the $n_0$ and $n_{ab}$ values pertaining to the solution of ten matrix problems for each case.

For $s = \infty$ the values of $b_1$ in Table III may be compared with the known analytical expressions, see Table I or Eq. (2.29). For Bravais lattices $b_1$ corresponds to $u_0$, and one observes that the agreement between $b_1$ and $u_0$ is much better than the one between $a_1$ (Table II) and $u_0^{-1}$, the former agreement extending in general over three decimal digits. Also our values agree well with those of Koiwa,[54] calculated for the d, bcc, and fcc lattices ($s = \infty$). We are therefore confident that for finite $s$ values ($s = 6$, 8, and 10) as well, the results for $b_1$ are in close agreement with the exact $u_0$. As a consistency check between the two (different) numerical methods, one can compare $b_1$ with $a_1^{-1}$ (Tables II and III). The agreement is better than within 1% in all cases.

One may also appreciate the smooth dependences of $b_1$ and $b_2$ on $Z$, the coordination number, as well as on $s$, the interaction range. The probability of returns to the origin decreases, as expected, when the range of interaction becomes larger (smaller $s$). The effect becomes more pronounced for smaller $Z$ values. Thus for the fcc lattice the probability of returns to the origin decreases only by a factor of 1.11 in going from $s = \infty$ to $s = 6$; the corresponding decreases are more pronounced for the other lattices; the factors are 1.15 for the bcc, 1.20 for the sc, 1.26 for the d, and 1.60 for the e lattice.

In Eq. (3.7), $\bar{t}_0$ is the average time spent at the origin until absorption, and $n_0$ in Eq. (3.9) is the mean number of steps from the origin. As was done in Sec. II we now proceed to show that we can obtain these values qualitatively from a diffusion model. It is intuitively evident from the findings of Sec. II that such an approach may be fruitful; there we found $M_n$, the average number of returns to the origin in a random walk of $n$ steps *without* absorption, to converge towards a finite value $M_\infty \equiv \lim_{n\to\infty} M_n$. We also expect $n_0$, calculated for increasingly larger spherically symmetrical sets $\zeta$, to converge to $M_\infty$, since enlarging $\zeta$ increases the distance between the origin and the absorbing boundary. Since the diffusion model led to reasonable values for $M_\infty$ and $M_n$, we expect the same to hold for $n_0$ and its correction terms. In fact, using the same parametrization as in Sec. II, we find relations between the leading terms of $M_n$ and of $n_0$, which are in excellent agreement with the numerically evaluated factors.

We start from the diffusion equation (2.31); here we need its solution in the presence of an absorbing boundary at $r = a$, i.e., $\tilde{\Psi}(a, t) = 0$. The initial condition is an instantaneous source of strength 1 at the origin for $t = 0$. The (radially symmetric) solution of this problem is given through[53,56]

$$\tilde{\Psi}(\mathbf{r}; t) = \frac{1}{2a^2 r}\sum_{n=1}^{\infty} n \exp\left(-\frac{n^2\pi^2 Dt}{a^2}\right)\sin(n\pi r/a) \ . \qquad (3.12)$$

In Ref. 56 this equation was used to obtain the mean passage time to a spherical surface. We employ it here to calculate the average time spent inside a spherical region.

The average time $T(\mathbf{r}; t)$ spent by the excitation at $\mathbf{r}$ between the times 0 and $t$ is again, as in Eq. (2.34):

$$T(\mathbf{r}; t) = \int_0^t d\tilde{t}\,\tilde{\Psi}(\mathbf{r}; \tilde{t}) = \frac{1}{2\pi^2 r D}\sum_{n=1}^{\infty}\frac{1}{n}\left[1 - \exp\left(-\frac{n^2\pi^2 Dt}{a^2}\right)\right]\sin(n\pi r/a) \ , \qquad (3.13)$$

and thus $T(\mathbf{r})$, the average time spent at $\mathbf{r}$ between $t = 0$ and $t = \infty$ is

$$T(\mathbf{r}) \equiv T(\mathbf{r}; \infty) = \frac{1}{2\pi^2 r D}\sum_{n=1}^{\infty}\sin(n\pi r/a)/n = \frac{1 - r/a}{4\pi r D} \ , \qquad (3.14)$$

where we used Eq. (27.8.6) of Ref. 46:

$$\sum_{n=1}^{\infty}\frac{\sin n\theta}{n} = \tfrac{1}{2}(\pi - \theta) \ , \quad (0 < \theta < 2\pi) \ . \qquad (3.15)$$

From Eq. (3.14), we obtain the mean lifetime of the excitation inside the sphere,

$$\bar{t} = \int_0^a 4\pi r^2 T(r)\, dr = \frac{a^2}{6D} \ , \qquad (3.16)$$

as well as the average time spent in a sphere of radius $R$ surrounding the origin,

$$\tilde{t}_0 = \int_0^R 4\pi r^2 T(r)\, dr = \frac{R^2}{2D} - \frac{R^3}{3Da} \ . \qquad (3.17)$$

Expressing $\tilde{t}_0$ as a function of $\bar{t}$, Eq. (3.16) we have

$$\tilde{t}_0 = \frac{R^2}{2D} - \frac{R^3}{3\sqrt{6}\,D^{3/2}}\bar{t}^{\,-1/2} \ . \qquad (3.18)$$

Comparing now Eqs. (2.37) and (3.18) we find immediately that the leading terms are identical. This was to be expected intuitively: letting the radius $a$ of the boundary go to infinity in Eq. (3.17) should lead to the same result as the long time behavior ($t \to \infty$) of the problem without an absorbing boundary. In the random-walk model this corresponds to the leading terms in $M_n$ [Eq. (2.19)] and in $n_0$ [Eqs. (3.10) ff.]. Our preceding discussions have shown that both terms should be identical.

More surprising, perhaps, is the relationship between the correction terms in Eqs. (2.37) and (3.18); the terms differ only by a factor of $\sqrt{6/\pi} = 1.382$. As we now proceed to show, the numerical results obtained by the matrix method give very closely this factor when compared to the exact values of Sec. II. This fact (the accuracy with which a *correction* term is obtained) illustrates the reliability of the numerical results of the matrix method.

In the case $s = \infty$ where the expressions for $M_n$ are given in Eq. (2.29) one verifies readily that the quotients of $b_2$ and of the coefficients of $n^{-1/2}$ in Eq. (2.29) vary between 1.374 and 1.377 for the d, sc, bcc, and fcc lattices. These ratios are given in Table III. The

quotient for the e lattice is 1.376 when the factor $\sqrt{2}$, which stems from the different occupancy times of the edge and of the main sc sublattice points, is accounted for. In Appendix B it is shown that for cubic lattices we can also obtain $u_1$ directly from the generating function for random walks which are not restricted to nearest neighbors (i.e., $s \neq \infty$). These $u_1$ values are given in Table III. The quantity $u_1/\sqrt{\pi}$ corresponds to the second term $b_2$ in the expression for $M_n$ [Eq. (2.19)]. The quotients between $u_1/\sqrt{\pi}$ and the numerically determined $b_2$ are also displayed in Table III.

For different $s$ we find the quotients to be independent of lattice type. Moreover, they depend only slightly on $s$: For $s=10$ and $s=8$ they are around 1.37, and they drop to 1.36 for $s=7$, and to 1.22 for $s=6$.

From a detailed analysis of the $b_2$ values we find that for $s=6$ they still change when the number of shells taken into account is increased from 100 to 150. Thus for $s=6$ the values $b_2$ are not yet completely stable, a fact which reflects the long-range character of the potential. An extrapolation to an infinite number of shells changes $b_2$ and increases the quotient in the fourth column in Table III to a value of 1.36, while the same procedure leaves $b_1$ almost unaffected.

In this section we have presented the numerical methods at our disposal and have listed the results obtained from them. We continue in the next section with a discussion and summary of the findings.

## IV. SUMMARY

In this work we have centered our attention on the determination of the quantities $S_n$ and $M_n$, the average number of different sites visited and the mean number of returns to the origin in a random walk of $n$ steps. These quantities are fundamental for each model considered and are intimately related to many topics of current interest, like the fluorescence and phosphorescence yields from doped materials in the problem of electronic and vibrational energy transfer and the trapping rate at the active site in photosynthesis.

The determination of $S_n$ and of $M_n$ may proceed via a number of distinct approaches, either through direct numerical simulation and numerical matrix methods, or indirectly using the generating-function formalism. In order to find out the advantages and drawbacks of each method, and also in order to present results which are nearer to the situations which may be encountered experimentally, we have considered several lattice types and have also allowed steps to other than nearest-neighbor sites. The latter extension of the model permits the description of incoherent transfers induced by multipolar interactions which depend on the intermolecular distances via a power law such that steps to more distant sites are also possible.

For nearest-neighbor random walks on cubic lattices and for a very large number of steps the generating-function formalism is certainly the superior method in determining the values of $M_n$ and $S_n$, since exact values are then available for the terms of the asymptotic expansions. However, the two leading terms may also be obtained with good accuracy from numerical approaches; we readily achieve an accuracy of one part in $10^4$ using the matrix inversion procedure, and of 1% using a direct and short simulation procedure (less than 5000 walks). Thus, in view of applications to realistic experimental situations the matrix method is certainly very satisfactory.

With increasing complexity of the model the generating-function approach becomes less appealing. For nearest-neighbor random walks on the diamond and the sparse-cubic e lattices one is still in the fortunate situation that the corresponding generating functions are related to those of the cubic lattices. In order to establish the exact connection, however, we had to investigate each lattice type separately. Thus, in still more complex cases, even *expressing* the generating function in its integral form may turn out to be difficult.

We also note that the relations which lead from the generating function to $S_n$ and to $M_n$ are different in the case of the two noncubic lattices considered. In contrast, the changes which we had to make in the numerical approaches were minimal, and we obtained the same accuracy in the results for the noncubic lattices as for the cubic ones.

Even in the framework of the generating-function formalism one has to resort to a numerical evaluation of the pertinent integrals if random walks with long-range transfer steps are involved. The advantage of the approach as a tool for obtaining the values $S_n$ and $M_n$ *analytically* no longer exists. Again the numerical methods are easily adapted to handle these problems, which clearly demonstrates their larger flexibility.

The Tables I, II, and III and Eqs. (2.29) and (2.30) summarize our findings. Both the average number of returns to the origin $M_n$ and the mean number of sites $S_n$ visited during a random walk of $n$ steps depend smoothly on the coordination number (number of nearest neighbors) of each lattice. This is true not only for the leading terms, but also for the correction terms which we evaluated. This result, although not necessarily compelling from physical arguments, appears plausible from a (continuous) diffusion model of the random walk. As we have shown, one can reformulate the (discrete) question regarding the number of visits to the origin as the problem of obtaining the *average time* spent at the origin. In a continuous model this corresponds to the average time spent in a certain region around the origin, a quantity which is readily evaluated from the solutions of the diffusion models. If the region is chosen to be spherical, the only parameter which enters is the radius of the sphere; a reasonable choice of this value reproduces quite well the exact results for all lattice types considered.

An increase in the range of the interactions [i.e., a decrease of the exponent $s$ in the rate law for the individual steps, Eq. (3.1)] increases the number of different sites visited and decreases the probability of returns to the origin. This trend is to be expected on intuitive grounds, since an increase of the interaction range enlarges the number of sites within reach of a single step;

thus the probability of stepping to a site already visited decreases. This effect also explains why an increase in the coordination number leads to an increase in $S_n$ and a decrease in $M_n$. Thus, the changes found in varying the interaction range are quantitative and are more pronounced in cases of *low* coordination numbers.

The behavior of the quantities considered does not change qualitatively, however. This is an important result, since we might view the edge lattice as a more "disordered" structure than the cubic lattices. In the study of random walks on disordered structures one is interested in how far the qualitative behavior changes from the one which obtains for ordered lattices. For three-dimensional disordered lattices the consensus is that no qualitative changes are expected for the (linear) time dependence of the mean squared displacement, for times long compared to the mean hopping rate.[9,57-60] However, these arguments are based on approximations which may not hold well for very long times (see Ref. 9 for a detailed discussion). Our results for the e lattice relate not only to the simple displacement from the origin, but to the more complex quantities $M_n$ and $S_n$; they are valid also for very long times and thus lend additional support to the above conjecture. Results on disordered lattices will be presented in additional papers.[61]

In summary, one has a series of very different methods for evaluating the experimentally relevant quantities of random-walk models. They range in sophistication from qualitative continuous approaches over numerical methods to generating functions. Here we have obtained a large number of results using these procedures under realistic conditions. These allowed us to investigate the merits and drawbacks of the approaches employed. We expect that these findings will facilitate the judicious choice of the method appropriate in each application.

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## APPENDIX A: NEAREST-NEIGHBOR RANDOM WALKS ON THE DIAMOND AND EDGE LATTICES

In this Appendix we will develop the formulas used in the text for the diamond and for the edge lattice.

(1) *Diamond lattice*: We start our considerations by determining first the generating functions of the random walk, and we follow here the approach of Ref. 47. A diamond lattice can be viewed as two shifted fcc sublattices. We denote with $P_j(\mathbf{r})$ the probability that on the $j$th step the random walker occupies the site $\mathbf{r}$ on the fcc sublattice which includes the origin; analogously $Q_j(\mathbf{r})$ is the probability for the occupancy of a site on the other fcc sublattice. One has for a nearest-neighbor walk:

$$P_{j+1}(\mathbf{r}) = \sum_{\mathbf{d}} p(-\mathbf{d}) Q_j(\mathbf{r}+\mathbf{d}) \,, \tag{A1a}$$

$$Q_{j+1}(\mathbf{r}) = \sum_{\mathbf{d}} p(\mathbf{d}) P_j(\mathbf{r}-\mathbf{d}) \,. \tag{A1b}$$

In Eqs. (A1), $\mathbf{d}$ is one of the vectors $(1,1,1)$, $(-1,-1,1)$, $(-1,1,-1)$, and $(1,-1,-1)$, and all $p(\mathbf{d})$ are equal to $1/4$. Introducing the generating functions:

$$P(\mathbf{r};z) = \sum_{j=0}^{\infty} z^j P_j(\mathbf{r}) \tag{A2a}$$

and

$$Q(\mathbf{r};z) = \sum_{j=0}^{\infty} z^j Q_j(\mathbf{r}) \,, \tag{A2b}$$

one obtains for a walk originating from $\mathbf{r}=0$ (i.e., on the $P$ sublattice):

$$P(\mathbf{r};z) = \delta_{\mathbf{r},0} + z \sum_{\mathbf{d}} p(-\mathbf{d}) Q(\mathbf{r}+\mathbf{d};z) \,, \tag{A3a}$$

$$Q(\mathbf{r};z) = z \sum_{\mathbf{d}} p(\mathbf{d}) P(\mathbf{r}-\mathbf{d};z) \,. \tag{A3b}$$

Multiplication with $e^{i\mathbf{k}\cdot\mathbf{r}}$ and summation over $\mathbf{r}$ lead to

$$P(\mathbf{k};z) = 1 + z\,\lambda(-\mathbf{k}) Q(\mathbf{k};z) \,, \tag{A4a}$$

$$Q(\mathbf{k};z) = z\,\lambda(\mathbf{k}) P(\mathbf{k};z) \,, \tag{A4b}$$

where $\lambda(\mathbf{k})$ is

$$\lambda(\mathbf{k}) = \sum_{\mathbf{d}} p(\mathbf{d})\, e^{i\mathbf{k}\cdot\mathbf{r}} = \tfrac{1}{2}[\cos(k_x+k_y)\, e^{ik_z} + \cos(k_x-k_y)\, e^{-ik_z}] \,. \tag{A5}$$

Inserting Eq. (A4b) in (A4a) and solving for $P(\mathbf{k};z)$ gives

$$P(\mathbf{k};z) = \frac{1}{1 - z^2 \lambda(\mathbf{k})\lambda(-\mathbf{k})} \,, \tag{A6a}$$

and with Eq. (A4b)

$$Q(\mathbf{k};z) = \frac{z\lambda(\mathbf{k})}{1 - z^2 \lambda(\mathbf{k})\lambda(-\mathbf{k})} \,. \tag{A6b}$$

The inverse Fourier transformation of Eq. (A6a) leads to $P(\mathbf{r};z)$:

$$P(\mathbf{r};z) = \frac{1}{(2\pi)^3} \iiint_{-\pi}^{\pi} \frac{e^{-i\mathbf{k}\cdot\mathbf{r}} d^3\mathbf{k}}{1 - z^2 |\lambda(\mathbf{k})|^2} \,, \tag{A7}$$

which is formula (2.9) of the main text.

For random walks starting on the $Q$ sublattice one obtains instead of Eqs. (A4a) and (A4b):

$$\tilde{P}(\mathbf{k};z) = z\,\lambda(-\mathbf{k}) \tilde{Q}(\mathbf{k};z) \,, \tag{A8a}$$

$$\tilde{Q}(\mathbf{k};z) = e^{i\mathbf{k}\cdot\mathbf{0}_Q} + z\lambda(\mathbf{k}) \tilde{P}(\mathbf{k};z) \,. \tag{A8b}$$

Here we assume the walk to start at $\mathbf{0}_Q$, the origin of the $Q$ sublattice and distinguish the different initial condition by a tilde. One has

$$\tilde{Q}(\mathbf{k};z) = \frac{e^{i\mathbf{k}\cdot\mathbf{0}_Q}}{1 - z^2 |\lambda(\mathbf{k})|^2} \tag{A9}$$

and therefore,

$$\tilde{Q}(\mathbf{r};z) = \frac{1}{(2\pi)^3} \iiint_{-\pi}^{\pi} \frac{e^{i\mathbf{k}(\mathbf{0}_Q - \mathbf{r})}}{1 - z^2 |\lambda(\mathbf{k})|^2} \,. \tag{A10}$$

From Eqs. (A7) and (A10) one obtains the relation

$$P(0;z) = \tilde{Q}(\mathbf{0}_Q;z) \,, \tag{A11}$$

which is also evident from symmetry arguments.

We are now in the position to show that for the d lattice $S(z)$ is also given through Eq. (2.4) of the main text. Let $F_j^P(\mathbf{r})$ and $F_j^Q(\mathbf{r})$ be the probabilities that site $\mathbf{r}$ is visited for the first time on step $j$. For walks starting at the origin:

$$P_j(\mathbf{r}) = \delta_{j,0}\delta_{\mathbf{r},0} + \sum_{k=1}^{j} F_k^P(\mathbf{r}) P_{j-k}(\mathbf{0}) \tag{A12a}$$

and

$$Q_j(\mathbf{r}) = \sum_{k=1}^{j} F_k^Q(\mathbf{r}) P_{j-k}(\mathbf{0}) \ . \tag{A12b}$$

The last line holds because of Eq. (A11). From Eqs. (A12) the generating functions

$$F^P(\mathbf{r}; z) = \sum_{n=1}^{\infty} z^n F_n^P(\mathbf{r}) \ , \tag{A13a}$$

$$F^Q(\mathbf{r}; z) = \sum_{n=1}^{\infty} z^n F_n^Q(\mathbf{r}) \ , \tag{A13b}$$

fulfill the relations

$$F^P(\mathbf{r}; z) = \frac{P(\mathbf{r}; z) - \delta_{\mathbf{r},\mathbf{0}}}{P(\mathbf{0}; z)} \ , \tag{A14a}$$

$$F^Q(\mathbf{r}; z) = \frac{Q(\mathbf{r}; z)}{P(\mathbf{0}; z)} \ . \tag{A14b}$$

Let $\Delta_n$ be the number of newly visited sites on the $n$th step:

$$\Delta_n = \sum_{\mathbf{r}}{}' [F_n^P(\mathbf{r}) + F_n^Q(\mathbf{r})] \ , \tag{A15}$$

where the sum extends over all sites with the exception of the origin. The generating function of the $\Delta_n$ is

$$\begin{aligned} \Delta(z) &= \sum_{n=1}^{\infty} z^n \Delta_n \\ &= -F^P(\mathbf{0}; z) + \sum_{\mathbf{r}} [F^P(\mathbf{r}; z) + F^Q(\mathbf{r}; z)] \\ &= -1 + [P(\mathbf{0}; z)]^{-1} \sum_{\mathbf{r}} [P(\mathbf{r}; z) + Q(\mathbf{r}; z)] \ . \end{aligned} \tag{A16}$$

In the last line of Eq. (A16) use was made of the relations (A14). Because of conservation of probability:

$$\sum_{\mathbf{r}} [P_n(\mathbf{r}) + Q_n(\mathbf{r})] = 1 \quad \text{(for all } n) \ , \tag{A17}$$

one has

$$\sum_{\mathbf{r}} [P(\mathbf{r}; z) + Q(\mathbf{r}; z)] = (1 - z)^{-1} \tag{A18}$$

and therefore

$$\Delta(z) = -1 + [(1 - z)P(\mathbf{0}; z)]^{-1} \ . \tag{A19}$$

The average number of sites visited during a random walk of $n$ steps is

$$S_n = 1 + \sum_{j=1}^{n} \sum_{\mathbf{r}}{}' [F_j^P(\mathbf{r}) + F_j^Q(\mathbf{r})] = 1 + \sum_{j=1}^{n} \Delta_n \ . \tag{A20}$$

Thus $\Delta_{n+1} = S_{n+1} - S_n$ and

$$\begin{aligned} \Delta(z) &= \sum_{n=0}^{\infty} \Delta_{n+1} z^{n+1} = \sum_{n=0}^{\infty} S_{n+1} z^{n+1} - z \sum_{n=0}^{\infty} S_n z^n \\ &= (1 - z)S(z) - 1 \ . \end{aligned} \tag{A21}$$

Therefore, with Eq. (A19):

$$S(z) = [(1 - z)^2 P(\mathbf{0}; z)]^{-1} \tag{A22}$$

which is identical to Eq. (2.4).

Using the same type of reasoning we now consider the average number of visits to the origin $M_n$, during a random walk of $n$ steps. Evidently since the origin is on the $P$ lattice:

$$M_n = \sum_{j=0}^{n} P_n(\mathbf{0}) \ , \tag{A23}$$

and therefore $P_{n+1}(\mathbf{0}) = M_{n+1} - M_n$, which leads to

$$P(\mathbf{0}; z) = \sum_{n=0}^{\infty} z^n M_n - z \sum_{n=0}^{\infty} z^{n-1} M_{n-1} = (1 - z)M(z) \tag{A24}$$

and thus,

$$M(z) = (1 - z)^{-1} P(\mathbf{0}; z) \ . \tag{A25}$$

This proof of the relation between $M(z)$ and the generating function appears simpler than the one advanced by Montroll and Weiss[35] in the study of Bravais lattices.

(2) *Edge lattice*: The edge (e) lattice results from a simple-cubic lattice whose unit vectors are $2\mathbf{e}_x$, $2\mathbf{e}_y$, and $2\mathbf{e}_z$ by adding to it the median points of the edges connecting nearest neighbors. The e lattice may also be viewed as consisting of a main sc lattice, denoted by $P$, which contains the origin, and of three sc sublattices, which result from the $P$ lattice through a displacement $\mathbf{e}_\mu$ ($\mu = x, y, z$) in the direction $\mu$. These sublattices will be denoted by $Q^\mu$.

The treatment of the e lattice is less straightforward than the one for the diamond lattice since the lattice points are not equivalent; points on $P$ have six nearest neighbors each, whereas the points on $Q$ have only two. One obtains for a nearest-neighbor walk, in analogy to Eqs. (A1):

$$P_{j+1}(\mathbf{r}) = \sum_{\mu} \sum_{\mathbf{d}_\mu} p_Q(\mathbf{d}_\mu) Q_j^\mu(\mathbf{r} - \mathbf{d}_\mu) \ , \tag{A26a}$$

$$Q_{j+1}^\mu(\mathbf{r}) = \sum_{\mathbf{d}_\mu} p(\mathbf{d}_\mu) P_j(\mathbf{r} - \mathbf{d}_\mu) \quad (\mu = x, y, z) \ . \tag{A26b}$$

Here $\mathbf{d}_\mu$ is either $+\mathbf{e}_\mu$ or $-\mathbf{e}_\mu$ ($\mu = x, y, z$) and the different $p$ and $p_Q$ correspond to the different step probabilities associated with the different numbers of nearest neighbors; for a symmetric walk,

$$p_Q(\mathbf{d}_\mu) = 1/2 \ , \quad p(\mathbf{d}_\mu) = 1/6 \ . \tag{A27}$$

Reverting now to the generating functions $P(\mathbf{r}; z)$ and $Q^\mu(\mathbf{r}; z)$ one has for walks which start on the $P$ lattice,

$$P(\mathbf{r}; z) = \delta_{\mathbf{r},\mathbf{0}} + z \sum_{\mu} \sum_{\mathbf{d}_\mu} p_Q(\mathbf{d}_\mu) Q^\mu(\mathbf{r} - \mathbf{d}_\mu; z) \ , \tag{A28a}$$

$$Q^\mu(\mathbf{r}; z) = z \sum_{\mathbf{d}_\mu} p(\mathbf{d}_\mu) P(\mathbf{r} - \mathbf{d}_\mu; z) \ , \quad (\mu = x, y, z) \ . \tag{A28b}$$

Multiplication with $e^{i\mathbf{k}\cdot\mathbf{r}}$ and summation over $\mathbf{r}$ lead to

$$P(\mathbf{k}; z) = 1 + z \sum_{\mu} \lambda_{Q_\mu}(\mathbf{k}) Q^\mu(\mathbf{k}; z) \ , \tag{A29a}$$

$$Q^\mu(\mathbf{k}; z) = z \lambda_\mu(\mathbf{k}) P(\mathbf{k}; z) \quad (\mu = x, y, z) \ , \tag{A29b}$$

with

$$\lambda_{Q_\mu}(\mathbf{k}) = \sum_{\mathbf{d}_\mu} p_Q(\mathbf{d}_\mu)\, e^{i\mathbf{k}\cdot\mathbf{d}_\mu} = \cos(k_\mu)\ , \tag{A30a}$$

$$\lambda_{\mu}(\mathbf{k}) = \sum_{\mathbf{d}_\mu} p(\mathbf{d}_\mu)\, e^{i\mathbf{k}\cdot\mathbf{d}_\mu} = \tfrac{1}{3}\cos(k_\mu)\ , \tag{A30b}$$

Inserting Eq. (A29b) into Eq. (A29a) one obtains the solution:

$$P(\mathbf{k};z) = \frac{1}{1 - z^2 \sum_\mu \lambda_{Q_\mu}(\mathbf{k})\lambda_\mu(\mathbf{k})} = \left[1 - (z^2/3)\sum_\mu \cos^2(k_\mu)\right]^{-1}\ . \tag{A31}$$

Furthermore, from Eq. (A29b):

$$Q^\mu(\mathbf{k};z) = \frac{z\cos(k_\mu)/3}{1 - (z^2/3)\sum_\mu \cos^2(k_\mu)}\ . \tag{A32}$$

The inverse Fourier transformation of Eq. (A31) gives the generating function for walks starting on the $P$ sublattice,

$$P(\mathbf{r};z) = \frac{1}{(2\pi)^3}\iiint_{-\pi}^{\pi} \frac{e^{-i\mathbf{k}\cdot\mathbf{r}}d^3\mathbf{k}}{[1 - (z^2/3)(\cos^2 k_x + \cos^2 k_y + \cos^2 k_z)]}\ , \tag{A33}$$

which is Eq. (2.14) of the main text.

Consider now random walks which do not start on the sublattice $P$. Since the three sublattices $Q^x$, $Q^y$, $Q^z$ are equivalent by symmetry we exemplify the procedure with $Q^x$. Let $\mathbf{0}_x$ be the origin of the $Q^x$ sublattice. Then for walks starting at $\mathbf{0}_x$ one has, instead of Eqs. (A28),

$$\tilde{P}(\mathbf{r};z) = z\sum_\mu \sum_{\mathbf{d}_\mu} p_Q(\mathbf{d}_\mu)\tilde{Q}^\mu(\mathbf{r}-\mathbf{d}_\mu;z)\ , \tag{A34a}$$

$$\tilde{Q}^x(\mathbf{r};z) = \delta_{\mathbf{r},\mathbf{0}_x} + z\sum_{\mathbf{d}_x} p(\mathbf{d}_x)\tilde{P}(\mathbf{r}-\mathbf{d}_x;z)\ , \tag{A34b}$$

$$\tilde{Q}^\mu(\mathbf{r};z) = z\sum_{\mathbf{d}_\mu} p(\mathbf{d}_\mu)\tilde{P}(\mathbf{r}-\mathbf{d}_\mu;z)\quad (\mu = y,z)\ , \tag{A34c}$$

Here the tilde denotes the new initial condition $Q_0^x(\mathbf{r}) = \delta_{\mathbf{r},\mathbf{0}_x}$. Thus one has

$$\tilde{P}(\mathbf{k};z) = z\sum_\mu \lambda_{Q_\mu}(\mathbf{k})\tilde{Q}^\mu(\mathbf{k};z)\ , \tag{A35a}$$

$$\tilde{Q}^x(\mathbf{k};z) = e^{i\mathbf{k}\cdot\mathbf{0}_x} + z\lambda_x(\mathbf{k})\tilde{P}(\mathbf{k};z)\ , \tag{A35b}$$

$$\tilde{Q}^\mu(\mathbf{k};z) = z\lambda_\mu(\mathbf{k})\tilde{P}(\mathbf{k};z)\quad (\mu = y,z)\ , \tag{A35c}$$

from which we obtain by inserting Eqs. (A35b) and (A35c) into (A35a):

$$\tilde{P}(\mathbf{k};z) = \frac{z\lambda_{Q_x}(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{0}_x}}{1 - z^2\sum_\mu \lambda_\mu(\mathbf{k})\lambda_{Q_\mu}(\mathbf{k})}\ , \tag{A36a}$$

and thus

$$\tilde{Q}^x(\mathbf{k};z) = e^{i\mathbf{k}\cdot\mathbf{0}_x}\left[1 + \frac{z^2\lambda_x(\mathbf{k})\lambda_{Q_x}(\mathbf{k})}{1 - z^2\sum_\mu \lambda_\mu(\mathbf{k})\lambda_{Q_\mu}(\mathbf{k})}\right]\ . \tag{A36b}$$

Therefore, the generating function for symmetric random walks starting on the $Q^x$ sublattice is

$$\tilde{Q}^x(\mathbf{r};z) = \frac{1}{(2\pi)^3} \times \iiint_{-\pi}^{\pi} \frac{1 - (z^2/3)(\cos^2 k_y + \cos^2 k_z)\, e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{0}_x)}d^3\mathbf{k}}{1 - (z^2/3)(\cos^2 k_x + \cos^2 k_y + \cos^2 k_z)}\ . \tag{A37}$$

We now calculate $Q^x(\mathbf{0}_x;z)$ by observing that for $\mathbf{r} = \mathbf{0}_x$ the integral is invariant with respect to the permutations $x \to y \to z \to x$. Thus

$$3\tilde{Q}^x(\mathbf{0}_x;z) = \frac{1}{(2\pi)^3}\iiint_{-\pi}^{\pi} \frac{3 - 2(z^2/3)(\cos^2 k_x + \cos^2 k_y + \cos^2 k_z)}{1 - (z^2/3)(\cos^2 k_x + \cos^2 k_y + \cos^2 k_z)} = 2 + P(\mathbf{0};z)\ , \tag{A38a}$$

i.e.,

$$\tilde{Q}^x(\mathbf{0}_x;z) = \tfrac{2}{3} + \tfrac{1}{3}P(\mathbf{0};z)\ . \tag{A38b}$$

The last relation may be compared to Eq. (A11) which obtains for the diamond lattice; evidently Eq. (A38) reflects the lower symmetry of the e lattice.

The calculation of $M(z)$ is now straightforward, since the arguments which we used in the derivation of Eq. (A25) for the diamond lattice apply here too. For walks starting on the $P$ sublattice one has

$$M(z) = (1-z)^{-1}P(\mathbf{0};z)\ , \tag{A39a}$$

whereas for walks which begin on a $Q$ sublattice, $M(z)$ is given by

$$M(z) = \tfrac{2}{3}(1-z)^{-1} + \tfrac{1}{3}(1-z)^{-1}P(\mathbf{0};z)\ . \tag{A39b}$$

The determination of $S(z)$ is more complicated. Let $F_j(\mathbf{r})$ be the probability that the site $\mathbf{r}$ on the $P$ sublattice is visited for the first time on step $j$, and let $F_j^\mu(\mathbf{r})$ correspondingly be defined for the sublattices $Q^\mu$. Then the equations similar to Eqs. (A12) are

$$P_j(\mathbf{r}) = \delta_{j,0}\delta_{\mathbf{r},\mathbf{0}} + \sum_{m=1}^{j} F_m(\mathbf{r})P_{j-m}(\mathbf{0})\ , \tag{A40a}$$

$$Q_j^\mu(\mathbf{r}) = \sum_{m=1}^{j} F_m^\mu(\mathbf{r})\tilde{Q}_{j-m}^\mu(\mathbf{0}_\mu)\quad (\mu = x,y,z)\ , \tag{A40b}$$

where we started the walk on the $P$ sublattice. $F_m(\mathbf{r})$ and $F_m^\mu(\mathbf{r})$ have the generating functions $F(\mathbf{r};z)$ and $F^\mu(\mathbf{r};z)$:

$$F(\mathbf{r};z) = \frac{P(\mathbf{r};z) - \delta_{\mathbf{r},\mathbf{0}}}{P(\mathbf{0};z)}\ , \tag{A41a}$$

$$F^\mu(\mathbf{r};z) = \frac{Q^\mu(\mathbf{r},z)}{\tilde{Q}^\mu(\mathbf{0}_\mu;z)}\ . \tag{A41b}$$

Introducing $\Delta_n$ as in Eq. (A15):

$$\Delta_n = \sum_{\mathbf{r}}{}' \left[F_n(\mathbf{r}) + \sum_\mu F_n^\mu(\mathbf{r})\right] = -F_n(\mathbf{0}) + \sum_{\mathbf{r}} F_n(\mathbf{r}) + \sum_\mu \sum_{\mathbf{r}} F_n^\mu(\mathbf{r})\ , \tag{A42}$$

one has for its generating function:

$$\Delta(z) = \sum_{n=1} z^n\Delta_n = -\left[1 - \frac{1}{P(\mathbf{0};z)}\right] + \sum_{\mathbf{r}} \frac{P(\mathbf{r};z) - \delta_{\mathbf{r},\mathbf{0}}}{P(\mathbf{0};z)} + 3\sum_\mu \sum_{\mathbf{r}} \frac{Q^\mu(\mathbf{r};z)}{2 + P(\mathbf{0};z)} = -1 + \sum_{\mathbf{r}} \frac{P(\mathbf{r};z)}{P(\mathbf{0};z)} + 3\sum_\mu \sum_{\mathbf{r}} \frac{Q^\mu(\mathbf{r};z)}{2 + P(\mathbf{0};z)}\ . \tag{A43}$$

Observing that for even steps the walker is on the $P$ sublattice and for odd steps on the $Q^\mu$ sublattices it follows

$$\sum_{\mathbf{r}} P_{2n}(\mathbf{r}) = 1 \; ; \; \sum_{\mathbf{r}} P_{2n+1}(\mathbf{r}) = 0 \; , \tag{A44a}$$

$$\sum_{\mu} \sum_{\mathbf{r}} Q^{\mu}_{2n}(\mathbf{r}) = 0 \; ; \; \sum_{\mu} \sum_{\mathbf{r}} Q^{\mu}_{2n+1}(\mathbf{r}) = 1 \; , \tag{A44b}$$

and thus

$$\sum_{\mathbf{r}} P(\mathbf{r}; z) = (1 - z^2)^{-1} \; , \tag{A45a}$$

$$\sum_{\mu} \sum_{\mathbf{r}} Q^{\mu}(\mathbf{r}; z) = z/(1 - z^2) \; . \tag{A45b}$$

Therefore,

$$\Delta(z) = -1 + [(1 - z^2) P(\mathbf{0}; z)]^{-1} + 3z \{(1 - z^2)[2 + P(\mathbf{0}; z)]\}^{-1} \tag{A46}$$

and $S(z)$ follows as above, Eqs. (A20) ff.:

$$S(z) = (1 - z)^{-2}(1 + z)^{-1} \left[ \frac{1}{P(0; z)} + \frac{3z}{2 + P(0; z)} \right] . \tag{A47}$$

Consider now walks starting on an edge, say on the $Q^x$ lattice from the origin $0_x$. One has then instead of Eqs. (A40):

$$\tilde{P}_j(\mathbf{r}) = \sum_{m=1}^{j} \tilde{F}_m(\mathbf{r}) P_{j-m}(0) \; , \tag{A48a}$$

$$\tilde{Q}^x_j(\mathbf{r}) = \delta_{j,0} \delta_{\mathbf{r}, \mathbf{0}_x} + \sum_{m=1}^{j} \tilde{F}^x_m(\mathbf{r}) \tilde{Q}^x_{j-m}(0_x) \; , \tag{A48b}$$

$$\tilde{Q}^{\mu}_j(\mathbf{r}) = \sum_{m=1}^{j} \tilde{F}^{\mu}_m(\mathbf{r}) \tilde{Q}^{\mu}_{j-m}(0_{\mu}) \quad (\mu = y, z) \; . \tag{A48c}$$

The generating functions $\tilde{F}(\mathbf{r}; z)$ and $\tilde{F}^{\mu}(\mathbf{r}; z)$ turn out to be

$$\tilde{F}(\mathbf{r}; z) = \frac{\tilde{P}(\mathbf{r}; z)}{P(\mathbf{0}; z)} \; , \tag{A49a}$$

$$\tilde{F}^x(\mathbf{r}; z) = \frac{\tilde{Q}^x(\mathbf{r}; z) - \delta_{\mathbf{r}, \mathbf{0}_x}}{\tilde{Q}^x(\mathbf{0}_x; z)} \; , \tag{A49b}$$

$$\tilde{F}^{\mu}(\mathbf{r}; z) = \frac{\tilde{Q}^{\mu}(\mathbf{r}; z)}{\tilde{Q}^{\mu}(\mathbf{0}_{\mu}; z)} \; . \tag{A49c}$$

With

$$\tilde{\Delta}_n = -\tilde{F}^x_n(\mathbf{0}_x) + \sum_{\mathbf{r}} \left[ \tilde{F}_n(\mathbf{r}) + \sum_{\mu} \tilde{F}^{\mu}_n(\mathbf{r}) \right] \tag{A50}$$

we obtain

$$\begin{aligned} \tilde{\Delta}(z) = \sum_{n=1}^{\infty} z^n \tilde{\Delta}_n &= -\left[ 1 - \frac{1}{\tilde{Q}^x(\mathbf{0}_x; z)} \right] + \sum_{\mathbf{r}} \frac{\tilde{P}(\mathbf{r}; z)}{P(\mathbf{0}; z)} \\ &\quad + \sum_{\mu} \sum_{\mathbf{r}} \frac{\tilde{Q}^{\mu}(\mathbf{r}; z)}{\tilde{Q}^{\mu}(\mathbf{0}_{\mu}; z)} - \frac{1}{\tilde{Q}^x(\mathbf{0}_x; z)} \\ &= -1 + \sum_{\mathbf{r}} \frac{\tilde{P}(\mathbf{r}; z)}{P(\mathbf{0}; z)} + 3 \sum_{\mu} \sum_{\mathbf{r}} \frac{\tilde{Q}^{\mu}(\mathbf{r}; z)}{2 + P(\mathbf{0}; z)} \; . \end{aligned} \tag{A51}$$

For even steps the walker is on the $Q^{\mu}$ sublattices and for odd steps on the $P$ sublattice. Therefore

$$\sum_{\mathbf{r}} \tilde{P}(\mathbf{r}; z) = z/(1 - z^2) \; , \quad \sum_{\mu} \sum_{\mathbf{r}} \tilde{Q}^{\mu}(\mathbf{r}; z) = (1 - z^2)^{-1} \tag{A52}$$

and

$$\tilde{\Delta}(z) = -1 + z[(1 - z^2) P(\mathbf{0}; z)]^{-1} + 3 \{(1 - z^2)[2 + P(\mathbf{0}; z)]\}^{-1} \; , \tag{A53}$$

from which $\tilde{S}(z)$ follows

$$\tilde{S}(z) = (1 - z)^{-2}(1 + z)^{-1} \left[ \frac{z}{P(0; z)} + \frac{3}{2 + P(0; z)} \right] . \tag{A54}$$

## APPENDIX B: ANALYSIS OF $P(0;z)$ FOR CUBIC LATTICES

In this Appendix we will use different methods to evaluate the first coefficients $u_i$ $(i = 1, 2, \ldots)$ in the expansion of $P(0; z)$, Eq. (2.17):

$$P(0; z) = u_0 - u_1(1 - z)^{1/2} + u_2(1 - z) - u_3(1 - z)^{3/2} + \cdots \tag{B1}$$

for the cubic lattices. We will not restrict ourselves to nearest-neighbor walks but will also consider the case of long-range steps. An elegant way to proceed is to rewrite $P(\mathbf{0}; z)$, Eq. (2.3) in the form [Ref. 35, Eq. (D2)]:

$$\begin{aligned} P(\mathbf{0}; z) &= \frac{1}{(2\pi)^3} \iiint_{-\pi}^{\pi} \frac{d^3\mathbf{k}}{1 - z\lambda(\mathbf{k})} \\ &= \frac{1}{(2\pi)^3} \iiint_{-\pi}^{\pi} \frac{d^3\mathbf{k}}{1 - \lambda(\mathbf{k})} \left[ 1 - \frac{(1 - z)\lambda(\mathbf{k})}{1 - z\lambda(\mathbf{k})} \right] \\ &= u_0 - \frac{(1 - z)}{(2\pi)^3} \iiint_{-\pi}^{\pi} \frac{d^3\mathbf{k}\, \lambda(\mathbf{k})}{[1 - \lambda(\mathbf{k})][1 - z\lambda(\mathbf{k})]} \; . \end{aligned} \tag{B2}$$

By comparing coefficients of $(1 - z)^{1/2}$ in Eq. (B1) and in Eq. (B2) one finds the coefficient $u_1$ to be given by

$$u_1 = \lim_{z \to 1} \frac{(1 - z)^{1/2}}{(2\pi)^3} \iiint_{-\pi}^{\pi} d^3\mathbf{k} f(\mathbf{k}) \; , \tag{B3}$$

with

$$f(\mathbf{k}) = \lambda(\mathbf{k}) / \{[1 - \lambda(\mathbf{k})][1 - z\lambda(\mathbf{k})]\} \; . \tag{B4}$$

Because of the factor $(1 - z)^{1/2}$ in front of the integral on the right-hand side of Eq. (B3), the only contributions to $u_1$ arise from the regions in $\mathbf{k}$ space for which the integral diverges. Thus only the regions around points in $\mathbf{k}$ space with $\lambda(\mathbf{k}) = 1$ must be considered; the remainder of the integral stays finite and, because of the limiting procedure $(z \to 1)$ and of the term $(1 - z)^{1/2}$, does not contribute to $u_1$.

For the random walks which we study the structure function $\lambda(\mathbf{k})$ has, according to Eqs. (3.1) and (2.6), the form

$$\lambda(\mathbf{k}) = \sum_{\mathbf{r}} p(\mathbf{r})\, e^{i\mathbf{k}\cdot\mathbf{r}} = \sum_{\mathbf{r}}{}' r^{-s}\, e^{i\mathbf{k}\cdot\mathbf{r}} \Big/ \sum_{\mathbf{r}}{}' r^{-s} \; . \tag{B5}$$

In the last expression the sums extend over all *lattice* sites $\mathbf{r}$ with the exception of the origin. One finds by inspection that $|\lambda(\mathbf{k})| \leq 1$, and that the equality $\lambda(\mathbf{k}) = 1$ is obtained only if $e^{i\mathbf{k}\cdot\mathbf{r}} = 1$ for all *lattice* sites $\mathbf{r}$. Because of the integration boundaries in Eq. (D3) we will be only concerned with sites $k = (k_1, k_2, k_3)$ for which $k_i \in [-\pi, +\pi]$ for $i = 1, 2, 3$. In the case of the sc lattice, only the point $\mathbf{k} = \mathbf{0}$ fulfills $e^{i\mathbf{k}\cdot\mathbf{r}} = 1$ and lies within the region of interest. However, in the cases of the bcc and fcc lattices constructed from the sc lattice by deleting sites (see Sec. II) also the $\mathbf{k}$ values $(\pm\pi, \pm\pi, 0)$, $(\pm\pi, 0, \pm\pi)$, $(0, \pm\pi, \pm\pi)$ for bcc, and $(\pm\pi, \pm\pi, \pm\pi)$ for fcc fulfill the above requirements. One satisfies oneself readily, however, that only the contribution from the origin needs

to be evaluated in Eq. (B3), since the additional terms can be accounted for by multiplying this result by a factor of 4 in the case of the bcc lattice, and by 2 in the case of the fcc lattice.

For points $\mathbf{k}$ in the neighborhood of the origin one has for $\lambda(\mathbf{k})$:

$$\lambda(\mathbf{k}) = 1 - \frac{1}{2}\sum_{\mathbf{r}}{}' r^{-s}(\mathbf{r}\cdot\mathbf{k})^2 \Big/ \sum_{\mathbf{r}}{}' r^{-s} + O(k^4)$$
$$= 1 - \beta k^2 + O(k^4)\,, \tag{B6}$$

where, due to the cubic symmetry:

$$\beta = \frac{1}{6}\sum_{\mathbf{r}}{}' r^{2-s} \Big/ \sum_{\mathbf{r}}{}' r^{-s}\,. \tag{B7}$$

It is now straightforward to determine the value of the integral (B3) in a small spherical region of radius $R_0$ around the origin. In this region we replace $\lambda(\mathbf{k})$ by its approximate form (B6). Then,

$$\int d^3\mathbf{k} f(\mathbf{k}) = 4\pi \int_0^{R_0} \frac{k^2 dk}{\beta k^2[1 - z + z\beta k^2]}$$
$$- 4\pi\beta \int_0^{R_0} \frac{k^4 dk}{\beta k^2[1 - z + z\beta k^2]}\,. \tag{B8}$$

The second integral on the right-hand side of Eq. (B8) stays finite for $z \to 1$. The contribution to $u_1$ thus arises only from the first integral which is equal to [Eq. (4.4.3) of Ref. 46]

$$\frac{4\pi}{\beta}\int_0^{R_0} \frac{dk}{1 - z + z\beta k^2}$$
$$= \frac{4\pi}{\beta^{3/2}\sqrt{z}(1-z)^{1/2}} \arctan\left(R_0\sqrt{\frac{z\beta}{1-z}}\right). \tag{B9}$$

Furthermore [Eq. (4.4.42) of Ref. 40]:

$$\arctan z = \frac{\pi}{2} - \frac{1}{z} + \frac{1}{3z^3} - \frac{1}{5z^5} + \cdots\,, \tag{B10}$$

and therefore, combining Eqs. (B3) and (B8)–(B10),

$$u_1 = \frac{\gamma}{4\pi\beta^{3/2}}\,, \tag{B11}$$

where $\gamma$ represents the number of times by which the contribution from the origin must be taken into account.

Equation (B11) is the main analytical result of this Appendix. For nearest-neighbor random walks it agrees with the corresponding expression in Ref. 35 when the factor $\gamma$ is accounted for. In this case the sums in Eq. (B7) are immediately evaluated, since only nearest neighbors are involved ($s = \infty$). One obtains $\beta = 1/6$, $\beta = 1/2$, and $\beta = 1/3$, for the sc, bcc, and fcc lattices, respectively. The coefficient $u_1$ is then as given in Eqs. (2.26) of the main text.

In the case of random walks with steps which are not restricted to nearest neighbors one has to perform the sums involved in Eq. (B7) numerically. We have evaluated these expressions for the cases $s = 6$, 8, and 10 for all three cubic lattices considered. These results are presented in Table III.

For the determination of the coefficients $u_2$ and $u_3$ in Eq. (B1), which correspond to higher-order terms, we have resorted to a numerical evaluation of the integral representation of the generating function. In principle one might envisage evaluating $P(0; z)$ according to Eq. (2.3) for a series of $z$ values in the neighborhood of $z = 1$ and then fitting the results to Eq. (B1). In practice, however, this allows only the determination of $u_0$ and of $u_1$ with sufficient accuracy. This is due to the fact that the power-law expansion in $(1 - z)^{1/2}$ forces one to choose $z$ values very close to 1, while on the other hand the integration of $P(0; z)$ cannot be performed with the required accuracy near $z = 1$ due to the pathological behavior of the integrand for $\lambda(\mathbf{k}) = 1$.

A more convenient procedure involves subtracting from $P(0; z)$ the terms $u_0 - u_1(1 - z)^{1/2}$, dividing by $(1 - z)$, and determining $u_2 - u_3(1 - z)^{1/2}$ from the remaining expression. This procedure follows readily when use is made of Eq. (B2). There the term $u_0$ is already separated and one is left with the evaluation of

$$I(z) = u_1(1 - z)^{-1/2} - \frac{1}{(2\pi)^3}\iiint_{-\pi}^{\pi} d^3\mathbf{k} f(\mathbf{k})\,, \tag{B12}$$

with $f(\mathbf{k})$ being given by Eq. (B4). Because of Eq. (B3) one sees that the first term on the right-hand side of Eq. (B12) plays only the role of removing the divergence of the second term at $z = 1$. The same role can be played by the following integral $\tilde{I}(z)$, calculated inside a sphere $S$ of radius $R_0$ around each singularity of $I(z)$:

$$\tilde{I}(z) \equiv \frac{1}{(2\pi)^3}\iiint_S \frac{d^3\mathbf{k}}{\beta(1-z)k^2 + \beta^2 k^4} = \frac{1}{2\pi^2\beta}\int_0^{R_0} \frac{dk}{1 - z + \beta k^2}$$
$$= \frac{1}{2\pi^2\beta^{3/2}(1-z)^{1/2}} \arctan\left(R_0\sqrt{\frac{\beta}{1-z}}\right). \tag{B13}$$

Viz., one has from Eqs. (B10) and (B11)

$$\tilde{I}(z) = \gamma^{-1}u_1(1 - z)^{-1/2}$$
$$- \frac{1}{2\pi^2\beta^2 R_0}\left[1 - \frac{(1-z)}{3R_0^2\beta} + \frac{(1-z)^2}{5R_0^4\beta^2} - \cdots\right]. \tag{B14}$$

The procedure is now obvious. We evaluate the integral

$$\tilde{\tilde{I}}(z) = \frac{1}{(2\pi)^3}\iiint_{-\pi}^{\pi} d^3\mathbf{k} F(\mathbf{k})\,, \tag{B15}$$

where $F(\mathbf{k})$ is

$$F(\mathbf{k}) = -f(\mathbf{k}) + [\beta(1-z)k^2 + \beta^2 k^4]^{-1} \tag{B16a}$$

for $\mathbf{k}$ inside the spherical domains, and

$$F(\mathbf{k}) = -f(\mathbf{k}) \tag{B16b}$$

for the remaining integration region. $\tilde{\tilde{I}}(z)$ has a finite value at $z = 1$ and can readily be compared to $u_2 - (\gamma/2\pi^2\beta^2 R_0) - u_3(1 - z)^{1/2}$. In expression (B13), $R_0$ is largely arbitrary but should be chosen as large as possible considering the singularities which are present in the case of the bcc and fcc lattices. We conveniently divide the integration region into cubes of sidelength $\pi/2$ and choose $R_0 = \pi/2$, i.e., we inscribe the largest possible sphere in such a cube. We perform the integrations separately inside the sphere, in the remaining cubical region, and in the cubes without singularities.

The value for $u_2$ is obtained directly as a result of the integral (B15) for $z = 1$, corrected for the term $[-\gamma/$

$(2\pi^2\beta^2 R_0)]$. The constant $u_3$ follows from a fit to a number of integrals (B15). In the numerical evaluation we chose $z$ to be in the range $0.995 < z < 1$.

For nearest-neighbor random walks we are thus able to calculate $u_2$ to five significant digits whereas for $u_3$ the numerical accuracy which we obtain with this method is one order of magnitude smaller. The accuracy was checked by comparison with the exact results of Sec. II.


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