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2000 J. Phys.: Condens. Matter 12 7199

(http://iopscience.iop.org/0953-8984/12/32/304)

J. Phys.: Condens. Matter **12** (2000) 7199–7204. Printed in the UK PII: S0953-8984(00)13398-3

Two-particle approximation to the diffusion coefficient of a tracer particle

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Received 19 April 2000

Abstract. In this paper we show that the diffusion behaviour of a tracer particle in a lattice gas of hard-core particles at a given concentration may be approximated, for the whole concentration range, by the diffusion behaviour of a tracer particle in a two-particle system with effective transition rates. In this approach, the other particle is an effective background particle with a dual particle–vacancy character. The diffusion constant obtained in the present approximation is shown to be equivalent to the one obtained by solving a set of coupled many-body rate equations with a second-order approximation, as originally given by Tahir-Kheli and Elliott. Our solution relies exclusively on random-walk methods and we give, in this framework, the *exact* solution for the diffusion coefficient of a tracer particle in a two-particle system with arbitrary transition rates.

1. Introduction

Diffusion in many-particle systems, either with or without static disorder, has received considerable attention over the years [1]. Notwithstanding, there are few instances in which exact solutions are available, most of them either for the limiting case of a single particle in a disordered medium [2] or for particular cases of one-dimensional many-particle systems [3].

The calculation of the diffusion coefficient of a tracer particle in a lattice gas of hard-core particles at arbitrary concentration c is a true many-body problem, for which no exact solution is known. Early attempts at approximate solutions were concerned with the limit of low concentration of vacancies [4]. Le Claire gives a comprehensive review of the earlier literature [5]. Later, asymptotically correct solutions for the limits $c \to 0$ and $c \to 1$ were derived through different methods [6–8].

For the case of arbitrary values of c, an early approximate solution has been given by Kikuchi and Sato [9]. More recently, approximate solutions based on the master equation approach, with varying methods, have been given by Feders and Sankey [10], Bender and Schroeder [11] and Nakazato and Kitahara [12]. Departing from a master equation, Tahir-Kheli and Elliott [13] proposed an approximate solution (TKE) based on a decoupling scheme of many-particle correlation functions, which proved to be very successful. Their solution correctly reproduces the single-vacancy and single-particle limits for general, but non-vanishing, values of the transition rates, J and J_0, of tracer and background particles, respectively. In the case of self-diffusion ($J_0 = J$), the theoretical results present remarkably

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0953-8984/00/327199+06$30.00

good agreement with Monte Carlo simulations results for the entire range of concentration of background particles [14]. Using a different approach in which the diffusion coefficient is expressed in terms of the velocity autocorrelation function, van Beijeren and Kutner [15] obtained a solution which is the same as the TKE solution.

In this paper our objective is to show that the TKE solution may also be derived from the random-walk theory applied to a system of two particles interacting in an effective medium. In what follows, we first briefly present the theoretical background of the problem; this is followed by a section on the effective medium. Then, we present the derivation of the two-particle random-walk approach and show its equivalence with the TKE solution for hypercubic lattices without static disorder. Finally, we make some concluding remarks.

2. Theoretical background

From general arguments of random-walk theory, it is possible to show that the tracer diffusion coefficient may be expressed as [16]

$$D = J_0 f_b f_c \tag{1}$$

where $f_b = (1 - c)$ is the blocking factor due to background particles and $f_c = (1 - Q)$ is the correlation factor, where the function Q is given by

$$Q = 2J_0 c\left(\frac{U_{ii} - U_{mi}}{E_0}\right). \tag{2}$$

Here, E_0 is a normalization constant which is conveniently chosen to be the maximum transition rate for a particle leaving a site in the system and U_{ij} are the usual generating functions for the probabilities of a random walker moving from site j to site i in a given number of hopping steps. In the limit of $c \to 0$ the difference $U_{ii} - U_{mi}$ is evaluated for the case in which a background particle interacts with the tracer particle while for $c \to 1$ it is evaluated for the case in which a single vacancy interacts with the tracer particle. Both these limits are reproduced correctly with the random-walk theory.

In the following, we show that the general case of arbitrary concentration c may be handled as well through a two-particle random-walk theory, at a level of approximation equivalent to that obtained with the TKE. The basic idea consists of setting up an effective two-particle system, containing a virtual background particle interacting with a tracer particle, in which the hopping rates are chosen in such a way that as c goes from zero to one the effective system gradually changes from a single-particle system to a single-vacancy system. Our demonstration consists of showing that (1) reproduces the TKE approximation for f_c, namely

$$f_c^{TKE} = \left(1 - \frac{2cJ_0\cos(\theta)}{J_2(1 + \cos(\theta))}\right)^{-1} \tag{3}$$

when Q is computed from (2) for the aforementioned effective system. In (3), $\cos(\theta)$ is a lattice-dependent geometrical factor. Here J_2 characterizes the relative motion of the tracer and a background particle or vacancy. In the mean-field approximation which includes only blocking effects on the tracer particle this reads

$$J_2 = J + J_0(1 - c). \tag{4}$$

An improvement which includes the correlation effects is to replace the effective tracer hopping rate by $J_0 f_c(1 - c)$ and solve for f_c self-consistently [14].

3. Effective medium

In the TKE approximation the hierarchy of many-body rate equations is truncated to the second-order equation and the original *infinite-particle* problem is then reduced to that of two interacting *virtual* particles in an effective medium. The effective interaction between the particles and the characteristics of the effective medium given by the approximation are such that both the *single-particle* and *single-vacancy* limits are correctly reproduced, as far as the blocking and correlation factors are concerned.

The derivation of (1), with Q given by (2), follows a different approach. It is derived by directly postulating a two-particle system with special characteristics. In it, a tracer particle interacts with a virtual particle, which represents the whole of the background particles. The concentration c of background particles defines the hopping rate of the virtual particle, such that the virtual particle may be seen as a normal background particle when $c \to 0$ and as a vacancy when $c \to 1$.

The effective system is defined as follows. The hopping rate for the virtual background particle remains unchanged, equal to J for any value of c, since this is the correct hopping rate for either a background particle or a vacancy. However, the tracer particle hopping rate is changed to $J_0(1 - c)$, since in the limit $c \to 1$ the tracer particle is immobile, while in the opposite limit it is a free particle with hopping rate J_0. The transition rates for exchanges between the virtual background particle and the tracer particle is set to J_0c. This definition ensures that in the limit $c \to 1$ the virtual background particle behaves like a vacancy while for $c \to 0$ it behaves like a normal background particle. Thus, the virtual background particle can be interpreted as having a concentration-dependent dual particle–vacancy character. Figure 1 shows a two-dimensional representation of the effective system that we are considering in this study.

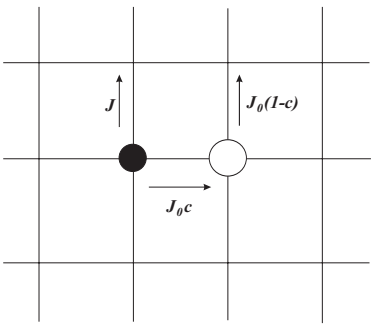

Figure 1. The effective two-particle random walk. The virtual particle is represented by the filled circle. The transition rate of the virtual particle in the empty lattice is always J. The corresponding value for the tracer particle is $J_0(1-c)$. The tracer particle swaps positions with the virtual particle with rate J_0c.

4. Two-particle random walk

The probability distribution functions associated with a system of two interacting particles may be obtained from a one-particle system in which one of the particles performs a random walk in an effective lattice while the other particle is at rest. The hopping rate with which the mobile particle moves is equal to the sum of the hopping rates of the two original particles. This could be considered as a '*change-of-reference-frame*-type' transformation applied to a

random-walk system. Such an approach is possible only when the lattice has translational symmetry. Figure 2 gives a graphical representation of the random walk of two particles in a lattice, where the reference frame has been changed.

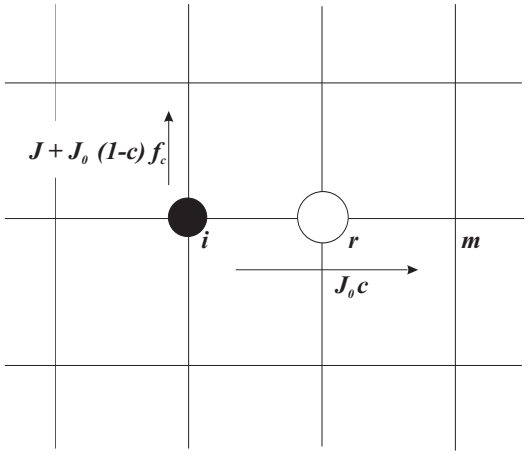

Figure 2. The two-particle random walk in a reference frame in which the tracer particle is at rest. For the definition of the transition rates, see figure 1. Note that the virtual particle may now jump directly from site i to site m and vice versa. The factor f_c multiplying $J_0(1-c)$ refers to the self-consistent approximation.

We now turn to the evaluation of $(U_{ii} - U_{im})/E_0$ for the effective system described above. The derivation given here will be restricted to a d-dimensional hypercubic lattice, for which the coordination number is $2d$. Since our derivation does not depend on the lattice geometry, extension to other lattice geometries is straightforward. Our strategy consists, essentially, of expressing the generating functions relative to the defective lattice in terms of the generating functions for a perfect lattice. Through simple manipulation of the series defining the generating functions U, as described previously [16–18], it can be shown that

$$\begin{aligned} U_{ii} &= 1 + U^{\Omega}_{ii}U_{ii} + U^{\Omega}_{im}U_{mi} \\ U_{im} &= U^{\Omega}_{ii}U_{im} + U^{\Omega}_{im}U_{mm} \\ U_{ii} - U_{im} &= \frac{1}{1 - (U^{\Omega}_{ii} - U^{\Omega}_{im})} \end{aligned} \tag{5}$$

where

$$U^{\Omega}_{ii} = \lambda p_{ii} + \lambda^2 \sum_{l \notin \Omega} p_{il}\, p_{li} + \cdots \tag{6}$$

$$U^{\Omega}_{im} = \lambda p_{im} + \lambda^2 \sum_{l \notin \Omega} p_{il}\, p_{lm} + \cdots \tag{7}$$

$$U_{ij} = \delta_{ij} + \lambda \sum_{l} p_{il} U_{lj}. \tag{8}$$

Here, p_{il} stands for the probability that a particle hops from site l to site i. These probabilities are related to the transition rates of the time-dependent picture through the expression $p_{il} = J_{il}/E_0$, where J_{il} is the probability per unit time for a particle hopping from site l to site i. Ω denotes the set of sites (i, r, m) while λ is the usual formal parameter in the definition of generating functions. Note that U^{Ω} is the same function as U, with the restriction that sites in the set denoted by Ω are not visited. In deriving (5) the symmetry relations

$U^{\Omega}_{mi} = U^{\Omega}_{im}$, $U^{\Omega}_{mm} = U^{\Omega}_{ii}$, $U_{mi} = U_{im}$ and $U_{mm} = U_{ii}$ have been used. Equation (5) is also valid for a perfect lattice, i.e., a lattice with only one particle and no defects. Hence we may write

$$[U_{ii}] - [U_{im}] = \frac{1}{1 - ([U^{\Omega}_{ii}] - [U^{\Omega}_{im}])} \tag{9}$$

where quantities enclosed in square brackets refer to a perfect lattice. From the definitions in (6) and (7), it may be checked that

$$U^{\Omega}_{ii} = \lambda(p_{ii} - [p_{ii}]) + [U^{\Omega}_{ii}] \tag{10}$$

$$U^{\Omega}_{im} = \lambda(p_{im} - [p_{im}]) + [U^{\Omega}_{im}]. \tag{11}$$

Following the conventional notation we set $([U_{ii}] - [U_{mi}])/2d = -\cos(\theta)$, for a d-dimensional hypercubic lattice. Here, $\cos(\theta)$ may be interpreted as the average cosine of the angle between two successive steps of a random walker. For our purposes, it is convenient to set $E_0 = 2dJ_2$. In this way, the probabilities $[p_{ii}]$ for the perfect system are equal to zero, which simplifies some of the equations. From (9) it is readily shown for $\lambda = 1$ that

$$[U^{\Omega}_{ii}] - [U^{\Omega}_{im}] = \left(1 + \frac{1}{2d\cos(\theta)}\right). \tag{12}$$

Noting that

$$\begin{aligned} p_{ii} &= 1 - \frac{(2d-1)J_2}{E_0} - \frac{J_0 c}{E_0} = \frac{1}{2d}\left(1 - \frac{J_0 c}{J_2}\right) \\ [p_{ii}] &= 0 \\ p_{im} &= \frac{J_0 c}{E_0} = \frac{J_0 c}{2dJ_2} \\ [p_{im}] &= 0 \end{aligned} \tag{13}$$

and making use of (9) and (12), the following result is obtained:

$$U^{\Omega}_{ii} - U^{\Omega}_{im} = \frac{1}{2d} - \frac{J_0 c}{dJ_2} + \left(1 + \frac{1}{2d\cos(\theta)}\right) \tag{14}$$

which upon substitution in (5) finally yields

$$(U_{ii} - U_{im})/2dJ_2 = -\frac{\cos(\theta)}{J_2(1+\cos(\theta)) - 2J_0\cos(\theta)}. \tag{15}$$

Equation (15) together with (1) and (2) give the TKE expression for f_c. In their calculation, Tahir-Kheli and Elliott use an effective interaction V between the tracer and the background. The first term in p_{ii} corresponds to the blocking effect of two neighbouring particles, while the second term in p_{ii} together with p_{im} represent the exchange of the pair.

5. Concluding remarks

Once a formal identity between the TKE approximation and a two-particle system has been established, one is naturally led to the question of whether any further improvements in the treatment of the tracer particle problem, in either ordered or disordered lattices, may be achieved through the present approach.

As for ordered lattices, we believe that we have demonstrated that the present approach gives good insight into the nature of the TKE approximation. It clearly shows that the latter works as a scheme for interpolation between two limits, i.e. the single-particle and single-vacancy limits, for which it gives exact results. The connection between the two limits is

accomplished by substituting for the set of background particles with a single *virtual* particle which changes its character from a normal background particle when $c \to 0$ to a vacancy when $c \to 1$. It is quite difficult to extract this interpretation directly from the set of rate equations and approximations from which the TKE has been originally derived. Despite the advantages in terms of the interpretation given by this framework, it is not evident how one could improve upon the TKE solution for the treatment of the dynamical correlations induced by the background particles.

With respect to systems with static disorder, such as bond- or site-disordered lattices, the present framework seems to open new possibilities for the treatment of the correlations induced by the static disorder in the tracer movement. Such possibilities are not directly discernible in the master equation approach. For instance, as a first approximation one may assume that the many-particle system can be reduced to an effective two-particle system, as above, independently of disorder in the lattice. One, then, is left with the task of treating the effect of the static disorder on the random walk of two particles. In references [17, 18] we provide an example of approximate methods for dealing with this problem. This assumes that the effective particles interact in an effective disordered medium where the correlation between successive steps $\overline{\cos(\theta)}$ is averaged over different environments and substituted into the formula for f_c. The good agreement between theory and simulation shown there indicates that the above prescription can, in some circumstances, describe quite successfully the effect of static disorder on the correlation factor.

Acknowledgment

LP and KK would like to express their thanks to the Academy of Finland for financial support.

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