Exact solution of the five frequency model of the vacancy-assisted impurity diffusion in the limit of vanishing vacancy concentration

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(Dated: February 9, 2022)

Abstract

The van Hove autocorrelation function of the impurity is obtained which is exact to the first order in the vacancy concentration. It is found that in the case of strong vacancy-impurity binding a singularity in the van Hove function corresponding to a resonant bound state develops on the unphysical sheet in the complex frequency plane close to the real axis. It is argued that this bound state corresponds to the defect-impurity pairs widely used in models of diffusion in semiconductors.

PACS numbers: 66.30.Dn, 66.30.Jt
FIG. 1: Frequencies of exchange of the vacancy (grey square) with atoms in the vicinity of the impurity (black circle) as defined in the five-frequency model: $\omega_1$ – exchange with the atoms in the first coordination sphere; $\omega_2$ – exchange with the impurity atom; $\omega_3$ – dissociative jumps away from the impurity into higher coordination spheres; $\omega_4$ – associative jumps from higher spheres into the first one. Not shown in the figure is the frequency $\omega_0$ of exchange with the atoms in the host bulk.

In close packed solids (like FCC crystals) the diffusion of atoms goes predominantly via their exchange with vacancies. Because the vacancy concentration is usually small, in the limit of infinite dilution a microscopic description of the diffusion reduces to the consideration of the two-body interactions and exchanges between a single vacancy and the atom of the diffusing species $1, 2, 3$.

When microscopic interactions are known, a two-body problem can usually be solved exactly. For example, in Ref. 4 a solution for the tracer Green function accurate to the leading orders in impurity and vacancy concentrations was obtained in the case of the self-diffusion problem. This success was due to the simplicity of the self-diffusion case where all vacancy hopping parameters are identical.

In the case of impurity, however, the vacancy in the host bulk and in its vicinity experiences different forces, so the number of parameters grows. This case is most frequently described in the framework of the so-called five-frequency model (5FM; see Fig. 1). Introduced by Lidiard 5 half a century ago, this model has become a conventional tool for the microscopic description of impurity diffusion.

The aim of the present Letter is to obtain the solution of the 5FM of impurity diffusion similar to that of Ref. 4 for the tracer diffusion and to show that under strong vacancy-impurity (V-I) binding the solution contains a resonant bound state which can be identified with the defect-impurity pairs widely used in the description of diffusion in semiconductors 6, 7.
To avoid awkward matrix formalism conventionally used in microscopic theories of diffusion [2, 3], the calculations of the present Letter will be based on the second quantization representation of stochastic dynamics [8]. This allows for the treatment of diffusion problems within the standard techniques of the quantum theory. A detailed exposition of this approach may be found in the review article [9]. The formalism which will be used in this Letter is presented in detail in Ref. [10], so below are listed only the formulas used in subsequent calculations.

In the second quantization approach the host lattice completely filled with the solvent atoms is considered to be the ground state ($|\text{host}\rangle$) of the diffusion problem. The impurity atoms and the vacancies are created (annihilated) on lattice site $i$ under the action of the so-called hard-core boson creation (annihilation) operators $a_i^+$ ($a_i$) and $b_i^+$ ($b_i$), respectively. These operators satisfy the canonical bosonic commutation relations in all cases except when on the same site in which case they satisfy the anticommutation relations [11]

$$\{d_i^+, d_i\} = 1 \quad \text{and} \quad d_i^2 = (d_i^+)^2 = 0$$  \hspace{1cm} (1)

(here $d_i$ stands either for $a_i$ or for $b_i$) to prevent multiple occupancy of the site by the same specie. The particle number operators as usual are

$$n_i = a_i^+ a_i \quad \text{and} \quad v_i = b_i^+ b_i$$  \hspace{1cm} (2)

and the average concentrations are their statistical averages $c_I = \langle n_i \rangle$ and $c_V = \langle v_i \rangle$.

The coherent state

$$|\rangle = \prod_i (1 + a_i^+)(1 + b_i^+) |\text{host}\rangle,$$  \hspace{1cm} (3)

comprises all possible configurations of impurities and vacancies with equal weight and is used below to compute statistical averages. The weak equivalences between the operators with respect to the conjugate coherent state

$$\langle a_i | = \langle |n_i; \quad a_i^+ = \langle |(1 - n_i)$$  \hspace{1cm} (4)

and similar relations for the vacancy operators are easily derived from Eqs. (1)–(3).

The matrix of transition probabilities $T$ governing the time evolution of a state vector

$$|t\rangle = \exp(Tt)|0\rangle,$$  \hspace{1cm} (5)
obeys the condition of probability conservation \[ \langle |T = 0. \] (6)

The van Hove autocorrelation function \( G_{l0} \) describes the evolution at equilibrium of an impurity atom initially placed at the origin of the lattice coordinates. It can be obtained as the \( c_I \rightarrow 0 \) limit of the impurity-impurity correlation function because in this limit only the autocorrelations survive:

\[
G_{l0} = \lim_{c_I \rightarrow 0} \left( c_I^{-1} \langle |n_t \exp(cI T)n_0 e^{-\mathcal{H}/kT}| \rangle \right),
\] (7)

where \( \mathcal{H} \) is the Hamiltonian of interparticle interactions which includes a normalization constant such that \( \langle |e^{-\mathcal{H}/kT}| \rangle = 1 \) \[10\]. With the use of Eq. (6) the last equation can be rewritten as a conventional retarded correlation function. For brevity, the following notation for such functions will be used:

\[
\langle A; B \rangle_t \equiv \lim_{c_I \rightarrow 0} \left( c_I^{-1} \langle |A(t)B(0)e^{-\mathcal{H}/kT}| \rangle \right),
\] (8)

where \( A(t) = e^{-cIT}Ae^{cIT} \). Thus, the evolution of the correlation function can be studied with the use of the Heisenberg equation

\[
\dot{A} = [A, T]
\] (9)

provided the transition matrix is known. According to Ref. [12], the transition matrix consists of two parts:

\[
T = T^{\text{in}} - T^{\text{out}},
\] (10)

where the first part describes intersite particle exchange while the second part is site-diagonal and depends only on the operators \( n_i \) and \( v_i \). In the case under consideration the “in” part can be written as

\[
T^{\text{in}} = \sum_{ij} \left( \omega_{ij} + \omega_{ij}^{\text{ex}} a_i^+ a_j \right) b_i^+ b_j.
\] (11)

Here the first term in the parenthesis corresponds to the vacancy exchanges with the host atoms while the second term describes the V-I exchanges. In general case the hopping frequencies entering Eq. (11) depend on the whole many-body configuration of vacancies and impurities. But in the double dilute limit under consideration it is sufficient to keep the dependence of \( \omega_{ij} \) on the position of only one impurity, while \( \omega_{ij}^{\text{ex}} \) does not depend on the configuration at all because the two participating particles are already present in the
transition matrix. So in the two-body approximation $\omega_{ij}^2$ can be identified with $\omega_2$ while $\omega_{ij}$ have the values shown in Fig. 1. It is important to note that $\omega_{ij} \neq \omega_{ji}$.

The “out” term in Eq. (10) can be easily obtained from Eq. (6) with the use of Eq. (4). But because it commutes with all site-diagonal operators, it will not be needed in the calculations below. Thus, substituting $A = n_i$ and $T^\text{in}$ into Eq. (9) and computing the average in Eq. (8) with $B = n_0$ to the leading orders in $c_I$ and $c_V$, with the use of Eq. (4) it is straightforward to obtain

$$dG_{l0}(t)/dt = \omega_2 \sum_\delta (\langle n_{l+\delta}v_l; n_0 \rangle_t - \langle n_{l}v_{l+\delta}; n_0 \rangle_t),$$

where by $\delta$ are denoted 12 different lattice vectors connecting nearest neighbor sites.

Similarly, by choosing $A = n_lv_j$ and $B = n_0$ in Eqs. (8) and (9) one arrives at a closed set of equations necessary to calculate the impurity van Hove function $G_{l0}(t)$ to the chosen order of approximation

$$(d/dt)\langle n_lv_j; n_0 \rangle_t = \omega_{jl}^x \langle n_jv_l; n_0 \rangle_t - \omega_{lj}^x \langle n_lv_j; n_0 \rangle_t$$

$$+ \sum_i \omega_{ji} \langle n_lv_i; n_0 \rangle_t - (\sum_i \omega_{ij}) \langle n_lv_j; n_0 \rangle_t.$$  (13)

The above two equations have the same formal structure as the corresponding equations of Ref. [4], so their solution can be found by a straightforward use of the techniques of that reference. Therefore, only notation and the points of departure from the solution of Ref. [4] will be explained in some detail.

The first step is to subject the equations to the Laplace (with respect to $t$) and spatial Fourier transforms (L-F transform). Their normalizations should be understood from the definition of $f_K(r)$ (cf. Ref. [4])

$$\langle n_lv_{l-r}; n_0 \rangle_t = \frac{1}{2\pi i} \oint dz \frac{1}{N} \sum_K f_K(r) e^{zt+iK \cdot r}$$

and a similar expression for $G_{l0}(t)$-$G_K(z)$ pair. The Laplace transform of derivatives contains the function values at $t = 0$. In the present case they are given by the equilibrium correlators in (8) which are $G_{l0}(0) = \delta_{l0}$ and

$$\langle n_lv_jn_0 \rangle_0 = c_V \delta_{l0}(1 - \delta_{lj})[1 + (e^{E_b/kT} - 1), \delta_{j-l},]$$

where the multiplier in the parentheses forbids simultaneous occupation of the same site by the impurity and the vacancy while the term in square brackets describes the enhancement
(suppression) of the vacancy concentration in the first coordination sphere of the impurity provided the V-I binding energy $E_b$ is positive (negative). The transformed Eq. (12) reads (cf. Eq. (5) of Ref. [4])

$$zG_K(z) = 1 - \omega_2 \sum_\delta [1 - \exp(iK \cdot \delta)] f_K(\delta).$$  \hspace{1cm} (16)

According to Ref. [4] it should be cast into the form of the diffusion propagator

$$G_K(z) = [z + c_V F(z, K) \epsilon_K]^{-1},$$  \hspace{1cm} (17)

with the $z$ and $K$-dependent diffusion correlation factor

$$F(z, K) = \omega_2 z \sum_\delta [1 - \exp(iK \cdot \delta)] f_K(\delta),$$  \hspace{1cm} (18)

where $\epsilon_K = \omega_0 \sum_\delta [1 - \exp(iK \cdot \delta)]$.

Eq. (13) under the L-F transform takes the form

$$zf_K(r) = c_V [1 - \delta(r)] [1 + (e^{\frac{E_b}{kT}} - 1) \sum_\delta \delta(r - \delta)]$$

$$+ \omega_2 \sum_\delta \delta(r - \delta) [\exp(-iK \cdot \delta) f_K(-r) - f_K(r)]$$

$$+ \sum_\delta [\omega(r - \delta, \delta) f_K(r - \delta) - \omega(r, \delta) f_K(r)],$$  \hspace{1cm} (19)

where $\omega(r, \delta)$ is the frequency of hopping from site $r$ to $r + \delta$. It is easy to see that $f_K(0) = 0$ satisfies this equation irrespective of $f_K(r)$ values at other sites because in the 5FM the vacancy hops onto or from the site occupied by the impurity are forbidden: $\omega(-\delta, \delta) = \omega(0, \delta) = 0$. Therefore, henceforth $f_K(0)$ will be excluded from the consideration. Furthermore, because in the absence of fluxes ($K = 0$) the system is at equilibrium, the values of $f_{K=0}(r)$ should be equal to the L-F transformed Eq. (15). The result can be written symbolically as

$$\vec{f}_0 = \vec{E}/z,$$  \hspace{1cm} (20)

where the vector components are the values of corresponding quantities at lattice sites $r$. Because the components of $\vec{E}$ coincide with the first line on the right hand side (RHS) of Eq. (19), $zf_0$ turns this line into identity. Thus, in order to satisfy the rest of equation the frequencies should be subject to the constraint [1, 2, 3]

$$\frac{\omega_3}{\omega_4} = \exp(-E_b/kT) \equiv \varepsilon$$  \hspace{1cm} (21)
as can be checked by a direct substitution of \( f_0 \) from Eq. (20) into the last line of Eq. (19).

The method of solution for general \( K \) proposed in Ref. [4] essentially consists in subtraction from both sides of Eq. (19) of the term which formally coincides with the equation last line but with all \( \omega(r, r') \) replaced with \( \omega_0 \). The result can be symbolically written as

\[
\hat{R}^{-1} \tilde{f}_K = \hat{E} + \hat{V} \tilde{f}_K,
\]

where matrix \( \hat{R} \) is composed of matrix elements

\[
R_{r, r'} = \frac{1}{N} \sum_{\lambda} \exp[-i\lambda \cdot (r - r')] \frac{z}{z + \epsilon_{\lambda}},
\]

the first line of Eq. (19) is represented by \( \hat{E} \) and the remaining terms are gathered into \( \hat{V} \tilde{f}_K \). The meaning of this transformation is that now on the RHS of Eq. (22) only a finite number of \( f_K(r) \) (54 in this case) with \( r \) belonging to the first four coordination spheres remain because beyond these spheres \( \omega(r, \delta) - \omega_0 \equiv 0 \), as can be seen from the definition of frequencies in Fig. [1] Now multiplying both sides of Eq. (22) with \( \hat{R} \)

\[
\tilde{f}_K = \hat{R} \tilde{E} + \hat{R} \hat{V} \tilde{f}_K
\]

and retaining only those equations which have at their left hand sides the same \( f_K(r) \) that are present on the RHS one obtains a linear system of 54 equations which can be solved, e. g. with the use of the Cramer’s rule

\[
f_K(r) = \Delta_r(z, K)/\Delta(z, K).
\]

Here \( \Delta(z, K) \) is the determinant of the system and \( \Delta_r(z, K) \) is the same determinant with the column corresponding to \( f_K(r) \) replaced by \( \hat{R} \tilde{E} \). Substituting \( f_K(\delta) \) thus obtained into Eqs. (18) and (7) one obtains \( G_K(z) \) for general values of \( z \) and \( K \). It can be used, e. g., to study the diffusion of Mössbauer impurities where the knowledge of the van Hove autocorrelation function at finite values of \( z \) and \( K \) is essential [13].

If one is interested only in the diffusion limit \( z, K \to 0 \), then the size of the system (24) can be reduced to 13 by the choice of a high symmetry direction \( K = (K, 0, 0) \) [4]. It can be shown that the correlation factor \( F(0, 0) \) in Eq. (18) can be expressed through the ratio of two determinants of size 13. The corresponding expression was derived and numerically checked on thousands of randomly generated frequency quintets. In all cases excellent agreement with the approximate expression due to Manning [2] was found. In
particular, it was numerically confirmed that in the case of strong V-I binding the correlation factor is always enhanced as $O(1/\omega_3)$. This might have been guessed on the basis of Eq. (20) which states that $f_{\mathbf{K}=0}(\delta) = \varepsilon^{-1}/z \propto 1/\omega_3$. A careful analysis shows that in Eq. (25) the $\omega_3^{-1}$ factor can originate only from the denominator because in the numerator the contribution due to $\hat{R}\hat{E}$ containing $\varepsilon^{-1}$ is suppressed in the limit $z \to 0$ by the factor $z$ in Eq. (18) (see Eq. (27) below). Thus, in the case of strong V-I binding the determinant $\Delta(0,0)$ should be proportional to $\omega_3$. Then it is reasonable to assume that at small $z$ and $|\mathbf{K}|$

$$\Delta(z, \mathbf{K}) \approx C_1\varepsilon + C_2 z + C_3 K^2,$$

(26)

where $C_k$ are some constants. From here it would follow that $F(z, \mathbf{K})$ develop a pole-like singularity at some small value of $z$.

To qualitatively assess the influence of this singularity on the impurity diffusion let us consider the simplest model with V-I binding: the so-called 2-frequency model (2FM)\cite{1, 2, 3} where all frequencies are equal to $\omega_0$ except $\omega_3$ which according to Eq. (21) should be equal to $\varepsilon\omega_0$. In this case the dimension of determinants reduces to 3 so with the use of exact relations between $R_{r,r'}$ derived in Ref.\cite{14} one arrives after some algebra to an expression which to leading orders in the small quantities reads

$$F_{2FM}(z, \mathbf{K}) \approx g + 0.5 \varepsilon^{-1} z + 2g\varepsilon + (\omega_0/6)(aK)^2,$$

(27)

where $g = (24R_{0,\delta})^{-1}$. Because $R_{0,\delta}$ has a square root singularity at $z = 0$\cite{14}, the pole shifts from the real axis on unphysical sheet on the distance $O(\varepsilon^{3/2}) \ll 1$, as can be seen from the denominator of Eq. (27).

The quasiparticle content of the van Hove function can be established by the substitution of $F_{2FM}$ into Eq. (18) and by approximating $g$ with a real constant $g_0 = g(z = 0)$. In this case the van Hove function acquires simple two-pole structure

$$G_K(z) \approx \frac{1 - \phi(K)}{z + z_1(K)} + \frac{\phi(K)}{z + z_2(K)},$$

(28)

where

$$z_1(K) \approx \frac{c_v}{2\varepsilon} \omega_0 (aK)^2 \equiv D_I K^2,$$

(29)

$$z_2(K) \approx 2g_0\varepsilon + (\omega_0/6)(aK)^2,$$

(30)

and

$$\phi(K) = (c_v/12\varepsilon) \omega_0^2 (aK)^4 / z_2^2(K).$$

(31)
FIG. 2: (color online) One-dimensional diffusion along (1,0,0) direction of the FCC lattice of initial \( \delta \)-function impurity distribution calculated in the two frequency model (see the text) for different values of diffusion length \( l_d = 2(D_I t)^{1/2} \). For definiteness, the parameters corresponding to the arsenic impurity in silicon at temperature \( T = 800^\circ C \) were used: \( E_b \approx 1.2 \text{ eV} \), \( c_V = 10^{-8} \), and \( a = 5.43 \text{ Å} \).

Thus, there are two diffusion poles. The one at \(-z_1\) corresponds to the interaction-enhanced impurity diffusion and the pole at \(-z_2\) can be identified with the V-I pair state. Indeed, being the part of the impurity autocorrelation function this state obviously contains an impurity. On the other hand, its diffusivity is independent of \( c_v \) which means that the vacancy is always present in this state. This is further confirmed by the diffusion profiles computed as inverse L-F transform of Eq. (28) and shown in Fig. 2. At small diffusion lengths they exhibit characteristic tails which in pair diffusion models \([6, 7]\) are attributed to the diffusing defect-impurity pairs.

Unfortunately, these profiles are not quite physical because at large distances they acquire small negative values. More accurate calculation of the inverse L-F transform is needed to deside on whether this deficiency is because of too crude approximations made above or that \( O(c_v) \) approximation is insufficient at large distances.

I am indebted to NATO for supporting my one year stay at IPCMS where the major part of this work was done. I express my gratitude to University Louis Pasteur de Strasbourg and IPCMS for their hospitality and to Hugues Dreyssé for collaboration. I am grateful to Réne Monnier for making possible my visit to ETH (Zürich) where this work was started. I would like to thank Jarek Dąbrowski for attracting my attention to the pair diffusion, Camilla Schmidt for useful bibliographical references, and Prof. A. B. Lidiard for interest in
the work.

[1] J. Philibert, *Atom Movements* (Les Éditions de Physique, Les Ulis, 1991).
[2] J. Manning, *Diffusion Kinetics for Atoms in Crystals* (Van Nostrand, Princeton, N. J., 1968).
[3] A. Allnatt and A. Lidiard, *Atomic Transport in Solids* (Cambridge University Press, Cambridge, 1993).
[4] R. A. Tahir-Kheli and R. J. Elliott, J. Phys. C **15**, L445 (1982).
[5] A. B. Lidiard, Phil. Mag. **46**, 1218 (1955).
[6] B. J. Mulvaney and W. B. Richardson, Appl. Phys. Lett. **51**, 1439 (1987).
[7] M. Orlowski, Appl. Phys. Lett. **53**, 1323 (1988).
[8] M. Doi, J. Phys. A **9**, 1465, 1479 (1976).
[9] D. C. Mattis and M. L. Glasser, Rev. Mod. Phys. **70**, 979 (1998).
[10] V. I. Tokar, Phys. Rev. E **53**, 1411 (1996).
[11] P. Grassberger and M. Scheunert, Fortschr. Phys. **28**, 547 (1980).
[12] L. P. Kadanoff and J. Swift, Phys. Rev. **165**, 310 (1968).
[13] S. Mantl, W. Petry, K. Schroeder, and G. Vogl, Phys. Rev. B **27**, 5313 (1983).
[14] M. Inoue, J. Math. Phys. **15**, 704 (1974).
[15] O. Pankratov, H. Huang, T. D. de la Rubia, and C. Mailhiot, Phys. Rev. B **56**, 13172 (1997).
[16] H. Bracht, J. F. Pedersen, N. Zangenberg, A. N. Larsen, E. E. Haller, G. Lulli, and M. Posselt, Phys. Rev. Lett. **91**, 245502 (2003).