Non-Fickian current enabling the uphill diffusion of impurities diffusing by the mechanism of mobile impurity-defect pairs

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Equations governing the diffusion mediated by the mobile pairs have been derived. In addition to known non-Fickian (n-F) behavior observable at small spatiotemporal scale under homogeneous defect distribution the equations predict another type of n-F diffusion that may take place only in the inhomogeneous case and can be operative at any scale. In the limit of slowly varying inhomogeneity the n-F diffusion current has been identified and shown to be able to induce the uphill diffusion. It has been argued that the latter should be observable in about one third of impurities in FCC metals.

The mechanism of diffusion via mobile impurity-defect (I-d) pairs was developed in Refs. [1–3] in order to explain the unusual exponential diffusion profiles of boron impurities in silicon. Its peculiarity in comparison with the conventional mechanisms of defect-mediated diffusion is that the impurity within the pair exists in a mobile state where it may perform not one but many consecutive migration steps due to the closeness of the diffusion-assisting defect. The mobile state, however, has a finite lifetime and as a consequence the distribution of the migration distances is not Gaussian as in the conventional Fickian diffusion but exponential in agreement with experiment [1]. Similar behavior was later found in B-Ge system [4] and in the diffusion of indium impurities in the copper (001) surface layer [5].

Another unusual phenomenon discovered in B-Si system is the uphill diffusion, that is, the diffusion along the concentration gradient in contradiction to the first Fick’s law. It was noted that the phenomenon is correlated with the steepness of the defect concentration gradients and may be enhanced by the presence of the mobile pairs, though no explicit mechanisms were suggested [2].

Deviations from Fick’s laws are of considerable interest from fundamental and practical standpoints which necessitates their thorough investigation. The aim of the present Letter is to show that in the systems where the impurity diffusion is underlain by the mechanism of mobile pairs an inhomogeneous distribution of defects induces a non-Fickian (n-F) contribution into the diffusion current which is enhanced by steep gradients of defect concentration. In contrast to the n-F exponential behavior restricted to short times, nanometer distances, and sharp impurity concentration profiles [1] the action of the n-F contribution can be observable at arbitrary scales and in smooth profiles. A most notable manifestation of the n-F current is the uphill diffusion that may arise under certain conditions. Because the n-F current should be operative in all systems with the pair diffusion mechanism the uphill diffusion should also be observable in all such systems.

Central to the mechanism is the diffusion of an individual I-d pair which in the continuum approximation can be described by the equation [1, 2, 3, 4, 5, 6–8, 9, 10]

\[
\frac{\partial}{\partial t}G_m(r, r_0, t) = D_m \nabla^2 G_m(r, r_0, t) - \epsilon G_m(r, r_0, t),
\]

where \(G_m\) is the probability density of finding the mobile pair at time \(t\) at point \(r\) if the pairing took place at point \(r_0\) at time zero; \(D_m\) and \(\epsilon\) are the pair diffusivity and the decay rate, respectively. In comparison with the macroscopic diffusion of impurities which is limited by the concentration of the point defects which is usually small, the pair diffusion is very fast because the mediating defect is permanently present within the pair. However, the mobile defects are also fast diffusers and so quickly escape the pair. Because of this the pair lifetime \(\tau = \epsilon^{-1}\) is short on the macroscopic scale. The latter can be characterized by the average time between successive I-d pairings \(t_p = g^{-1}\), where \(g\) is the I-d pairing rate [1]. The pairing rate is limited by the small defect concentration \(c_d\) because \(g = O(c_d)\) [1, 10] and so is also small.

To derive the equation governing the evolution of the impurity profile \(C(r, t)\) we first note that the macroscopic diffusion proceeds on the time scale \(t = O(t_p) \gg \tau\). At this scale the time step \(\Delta t\) in the governing equation can be chosen in such a way that it was microscopically large but still small at the macroscopic scale:

\[
t = O(g^{-1}) \gg \Delta t \gg \tau.
\]

For example, in experiments of Ref. [8] the characteristic interval between the defect jumps was \(10^{-8}\) s. During the pair lifetime the impurity made on average \(\sim 10\) steps so \(\tau\) was of \(O(10^{-7})\) s. The mean time between the impurity pairings, on the other hand, was \(\sim 10\) s, so with the choice of \(\Delta t = 10^{-3}\) s Eq. (2) can be easily satisfied. Because of the four orders of magnitude difference between \(\Delta t\) and \(\tau\) in this example, the creation and the decay of the pair are fully confined within \(\Delta t\) with the relative error of \(O(10^{-4})\). So on the macroscopic time scale the redistribution of the impurity density due to the pair diffusion looks as instantaneous. This means that within \(\Delta t\) the distribution of the impurity due to one I-d encounter
can be approximated by the integral \[ P(r, r_0) = \epsilon \int_0^\infty G_m(r, r_0, t) dt. \] (3)

The equation satisfied by \( P \) can be obtained by integrating Eq. (1) over \( t \) and using the initial condition \( G_m(r, r_0, 0) = \delta(r - r_0) \) as

\[ -\lambda^2 \nabla^2 P(r, r_0) + P(r, r_0) = \delta(r - r_0), \] (4)

where \( \lambda = \sqrt{D_m/\epsilon} \) is the mean migration distance \([1, 8]\). Because the pair carries an impurity, the impurity conservation forbids the pairs to cross the system boundaries which leads to the zero Neumann boundary condition for the pair current

\[ n \cdot \nabla P(r, r_0)|_{\text{boundary}} = 0, \] (5)

where \( n \) is the vector normal to the boundary.

Thus, on the macroscopic time scale the diffusion of substitutional impurity is seen as its disappearance at some point due to the pairing with a defect followed by its instant redistribution in the vicinity of that point according to the probability density \( P \). By analogy with the second Fick’s law the equation governing the diffusion under the mechanism of mobile pairs can be written down in the form of the conservation law

\[ \frac{\partial}{\partial t} C(r, t) = -g(r, t)C(r, t) + \int P(r, r_0)C(r_0, t)g(r_0, t)dr_0, \] (6)

where the first term on the right hand side describes the loss of impurities by the concentration profile due to the pairings and the second term its replenishment by the decayed pairs. Under inhomogeneous defect distribution the pairing rate \( g \) depends on time and space variables. The impurity conservation is obtained by integrating Eq. (6) over \( r \) with the use of Eqs. (1) and (5).

Eq. (6) effectively generalizes the physical picture of Ref. [1] on the inhomogeneous case. To see this let us consider the limit of slowly varying \( C \) and \( g \) when the integral in Eq. (6) can be approximated by a local expression. Formally this can be achieved by expanding Eq. (6) in powers of \( \lambda \) but if the characteristic scale, say, \( \Lambda \) of the spatial variation of both functions is assumed to be much larger then the migration distance, the expansion will be, factually, in the powers of \( \lambda/\Lambda \). This is implicitly accounted for in the expansion below in the small values of the spatial derivatives while \( \lambda \) is supposed to have its physical value.

At the distances of \( O(\Lambda) \) from the system’s boundaries the kernel \( P \) can be approximated by the inverse Fourier transform of Eq. (1) in the unbounded space

\[ P(r - r_0) = \frac{e^{-|r - r_0|/\lambda}}{4\pi \lambda^2 |r - r_0|}. \] (11)

With the use of this expression the integral in Eq. (6) can be calculated to leading orders in \( \lambda \) as

\[ \int dr_0 P(r - r_0)\phi(r_0, t) = \int d\xi \frac{e^{-|\xi|}}{4\pi |\xi|} \phi(r + \lambda \xi, t) = \phi(r, t) + \lambda^2 \nabla^2 \phi(r, t) + \ldots, \] (12)

where \( \phi = Cg, \xi = (r_0 - r)/\lambda \), and the terms linear in \( \lambda \) as well as the cross-derivatives of the second order vanish due to the kernel symmetry.
Thus, Eq. (13) in the small $\lambda/\Lambda$ approximation reads
\[
\frac{\partial C(r,t)}{\partial t} \simeq \lambda^2 \nabla^2 [C(r,t)g(r,t)] \\
= -\nabla \cdot [-D(r,t)\nabla C(r,t) - \lambda^2 C(r,t)\nabla g(r,t)],
\]
where
\[
D(r,t) = \lambda^2 g(r,t)
\]
(14). The first term in the brackets on the second line of Eq. (13) is the Fickian diffusion current Eq. (4) while the second term is the n-F contribution. It is interesting to note that equation similar to Eq. (13) was used in Ref. 4 in simulations of boron diffusion in amorphous silicon mediated by the dangling bonds which may hint at a similar underlying mechanism.

With the use of Eq. (14) the diffusion current from Eq. (15) can be cast in the form
\[
J = -D(r,t)C(r,t)[\nabla \ln C(r,t) + \nabla \ln g(r,t)].
\]
(15)

As is seen, if the logarithmic derivative of $g$ exceeds that of $C$ and has opposite sign the uphill diffusion follows. The stationarity condition $J = 0$ is satisfied by Eq. (10) also in this approximation.

To asses the strength of the n-F contribution in physical terms, model 1D diffusion profiles has been simulated using Eq. (12) with and without the n-F term. The main difficulty poses the problem of finding explicit expression for $g$. To find $g$ in realistic simulations one has to solve the problem of the defect capture by the immobile impurity given the defect distribution profile $c_d(r,t)$. This in turn would require knowledge of details of the defect kinetics and of the I-d interactions. In homogeneous case, however, the problem simplifies because $c_d$ is constant and $q$ can be found from the Smoluchowski-type formula 1, 10 according to which $g$ is proportional to the defect concentration. This should be roughly valid also in the case of slowly varying $c_d(r,t)$. Because Eq. (12) has been derived under this assumption, we will use approximation $g \propto c_d$ in our estimates. The diffusion constant in Eq. (15) can be assessed as the product of the equilibrium diffusion constant multiplied by the supersaturation $c_d(r,t)/c_d^2$ ($c_d^2$ is the equilibrium value) 1 while the logarithmic derivative of $g$ in this approximation will depend only on $c_d$.

For concreteness some characteristic numbers from Refs. 1, 3, 11 were used in the simulations as the input parameters. The stationary defect profile was modeled departing from the fact that in Ref. 11 strong gradients of the defect concentration were observed at depth below 10 nm. So $c_d$ was assumed to be constant in Si bulk with the supersaturation maintained during the experiment, e. g., by the defect clusters 3, at the level of $10^2$ 1 but starting from the depth 10 nm $c_d$ linearly dropped to the equilibrium value at the surface 3. The equilibrium diffusion constant was calculated according to Ref. 12.

The results of simulated diffusion shown in Fig. 1 are qualitatively similar to the experimental profiles of Ref. 3. As is seen, the n-F contribution accounts for all of the uphill diffusion and the profiles tend to reach the stationary distribution Eq. (10). The simulated system was assumed to be unbounded in the positive $x$ direction so at large times the impurity profile will eventually vanish. In a finite system the steep decrease of the defect concentration at the other end of the system should cause the appearance of another peak in the impurity concentration, as observed experimentally 3. If the inhomogeneous defect distribution persists sufficiently long, at large times the equilibrium distribution would be reached. Experimentally this may be achieved, e. g., with the use of externally imposed constant temperature gradient.

The fact that exponential profiles were seen so far only in a few systems may be because the values of $\lambda$ in known cases were restricted to a few nanometers and observations at this scale require the use of sophisticated experimental techniques. The uphill diffusion, in contrast, should be realizable at arbitrary length scales which may considerably increase the number of systems suitable for the study of the pair diffusion. For this end it would be helpful to establish some criteria facilitating the search for such systems. In Refs. 1, 2 it was suggested that the value of $\lambda$ that can be assessed from the impurity diffusion constant (see Eq. (14)) may serve as such a criterion. Large $\lambda$ means large number of joint I-d steps, hence, high
mobility. If, on the other hand, $\lambda$ is small and the I-d encounter amounts to only $\sim 1$ step the diffusion should be Fickian [4]. Thus, the pair mechanism should be sought among fast diffusers. This criterion, however, may be too restrictive in some cases.

For example, in the vacancy-mediated diffusion in the FCC hosts that microscopically can be described by the five frequency model (5FM) [13] the vacancy can be tightly bound to the impurity but the latter may still diffuse slowly because of the small value of the frequency $w_2$ of the I-v (“v” for vacancy) exchanges that drive the impurity diffusion. The strength of the I-v pairing is characterized in the model by the binding energy $E_b > 0$ which can be found from the detailed balance condition for the associative ($w_3$) and dissociative ($w_4$) jump frequencies as [13]

$$w_3/w_4 \simeq \exp(-E_b/k_B T).$$

Strong I-v pairing (small decay rate) corresponds to large ratio $E_b/k_B T$. Thus, for example, in the experiments on Fe-Al system [14] $E_b = 0.29$ eV was rather large but $w_2$ was so small that the number of impurity steps during the pair lifetime was equal to one (see discussion in Ref. [4]). However, due to the strong binding and large frequency $w_1$ of the vacancy jumps in the first coordination shell of the impurity the vacancy makes many random steps around the impurity before the single diffusive step occurs so the information on the direction of approach of the defect wipes out. Correspondingly, the distribution of the impurity jumps will be symmetric as in the large-$\lambda$ case (see Eq. (11)) which is sufficient for the derivation of Eq. (6) and all ensuing equations even in the case of small $\lambda$.

If, however, the I-v interactions are weak and the diffusion is similar to the self-diffusion, the one I-v exchange may be only in the direction of the vacancy that approached the impurity [12]. So if the vacancy distribution is inhomogeneous, the diffusive steps will be more probable toward higher vacancy concentration, that is, in the direction opposite to that predicted by the n-F term in Eq. (15). Such diffusion will also be n-F but in a qualitatively different way.

Thus, the main requirements for the n-F contribution into the diffusive current of the type of Eq. (15) is a strong I-v binding, that is, sufficiently large $E_b$ and sufficiently small temperature. The binding energies can be estimated with the use of Eq. (16) from the database of Ref. [16] where the 5FM frequencies obtained in ab initio calculations for 228 FCC systems are summarized. Though the data are not sufficiently reliable for concrete systems (for example, they predict weak repulsion in the Fe-Al system instead of the experimentally observed attraction), the ab initio calculations are believed to correctly predict general trends. According to the database $E_b \gtrsim 0.1$ eV in almost third of the systems so at sufficiently low temperatures the diffusion via mobile pairs may be sought in more than 70 impurities in FCC metals.

To sum up, in the present Letter the equations governing diffusion of impurities via the mechanism of mobile pairs have been derived and shown to exhibit two types of n-F behavior. The first one is the known behavior responsible for the exponential diffusion profiles observed at small times and the nanometer scale distances in boron diffusion in semiconductors. It was described theoretically in Ref. [1] within the pair diffusion mechanism under homogeneous defect distributions. In contrast, the behavior of the second type is predicted to be observable only in systems with inhomogeneous distribution of the diffusion mediating defects and at arbitrary spatiotemporal scales. Its most distinct manifestation is the uphill diffusion [6] which is predicted to take place under appropriate conditions in all systems with the diffusion mediated by the mobile pairs, in particular, in many FCC impurity-host systems.

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