PVRD-FASP Documentation

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ABOUT

1.1 Introduction

There are many software tools available to understand and study the transport of charge carriers namely electrons and hole in materials. Very few tools exist to study the transport of point defects in materials. Moreover, the chemistry of point defects are addressed in almost no tool.

In our tool we developed a novel approach to study the transport of charge carriers and point defects on an equal footing along with the incorporation of point defect chemistry.

1.2 Theory

The equation used for describing the transport of charge carriers are

$$\frac{\partial n}{\partial t} = -\nabla \cdot \overrightarrow{J_n} + G_n - R_n \tag{1.1}$$

$$\overrightarrow{J_n} = -\mu_n n \overrightarrow{E} - D_n \nabla n \tag{1.2}$$

$$\frac{\partial p}{\partial t} = -\nabla \cdot \overrightarrow{J_p} + G_p - R_n \tag{1.3}$$

$$\overrightarrow{J_p} = \mu_p p \overrightarrow{E} - D_p \nabla p \tag{1.4}$$

$$\nabla \cdot (\varepsilon \nabla \phi) = -p + n - N_D + N_A \tag{1.5}$$

where $\overrightarrow{J_n}$, $\overrightarrow{J_p}$ are the flux densities instead of the usual current densities used in semiconductors, $\overrightarrow{E}$ is the electric field, ϕ is the electrostatic potential, G and R are the generation and recombination rates modeled for radiative, SRH, Auger etc., N_D and N_A are the net donor and acceptor concentrations. For heterostructures, an additional gradient term should be added to the drift-diffusion equation (1.2) and (1.4). The transport of point defects also follow the similar equations.

We can arrive at the same equations by treating diffusion flux as negative gradient of electro chemcial potential (μ) defined as

$$\mu = G_f^0 + q\phi + kT \ln \left(\frac{u}{N_s} \right) \tag{1.6}$$

where G_f^0 is the formation energy of the species, ϕ is the electrostatic potential, q is the charge of the species, T is the temperature, k is the Boltzmann constant, u is the concentration of the species and N_s is the maximum number of microstates the species can occupy. The diffusion flux is given as

$$\overrightarrow{J} = -\frac{D}{kT} u \nabla \mu. \tag{1.7}$$

Please note that we used Einstein relationship between mobility and diffusivity in writing (1.6) and (1.7). Thus the transport equation are given as

$$\frac{\partial u_i}{\partial t} = -\nabla \cdot \overrightarrow{J_i} + G_i - R_i \tag{1.8}$$

$$\overrightarrow{J_i} = -\frac{D}{kT} u_i \nabla \left(G_{f,i}^0 + q_0 z_i \phi + kT \ln \left(\frac{u_i}{N_{s,i}} \right) \right) \tag{1.9}$$

$$\nabla \cdot (\varepsilon \nabla \phi) = q_0 \sum_i z_i u_i \tag{1.10}$$

where i is the index of the species, q_0 is the charge of an electron, z_i stands for the ionization number of the charge state with sign. The above equations can be applied to both charge carriers as well as point defects. The (1.8) requires the computation of generation and recombination rates $G_i - R_i$. For charge carries these rates are well known and can be computed with algebraic expressions. For example if the charge carriers involve in radiative recombination then the $G_i - R_i$ is given as

$$(G_i - R_i)|_{radiative} = B \left(n_i^2 - np \right) \tag{1.11}$$

For trap assisted recombination (SRH) we have

$$(G_i - R_i)|_{SRH} = \frac{n_i^2 - np}{\frac{n+n_1}{C_p} + \frac{p+p_1}{C_n}} \tag{1.12}$$

where

$$n_1 = N_c e^{-\frac{E_C - E_T}{kT}} \tag{1.13}$$

$$p_1 = N_v e^{\frac{E_V - E_T}{kT}} \tag{1.14}$$

Here N_C, N_V are conduction and valence band density of states, E_C, E_V and E_T are conduction band, valence band and trap energy levels respectively.

For point defects these rate are generally not known. We employ defect chemical reaction formalism and use chemical reaction kinetics to compute the generation and recombination rate for point defects. Considering charge carries as a point defect species we can show that generation and recombination rates obtained from reaction kinetics are equivalent to the general expressions given in (1.11) and (1.12).

The interactions between point defects (including charge carriers) can be represented as defect chemcial reaction. Considering a general reaction

$$\text{aA} + \text{bB} \underset{K_b}{\overset{K_f}{\rightleftharpoons}} \text{cC} + \text{dD} \tag{1.15}$$

The rate equation can be written as

$$-\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} == \frac{1}{d}\frac{d[D]}{dt} = K_f[A]^a[B]^b - K_b[C]^c[D]^d \tag{1.16}$$

In our tool we consider only point defect chemical reaction with atmost 2 reactants or atmost 2 products with stoichiometric coefficients a,b,c and d to be either 1 or 0. For such point defect reactions we show our method of computing the generation recombination rates. If any of the species is involved in more than one reaction then the rate equation for that species have contributions from all the invovled reactions.

Consider the following reaction system which represent almost all reactions considered in our tool.

$$\text{A} + \text{B} \underset{K_{b1}}{\overset{K_{f1}}{\rightleftharpoons}} \text{C} + \text{D} \tag{1.17}$$

$$\text{A} \underset{K_{b2}}{\overset{K_{f2}}{\rightleftharpoons}} \text{E} + \text{F} \tag{1.18}$$

$$\text{Null} \underset{K_{b3}}{\overset{K_{f3}}{\rightleftharpoons}} \text{A} + \text{G} \tag{1.19}$$

Here species A is invovled in the 3 reactions as shown. Thus for this we write the rate equation as

$$\frac{d[A]}{dt} = -K_{f1}[A][B] + K_{b1}[C][D] - K_{f2}[A] + K_{b2}[E][F] + K_{f3} - K_{b3}[A][G] \tag{1.20}$$

Once this rate equations are formed we systematically rewrite them as

$$\frac{d[A]}{dt} = U^T Q_A U + P_A U + K_A \tag{1.21}$$

where U is a concentration vector (column) of length 7 (total number of species in the system),

$$U = ([A], [B], [C], [D], [E], [F], [G])^T \tag{1.22}$$

Q_A is a 7X7 matrix with all zero elements except for

$$q_{12}^A = q_{21}^A = -\frac{K_{f1}}{2}, q_{34}^A = q_{43}^A = \frac{K_{b1}}{2}, q_{56}^A = q_{65}^A = \frac{K_{b2}}{2}, q_{17}^A = q_{71}^A = -\frac{K_{b3}}{2} \tag{1.23}$$

P_A is a row vector of length 7 with all elements zero except

$$p_1^A = -K_{f2} \tag{1.24}$$

and K_A is the constant term given as K_{f3}.

The above representation of rates as (1.21) can be extended to any species and we can write the corresponding Q, P, K variables as functions of reaction rate constants. For a general reaction system with M species, the rate equation for the i species is given as

$$\frac{du_i}{dt} = \sum_{k=1}^{M} \sum_{j=1}^{M} a_{jk}^i u_j u_k + \sum_{j=1}^{M} b_j^i u_j + c^{i`} \tag{1.25}$$

for $i = 1, 2, ..., M$, and a,b,c are the reaction rate constants in which the i species is involved.

Then the variables Q^i, P^i, K^i can be calculated as

$$q_{jk}^i = q_{kj}^i = \begin{cases} \frac{1}{2} a_{jk}^i, & \text{if } j \neq k \\ a_{jk}^i, & \text{if } j = k \\ 0, & \text{otherwise} \end{cases} \tag{1.26}$$

$$p_j^i = b_j^i, K = c^i. \tag{1.27}$$

Thus, the generation recombination expression for any point defect species (including free carriers) can be expressed as

$$G_i - R_i = \left. \frac{du_i}{dt} \right|_{reactions} = U^T Q^i U + P^i U + K^i \tag{1.28}$$

The net rate as reaction operator $R(U)$ can be written as

$$R(U) = U^T Q U + P U + K \tag{1.29}$$

where Q is MxMxM array, P is MxM array and K is Mx1 array.

The major advantage of writing $R(U)$ in the above form is that we can calculate the Jacobian of the reaction operator with the formula

$$J_R(U) = (Q + Q^T) U + P \tag{1.30}$$

We thus showed you how we calculate the generation reaction term for point defects using the point defect chemical reaction formalism.

1.2.1 Equivalence

In this section we show you the equivalence of writing radiative process and trap assisted process (SRH) as defect chemical reaction. The radiative generation and recombination rate and SRH rates are given as (1.15) and (1.16) respectively.

We represent radiative process as

$$\text{Null} \underset{K_b}{\overset{K_f}{\rightleftharpoons}} e_c^- + h_v^+ \tag{1.31}$$
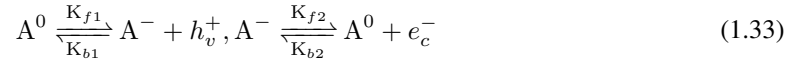
where e_c^- and h_v^+ denote the free electron and hole in conduction and valence band of the material. Hence the rate equation is given as

$$\frac{d[e_c^-]}{dt} = \frac{d[h_v^+]}{dt} = K - K_b[e_c^-][h_v^+] = K_b\left(\frac{K_f}{K_b} - [e_c^-][h_v^+]\right) \tag{1.32}$$

Thus, if the ratio of forward to backward rate constant is n_i^2 we can easily see that $eq11$ and $eq29$ are equivalent. The thermodynamics of reactants and products results in such condition for the ratio. This will be shown in next section.

The equivalent reaction representing the SRH process in case of acceptor type specis can be written as

$$A^0 \underset{K_{b1}}{\overset{K_{f1}}{\rightleftharpoons}} A^- + h_v^+, A^- \underset{K_{b2}}{\overset{K_{f2}}{\rightleftharpoons}} A^0 + e_c^- \tag{1.33}$$

The rate equations can be written as

$$\frac{d[A^0]}{dt} = -\frac{d[A^-]}{dt} = -K_{f1}[A^0] + K_{b1}[A^-][h_v^+] + K_{f2}[A^-] - K_{b2}[A^0][e_c^-], \tag{1.34}$$

$$\frac{d[e_c^-]}{dt} = K_{f2}[A^-] - K_{b2}[A^0][e_c^-], \tag{1.35}$$

$$\frac{d[h_v^+]}{dt} = K_{f1}[A^0] - K_{b1}[A^-][h_v^+]. \tag{1.36}$$

From (1.34) we note that $[A^0] + [A^-]$ is constant in time (say D). Hence in steady state equilibrium for $[A^0]$ and $[A^-]$ we have

$$[A^0] = \frac{K_{f2} + K_{b1}p}{K_{f1} + K_{f2} + K_{b1}p + K_{b2}n}D, [A^0] = \frac{K_{f1} + K_{b2}n}{K_{f1} + K_{f2} + K_{b1}p + K_{b2}n}D \tag{1.37}$$

where $[h_v^+] = p$ and $[e_c^-] = n$ is used for notational simplicity.

Using (1.37) in (1.35) and (1.36) with few algebraic simplifications we can write

$$\frac{dn}{dt} = \frac{dp}{dt} = \frac{K_{f1}K_{f2} - K_{b1}K_{b2}np}{K_{f1} + K_{f2} + K_{b1}p + K_{b2}n} \tag{1.38}$$

Now if the ratio of the reaction rates is restricted as

$$\frac{K_{f1}}{K_{b1}} = p_1 = N_V e^{\frac{E_V - E_T}{kT}} \frac{K_{f2}}{K_{b2}} = n_1 = N_c e^{-\frac{E_C - E_T}{kT}} \tag{1.39}$$

then (1.38) can be simplified further as

$$G - R = \frac{n_i^2 - np}{\frac{n+n_1}{K_{b1}} + \frac{p+p_1}{K_{b2}}} D \tag{1.40}$$

which is equivalent to (1.16). The thermodynamics of reactants and products will result in (1.39) which will be shown in the next section. A similar equivalence can be shown for donor type centers as well.

1.2.2 Thermodynamic Relationship between Forward and Backward Rate Constants

Consider a general reaction

$$\sum_{i=1}^{V} x_i X_i \underset{K_b}{\overset{K_f}{\rightleftharpoons}} \sum_{j=1}^{M} y_j Y_j \tag{1.41}$$

with N reactants and M products. At thermodynamic equilibrium the difference in the chemical potential of reactants and products should be zero. Thus, we have

$$\Delta_r G = \sum_{i}^{N} x_i \mu_{X_i} - \sum_{j=1}^{M} y_j \mu_{Y_j} \tag{1.42}$$

where $\Delta_r G$ is the Gibb's free energy change of reaction, μ is the chemical potential of the species which can be written from (1.6) neglecting the electrostatic potential as

$$\mu_{X_i} = G_{f,X_i}^0 + kT \ln\left(\frac{[X_i]}{N_{s,X_i}}\right) \tag{1.43}$$

Thus, at equilibrium we have

$$\sum_{i=1}^{N} \left(x_i G_{f,X_i}^0 + kT \ln\left(\frac{[X_i]_{eq}^{x_i}}{N_{s,X_i}^{x_i}}\right) \right) = \sum_{j=1}^{M} \left(y_j G_{f,Y_j}^0 + kT \ln\left(\frac{[Y_j]_{eq}^{y_j}}{N_{s,Y_j}^{y_j}}\right) \right) \tag{1.44}$$

Upon simplification we get

$$\frac{\prod_{j=1}^{M} [Y_j]_{eq}^{y_j}}{\prod_{i=1}^{N} [X_i]_{eq}^{x_i}} = \frac{\prod_{j=1}^{M} N_{s,Y_j}^{y_j}}{\prod_{i=1}^{N} N_{s,X_i}^{x_i}} e^{-\frac{\Delta_r G^0}{kT}} \tag{1.45}$$

where $\Delta_r G^0$ is the standard enthalpy change of reaction or standard reaction Gibb's energy defined as

$$\Delta_r G^0 = \sum_{j=1}^{M} y_j G^0_{f,Y_j} - \sum_{i=1}^{M} x_i G^0_{f,X_i} \tag{1.46}$$

We also know that at equilibrium we have

$$K_f \prod_{i=1}^{N} [X_i]^{x_i} eq - K_b \prod_{j=1}^{M} [Y_j]^{y_j}_{eq} = 0 \tag{1.47}$$

Hence using (1.45) and (1.47) we can write

$$\frac{K_f}{K_b} = \frac{\prod_{j=1}^{M} N^{y_j}_{s,Y_j}}{\prod_{i=1}^{N} N^{x_i}_{s,X_i}} e^{-\frac{\Delta_r G^0}{kT}} \tag{1.48}$$

Therefore, the reaction rate constants should have a fixed ration. Applying this to the reaction (1.31) we have

$$\frac{K_f}{K_b} = N_{s,e_c^-} N_{s,h_v^+} \exp\left(-\frac{G^0_{f,e_c^-} G^0_{f,h_v^+}}{kT} \right) \tag{1.49}$$

The number of microstates for electrons in conduction band and hole is valence band are N_C and N_V respectively. The formation energies of electrons in conduciton band and holes in valence band referenced from vacuum level is

$$G^0_{f,e_c^-} = -\chi, G^0_{f,h_v^+} = \chi + E_g \tag{1.50}$$

where χ is the electron affinity of the material and E_g is the band gap of the material. Thus, we have the ratio as

$$\frac{K_f}{K_b} = N_C N_V \exp\left(-\frac{E_g}{kT} \right) \tag{1.51}$$

Considering the reactions in (1.33) we have

$$\frac{K_{f1}}{K_{b1}} = \frac{N_{s,A^-} N_{s,h_v^+}}{N_{s,A^0}} \exp\left(-\frac{G^0_{f,A^-} + G^0_{f,h_v^+} - G^0_{f,A^0}}{kT} \right) \tag{1.52}$$

$$\frac{K_{f2}}{K_{b2}} = \frac{N_{s,A^0} N_{s,e_c^-}}{N_{s,A^-}} \exp\left(-\frac{G^0_{f,A^0} + G^0_{f,e_c^-} - G^0_{f,A^-}}{kT} \right) \tag{1.53}$$

where the formation energies are given as

$$G^0_{f,A^0} = E_{f,A^0} - \chi - E_g,$$
$$G^0_{f,A^-} = E_{f,A^0} - sign(A^-)E_T - \chi - E_g \tag{1.54}$$
$$G^0_{f,e_c^-} = -\chi, G^0_{f,h_v^+} = \chi + E_g$$

Here $sign(A^-)$ is the sign of the charge on the species, E_T is the trap level (transition level from 0/-) with respect to vacuum and E_{f,A^0} is the defect formation energy of neutral species calculated through Density Functional Theory (DFT) referenced with respect to valence band. Assuming that the microstates for neutral and charged species are nearly same, we get

$$\frac{K_{f1}}{K_{b1}} = N_V \exp\left(-\frac{\chi + E_g + E_T}{kT}\right) = N_V \exp\left(\frac{E_V - E_T}{kT}\right)$$
$$\frac{K_{f2}}{K_{b2}} = N_C \exp\left(\frac{-\chi - E_T}{kT}\right) = N_C \exp\left(-\frac{E_C - E_T}{kT}\right)$$

(1.55)

where we have used the relations

$$E_C = -\chi, E_V = -\chi - E_g$$

(1.56)

Hence, for SRH process, the thermodynamics guarantees the equivalence as a chemical defect reaction.

1.3 Models

We have presented the theory behind our approach and the differential equations involved in the transport of charge carries and point defects. In this section we give the models we have employed in our solver.

1.3.1 Reaction Models

Although thermodynamics provides the ratio of forward and backward rate constants, we still have to find either one of the rate constants. For this we use reaction models that provide the rate constant of the reaction either forward rate or backward rate. Consider a general reaction

$$A^{z_A} + B^{z_B} \xrightarrow{K} C^{z_C} + dD^{z_D}$$

(1.57)

where d can be 0 or 1 with 0 being single product reaction and 1 being two product reaction, z_X is the ionization of species X. The diffusion-controlled reaction rate constant for the above reaction is given as

$$K = 4\pi R_{capt}(D_A + D_B)\exp\left(-\frac{E_A}{kT}\right)$$

(1.58)

where R_{capt} is the capture radius, D_X is the diffusivity of species X, E_A is the activiation energy of reaction ($E_A \geq 0$) representing the probability of a collision resulting in the formation of product.

The various types of reaction models used in the solver are as given below

- Diffusion Limited with Attraction Model:
$$K = q\frac{|z_A z_B|}{\varepsilon kT}(D_A + D_B) \text{ where model is applicable only if } z_A \times z_B < 0$$

(1.59)

- Capture Radius Limited Model:
$$K = 4\pi R_{capt}(D_A + D_B) \text{ where model is applicable only if } z_A \times z_B \geq 0$$

(1.60)

- Capture Cross Section Limited Model:

$$K = \sigma_{e/h} v_{th,e/h} \text{ where model is applicable whenever one reactant}$$
$$\text{is either electron or hole and only if} z_A \times z_B \geq 0 \quad (1.61)$$

- Thermal Generation-Recombination Model:

$$K = B_0 \text{ where model is applicable only when the reactants are both electron}$$
$$\text{and hole. Here } B_0 \text{ is the band to band recombination rate} \quad (1.62)$$
$$\text{coefficient of the material}$$

- Barrier Limited Model:

$$K = \nu \exp\left(-\frac{E_b}{kT}\right) \text{ where model is applicable with sigle reactant and single product}$$
$$\text{Here } \nu \text{ is the attempted frequency} \quad (1.63)$$
$$E_b \text{ is the reaction activation barrier}$$

1.3.2 Diffusion Models

The diffusion coefficient of species is assumed to have Arrhenius relationship with temperature given as

$$D(T) = D_0 \exp\left(-\frac{E_D}{kT}\right)$$

The diffusion coefficient of free carriers are assumed to follow Einstein relationship given as

$$D_{e/h} = \mu_{e/h} \frac{kT}{q}$$

The mobility of free carriers are assumed to follow the relationship

$$\mu_{e/h} = \mu_{e/h,300K} \left(\frac{T}{300}\right)^{\frac{3}{2}}$$

1.3.3 Band Gap Models

We use Varshni model for the temperature dependence of band gap given as

$$E_g(T) = E_0 - \alpha\left(\frac{T^2}{T + \beta}\right)$$

where E_0 is the band gap at 0K, α and β are fitting parameters.

1.3.4 Density of States Models

For charge carriers the density of states are given as

$$2\left(\frac{2\pi m_{eff,e/h} m_0 kT}{h^2}\right)^{\frac{3}{2}}$$

For defect species the density of microstate are given as

$$N_s = g_{atom} \times g_{elec} \times N_0$$

where g_{atom}, g_{elec} are the atomic and electronic degeneracy factors, N_0 is the lattice site density of the host material. The sites available to the point defects in the host material depends on the host crystal structure, size of the point defect etc. Hexagonal site, tetrahedral site etc are examples of lattice sites in zincblende crystal structure.

1.3.5 Formation Energy of Species Models

For charge carriers the formation energy is given as

$$\Delta H_f(e) = -\chi, \Delta H_f(h) = \chi + E_g(T)$$

For point defect species the formation energy is

$$\Delta H_f(X^{z_x}) = \Delta H_f(X^0) - sign(z_x) * \left(\frac{T}{300} \Delta E_T - \chi - E_g(T) \right)$$

This completes the description of the solver.

INSTALLATION

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