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Letter to the Editors

A comparison of the effective medium and modified Smoluchowski equations for the reaction rate of the diffusion-controlled reactions

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Abstract

We demonstrate the equivalence of the effective-medium approach and the modified Smoluchowski equations for the reaction rate of the bimolecular $A + B \to B$ process. This fact encourages us to use the latter, flexible formalism for a study of complicated spatial distributions of traps.

1. Introduction

The effective medium theory (EM) [1,2] is nowadays widely used for the description of bimolecular, diffusion-controlled reaction kinetics, e.g., for Frenkel defects in irradiated solids, $A + B \to 0$, and for energy transfer, $A + B \to B$, in solids from donors A to unsaturable acceptors (sinks) B [3]. In fact, this approach is based on Maxwell's old idea [4] of considering a whole reaction volume as a homogeneous reactive medium containing a number of isolated point defects. The reaction rate is here calculated using a coupled set of equations for diffusion/reaction inside the reaction sphere around the defect and for those outside this region where there is no reaction.

Another approach to the $A + B \to B$ reaction with immobile sinks B has been presented in Refs. [5–7]. The latter formalism is based on the modified Smoluchowski (MS) equation derived using the Kirkwood superposition approximation for three-particle correlation functions [6–8]. It could be applied to any spatial distribution of sinks. In this Letter we compare the two approaches and show that EM theory is a particular case of MS theory. We also compare these two theories with the results for the exact Wigner–Seitz model developed for a regular (periodic) sink distribution [9].

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2. Two basic approaches

The EM theory characterizes an isolated sink by the reaction (trapping) radius r_0 which is surrounded by the sphere of a larger radius R. It is assumed that no other sinks are present within this large sphere, $0 \le r \le R$, i.e., there is a depletion of sinks in this region. Following Ref. [2], one gets the following kinetic equations for the concentration of defects A at the distance r from a sink placed at the coordinate origin

$$D_A \Delta c(r) + \lambda = 0, \quad r_0 \le r \le R, \tag{1}$$

$$D_A \Delta c(r) + \lambda_{\text{eff}} - k_{\text{eff}} n_B c(r) = 0, \quad r \ge R. \tag{2}$$

Here Δ is the Laplace (diffusion) operator, D_A is the diffusion coefficient, λ, λ_{eff} are the defect production rates within sphere R and in the surrounding effective medium, respectively, k_{eff} is the effective reaction rate sought for, and n_B is the sink concentration. Since defects AB are not spatially correlated at long relative distances, the local concentration asymptotically approaches the average, macroscopic concentration: $c(r \to \infty) = \bar{c}$. If there is no defect production within a recombination sphere of radius r_0, $\lambda_{\text{eff}} = \lambda(1 - \Phi)$ where reaction volume's fraction covered by sinks is $\Phi = \frac{4}{3}\pi r_0^3 n_B$. Hereafter we neglect the

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difference between λ and λ_{eff} assuming $\Phi \ll 1$. The quasi-steady reaction rate is determined by a flux of particles A over the reaction sphere

$$k_{\mathrm{eff}} = 4\pi D_A r_0^2 \left[\frac{\partial c(r)}{\partial r} \right]_{r=r_0} = \beta c(r_0), \tag{3}$$

where β is the parameter of the radiation boundary condition (a grey recombination sphere).

In its turn, in the MS approach we start from the following steady-state kinetic equations for the joint, sink-particle correlation function [5–7]

$$D_A \Delta Y(r) + k_{\mathrm{eff}} n_B Y(r)[1 - Z(r, r_0)] + \frac{\lambda}{\bar{c}}(1 - Y(r)) = 0, \tag{4}$$

where the functional $Z(r, r_0)$ in Eq. (4) takes into account spatial correlations between sinks. It reads [8]

$$Z(r, r_0) = \frac{1}{2 r r_0} \int_{r-r_0}^{r+r_0} X_B(\rho) \rho \, \mathrm{d}\rho, \tag{5}$$

and the reaction rate is

$$k_{\mathrm{eff}} = 4\pi D_A r_0^2 \left[\frac{\partial Y(r)}{\partial r} \right]_{r=r_0}. \tag{6}$$

Here $X_B(\rho)$ is the trap–trap, joint correlation function. It is normalized by the unity as the relative distance between sinks $\rho \to \infty$. From the law of mass action one gets that at the saturation, $(t \to \infty)$, the macroscopic (average) concentration of particles A is $\bar{c} = \lambda / k_{\mathrm{eff}} n_B$.

These equations permit us to get the EM model as the particular case of MS theory. Indeed, let us assume that there are no sinks at $r \le R$:

$$X(\rho) = \Theta(r - R), \tag{7}$$

where $\Theta(z)$ is Heaviside step-function: $\Theta(z) = 1$, $z \ge 0$, and zero otherwise. Substitution of Eq. (7) into Eqs. (4) and (5) yields [5–7]

$$D_A \Delta Y(r) + k_{\mathrm{eff}} n_B Y(r) + \frac{\lambda}{\bar{c}}[1 - Y(r)] = 0, \quad r_0 \le r \le R, \tag{8}$$

$$D_A \Delta Y(r) + \frac{\lambda}{\bar{c}}[1 - Y(r)] = 0, \quad r > R. \tag{9}$$

Taking into account that $Y(r) = c(r)/\bar{c}$, i.e., $Y(r \to \infty) = 1$, and that $\bar{c} = \lambda / k_{\mathrm{eff}} n_B$, one immediately arrives at Eqs. (1) and (2) of the EM theory. This demonstrates that MS and EM theories are in fact equivalent.

For a random trap distribution, $R = r_0$, one gets the reaction rate with the correction linear in the trap concentration [5]:

$$k_{\mathrm{eff}} = 4\pi D_A r_0 (1 + 1.53\Phi). \tag{10}$$

Let us now consider another, *regular* sink distribution assuming that $R = R_B$ where $R_B = n_B^{-1/3}$ is the mean distance between traps. Employing Eqs. (1) and (2) (or Eqs. (4)–(6)), both EM and MS approaches here yield the sink concentration correction to the reaction rate

$$k_{\mathrm{eff}} = 4\pi D_A r_0 (1 + 3.9\Phi^{1/3}), \tag{11}$$

which is proportional to $n_B^{1/3}$. The exact solution for this case has been given earlier using the Wigner–Seitz model [9] well-known in the band structure theory of crystals (see also Ref. [10])

$$k_{\mathrm{eff}} = 4\pi D_A r_0 (1 + 1.85\Phi^{1/3}). \tag{12}$$

Note that the only difference between Eqs. (11) and (12) lies in the numerical co-factor. In fact, the discrepancy arises from our choice of the parameter R; these equations would coincide if $R = 0.69 R_B$. The latter estimate of the effective radius R seems to be more exact than just $n_B^{-1/3}$ keeping in mind that *each* trap in a regular distribution is surrounded by the reaction sphere and such the spheres should not significantly overlap.

3. Conclusion

We have demonstrated for the first time the *equivalence* of the effective medium and modified Smoluchowski equations and applied them to the particular cases of the random and regular (periodic) sink distribution. This equivalence is not surprising since the latter theory is also based on the effective medium ideas. The advantage of the modified Smoluchowski theory is that it allows one easily to treat any spatial distribution of sinks. This will be demonstrated in a separate publication [7].

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