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The Cell-Jamp Formalism of Multicomponent Nonlinear Diffusion

A.N. Gorban[1], H.P. Sargsyan[2*] and H.A. Wahab[1]

[1]*Department of Mathematics, University of Leicester, Leicester, LE1 7RH, UK*
[2]*Institute of Chemical Physics NAS RA, 5/2Paruir Sevak Str., 0014, Yerevan, Armenia,*
E-mail: *hrachya_sargsyan@mail.ru

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Abstract. In this paper, based on the idea of the mechanism of the elementary diffusion act, borrowed from chemical kinetics, an approach was developed to describe the nonlinear multicomponent diffusion. This approach allows to construct a matrix of diffusion coefficients, the members of which represent all possible variants of crisscrossed coefficients of diffusion. It was shown that diffusion coefficients have the form of a polynomial function of the concentrations of the system components. The developed approach differs from the generalized diffusion equations for multicomponent systems based on the Fick's law, the application of which often leads to discrepancy (balance relations are violated).This formalism allows to perform numerical modelling of complex diffusion processes in multicomponent systems.

Keywords: nonlinear diffusion, complex process, elementary processes, stoichiometry of diffusion, transport equation

1. Introduction

The physical idea of the quasi-chemical representation of diffusion in solids belongs to Yakov Frenkel [1, 2]. He introduced both the vacancy and the interstitial mechanisms of diffusion and found some rate constants from experimental data. Thirty years later, F.C.Frank and D. Turnbull developed the Frenkel theory further [3]. They studied the diffusion of copper in germanium. This diffusivity is very rapid. They proposed that the copper could be dissolved in two states, interstitial and substitutional. For the interstitial state the solubility of copper is two orders of magnitude less and the diffusivity many orders of magnitude greater than in the substitutional state. The conversion of these states is effected by lattice vacancies. The quasi-chemical theory of diffusion and viscosity was developed also by H. Eyring with co-authors [4]. Eyring developed the theory of absolute reaction rates for chemical reactions in gases [5] and in condensed phase [6] and then applied these ideas to transport phenomena. In this theory, the transport process is represented by an ensemble of elementary events. Each elementary event is represented by the creation or disintegration of an activated complex. The rate of the elementary process is given by the concentration of activated complexes, multiplied by the rate at which they decompose. The main constructive hypothesis is that it is possible to calculate the concentration of activated complexes by equilibrium statistical thermodynamics: the complex concentrations in quasi-equilibrium with the stable components. Each complex has its "internal translational" degree of freedom. On the surface of potential energy this corresponds to the “reaction path”. Complexes move along this path. The velocity of this motion is assumed to be just a thermal velocity and is proportional to $\sqrt{\mathbf{T}}$. The additional reaction path degree of freedom has its own kinetic energy and, therefore, increases the complex heat capacity. We have to take this into account in the calculation of the equilibrium constant. Collective models of diffusion were proposed too. One of the earliest collective model is the Z. Jeffries “ring mechanism” with 4 or more atoms. More on the history of solid-state diffusion is presented in the review [7] and in a modern textbook [8]. On the surface, there are various mechanisms for collective diffusion [9] as well. Elementary events for these mechanisms involve many atoms simultaneously. A dynamic description of nonlinear multicomponent diffusion requires a unified framework that should satisfy basic physical principles.

2. Mechanisms as Collections of Elementary Processes

In this article, we extend the area of applications onto nonlinear multicomponent diffusion [10]. A complex process can be disassembled into several elementary processes. The dependence of the process rate (the flux) on the state (concentrations, chemical potentials and their gradients) is simple for elementary processes. The model of the whole process is assembled from these elementary “details”. This idea was developed in chemical kinetics. In 1862–1867, Guldberg and Waage proposed the mass action law for equilibrium. In 1879 they developed the mass action law for dynamics.

This idea was developed further by many researchers and after several dozen years it was transformed into a technology for the representation of complex processes: A complex reaction is represented as an ensemble of elementary reactions. The reaction rate has a simple monomial dependence on concentration.

3. Stoichiometry of Diffusion Jumps

We represent the physical space as a network of compartments [10]. Each compartment is modelled as a cubic cell with an edge size l. The stoichiometric equations of diffusion describe interaction of two neighbouring cells. To distinguish the quantities related to these two cells we use the upper indexes I and II .

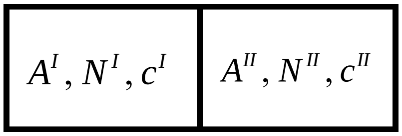

Figure: Cell Jump Model

The general stoichiometric equation for an elementary event of diffusion is:

$$\sum_i \alpha^I_{ri} A^I_i + \sum_i \alpha^{II}_{ri} A^{II}_i \to \sum_i \beta^I_{ri} A^I_i + \sum_i \beta^{II}_{ri} A^{II}_i , \qquad (1)$$

Coefficients $\alpha_{ri}^{I,II}$; $\beta_{ri}^{I,II}$ are nonnegative. Usually, we assume that they are integers but in some situations real numbers are needed.

Elementary events (1) describe diffusion and do not include the transformation of components (reactions). Therefore, the total amounts of each component A_i coincide in the left and the right hand sides of (1):

$$\alpha_{ri}^{I} + \alpha_{ri}^{II} = \beta_{ri}^{I} + \beta_{ri}^{II}. \tag{2}$$

Each elementary process (1) has two loss vectors $\alpha_{ri}^{I,II}$ with coordinates $\alpha_{r}^{I,II}$ and two output $\beta_{r}^{I,II}$ vectors, with coordinates $\beta_{ri}^{I,II}$. Because of the conservation of particles of all types (2), the stoichiometric vectors of processes for the cells differ just by the sign of coordinates:

$$\gamma_r = \gamma_r^{I} = \gamma_r^{II} = \beta_r^{I} - \alpha_r^{I} \tag{3}$$

- Fick's diffusion $A_i^I \to A_i^{II}$; $A_i^{II} \to A_i^I$;
- The exchange of particles $A_i^I + A_j^{II} \to A_i^{II} + A_j^I$;
- Clustering (diffusion with attraction) $A_i^I + sA_i^{II} \to (s+1)A_i^{II}$;
  $sA_i^I + A_i^{II} \to (s+1)A_i^I$; $s > 1$;
- Diffusion with repulsion $(s+1)A_i^I \to sA_i^I + A_i^{II}$;
  $(s+1)A_i^I \to A_i^I + sA_i^{II}, (s > 0)$.

Formally, diffusion with repulsion is the time-inverted process of diffusion with attraction (the porous medium model) but for $s = 1$ diffusion with attraction has no sense (the exactly uniform state cannot produce the nonuniform distribution). Therefore, the restrictions on $s$are different.

4. Mass Action Low (MAL) Equations for Diffusion

Let us consider the system of stoichiometric equations (1) as a reaction mechanism for MAL [10]. If we apply MAL then the rate of the elementary diffusion process is

$$w_r(c^I, c^{II}) = k_r \prod\nolimits_i (c_i^I)^{\alpha_{ri}^I} \prod\nolimits_i (c_i^{II})^{\alpha_{ri}^{II}}, \tag{4}$$

For example, for Fick's diffusion, we have two elementary processes, $A_i^I \to A_i^{II}$ and $A_i^{II} \to A_i^I$. The corresponding reaction rates are $k_1 c_i^I$ and $k_2 c_i^{II}$.

The composition of each cell is vector $N^{I,II}$. Components of this vector $N^{I,II} = V^{I,II} C^{I,II}$ areamounts of A_i in the corresponding cell and $V^{I,II}$ are volumes of cells. We describe the dynamicsof the compositions of two cells by the equations:

$$\frac{dN^{I}}{dt}=-\frac{dN^{II}}{dt}=S^{I,II}\sum_{r}\gamma_{r}w_{r}(c^{I},c^{II}) \tag{5}$$

Where $S^{I,II}$ is the area of the boundary between cells *I* and *II*. If there are many cells then

$$\frac{dN^{I}}{dt}=\sum_{J}S^{I,J}\sum_{r}\gamma_{r}w_{r}(c^{I},c^{J}) \tag{6}$$

with summation through all interacting pairs (I,J).

For example, for Fick's diffusion, we have two elementary processes, $A_i^{I}\to A_i^{II}$ and $A_i^{II}\to A_i^{I}$.

The corresponding reaction rates are $k_1c_i^{I}$ and $k_2c_i^{II}$. Equations (5) give

$$\frac{dN_i^{I}}{dt}=-S^{I,II}k_1c_i^{I}+S^{I,II}k_2c_i^{II} \tag{7}$$

The diffusion processes for which *space-inverted elementary processes coincide with the inverse processes* have a fundamental property: The entropy production is positive for the corresponding mass action law diffusion equations.

Let us consider a complex diffusion process in a bounded domain with smooth boundary and without external fluxes. We prove the following theorem [10]:

Theorem. Let a complex diffusion process consist of elementary processes, which satisfy the following property: the space-inverted elementary process coincides with the inverse process. Then, for the mass action law equation of diffusion (6), the principle of detailed balance is valid, the global convex Lyapunov functional exists and the uniform distribution is asymptotically stable.

5. Mechanisms of Transport and the General Forms of Macroscopic Equation

We developed a formalism of the mechanism of diffusion and heat conduction represented by the system of stoichiometric equations with the simple kinetic law $\exp(\alpha,\mu/RT)$ and the balance condition (complex balance for the general Markov microscopic kinetics and detailed balance for systems with microreversibility) [10]. This formalism produces equations which are particular cases of the general nonequilibrium thermodynamic equations [11, 12]. It is a very simple task to demonstrate that our transport equations are particular cases of the GENERIC formalism [12, 13]. Due to this two–generator formalism, evolution of any smooth function A of the state variables x is given by

$$\frac{dA}{dT}=\{A,E\}+[A,S] \tag{8}$$

Where E and S are the total energy and entropy, and $\{\,\cdot\,,\,\cdot\,\}$ and $[\,\cdot\,,\,\cdot\,]$ are Poisson and dissipative brackets, respectively.

The formulas for fluxes produced in this Section have the form of dissipative brackets:

$$[A,S]=\frac{\delta A}{\delta x}M\frac{\delta S}{\delta x} \tag{9}$$

where M is a symmetric positively semidefinite operator, "the friction matrix".

The general form of the "dissipative brackets with constraints" in application to multicomponent diffusion was produced very recently [14]. The flux of the i-th component J_i in that formalism was presented by formula [14]:

$$J_i=-\sum_j \Lambda_{ij}^c\left[\nabla\left(\frac{\mu_j}{T}\right)+\Lambda_j^{'}\nabla\left(-\frac{1}{T}\right)\right] \tag{10}$$

Our formulas belong to this type and give particular expressions for coefficients Λ. In the paper [14] a precise comparison of this formula with the classical expressions from [11] was presented and the equivalence of these general forms was proven. Now, we can just refer to these results. In addition to the general form, our approach gives the possibility to build the model from the elementary processes. This construction also satisfies the "constrains" (conservation laws) of diffusion because these conservation laws are implemented in the algebra of the stoichiometric coefficients.

6. Conclusion

We have demonstrated how an approach based on the mechanism of the elementary diffusion act allows to describe diffusion in a multicomponent system. It has been established that in order to satisfy the thermodynamic constraints the kinetic law of an elementary process cannot have an arbitrary form, that is, for the pre-exponential factor in the generalized law of mass action, additional conditions are necessary [10]. There are two main sets of these conditions. The first one, the condition of detailed equilibrium, runs from the property of the underlying microscopic dynamics - micro reversibility [15–17]. The second and more general condition is called "semi-detailed balance" or "complex balance". The theoretical principles underlying these conditions were discovered in [18–20]. Recently, it was demonstrated how these conditions can be derived using the Markov equations [21] in the approximation of a quasi-equilibrium and quasi-stationary state. Explicit formulas obtained in current work, in combination with elementary processes, can help in the modelling practice [22]. The formalism developed in this work makes possible to implement effective numerical modelling of complex diffusion processes in multicomponent systems.

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