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DIFFERENCE SCHEME FOR DYNAMIC SIMULATION DESCRIBING STOCHASTIC KINETICS OF MOLECULES IN CERAMICS

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ABSTRACT

A conservative and monotonous finite difference scheme is proposed for solving PDE describing the kinetics of molecules in ceramics. Numerical results of computational experiments are presented.

1. INTRODUCTION

Mathematical model of gas-liquid type phase transition in a self-interacting molecular gas in non-homogeneous temperature field is considered. Such transition creates the stochastic molecular motion [1]. It is considered that the molecules are emitted from the surfaces. The system has cylindrical symmetry and only one-dimensional motion of molecules is examined. The applied temperature T gradient causes the motion of molecules. Then the equation of flux of molecules can be written as [2]:

$$\begin{aligned} J &= -\Omega_0 a \frac{\partial c}{\partial x} ch \left[\frac{q}{k} \left(\frac{c(x+a)}{T(x+a)} - \frac{c(x)}{T(x)} \right) \right] + \\ &+ 2\Omega_0 c(1-c) sh \left[\frac{q}{k} \left(\frac{c(x+a)}{T(x+a)} - \frac{c(x)}{T(x)} \right) \right], \end{aligned} \tag{1.1}$$

where Ω_0 is a transition frequency of particle from one site to another; $c(x) \in [0,1]$ is the concentration of molecules; q is the interaction energy; and k is the Boltzmann constant. The force created by temperature gradient is included into the equation (1.1). Otherwise phase transition cannot go without inclusion of fluctuations. Such external force appears due to the fact that molecules jump faster from sites with higher temperature (see, e.g., thermal electricity). Of course it depends substantially on the material. The conservation law of molecules is expressed in the form of flux continuity equation:

$$\frac{\partial c}{\partial t} + \frac{\partial J}{\partial x} = 0. \tag{1.2}$$

The system of equations (1.1), (1.2) is essentially non-linear. The concentrations on boundaries are fixed.

As it is known not for all difference schemes unambiguous physical solutions are obtained. Especially, this problem is actual for stochastic processes, when the stochasticity can occur as a result of physical process or the realization of the difference scheme as well. In order do separate the physical and "mathematical" stochasticities, the difference scheme must be conservative, monotonous and desirably absolutely stable. In this article conservative, monotonous, and absolutely stable difference scheme is proposed for description of stochastic processes.

2. DIFFERENCE SCHEME

We will substitute the concentration $c(x)$ by $W(x)$:

$$c(x) = W(x) exp\left\{\int_{x_0}^{x} dx \frac{2(1-c)}{a} th\left[\frac{q}{k}\left(\frac{c(x+a)}{T(x+a)} - \frac{c(x)}{T(x)}\right)\right]\right\}, \tag{2.1}$$

where x_0 is an arbitrary constant which don't affect the coefficients of the difference scheme. Then the flux can be written as:

$$\begin{aligned} J &= -\Omega_0 a \cdot ch\left[\frac{q}{k}\left(\frac{c(x+a)}{T(x+a)} - \frac{c(x)}{T(x)}\right)\right] \\ &\times exp\left\{\int_{x_0}^{x} dx \frac{2(1-c)}{a} th\left[\frac{q}{k}\left(\frac{c(x+a)}{T(x+a)} - \frac{c(x)}{T(x)}\right)\right]\right\} \frac{dW}{dx}. \end{aligned} \tag{2.2}$$

Using the balance method and substituting (2.1) we obtain the following difference scheme

$$A_i c_{i-1}^{l+1} + B_i c_{i+1}^{l+1} - Q_i c_i^{l+1} = -\frac{c_i^l}{\tau}, \quad i = 1, 2, ..., M-1, \tag{2.3}$$

where l is the time step index. The coefficients are

$$A_i = \frac{\Omega_0 a \cdot ch\left[\frac{q}{k}\left(\frac{c_i}{T_i} - \frac{c_{i-1}}{T_{i-1}}\right)\right]\beta_{i-1/2}}{h_i^*\left[1 - \exp(-\beta_{i-1/2})\right]}, \tag{2.4}$$

$$B_i = \frac{\Omega_0 a \cdot ch\left[\frac{q}{k}\left(\frac{c_{i+1}}{T_{i+1}} - \frac{c_i}{T_i}\right)\right] \beta_{i+1/2} \exp(-\beta_{i+1/2})}{h_i^* \left[1 - \exp(-\beta_{i+1/2})\right]}, \tag{2.5}$$

$$Q_i = A_{i+1} + B_{i-1} + \frac{1}{\tau}, \tag{2.6}$$

where

$$\beta_{i+1/2} = \frac{2q}{k}(1-c)_{i+1/2}\left(\frac{c_{i+1}}{T_{i+1}} - \frac{c_i}{T_i}\right). \tag{2.7}$$

The elaborated difference scheme is conservative, the coefficients A, B, Q obey the known monotonous conditions, and as shown by the numerical calculations it is absolutely stable. The difference scheme (2.3-2.7) with respective boundary conditions of the first-type is solved numerically by the factorisation method.

3. NUMERICAL RESULTS

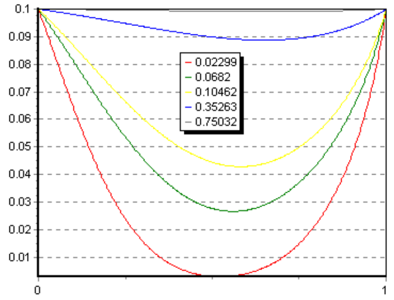

Figure 1. The distribution of concentration along x-axis at various time moments

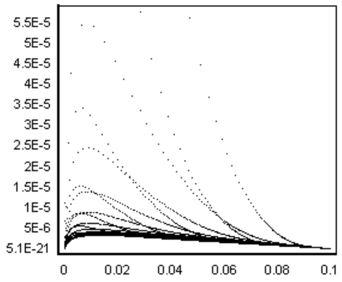

Figure 2. Total phase diagram

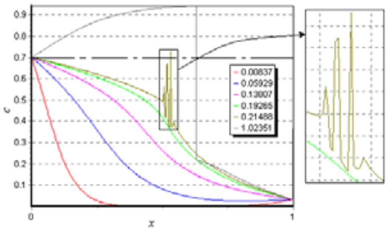

Figure 3. The distribution of concentration along x-axis at various time moments

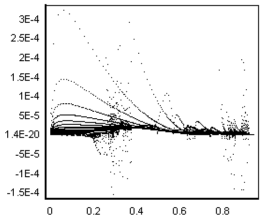

Figure 4. Total phase diagram

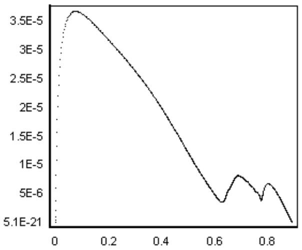

Figure 5. Phase diagram at $x = 0.3$

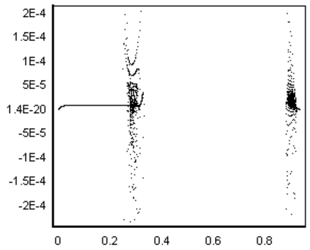

Figure 6. Phase diagram at $x = 0.6$

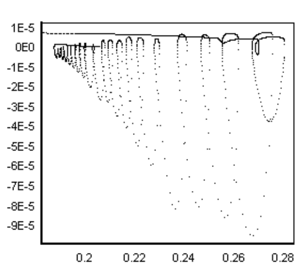

Figure 7. Phse diagram at $x = 0.65$

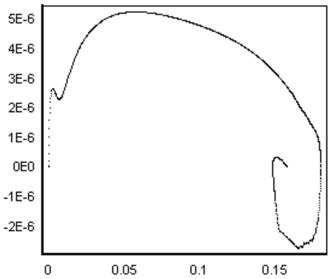

Figure 8. Total phase diagram

The calculations are provided in two cases - with smaller concentration than critical one on the boundaries, when the system reaches the homogeneous concentrations which are equal to the boundary concentration, and with the concentration at boundary higher than critical concentration. In our case the critical concentration can be estimated as 0.2.

The results of numerical simulations are shown in Fig.1-2. The grid-step h_i is chosen to be a constant but the size (undimensional value) of the system equal to 1. Temperature varies from $q/kT = 0.2$ to $q/kT = 1.8$ on the boundaries. Initial concentration is zero inside the ceramics material. It is considered that the boundary conditions are changed to $c_0 = c_M = 0.1$ at time moment $t = 0$ in Fig.1. The unstationary concentration distribution is shown in Fig.1. It must be mentioned that the concentration in this case is less than critical one and the physical solution is $c(x) = 0.1$ which is also the trivial solution of such problem. The asymmetry of the curves is created by the temperature gradient. As shown by the numerical calculations the stationary solution remains as trivial solution independently from the value of time step and it means that the difference scheme is absolutely stable.

Fig.2 shows the total phase diagram. It is the sum of phase diagrams at various cross-sections of coordinate x. Each phase diagram shows $\dot{c}$ vs. c at appropriate time moments and given spatial coordinate. Each phase curve is regular in Fig.2, meaning that the process is deterministic. concentrations to $c_0 = c_M = 0.7$ at time moment $t = 0$. These boundary concentrations are more than critical ones. In this case the motion of molecules has a stochastic nature as shown in Fig.3-8. The unstationary concentration distribution is shown in Fig.3, where the creation of the initial irregular nature of concentration motion is shown in the small box. The total phase diagram is shown in Fig.4 at the same cross-sections as in previous case. At some cross-sections the curves are irregular as shown in Fig.5-8. In Fig.5 the curve of phase diagram is regular and the process is deterministic at every time moment. Such behaviour is characteristic also for the cross-section near the second boundary as shown in Fig.8. In Fig.6-7 irregular processes are shown and the motion of molecules is characterized by stochastic motion.

As can be seen from figure Fig.3, the process of kinetic can be divided into three time periods: initially the process is in time and space determined, then it becomes stochastic, and finally the process is deterministic again - liquid-gas system is formed.

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