MONTE-CARLO MODELING OF SOLID ELECTROLYTES WITH INTERGRAIN BOUNDARIES

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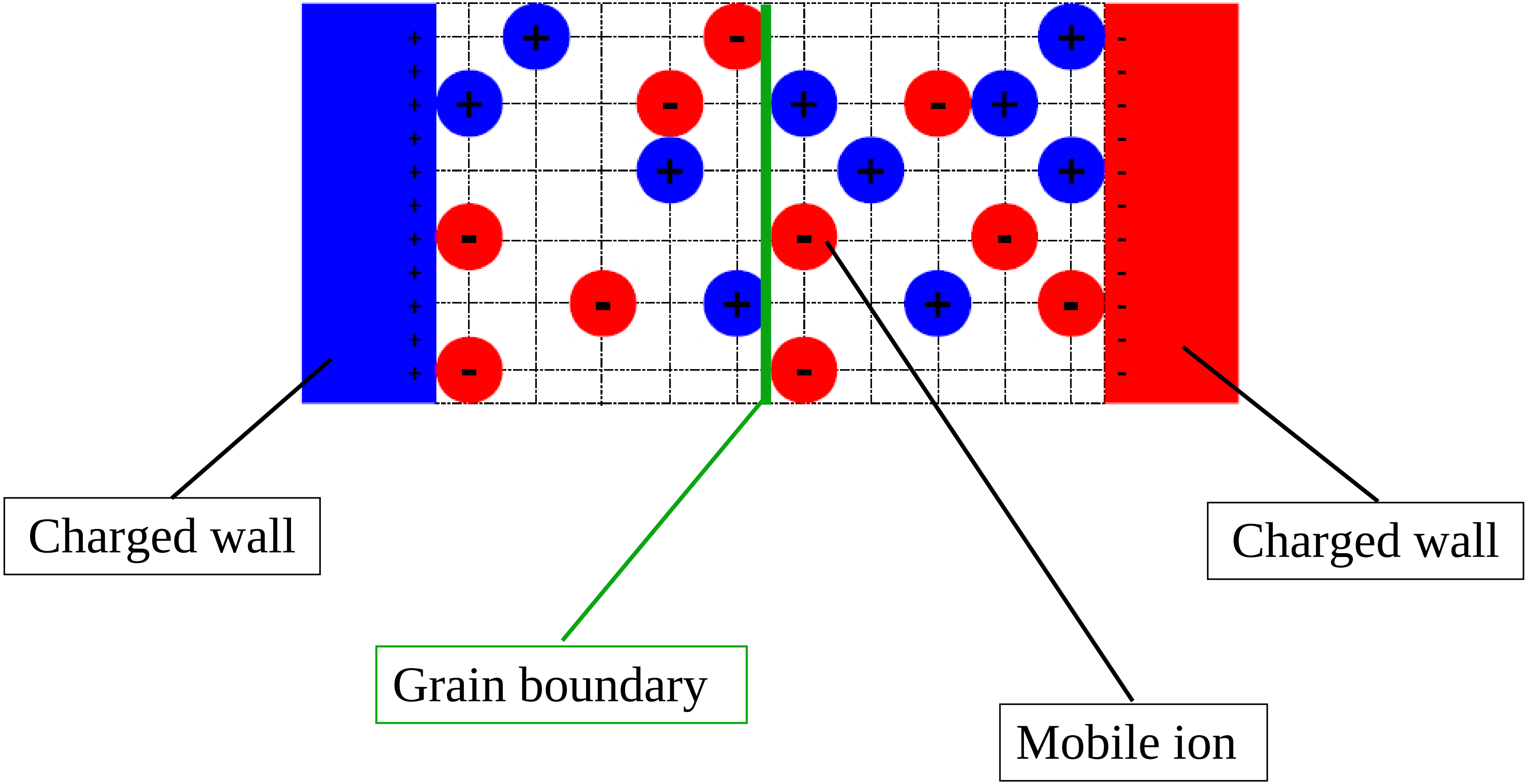
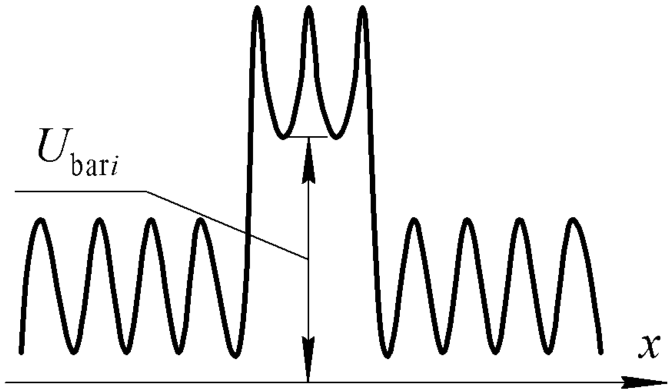
Model

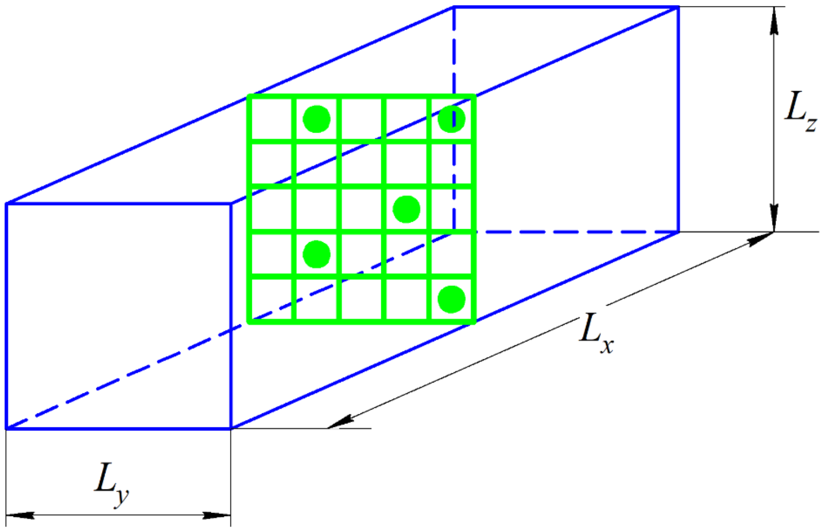


Methods of modeling a grain boundary

1. Potential profile of the host



2. Intergrain particles (IGP)



The concentration of intergrain particles

$$c_{IGP} = \frac{N_{IGP}}{L_y L_z}$$

The charge on the walls is set by N_w "frozen" particles with a concentration

$$c_w = \frac{N_w}{L_y L_z} \qquad (1)$$

To simulate the system, an ion located at site j is randomly selected. The direction of its possible transition is determined randomly in one of free sites i.

The probability of a particle jump is proportional to

$$w_{jl} = \exp\left(-\frac{(U_{\mathrm{bar}i} - U_{\mathrm{bar}j}) + J(z_j - z_i) + \Delta U_{\mathrm{Coul}}}{k_{\mathrm{B}} T} \right) \qquad (2)$$

$U_{\mathrm{bar}i}$ is inter-site energy barriers.

J is the energy of van der Waals attraction of the nearest neighbors;
z_j, z_i is the number of nearest neighboring particles of the j-th and i-th sites, respectively.

The contribution of the Coulomb interaction is determined by Ewald's summation

$$U_{\text{Coul}} = \frac{1}{4\pi\varepsilon\varepsilon_0}\left[\frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\left(q_i q_j \frac{\operatorname{erfc}\left(\alpha\left|\mathbf{r}_{ij}\right|\right)}{\left|\mathbf{r}_{ij}\right|} + \right.\right.$$

$$\left.\left. + \frac{1}{\pi V}\sum_{\mathbf{k}\neq 0} q_i q_j \frac{4\pi^2}{\alpha^2}\exp\left(-\frac{k^2}{\alpha^2}\right)\cos\left(\mathbf{k}\cdot\mathbf{r}_{ij}\right)\right) + \frac{2\pi}{V}\left|\sum_{i=1}^{N} q_i \mathbf{r}_i\right|^2\right], \qquad (3)$$

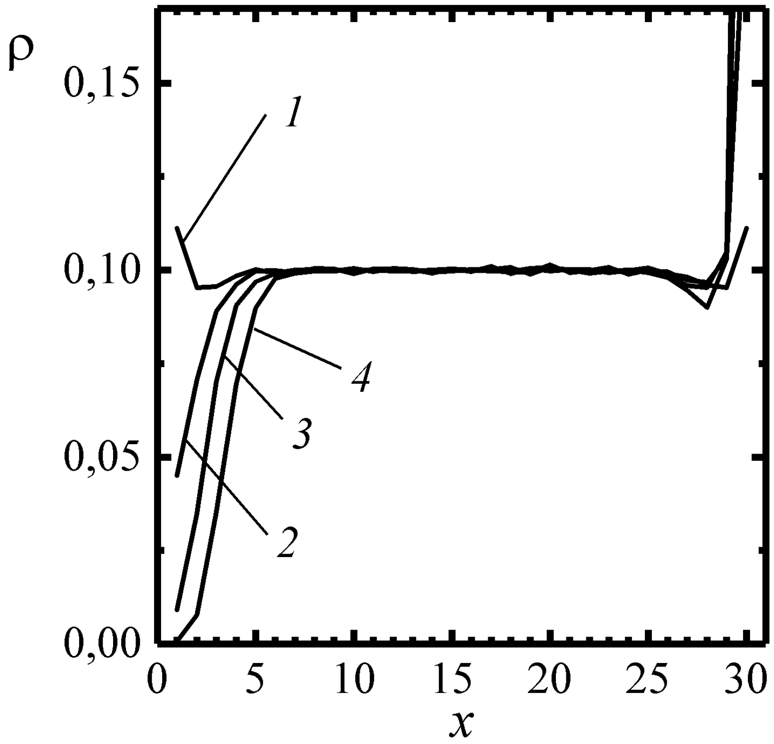
α is Ewald's parameter,

$\mathbf{r}_{ij}$ is the radius vector of particle j with respect to particle i,

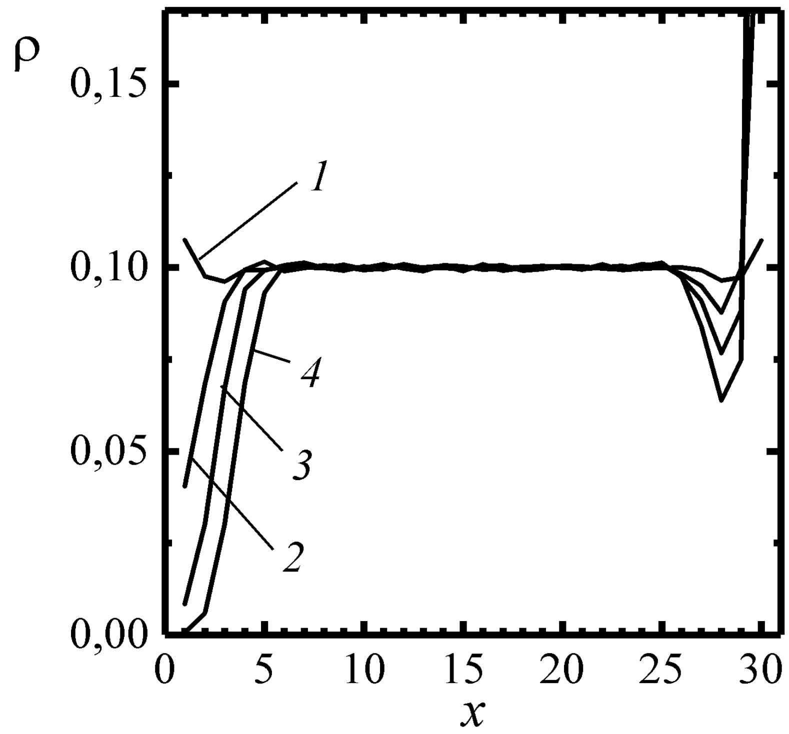
$V = L_x L_y L_z$ is the system volume,

$\mathbf{k} = 2\pi(\gamma'_x / L_x,\ \gamma'_y / L_y,\ \gamma'_y / L_y)$ is the reciprocal lattice vector.

For the grain boundary defined by the potential profile



The concentration profile of mobile ions with ρ = 0.1, in the absence of attraction of the nearest neighbors and the absence of an intergrain boundary: *1* – $c_w = 0$; *2* – $c_w = 0{,}1$; *3* – $c_w = 0{,}2$; *4* – $c_w = 0{,}3$



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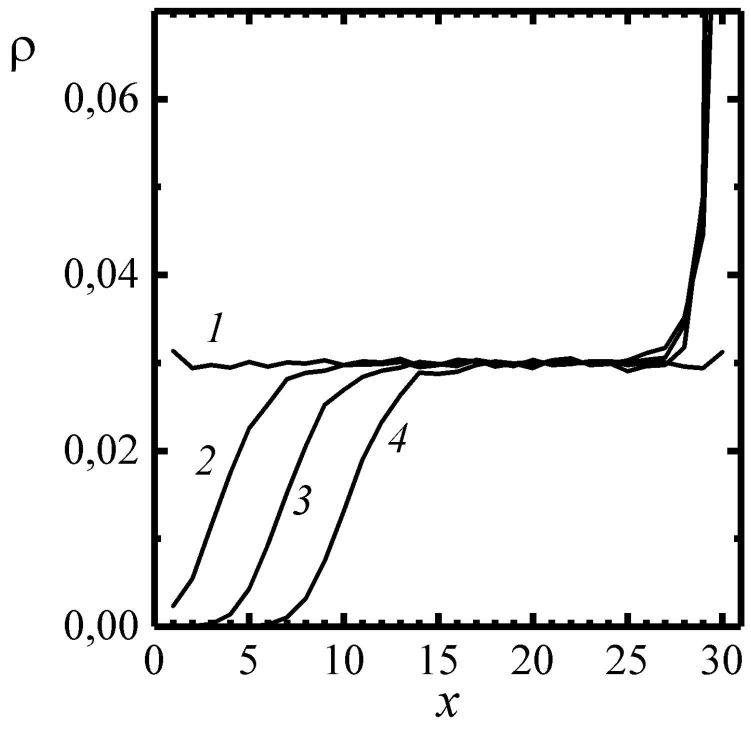
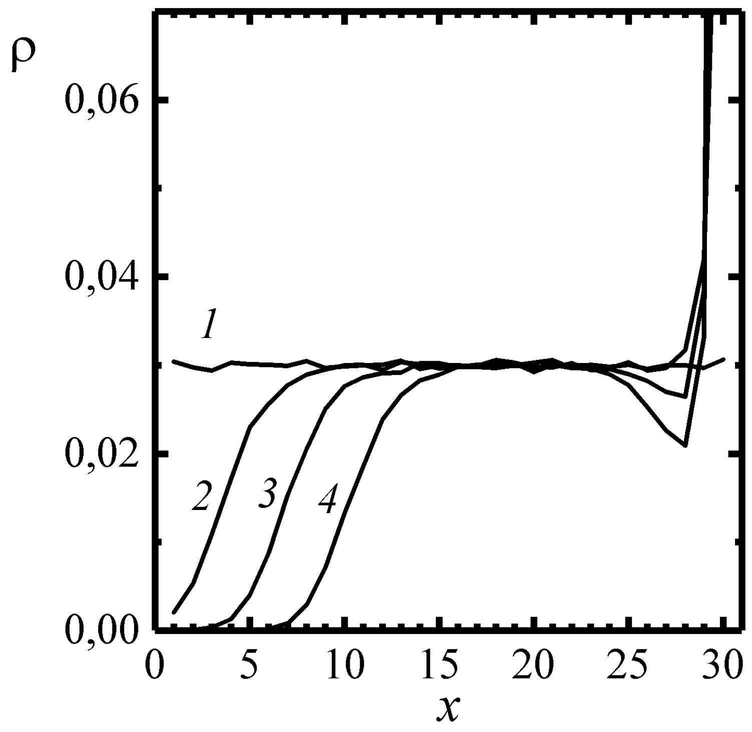
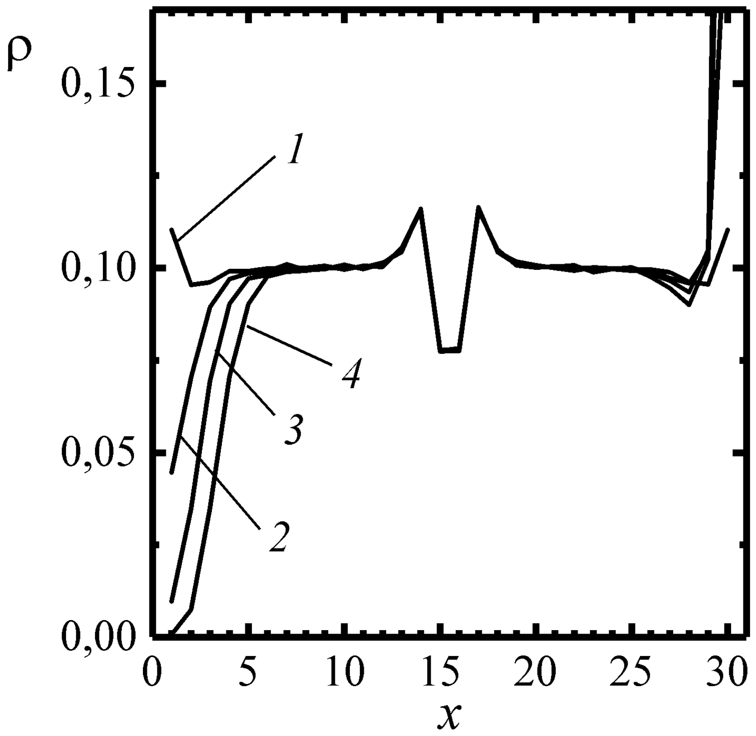
	
The concentration profile of mobile ions with ρ = 0.03, in the absence of attraction of the nearest neighbors and the absence of an intergrain boundary: *1* – c_w = 0; *2* – c_w = 0,1; *3* – c_w = 0,2; *4* – c_w = 0,3	The concentration profile of mobile ions with ρ = 0.03, in the presence of attraction of the nearest neighbors and the absence of an intergrain boundary: *1* – c_w = 0; *2* – c_w = 0,1; *3* – c_w = 0,2; *4* – c_w = 0,3



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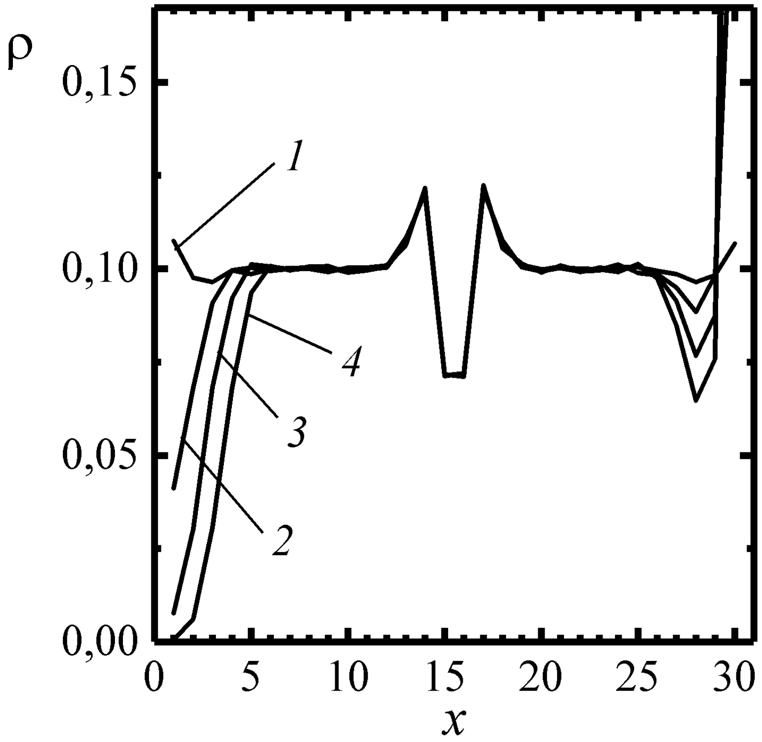

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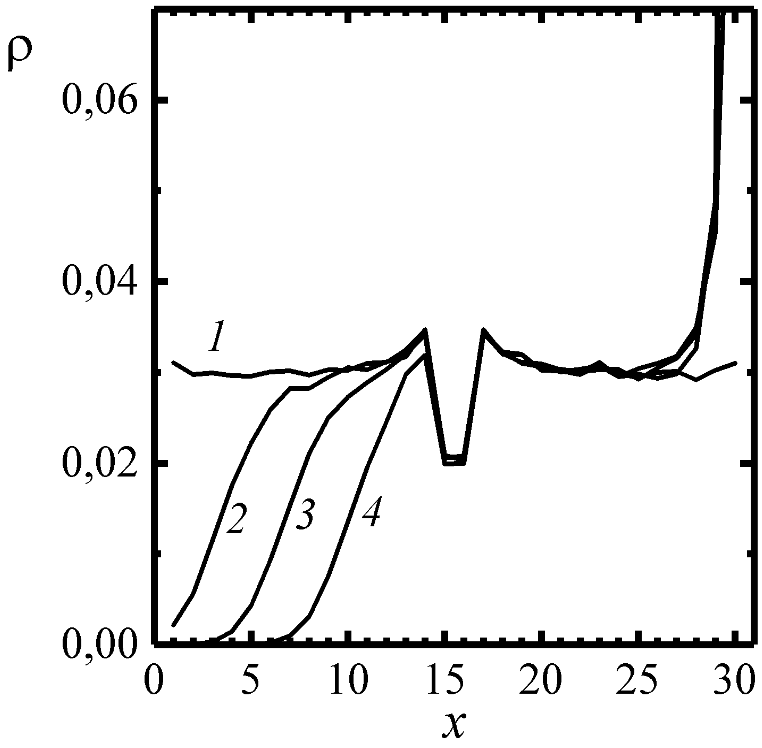

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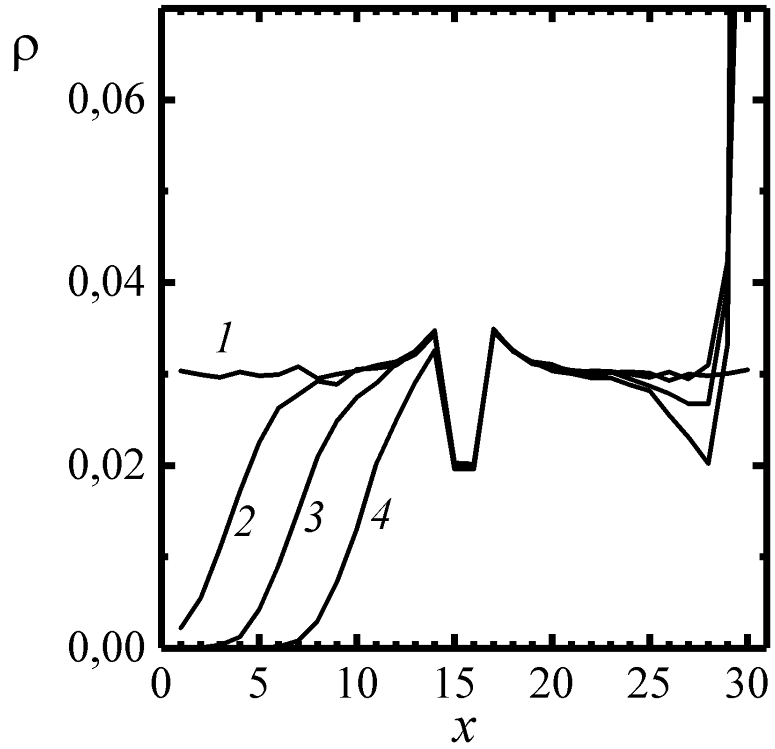

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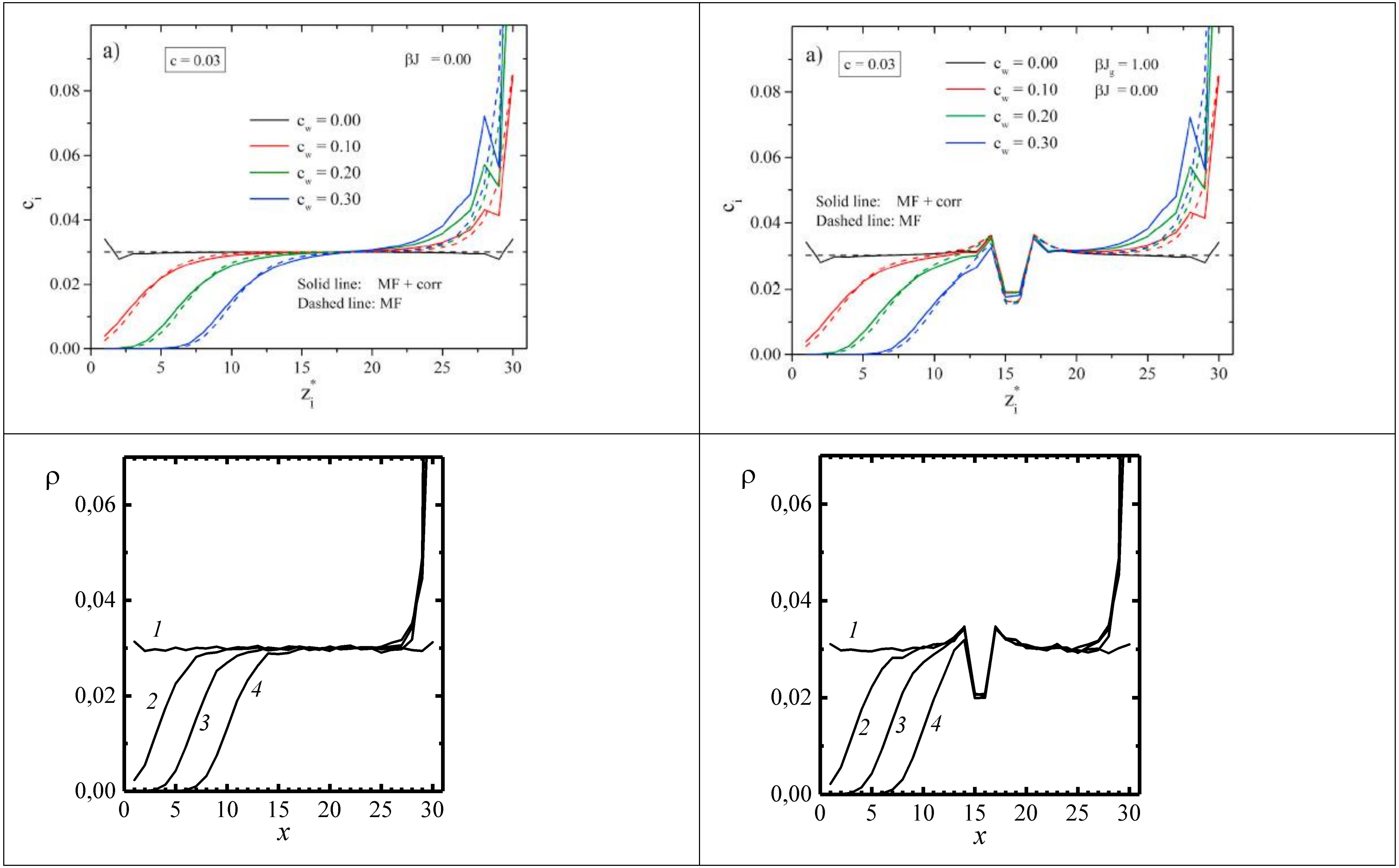
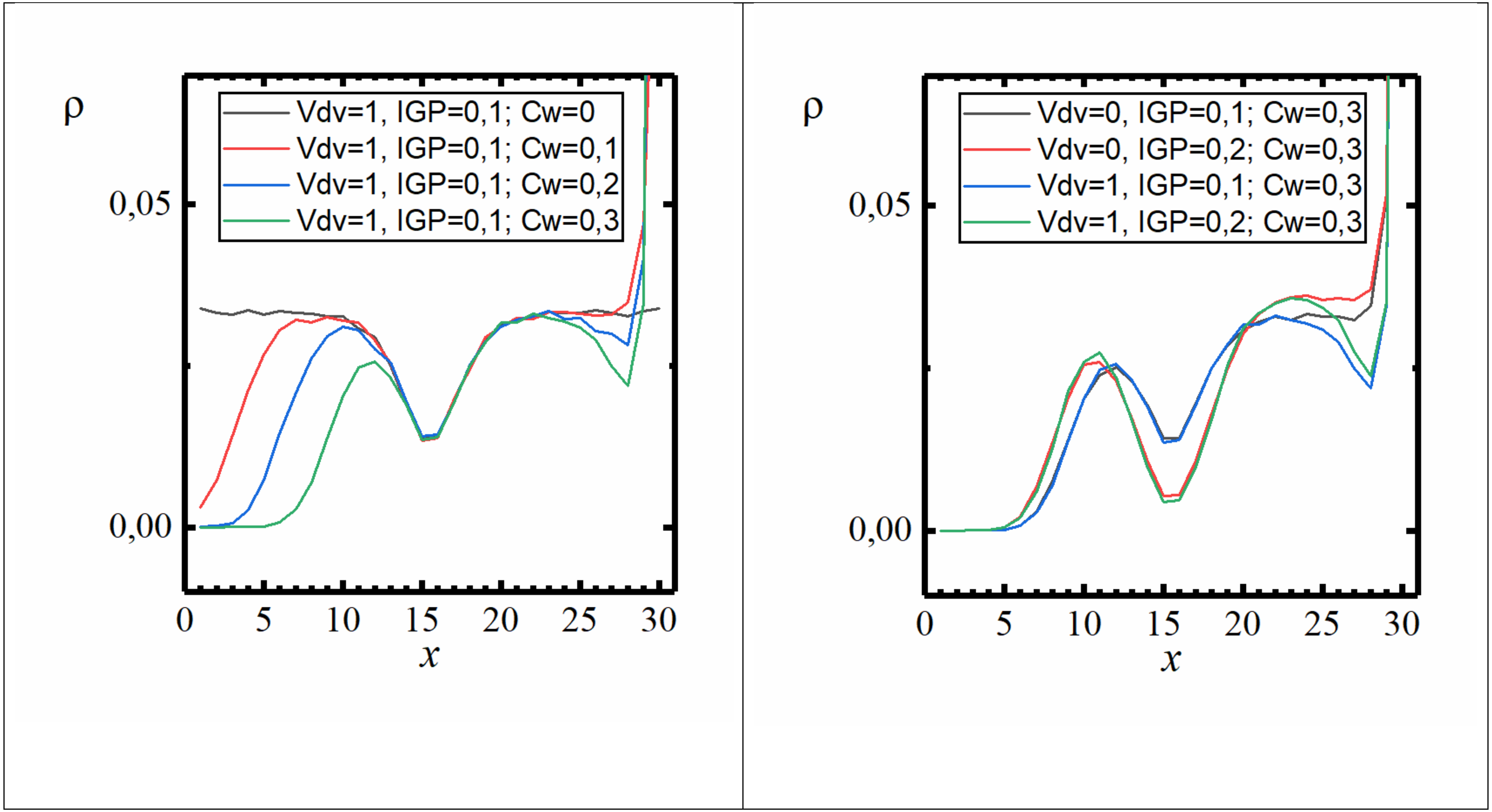


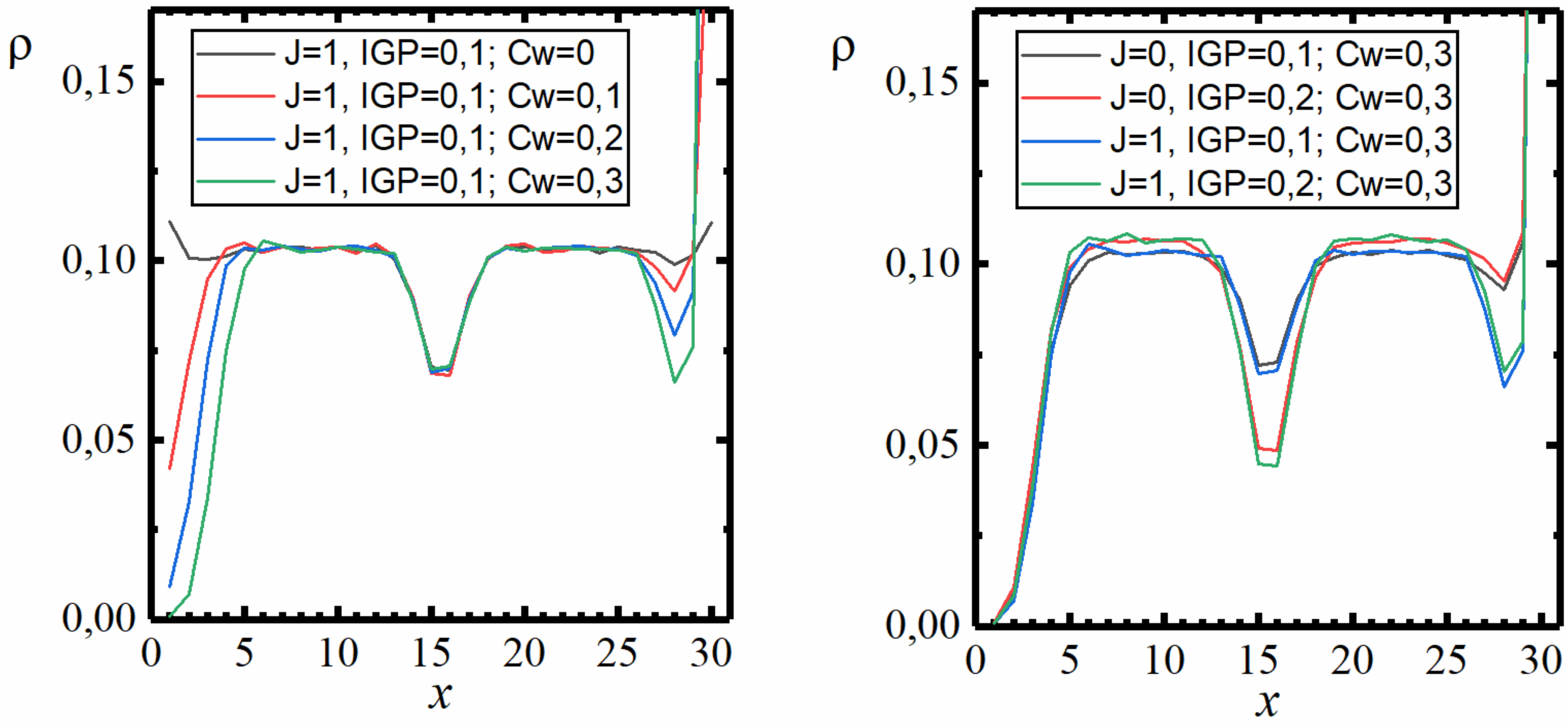
Color figures from: Patsahan T., Bokun G., di Caprio D., Holovko M., Vikhrenko V. *Solid State Ionics*. 2019, vol. 335, P. 156–163.

On the left positively charged wall, the width of the layer of reduced concentration increases with increasing charge on the wall. At the same time, ions accumulate on the opposite wall. A layer with a reduced concentration appears due to Coulomb repulsion from the left wall and the condition of electroneutrality. In addition, the short-range attraction between the ions leads to a larger concentration dip near the right wall.

At large enough the system size, the presence of a grain boundary practically does not affect the concentration distribution near the walls and vice versa.

Grain boundary defined by the intergrain charged particles





The distribution profile of mobile ions is similar in both cases.

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Thank you for the attention