SIMULATION OF NON-EQUILIBRIUM SORPTION DYNAMICS OF THE INTERACTING PARTICLES

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The set of two nonlinear equations which describes the gas sorption dynamics of nondissociative molecules is investigated. The results were obtained for different values of adatoms interaction energy. The comparison of three approximations in particle correlation effects is carried out.

The investigation has been performed at the Laboratory of Computing Techniques and Automation, JINR.

Моделирование динамики сорбции взаимодействующих частиц

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Исследована система нелинейных уравнений, описывающая динамику сорбции газа недиссоциирующихся молекул. Результаты получены для различных значений энергии взаимодействия между сорбируемыми частицами. Приводятся сравнения результатов в рамках трех приближений учета корреляционных эффектов.

Работа выполнена в Лаборатории вычислительной техники и автоматизации ОИЯИ.

The processes within two or more phases play an essential role in a wide class of physical and chemical phenomena [1]. Here, first of all, one can include the adsorption and desorption processes. In this work we present the results on simulation of gas sorption dynamics taking into account the interaction between adatoms.

For the sorption dynamics of gas, which is transferred with the constant velocity, we have the following system of nonlinear equations:

$$v \frac{\partial v}{\partial \xi} + \frac{\partial v}{\partial \tau} + \frac{\partial \theta}{\partial \tau} = d \frac{\partial^2 v}{\partial \xi^2}, \quad (\tau = t/\tau_0), \qquad (1)$$

$$\frac{\partial \theta}{\partial \tau} = \left(\frac{v}{ap_0} - 1 \right) f(\theta), \quad (v = n\gamma), \qquad (2)$$

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$$v(\xi, \tau = 0) = 0, \quad \theta(\xi, \tau = 0) = 0, \quad 0 \leq \xi \leq k_1, \tag{3}$$

$$v(\xi = 0, \tau) = v_0, \quad v(k_1, \tau) + c\frac{\partial v(k_1, \tau)}{\partial \xi} = 0, \quad 0 \leq \tau \leq k_2. \tag{4}$$

Here v is dimensionless gas concentration, θ — cover in terms of adsorption ($0 < \theta < 1$), a is the adsorption coefficient, p_0 — the equilibrium pressure corresponding to the surface coverage θ, and $f(\theta)$ expresses the correlation effects between adatoms.

The equation (2) is obtained on the basis of the Hamiltonian for adsorbat-adsorbent open system [2],

$$H = -\mu \sum_f N_f - \varepsilon \sum_{\langle fg \rangle} N_f N_g,$$

where ε is the effective adatoms interaction parameter ($\varepsilon > 0$ corresponds to physical adsorption; $\varepsilon < 0$, to chemisorption), μ is the effective chemical potential, $N_f = 0,1$, respectively, means the free and the occupied active center on surface. It is to be noted that $\theta = \langle N_f \rangle$, and, on the other hand, θ unambiguously defines the mean value of sorbat concentration in the sorbent pores.

The equation (2) is the kinetic equation for the monolayer coverage

$$\frac{\partial \theta}{\partial t} = v_{ads} - v_{des}, \tag{5}$$

where v_{ads} and v_{des} are, respectively, the adsorption and the desorption velocities.

To derive the equation (2) we used the expressions v_{ads} and v_{des} for nondissociative (one-central) adsorption and desorption [3]:

$$v_{ads} = r_A f(\theta), \quad v_{des} = r_D f(\theta), \tag{6}$$

$$r_A = \frac{J^* P \exp(-\beta(\varepsilon_k - \varepsilon_0))}{J_0 h a p_0}, \quad r_D = \frac{J^* \exp(-\beta \varepsilon k)}{J_a h \beta}, \tag{7}$$

Here $J*$, J_0 and J_a are, respectively, statsums of activated complex, of the particles in a gas phase and in adsorbate, P is the pressure in adsorptional systems, ε_0 and ε_k are the adatom binding and the adsorption activation energies, $\beta = (k_B T)^{-1}$, h is the Planck constant (for ideal gas to be adsorped we have $P\beta = n$).

Thus taking into account the formulas (6)—(7) one can obtain from (5) the equation which can easily be reduced to the form of (2):

$$\frac{\partial \theta}{\partial t} = \frac{1}{\tau_0} \left(\frac{P\beta\gamma}{ap_0} - 1 \right) f(\theta),$$

where $\tau_0 = \dfrac{J_a h\beta}{J*} \exp(\beta\varepsilon_k)$ have the time dimension and $\gamma = \dfrac{J_a}{J_0} \exp(\beta\varepsilon_0)$ have the dimension inverse to concentration and it connects the statsums of the molecules in the gas phase and in the adsorbate.

The expressions for ap_0 and $f(\theta)$ are concretized for the different approximations in particle correlation effects (e.g., molecular field approximation (MFA), polynomial fission (PF), quasichemical approximation (QCA) and so on). In particular, in QCA we have [4]:

$$\frac{1}{ap_0} = \frac{1 - \theta}{\theta} [1 - r + r \exp(-\beta\varepsilon)]^{-z}, \tag{8}$$

$$r = \frac{\delta - 1 + 2\theta}{\delta + 1}, \quad \delta = \sqrt{(1 - 2\theta)^2 + 4\theta(1 - \theta) \exp(\beta\varepsilon)},$$

$$f(\theta) = \theta(1 + yr)^z, \quad y = \exp(\beta(\varepsilon_1 - \varepsilon)) - 1.$$

We solved the set of equations (1)—(4) numerically. For the numerical solution we used the following difference scheme [5]:

$$\frac{v_m^{n+1} - v_m^n}{\Delta\tau} + v \frac{v_m^{n+1} - v_{m-1}^{n+1}}{\Delta\xi} = - F(v_m^n, \theta_m^n),$$

$$\frac{\theta_m^{n+1} - \theta_m^n}{\Delta\tau} = F(v_m^n, \theta_m^n),$$

$$F(v_m^n, \theta_m^n) = \left(\frac{v_m^n}{ap_0} - 1 \right) f(\theta_m^n).$$

As an initial approximation we consider the stationary values of the coverage, i.e., $\dfrac{\partial \theta}{\partial \tau} = 0$. In this case for the given distribution of the gas concentration we have the isotherm $\theta = \theta(v)$. The numerical results for the fixed values of the particles interaction energy ε (eV) and the temperature
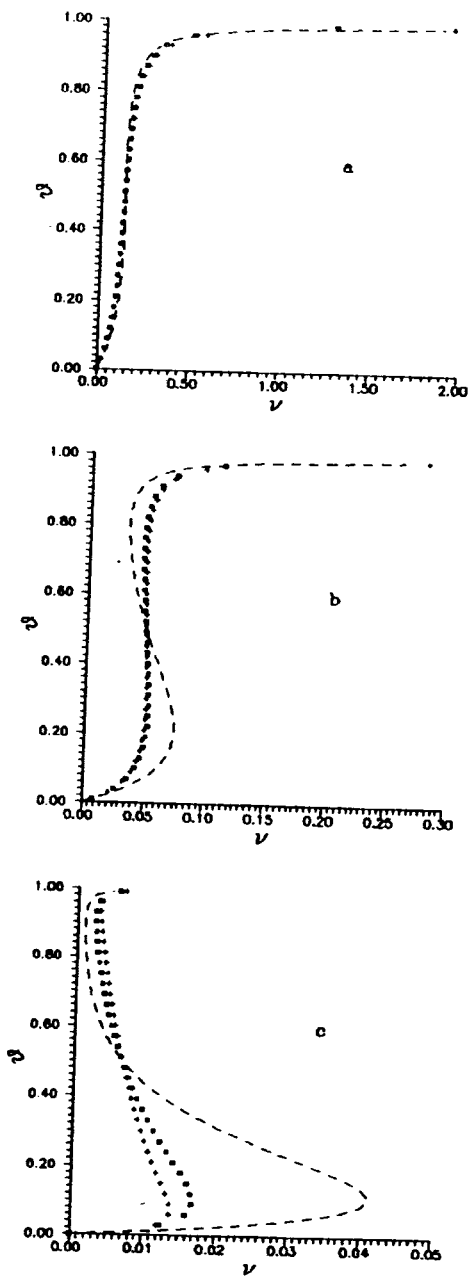
Fig.1. The sorption isotherms for $\beta\varepsilon = 1.0$(a), 1.5(b) and 2.5(c).
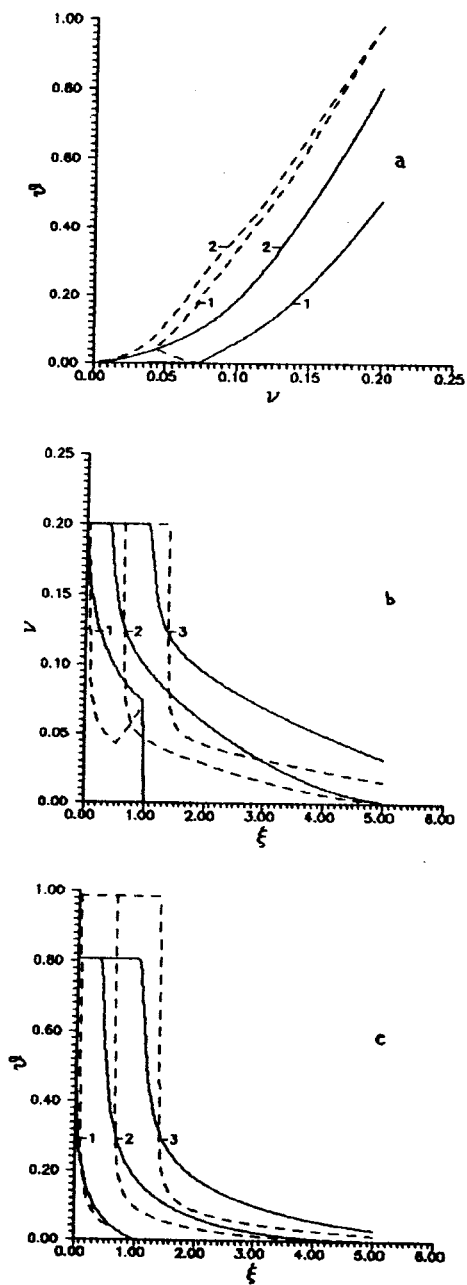
Fig.2. The sorption isotherms of dynamical equations
(1)—(4) for $\beta\varepsilon = 1.0$(- -) and 1.5 (—).

30

of the system $\beta = (k_B T)^{-1}$ (eV)$^{-1}$, such that $\beta\varepsilon = 1.0$, 1.5 and 2.5, are, respectively, shown in Fig.1a, b and c.

The results for the QCA, i.e. the computations with the formulas (8), are drawn by markers ^^^. In Fig.1, for comparison, the results obtained in the approximation of PF (the signs "+") and in MFA (the dashed line) are also plotted. The results show that with the increase of the adatoms interaction parameter $\beta\varepsilon$ the sorption isoterms become essentially nonlinear.

In Fig.2a, b and c we present the results of the direct solutions of the equations (1)—(4) for non-equilibrium sorption dynamics (the solid lines for $\beta\varepsilon = 1.0$, the dashed lines for $\beta\varepsilon = 1.5$). The evolutions of $v(\xi, \tau)$ and $\theta(\xi, \tau)$ (Fig.2b and c) in the interval $\xi \in [0,5]$ are shown at three moments: 1 — for $\tau = 1.0$; 2 — for $\tau = 5.0$; 3 — for $\tau = 10.0$. The Tables 1 and 2 give a convergence of the difference scheme applied with the Runge rule [6]:

$$\sigma = \frac{Y_i(\Delta\tau) - Y_i(\Delta\tau/2)}{Y_i(\Delta\tau/2) - Y_i(\Delta\tau/4)}.$$

Table 1. The convergence of the numerical values of θ

ξ	$\theta(\Delta\tau)$	$\theta(\Delta\tau/2)$	$\theta(\Delta\tau/4)$	σ
2.0	0.1798875	0.1816078	0.1824608	2.016764
4.0	0.0564381	0.0569365	0.0571856	2.000803
6.0	0.0140383	0.0142581	0.0143684	1.992747
8.0	0.0012153	0.0012625	0.0012865	1.966666
9.0	0.0001261	0.0001348	0.0001393	1.933333

Table 2. The convergence of the numerical values of v

ξ	$v(\Delta\tau)$	$v(\Delta\tau/2)$	$v(\Delta\tau/4)$	σ
2.0	0.0939182	0.0943445	0.0945539	2.035817
4.0	0.0490738	0.0493528	0.0494917	2.008639
6.0	0.0182292	0.0184387	0.0185435	1.999045
8.0	0.0025861	0.0026634	0.0027025	1.976982
9.0	0.0004115	0.0004328	0.0004438	1.936353

Conclusions

1. The equation for external diffusive kinematics of gas sorption is obtained. The sorption dynamics of the interacting particles is investigated.

2. The numerical analysis of the sorption equations and the convergence of the difference scheme is carried out.

3. The nonlinear behaviour of the sorption isotherms depending on adatoms interaction parameters is found.

References

1. Nicolis G., Prigogine I. — Exploring Complexity. W.H.Freeman and Company, New York, 1989, p.313.
2. Fedyanin V.K. — J.Chem.Phys., 1972, 46, No.1, p.119 (in Russian).
3. Tovbin Yu.K., Fedyanin V.K. — Kinetika i kataliz, 1978, 19, 4, p.989 (in Russian).
4. Tovbin Yu.K., Fedyanin V.K. — Kinetika i kataliz, 1978, 19, 5, p.1202 (in Russian).
5. Samarskiy A.A., Popov Yu.P. — The Difference Method for Solution of the Gasodynamic Problems. M.: Nauka, 1992, p.423 (in Russian).
6. Kalitkin N.N. — Numerical Methods. M., Nauka, 1978, p.457 (in Russian).