

THE DYNAMICS OF SORPTION OF INTERACTING PARTICLES

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Specific features of particles transport when their sorption is taken into account by the surface are analyzed: flows of gas or liquid in systems of different geometry; (for definiteness, the formulae are given for the flow through a tube of length L). An activated complex is treated as an admixture. The quantum statistical Hamiltonian of adsorption is taken as an effective Hamiltonian of an open system. The kinetic equation of sorption, except for the case of Henry's isotherm, is essentially nonlinear in coverage, which provides a high degree of nonlinearity for differential equations and concentration of particles in the flow. Solutions for Henry's isotherm and the asymptotics of solutions for the wave front of Langmuir's isotherm are analytically analyzed. It is important to take into account an interaction in the adsorbate, and for chemisorption it allows one to show that starting from some coverages desorption dominates over adsorption. This is especially essential for dissociative adsorption ($A_n \rightarrow n[A]^*$). Certain relations between the interaction of adatoms and adatoms with the activated complex may lead to the formation of chemical waves of concentration in the flow and appearance of strange attractors.

The investigation has been performed at the Laboratory of Theoretical Physics, JINR.

Динамика сорбции взаимодействующих частиц

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Исследуется влияние активной поверхности на поток газа или жидкости через среду различной геометрии (формулы приведены для потока через трубу длины L радиуса R_0). Активные комплексы поверхности рассматриваются как примеси. При анализе используется эффективный квантостатистический гамильтониан открытой системы адсорбат — адсорбент. Для всех изотерм адсорбации, кроме изотермы Генри, кинетические уравнения сорбции существенно нелинейны, что обуславливает высокую нелинейность концентрации в потоке. Аналитически проанализирована адсорбция Генри и, в приближении фронта волны, Ленгмюра. Учет взаимодействия в адсорбате позволяет сделать вывод, что, начиная с определенных покрытий десорбция превалирует над адсорбцией. Это весьма существенно для диссоциативной хемисорбции ($A_n \rightarrow n[A]^*$). При определенных соотношениях взаимодействий между адатомами и адатомами с активными центрами возможно возникновение автоволн концентрации и странных аттракторов.

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The quantum statistical Hamiltonian of absorption is taken as an effective Hamiltonian of an open system

$$H = -\nu \sum_f N_f - \varepsilon \sum_{\langle fg \rangle} N_f N_g \quad (1)$$

Here ε is an effective parameter of the interaction ($\varepsilon \sim 0.05$ eV for the physical adsorption, often $\varepsilon > 0$, $|\varepsilon| \sim 0,1 + 0,2$ for the chemical adsorption, that is, $\varepsilon < 0$); ν is an effective chemical potential of the system adsorbate-adsorbent, defined by the chemical potential of the adatom of the open system $\mu(A_n)$: $\mu(A_n) = n\mu[A]$, and by the characteristics of the adsorbent-adsorbate system [1]. For dissociative adsorption we take the gas $A_n \rightarrow n[A]$

$$\nu = k_B T \left[p_0 \frac{\exp \beta(\varepsilon_0 + \delta\mu_e) \cdot J_a^n}{k_B T J_0(\beta)} \right]^{1/n} = k_B T (ap_0)^{1/n}, \quad (2)$$

a is the coefficient of the adsorption, p_0 is the equilibrium of the pressure for the coverage $\theta = \theta(p_0, T/\varepsilon) = \langle N_f \rangle$, ε_0 is the binding energy of the adatom, J_a, J_0 are the partition functions of the adatom and of the particle for a gas, $\delta\mu_e$ is the change of the chemical potential of the electronic subsystem [2], T is the temperature, k_B is the Boltzmann constant. In the equation (1) $N_f = 0,1$ ($N_f = 0$ is the case of the open sites; $N_f = 1$, of the packing sites, and the summation is carried out over all adsorption sites on the surface (f) and out over all ($g = 1,2,\dots,z$) sites (f,g). The Hamiltonian (1) may be deduced from the first principles in the framework of an Anderson-Ising composite model [3]. Within the composite Hamiltonian method the coverage dependence of the chemisorption characteristic for a single hydrogen-like adatom on the transition metal surface like the chemisorption energy, ε_0 changes of the Fermi level $\delta\mu_e$, the electric charge $e[1 - \bar{n}_{f\uparrow} - \bar{n}_{f\downarrow}]$ and $\mu_e[1 - \bar{n}_{f\uparrow} - \bar{n}_{f\downarrow}]$ magnetic moment at adsorbed atoms are investigated [2]; $\bar{n}_{f\sigma} = \langle N_{f\sigma} n_{f\sigma} \rangle_M \cdot \theta^{-1}$, $n_{f\sigma} = a_{f\sigma}^+ a_{f\sigma}$. The unusual form of the average $\bar{n}_{f\sigma}$ arises from the fact that the configuration of adatoms is not fixed and the electronic correlation function $\bar{n}_{f\sigma}$ should be interpreted as the probability of finding an electron with the spin $\sigma = \pm 1/2$ at the adsorption center « f » when the latter is already occupied.

This fact is discussed in detail in [2,3]. We should remark that $\varepsilon_0, |\varepsilon|$ weakly depend on θ and T .

If for the calculation of the equilibrium characteristics of the adsorption important are $\langle N_f \rangle, \langle N_f N_g \rangle$, for the calculation of the adsorption and desorption rates we must have the correlation functions

$F_k(\theta) = \langle N_f \prod_1^k N_g \rangle, k = 1, \dots, z$ for the one-site adsorption [4] and

$F_k^{(h)} = \langle N_f \prod N_g \prod N_k \rangle, k = 1, \dots, z, j$ are the numbers for the next-neighbour sites [5] for dissociative two-site adsorption.

The kinetic equation of sorption (for simplicity we take the case of the one-site adsorption) has the form [4]

$$\begin{aligned} \partial_t \theta &= V_{ads} - V_{des} \\ V_{ads} &= r_A F(\theta), \quad V_{des} = r_D F(\theta) \\ F(\theta) &= \sum_{k=0}^z \frac{x^k}{k!} F_k(\theta), \quad x = \exp[\beta(\varepsilon_1 - \varepsilon)] - 1 \\ r_A &= \frac{J^* P \exp[-\beta(\varepsilon_k - \tilde{\varepsilon}_0)]}{J_0 h \sigma a p_0}, \quad r_D = \frac{J^* \exp(-\beta \varepsilon_k)}{J_a h \beta \sigma}, \end{aligned} \quad (3)$$

J^*, ε_k is the partition function and the energy of an activated complex, P is the pressure in the system, ε_1 is the interacting energy of the adatom with an activated complex; $\tilde{\varepsilon}_0 = \varepsilon_0 + \delta \mu_e$. The $F(\theta)$ is some function of the coverage θ . The expressions V_{ads} and V_{des} for dissociative adsorption are taken from [5]. The difference between r_A and r_D lies in that the activated complex of the adsorption is in equilibrium with the gas molecules; and of the description activated complex, with the adatoms.

There is the equation of the transfer. For the gas sorption we have the equation (with the diffusion)

$$\partial_t \theta + \partial_t v = -V_0 \partial_x v + D \partial_{xx} v, \quad (4)$$

V_0 is the velocity, D is the coefficient of the diffusion.

There are initial and boundary conditions:

$$v(x,0); \dot{v}(x,0); v(0,t) \equiv v_0(t), \dot{v}(0,t) = \dot{v}_0(t). \quad (5)$$

For the ideal gas, $P = \frac{n(x,t)R_A T}{V}$, $n(x,t)$ is the number of the mol. on the place « x » and on the time « t »,

$$v(x,t) = u(x,t) \frac{V_0}{\Delta}, \quad u(x,t) = \frac{n(x,t)N_A}{V}, \quad (4')$$

V_0 is the volume of the gas molecule; Δ , a geometrical factor; $\Delta \sim \frac{2}{3} \frac{1 - d/R_0}{(1 - d/D)}$ is the same effective parameter of the adsorption region, d , $D = 2R_0$, R_0 is the radius of the tube. The parameter μ^{-1} has the dimension of the time

$$\partial_t \theta = \mu \left[\frac{P \cdot a}{P_0 \cdot a} - 1 \right] F(\theta), \quad \mu = \frac{k_B T J^* \exp(-\beta \varepsilon_k)}{\sigma h J_a} \quad (6)$$

and can be «a chemical time».

In the self-consistent approximation [4,6] we have for the equation (6)

$$\frac{1}{ap_0} = \frac{1 - \theta}{\theta} \exp(\beta z \varepsilon \theta), \quad F(\theta) = \theta(1 + x\theta)^z$$

$$\partial_t \theta = \tau_0^{-1} [(1 - \theta) \cdot v \exp(\beta z \varepsilon \theta) - \delta \cdot \theta] (1 + x\theta)^z$$

$$\tau_0 = \frac{\sigma h J_0 v_0}{k_B T J^* \Delta} \exp[-\beta(\tilde{\varepsilon}_0 - \varepsilon_k)], \quad \delta = \frac{V_0 J_0}{\Delta J_a} \exp(-\beta \tilde{\varepsilon}_0), \quad (7)$$

z is the number of the sites ($z = 3.4.6$). The r_0 can be called «an adsorption time». From the physical point of view $\delta \ll 1$. When $\varepsilon = \varepsilon_1$ and for the case of Henry's isotherm ($v \ll 1$, $\theta \ll 1$) we have

$$\partial_t \theta = \tau_0^{-1} (v - \delta \theta),$$

$$\partial_t \theta + \partial_t v = -V_0 \partial_x v + D \partial_{xx} v, \quad v(0,t) = v_0(t). \quad (8)$$

The case of Langmuir's isotherm ($\varepsilon = \varepsilon_1 = 0$, $0 \leq \theta \leq 1$) we have

$$\partial_t \theta = \tau_0^{-1} [1 - \theta] \cdot v - \delta \cdot \theta],$$

$$\partial_t \theta + \partial_t v = -V_0 \partial_x v + D \partial_{xx} v, \quad v(0,t) = v_0(t), \quad (9)$$

The kinetic equation (7) is essentially nonlinear in coverage, which provides a high degree of nonlinearity for differential equations and concentration of particles in the flow.

Solutions for Henry's isotherm and the asymptotics of solutions for the wave front of Langmuir's isotherm [7]

$$\tau = t - \frac{x}{V_0}, \quad \sigma = \frac{x}{V_0} \quad (10)$$

with the help of the Laplace transformation are analytically analyzed. In the last case we can introduce the «potential function» $\psi(x,t)$ and by the

$$v = \partial_t \psi, \quad \theta = -\partial_\sigma \psi \quad (11)$$

and Koul-Hopf like operation

$$\psi = \tau_0 \ln \chi(x,t). \quad (12)$$

we obtaine for the Langmuir's case the equation

$$\chi_{\tau\sigma} + \tau_0^{-1} \chi_\tau + \mu \chi_\sigma = 0. \quad (13)$$

For the case of the (x,t) -variables

$$\frac{\tau_0}{1+\delta} [\chi_{tt} + V_0 \chi_{tx}] + \chi_t + V_0 \frac{\delta}{1+\delta} \chi_x = 0. \quad (14)$$

For the hyperbolic equation of second order (14) we have the succession of times

$$\tau_1 < \tau_0 < \tau_2, \quad \tau_1 = \frac{\tau_0}{1+\delta}, \quad \tau_2 = \frac{\tau_0}{\delta(1+\delta)}. \quad (15)$$

The «wave of the second order» transfer of the initial profile with the velocity V_0

$$\chi_2(x,t) = \chi_0(\tau) \exp\left(-\frac{x}{\tau_2 V_0}\right). \quad (16)$$

For $t \gg \tau_1$ there is a «wave of the first order» which has the velocity

$$V_1 = V_0 \frac{\delta}{1+\delta} \ll V_0$$

$$\chi_1(t,x) = \chi_0\left(t - \frac{x}{V_1}\right). \quad (17)$$

Both eq. (16) and eq. (17) can be derived asymptotically by the Laplace-transformation ($s \rightarrow \infty$ for eq. (16) and $t \gg \tau_1$ for eq. (17)).

It is important to take into account an interaction in the adsorbate, and for the chemisorption ($\epsilon < 0$) it follows one to show that starting from some coverages desorption dominates over adsorption. This is especially essential for dissociative adsorption ($A_n \rightarrow n[A]$, O_2 ; for O_2 , H_2 , N_2 «n» equals two). For the chemisorption of the interacting adatoms in eq. (7) $\exp(\beta z \epsilon \theta) \equiv \equiv \exp(-\beta z |\epsilon| \theta)$ and $\beta z |\epsilon| \theta \approx 15 + 25$ for typical systems adsorbate-adsorbent [1].

Certain relations between the interaction of adatoms and adatoms with the activated complex may lead to the formation of chemical waves of the concentration in the flow and appearance of strange attractors for $(r_0)_+ \rightarrow 0$ (maybe it is a case of physical adsorption). From this point of view we must analyse the equation

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