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Probe mössbauer diagnostics of dynamic properties of 2D-dimensional water layers in montmorillonite

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On the basis of Mössbuer spectroscopy, a methodological approach has been developed and tested that makes it possible to separate surface forces of various nature — electrostatic, dispersive, structural and hydrophobic, present in thin films of bound water in a clay mineral. For surface ice, two melting scenarios have been established that are characteristic of a second-order phase transition. The probe technique makes it possible to detect the presence of white and flicker noise in water films. Based on the results of the experiment, a specific type of scenario for the transition to dynamic chaos in a deterministic system was established.

Keywords: surface forces, melting scenarios, dynamic chaos, $1/f$-noise.

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The behavior of surface processes in a clay mineral (montmorillonite) cannot be correctly described within the framework of the Deryagin-Landau-Verwey-Overbeek (DLFO) theory [1]. This happens because at the considered distances the situation is complicated by the appearance of so-called „non-DLVO" forces, which can be monotonically attractive, repulsive, or even oscillating. Moreover, in absolute value they can be much stronger than any of the „classical" forces, used in the DLVO theory.

The purpose of this article is to demonstrate a newly created approach based on probe Mössbauer spectroscopy (MS), which allows one to separate surface forces of different nature and simultaneously study the dynamic properties of 2D-dimensional water layers in the „ice-water-clay" model system. To solve the problems posed two valence states of the Mössbauer probe ^{57}Fe were chosen. The experimental spectrum of the first type is characteristic of ferric iron, consisting of iron dimers and amorphous polymer films („clusters") (*1* and *2* in Figure 1, *a*, respectively). The second type was a superposition of two partial spectra with parameters typical of cations Fe^{2+} located in a high-spin state and in two nonequivalent positions (forms 1, 2 in Figure 1, *a*). Let us proceed to discuss the results obtained.

1. Mössbauer diagnostics of surface forces

As a first approximation, the contribution of surface forces (attraction and/or repulsion) acting in water films h thick to the disjoining pressure $\Pi(h)$ is considered additive [1]:

$$\Pi(h) = \Pi_e(h) + \Pi_m(h) + \Pi_s(h), \qquad (1)$$

where $\Pi_e(h)$ — the electrostatic component due to the overlap of diffuse ionic layers of charged surfaces of particles and their repulsion, $\Pi_m(h)$ — the molecular component due to the dispersion interaction of the solid substrate through a thin film of liquid, $\Pi_s(h)$ — structural component caused by the overlap of adsorption layers of liquid with a changed structure.

Let us immediately note that when studying films of bound water (and thicknesses no more than 4−6 nm) in clay, it is more correct to give preference to the concept of structural forces ($\Pi_s(h)$) compared to electrostatic forces ($\Pi_e(h)$). Then the structural forces acting in the water sublayer, according to the contact theorem [2] are described by the expression for

$$\Pi_s(h) = k_B T\left[\rho_s(h) - \rho_s(\infty)\right],$$

where $\rho_s(h)$ — the numerical density of a liquid sublayer of thickness h, and $\rho_s(\infty)$ is the numerical density of the liquid on the outer side of the plate). To estimate $\Pi_s(h)$ we use data on the density of interlayer water obtained using the MS method (Figure 2, *a*). It was established that the nature of the interaction between aluminosilicate surfaces with a water film in the gap (thickness 4−6 nm maximum) is similar to electrostatic repulsion. However, the value $\Pi_s(h)$ turned out to be by order of magnitude greater than the value of the component $\Pi_e(h)$. Reducing the film thickness to two water layers did not lead to a noticeable change in the absolute value of the component $\Pi_s(h)$, but the nature of the interaction of the plates changed. At the same time, a hydrophobic attraction is established between them, which can be explained by the dominant manifestation of another type of „non-DLVO" forces, which is of an oscillating nature [2]. Note that from a physical point of view, the presence of such oscillations $\Pi_s(h)$ in the interlayer film makes it possible to develop in practice an effective method for monitoring its thickness, which we implemented when preparing samples. In order to confirm the estimate $\Pi_s(h)$ ($\cong 2.22 \cdot 10^7$ Pa) we will use the result of theoretical paper [3], in which the approach is

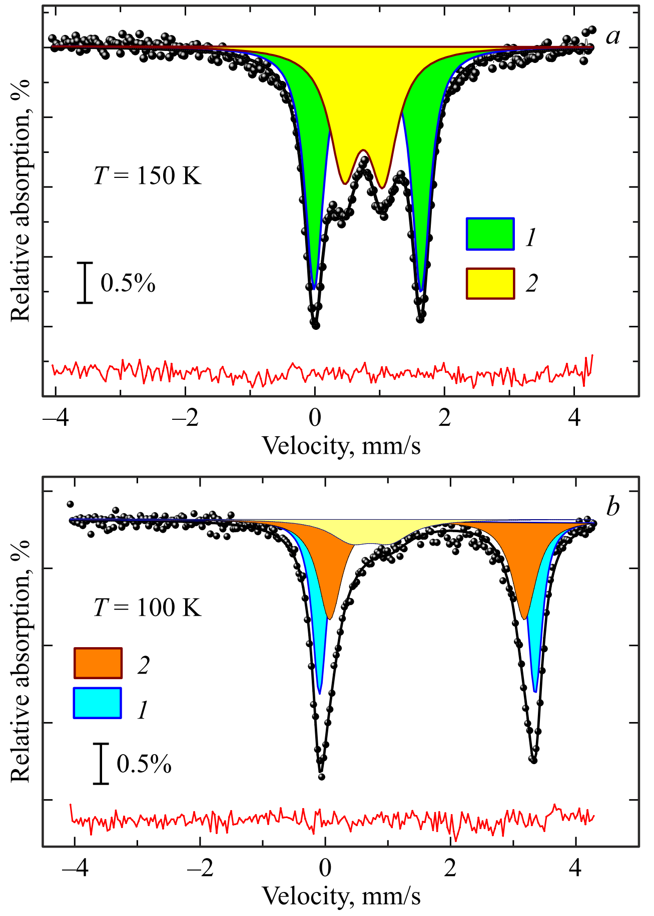

Figure 1. Model interpretation of Mössbauer spectra of probe atoms ^{57}Fe in the system „ice-montmorillonite surface": *1* — iron dimers $\langle[Fe_2^{3+}(OH)_2^-\rangle]^{4+}$, *2* — iron clusters (*a*). *1* — form 1 for Fe^{2+} *2* — form 2 for Fe^{2+} (*b*).

implemented of expanding the free energy into a series as per powers of order parameter η. From a physical point of view, our choice is due to its wide application in the theory of phase transitions (PTs) of second kind (see Figure 3, *a*). On the other hand, in the methodological aspect, the traditional use of exponential dependence $\Pi_s(h)$ would not be entirely correct (see, for example, [1]). Therefore, for the analysis we used the expression for $\Pi_s(h)(= K/4sh^2(h/2l))$ in conjunction with the data obtained from the Mössbauer experiment. Indeed, the values of the thickness of water layers (h) (for the MS-based method, see [4]) and the correlation length parameter (l) from the analysis of diffusion processes (Figure 2, *b*), allowed us to estimate the value of the parameter K. The result obtained for the parameter $K(\cong 6 \cdot 10^8\,\text{din/cm}^2$ at $l = 1.19\,\text{nm})$, showing the state of surface ordering of water films, was in satisfactory agreement with experimental data obtained by other methods for water near silicate surfaces [1,2].

The probe MS method allows us to make quantitative estimates of the molecular component $\Pi_m(h)$ for disjoining pressure $\Pi(h)$. According to [5] and taking into account the specifics of our system, we use the asymptotic expression for

$$\Pi_m(h) = -(A(h))/(6\pi h^3),$$

where $A(h)$ — constant of dispersion forces in undelayed limit ($h \ll \lambda_0/2\pi$), and λ_0 is the main wavelength in the absorption spectra of contacting media). The main problem that arises when performing the estimation procedure $\Pi_m(h)$ is associated with the definition of the constant $A(h)$ (or the Hamaker constant A_{132}), which is not universal. A rather wide scattering in values (Table 1 or see, for example, the review [5]), as well as the use of more accurate formulas (in contrast to the asymptotics we use for $\Pi_m(h)$) did not improve the situation much. In order to obtain an adequate answer for the desired value $A(h)$, an approach is proposed, based on the one hand on the MS method (temperature dependence of the asymmetry

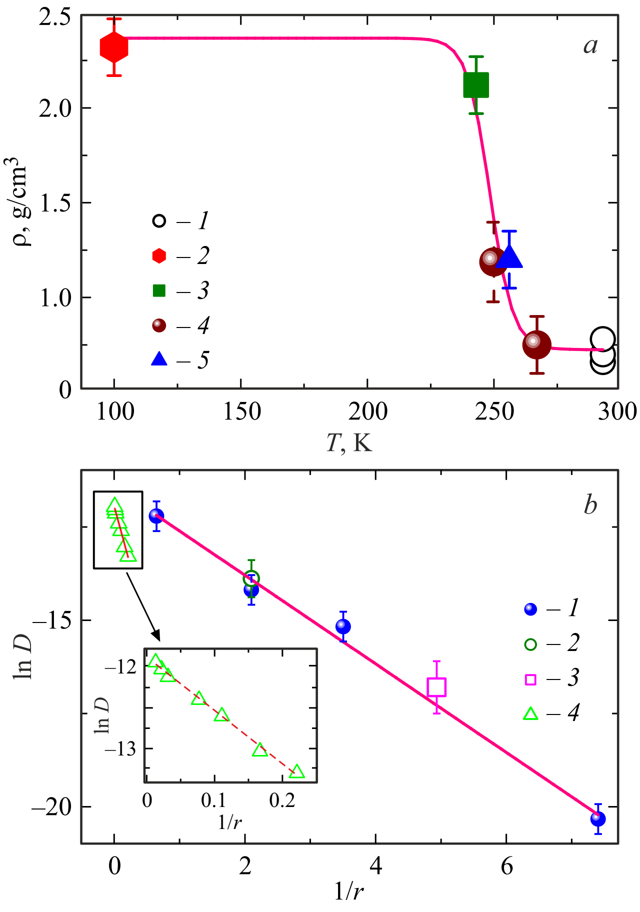

Figure 2. (*a*) Correlation of density for a quasi-liquid layer of water in montmorillonite, obtained using the MS method, with other experimental study methods in various systems: *1* — bound water in clays, *2* — modified water (according to Deryagin), *3* — polymorphic modified water (*A*-phase) in ice-containing clouds (according to Nevzorov), *4* — density values from this paper, *5* — high-density amorphous ice; (*b*) — Linearization of the dependences of the diffusion coefficient D on the radius of montmorillonite pores when using various Mössbauer probes: *1* — $Fe(ClO_4)_2$; *2* — $Fe(ClO_4)_2$ + organic; *3* — $FeCl_3 \cdot nH_2O$. Insert — points 4 are presented in accordance with data on the diffusion of salt $CoCl_2$ in porous glass membranes [10].

Table 1. Comparison of probe MS experimental data with Hamaker constant (A_{132}) and surface energy (γ) taken from literature sources

№	Object	A_{132}, (10^{-20} J)	γ, (mJ/m^2)	Lit. source
1	Ice–water–silicon	−0.17	–	[5]
2	Ice–water–quartz	0.003	–	[5]
3	Ice–water–gold	0.16	–	[5]
4	Silicon–water–silicon	12	–	[5]
5	Quartz–water–quartz	0.85	–	[5]
6	Ice	–	75	[2]
7	Water	3.7	–	[2]
8	Ice–water–montmorillonite	1.4	–	Present. article
9	Quasi-liquid layer of water on surface ice in montmorillonite	–	6.5	Present article

parameter ($A(T) = S_{3/2}/S_{1/2}$) of absorption line for the Fe^{3+} probe), and on the other hand — taking into account the features of the physical processes of surface ice melting (see, below p. 2). As a result, the obtained constant $A(h)$ did not contradict the literature data (Table 1 and additional footnotes in [5]), and this, in turn, made it possible to estimate the component $\Pi_m(h)$ ($\cong 16.7 \cdot 10^5$ Pa). To check the result, let's estimate the surface energy of the liquid layer of water in our system. To solve the set problem, we will use the method [2], tested on a large amount of factual material. In particular, using the formula for γ ($= A_{123}/(12\pi D_0^2)$, where γ — surface energy, and D_0 — constant) made it possible to obtain an estimate of the surface energy for films, the value of which differs from bulk water (Table 1). On the other hand, from an energy point of view, the difference in γ does not contradict the presence in our system of a whole cascade of phase temperatures. However, there is an alternative explanation, but only in the form of a hypothesis. Thus, in [6] it is theoretically shown that in the Casimir approximation ($h \gg \lambda_0/2\pi$) the oscillating function for the chemical potential $\mu(l)$ can lead to the formation of film that is stable only in a certain range of its thickness. Such a non-monotonic dependence $\mu(l)$ may be precisely responsible for the appearance of a sequence of discrete phase transitions in the film. Therefore, we can state that the hypothesis from [6] found its reliable confirmation in the Mössbaer experiment.

2. Diagnostics of 2D-dimensional ice layers on montmorillonite substrate

From a wide range of experimentally obtained data, the difference in physical properties between 2D and 3D measurements is most effectively manifested in the study of ice melting processes. Indeed, if in the case of „bulk“ (or 3D) ice the melting always occurs through PT of first kind, then in „surface“ (or 2D) ice — the process can consist of many variants of melting scenarios. The first and most well-known scenario for 2D systems melting is a two-step process consisting of two continuous Berezinsky, Kosterlitz and Thouless transitions (or BKT transitions) with an intermediate anisotropic liquid — hexatic phase (HP) [7]. The implementation of such a melting scheme can be illustrated by the temperature dependence of the Lamb–Mössbauer factor ($f' \approx S(T)$) for the probe Fe^{3+}, previously divided according to the assumed scenario into the corresponding regions (Figure 3, *a*). On the other hand, there is a second scenario (based on the results of computer modeling [8]), according to which melting can occur through two transitions with an intermediate one, but unlike the first scenario, the crystal goes into the HP through continuous BKT-transition, and the hexatic turns into an

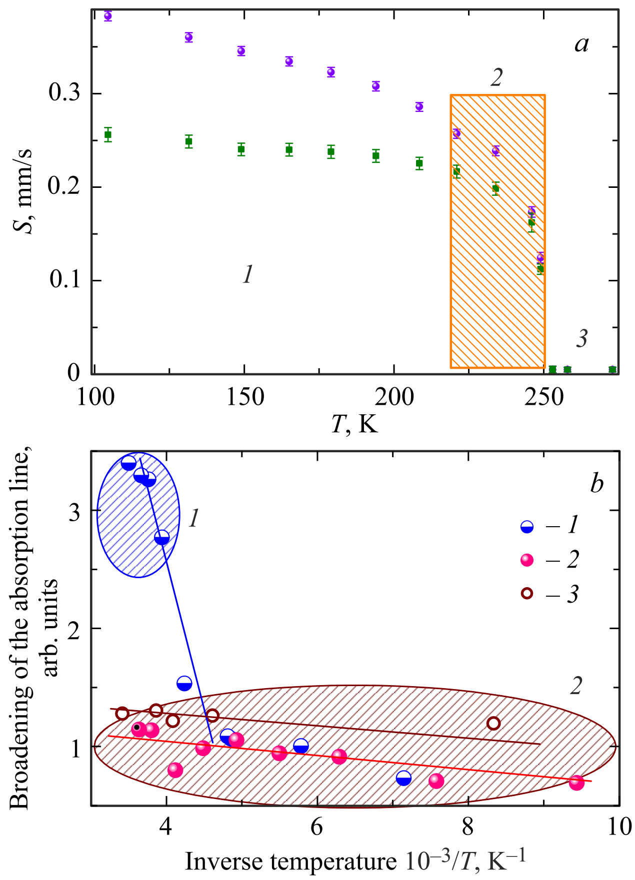

Figure 3. (*a*) 2D ice melting scenario based on the temperature behavior of the Mössbauer effect probability ($f' \propto S$): *1* — quasicrystalline phase; *2* — hexatic phase; *3* — isotropic phase. (*b*) Scheme of possible noise regions in the system „frozen solution-montmorillonite“ and based on the temperature behavior of the parameter $\Delta\Gamma(T)$ of spectrum for Mössbauer probes under various conditions (*1* — $Fe(ClO_4)_2$ in the presence of bound water in the mineral; *2* — $FeCl_3$ without water; *3* — $Fe(ClO_4)_2$ in a mineral without bound water: *1* — „pink“ noise region; *2* — region of „white“ noise.

Table 2. Values of the universal parameter (δ) for various scenarios of transition to chaos

№	δ	Type of scenario	Method of obtaining
1	4.6692016...	Period doubling	Mathematical experiment (One-dimensional display)
2	4.19244418	Period doubling	Mathematical experiment (two-dimensional display)
3	2.83361...	Quasiperiodic	Mathematical experiment (mapping circle onto itself)
4	2.8	Quasiperiodic	Physical experiment (Rayleigh-Benard system)
5	2.833(3)	Quasiperiodic	Physical experiment (MS method)

isotropic liquid through PT of first kind. Based on modern data on ice forms in combination with the methodological capabilities of MS, we established that in 2D ice, depending on the water layer thickness, both ice melting scenarios can be realized. In this case, the HP is a hexatic glass, and the quasicrystalline phase is a mixture of crystalline „bulk" (I_c, I_h) and metastable (amorphous) forms of low-density ice.

3. Diagnostics of the main types of noise using MS method

All experimental material was previously divided into two groups. The first group is due to the fact that when describing equilibrium fluctuations in the studied media, a model was used that assumed the action of random forces on the particles of the medium, having a „white" noise (WN) spectrum in the low-frequency part. The second group is characterized by another type of fluctuations, which was described by flicker noise (FN) (or $1/f$-noise), usually observed in locally nonequilibrium media and characterized by very strong time correlations.

The use of the MS method made it possible to reliably establish two noise regions realized in the „frozen solution-montmorillonite system" (Figure 3, *b*). To monitor the presence of flicker noise ($1/f$-noise) in the system the Hooge parameter [9] was used. The analysis was carried out on two series of experimental data, in which the first group was the result of the „pure" use of the MS method for our system. For the second group, a classic experiment was used, typical when the flicker-noise spectroscopy method is used, but only with monitoring of the necessary experimental parameters using the MS method. The resulting range of values for the Hooge parameter ($\alpha = (1.07-1.64) \cdot 10^{-3}$) allows us to confidently state the $1/f$-noise presence in our system.

Solving the problem of determining a specific type of chaos development scenario requires conducting numerical studies or mathematically science-intensive experiments. Therefore, quite extensive literature data were summarized in advance and, for convenience, presented in Table 2 (lines № 1–4). Therefore, in order to carry out the most effective solution to the problem posed, and to obtain at the same time „quick" answer from it, a special method was developed, tested with data from the Mössbauer experiment. As a result, a quasiperiodic scenario of transition to chaos was established, which is confirmed by the obtained value of the universal parameter (δ) (see line № 5).

In conclusion, note that the probe MS method presented in this paper removes some controversial points in surface physics and makes it possible to supplement other branches of physics with relevant information.

Conflict of interest

The authors declare that they have no conflict of interest.

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