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ANOMALOUS DENSITY FLUCTUATIONS
ACCOMPANYING SURFACE ROUGHENING
IN NONEQUILIBRIUM GAS — ADSORBATE SYSTEM

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Anomalous Density Fluctuations Accompanying Surface
Roughening in Nonequilibrium Gas - Adsorbate System //

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The particles density fluctuations which are anomalously great as compared with equilibrium ones by a factor of more than 10^2 , were observed in a far-from-equilibrium rarefied Xe gas interacting with its multilayer adsorbate. The density-density autocorrelation function was found to exhibit a maximum at the frequency $\omega \approx 3.3 \cdot 10^{-2} \text{ sec}^{-1}$. The phenomenon discovered could be explained as a result of the nonequilibrium phase transition in the adsorbate controlled by the flux of gas molecules. Microscopic mechanism of fluctuations is suggested.

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During recent years the problem of rough surface growth subjected to far-from-equilibrium conditions has attracted great interest [1 - 7]. The interface growth characterized by interface height fluctuations $\langle (h - \langle h \rangle)^2 \rangle^{1/2}$ averaged over the surface has been of particular interest of the researchers. For example, this value has been measured in electrochemical deposition [7]. But the dynamics of spatial nonuniformities rise and relaxation on rough surface has not been studied yet. It should be noted these spatial nonuniformities are examined conventionally as interface height fluctuations, but hereafter they are considered as fluctuations of particles density.

We present here the preliminary results of investigations of a dynamics of particles density fluctuations on surface in new experimental positions. Our aim was to investigate fluctuations in a closed far-from-equilibrium stationary system "gas - multilayer adsorbate." As the number of particles in such system is constant, it could be supposed that fluctuations of particles number in the adsorbate result in the rise of pressure fluctuations in gas phase. We discovered such fluctuations for xenon coverages larger than the critical value $\theta_{cr} \approx 1$. The fluctuations were observed under the condition of gas nonequilibrium when the molecular flux towards the surface covered by adsorbed xenon exceeded the equilibrium value for surface temperature. Earlier the alterations in isotherms of multilayer xenon and argon adsorption caused by the roughening transition were observed in Refs. [8, 9]. Unlike these works we present the results of the dynamics of surface fluctuations investigations for multilayer Xe adsorbate. They were performed for a large scale of values of particles fluxes towards the surface and particles density of adsorbate. The theoretical analysis of the phenomenon fulfilled within the framework of the density functional technique [10] resulted in the possibility to explain qualitatively the essential peculiarities of the experimental data.

The system examined is the highly rarefied gas in a

gap between cold (temperature T_1) and hot (T_2) plates and adsorbate on the surface of cold plate. The deviation of the value of the gas flux towards the cold surface from its equilibrium one (the degree of non-equilibrium of the system) is determined by the temperature difference $\Delta T = T_2 - T_1$. To create such conditions special device was used. It was mounted in a stainless-steel chamber with the volume of 300 cm^3 . The device construction was described in details in Ref. [11]. It is a flat temperature sensitive element (hot plate) placed in a gap between two massive stainless-steel plates (cold plates) covered by Au film. The thermal element is a thermistor formed by Au film deposited in vacuum on the both sides of mica plate ($40 \times 50 \times 5 \cdot 10^{-3} \text{ mm}^3$). The distance between the thermal element and each of the plates equals 0.12 cm. The temperature of the element was varied within the range 78 - 300 K and controlled by means of thermistor resistance measurements. Stainless-steel plates were in good heat contact with liquid N_2 thermostat and their minimum temperature was 78 K. This temperature could be regulated with the help of a tungsten heater and was measured with a platinum thermistor. Analogous device was used for the system pressure measurements. Pressure was also measured with standard thermocouple and ion gauges. These gauges allowed to register pressure fluctuations within the range of ($10^{-4} - 10^{-8}$) Torr at the mean pressures in the range ($10^{-2} - 10^{-6}$) Torr. Their response times were within the range from 0.1 up to 10 sec. Spurious noise didn't exceed several percents of fluctuations value in gaseous phase. Gas composition control was carried out using a mass-spectrometer. This device was also used to control the composition of the adsorption layer by the thermodesorption method. The system was pumped at a temperature of 300°C for 48 hours. After that the pressure measured value (ion gauge) was found to be less than 10^{-8} Torr.

For several values of Xe coverage θ of the cold surface within the range from 10^{-1} to 10^4 monolayers we got the time dependence $p(t)$ of gas phase pressure. Fig.1 shows the pressure fluctuations dependencies $\Delta p(t) = p(t) - \langle p \rangle$ ($\langle p \rangle$ is the

mean pressure averaged over the experiment time) measured with the ion gauge under the conditions $\theta \sim 10^4$ monolayers, $T_1 = 78$ K and T_2 equal: (a) 280 K, (b) 140 K, (c) 78 K. Under such conditions mean system pressure was $2.5 \cdot 10^{-3}$ Torr and xenon adsorbate on the cold surface was in solid state. Analogous dependencies (but smoothed over response time about 10 sec for thermal element) were obtained with a special highly sensitive film thermistor [11] described above. Fig.1 demonstrates the decrease of hot surface temperature T_2 from 280 K down to 140 K results in significant decrease of fluctuations amplitude (by a factor of 10). Fig.1(c) is for equilibrium gas - adsorbate system. The visible fluctuations are apparently due to spurious noise. It should be noted that in this case numerical estimations of equilibrium fluctuations give the value of about 10^{-10} Torr. It was found that for temperatures $T_1 = 78$ K and $T_2 = 280$ K the value of pressure fluctuations is anomalously great when xenon coverage exceeds the critical value $\theta_{or} \approx 1$. At θ greater than θ_{or} the alterations of coverage don't result in changes of the mean value $\langle |\delta p(t)| \rangle$ of pressure fluctuations. The value $\langle |\delta p(t)| \rangle$ decreases by a factor of 10^2 for $\theta < \theta_{or}$. In this case the dependence $\delta p(t)$ is similar to the dependence presented in Fig.1(c) for any values of T_2 .

Autocorrelation function $S(t)$ of pressure fluctuations was calculated in accordance with the formula:

$$S(n\tau) = [1/(N+1)] \sum_{k=0}^{N-n} \delta p(k\tau) \delta p((k+n)\tau). \quad (1)$$

The value of τ (about 1 sec) was less than the characteristic time of visible fastest pressure fluctuations. The experiment duration $T = N\tau$ (about $7 \cdot 10^3$ sec) exceeded the characteristic time of the slowest fluctuations observed and its further increase has not resulted in changes of the dependence $S(t)$. The Fourier transform $S(\omega)$ of correlator $S(t)$ calculated for data obtained under the conditions $\theta \sim 10^4$, $T_1 = 78$ K, $T_2 = 280$ K, $\langle p \rangle = 2.5 \cdot 10^{-3}$ Torr is presented in Fig.2. A local maximum centered at the frequency $\omega_0 \approx 3.3 \cdot 10^{-2} \text{ sec}^{-1}$ on

the background of monotone decreasing of $S(\omega)$ is clearly seen. Possible mechanism and qualitative description of observed phenomenon is considered below.

The experimentally observed particles density fluctuations in gaseous Xe could be explained assuming that a nonequilibrium phase transition into inhomogeneous state takes place in the adsorbed Xe upper monolayer. That transition is controlled by the flux of molecules towards the surface determined by the temperature difference of hot and cold plates. As the system is closed it could be supposed that the fluctuations in the gas phase are due to the particles density fluctuations in the adsorbate. Note that by virtue of the fact that the vacancy formation energy in solid Xe ($E_a \approx 0.03$ eV [12]) is a small one the subsurface layers of Xe (when $\theta \gg 1$) are essentially rich in vacancies ($n_v/n \approx 10^{-2}$). As a consequence of the notably fast escape of vacancies from the first monolayer ($\omega\tau \approx 10^{-7}$, where ω is the characteristic fluctuations frequency in gaseous phase and τ the characteristic vacancies escape time, $\tau \approx 10^{-5}$ sec for $T=80$ K [12]) the vacancies distribution in Xe film for $\theta \gg 1$ is determined by fast vacancies diffusion and gaseous flux towards the film. As a result for fairly large θ the mean particles concentration in the upper monolayer is independent of θ . For $\theta \gg 1$ the investigated system can be considered as a system with quite a "friable" near-surface layers and the slow fluctuations considered can be treated as those occurring within the upper monolayer and in the gas interacting with it.

Now let us find the particle-density fluctuations in the adsorbate. For this purpose we use the relaxation equation for an arbitrary density system:

$$\frac{dn}{dt} = \int \varepsilon(\vec{r}-\vec{r}', t-t') \frac{\delta F}{\delta n} d\vec{r}' dt' + \gamma j, \quad (2)$$

where n is the particles number density in the upper monolayer, ε - the kinetic coefficient, γ - the sticking coefficient of particles to the surface in nonequilibrium system and F is the free energy of the dense system [10]. The value of j is defined

for a strong rarefied gas by an expression given in Ref. [13] as:

$$j = J - J_{eq} = KN, \quad K = (2T_1/\pi m)^{1/2} [T_2^{1/2} (T_1^{1/2} + T_2^{1/2})^{-1} - 1/2] \quad (3)$$
 where J and J_{eq} are the molecular fluxes towards the cold surface for the nonequilibrium and equilibrium systems respectively, N - the particles number density in the gas phase.

It should be noted that in equilibrium ($j=0$) the equation (2) describes both the process of particle escape from the surface and arrival due to the presence of an equilibrium vapor over the surface and of an equilibrium distribution of vacancies in the multilayer adsorbate. The unknown kinetic coefficient ε in Eq. (2) can be calculated by comparing in equilibrium ($j=0$) the Eq.(2) with the equation for n in the gas approximation:

$$\frac{dn}{dt} = D\Delta n - \alpha(n - n_{eq}), \quad (4)$$

where D is the diffusion coefficient of adatoms, α is the frequency of particles escape into the gas and the second layer of adsorbate, n_{eq} is the equilibrium upper monolayer density. Taking into account the connection between the free energy F and the response function $\beta(\vec{r}, \vec{r}')$ [10]:

$$\beta^{-1}(\vec{r}, \vec{r}') = - \frac{\delta^2 F}{\delta n(\vec{r}) \delta n(\vec{r}')}, \quad (5)$$

and proceeding to Fourier transform one can write:

$$\varepsilon(\vec{k}, \omega) = \beta_{eq}(\vec{k}, \omega) (Dk^2 + \alpha), \quad (6)$$

where \vec{k} is a wave vector, β_{eq} is the response function for $n=n_{eq}$.

To find the spectrum of particles density fluctuations in the adsorbate it is necessary to find the stationary solution

($n = n_0$) of Eq.(2). It could be obtained from the equation

$$\int \frac{\delta}{\delta n} (\epsilon F + \gamma j n) d\vec{r}' dt' = 0. \quad (7)$$

When Eq.(3) is substituted into Eq.(7) we obtain the nonequilibrium phase diagram for adsorbate in the variables n , T_1 , T_2 and the gas parameters.

Eq.(2) permits to connect the spectrum of the particles density fluctuations in the upper monolayer (δn) with the flux fluctuations (δj) and hence according to (3) with the spectrum of the particles density fluctuations in the gaseous phase (δN). In fact, assuming $n=n_0+\delta n$, $j=j_0+\delta j$, $N=N_0+\delta N$ we obtain:

$$\langle \delta N \delta N \rangle_{\omega} = (\epsilon^2 \beta_0^{-2} + \omega^2) \langle \delta n \delta n \rangle_{\omega} / k^2 \gamma^2, \quad (8)$$

where β_0 is the response function for $n=n_0$. The spectrum of particles density fluctuations in the adsorbate can be calculated starting from the relaxation equation (2) with the help of introducing a noise term into its right hand side [14]. Averaging over the surface S covered by adsorbate by means of the procedure described in Ref. [14] we obtain the following expression:

$$\langle \delta n \delta n \rangle_{\omega} = (\pi/2\pi\omega)^{1/2} \int \frac{2\omega(k)}{\omega^2 + \omega^2(k)} \exp(-\omega(k)/2\omega) dk (n_0/S) \quad (9)$$

where $\omega(k)$ is the relaxation frequency of density fluctuations $\delta n(k)$:

$$\delta n(k) \sim \delta n_0 \exp(-\omega(k)t), \quad \omega(k) = \tilde{D}(k)k^2 + \tilde{\alpha}(k). \quad (10)$$

Here $\tilde{D}(k)$ and $\tilde{\alpha}(k)$ have a meaning of the effective diffusion coefficient and of the effective frequency of particles escape, respectively, for interacting adatoms. The value $\omega^{-1}(k)$ is the characteristic time for the particle to stay in a particular surface region with the dimension of $r \sim 2\pi/k$. Its dependence versus k results from the influence of particles interaction on the potential wells depth for diffusion in upper monolayer and for escape from it and since on the probability of particles escape from potential well. The

exponential dependence of the desorption probability upon the depth of the potential well causes the increase of fluctuations value as compared with equilibrium one for the space-inhomogeneous state of adsorbate. Eqs. (8) and (9) give a possibility to analyze the features of the fluctuations observed in our system.

To get estimates one should calculate the effective diffusion coefficient in the random phase approximation [15]. So we have

$$\tilde{D}(k) = D(1 + n_0 V(k) / 2T_1 u), \quad (11)$$

where $V(k)$ is the Fourier transform of the pair interaction potential $V(r)$, u the interplanar distance between adsorbate monolayers. The pair interaction of noble gas atoms is usually described by a Leonard-Jones type potential [12]. For the sake of simplicity we use a type of square well approximation of the interaction potential:

$$V(r) = \begin{cases} \Lambda, & r < a; \\ E, & a \leq r \leq b; \\ 0, & r > b. \end{cases} \quad (12)$$

Here $E \approx -100$ K, $a \approx 5$ Å, $b \approx 9$ Å.

The value (Λ) was obtained using the condition of macroscopic system stability that is $V(k=0) \geq 0$ and it formed the value $\Lambda \approx 900$ K.

The dependence of $\tilde{\alpha}(k)$ must take into account the increase of characteristic particle residence time for large spatial scales ($k \rightarrow 0$) due to the emergence of an attractive mean field in a dense adsorbate. For simplicity it was chosen in the form:

$$\tilde{\alpha}(k) = \alpha_0 k^2 (1 + \alpha_1 k^2)^{-1} \quad (13)$$

where α_0 and α_1 are the constant values.

The Fourier transform $V(k)$ of the potential (12) exhibits at $k \neq 0$ the first minimum at $k_{or} \approx 1.1$ Å⁻¹. As it follows from Eq. (11) for temperature $T_1 = 78$ K the diffusion coefficient is vanished (critical slowing-down) at $k = k_{or}$ if particles concentration in the upper layer $n_{or} \approx 2 \cdot 10^{14}$ cm⁻², which corresponds to about one monolayer. So the relaxation frequency

(10) of fluctuations $\delta n(k_{or})$ in the surface region with the characteristic size $r \approx 2\pi/k_{or}$ is determined at $n = n_{or}$ only by the escape frequency $\tilde{\alpha}(k_{or})$ of particles from the upper monolayer. The fluctuation spectrum $\langle \delta n \delta n \rangle_{\omega}$ calculated with the help of Eq. (9) is presented in Fig. 2 (solid curve corresponds to $\alpha_0 = 6 \text{ \AA}^2/\text{sec}$ and $\alpha_1 = 100 \text{ \AA}^2$). The maximum in fluctuation spectrum $\langle \delta n \delta n \rangle_{\omega}$ and consequently in the fluctuation spectrum of particles number density in the gas phase $\langle \delta N \delta N \rangle_{\omega}$ is due to the critical slowing-down of the diffusion mode for $k = k_{or}$ which corresponds to the possible formation of clusters with the mean size $r_{or} = 2\pi/k_{or}$ and their slow decay during the adatoms residence time at the surface $\tau \approx \tilde{\alpha}^{-1}(k_{or})$. As it was noted above the steady concentration (n_{or}) of particles in the upper monolayer is independent on θ . Consequently the critical slowing-down of relaxation of density fluctuations $\delta n(k_{or})$, when $\tilde{D}(k_{or}) = 0$, must take place for any quite large coverages θ and the characteristic relaxation frequency wouldn't be on θ dependence. It was observed in experiment.

The characteristic frequency for the maximum in the spectral density of Xe pressure fluctuations to appear can be estimated based on the ω versus k dependence: $\omega \approx Dk^2 - \alpha$. The diffusion coefficient value for Xe in the solid phase at the temperature $T \approx 78 \text{ K}$ is $D \approx 10^{-18} \text{ cm}^2/\text{sec}$ and $k_{or} \approx 1 \text{ \AA}^{-1}$ which results in the value of the frequency $\omega \approx 10^{-2} \text{ sec}^{-1}$. This frequency value coincides with the reverse life-time of Xe atom on the surface.

Thus the dependences (8) and (9) give a qualitative description for low frequencies of the fluctuations spectral density in the gas phase as measured in the experiments.

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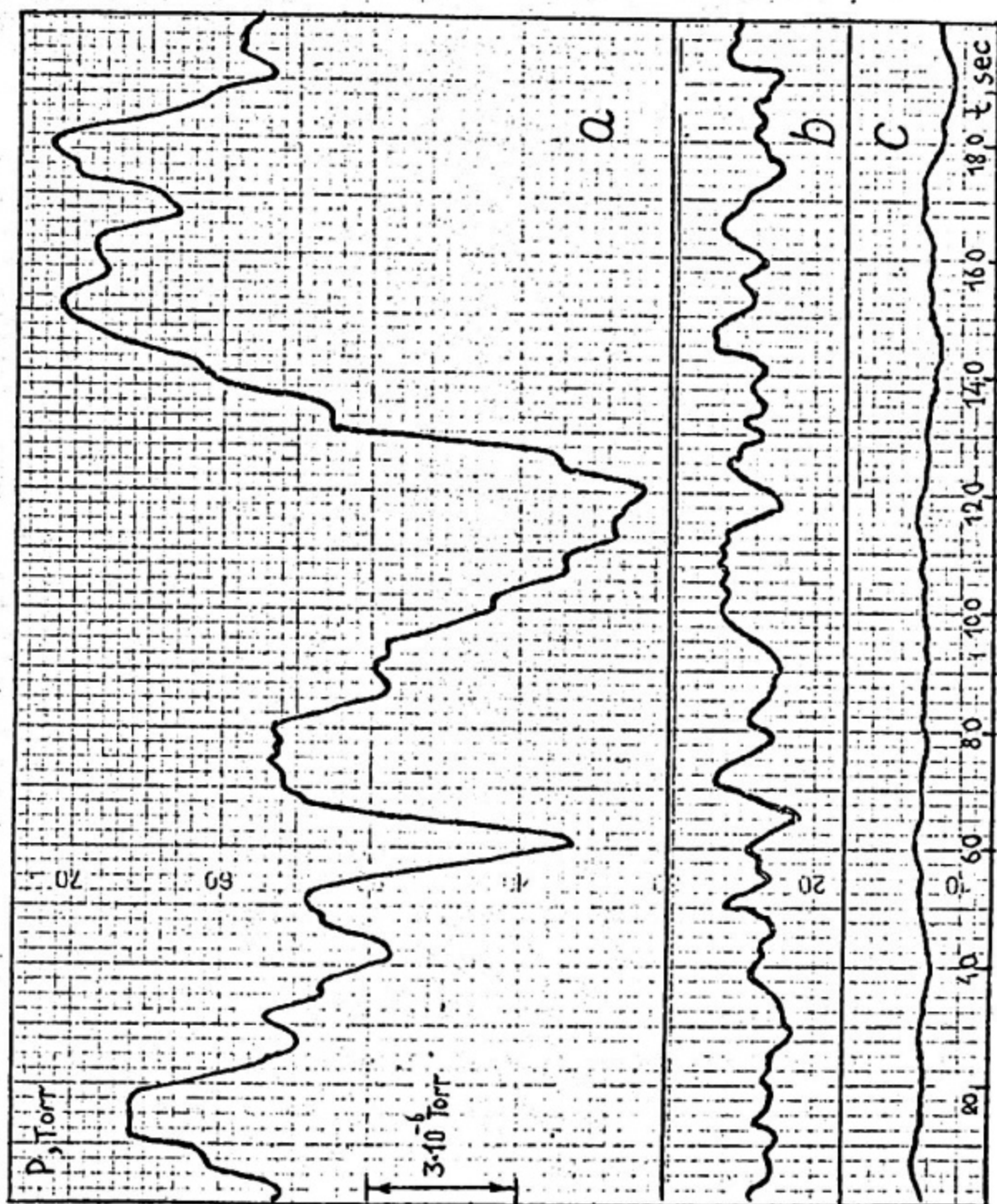


Fig.1. Pressure fluctuations dependence vs time. Cold surface coverage: $\theta=10^4$ monolayers; temperature of cold surface $T_1=78$ K; mean pressure: $\bar{p}=2.5 \cdot 10^{-3}$ Torr; temperature of hot surface T_2 : (a) 280 K, (b) 140 K, (c) 78 K

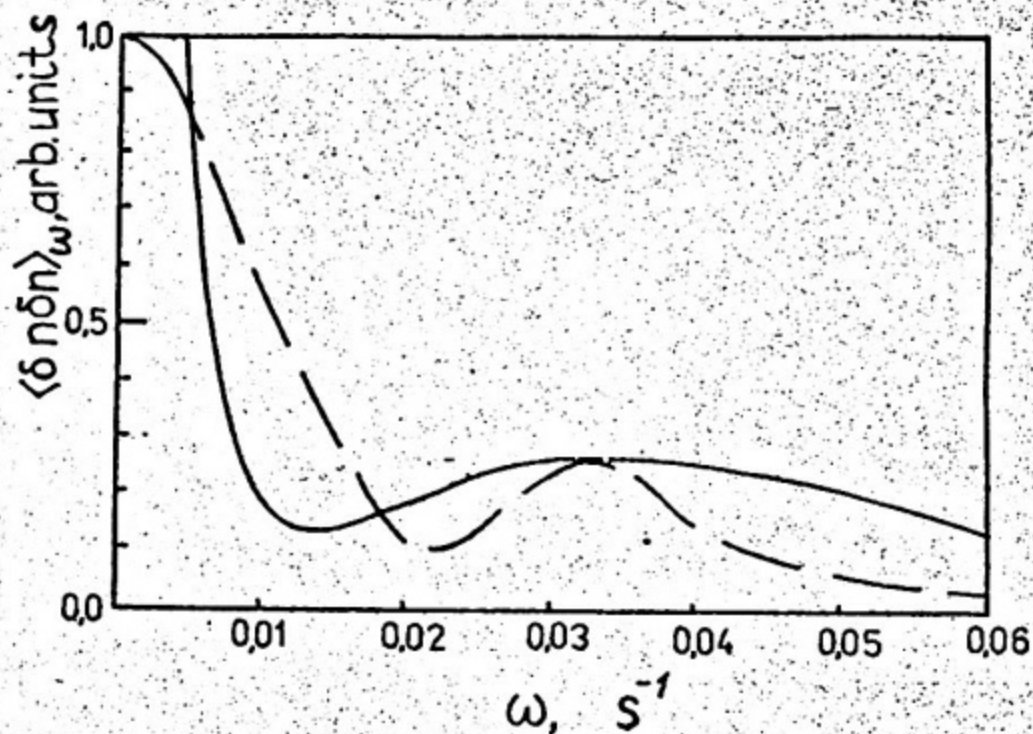


Fig.2. The dimensionless fluctuations spectrum calculated in accordance with Eq.9 (solid curve) and the experimental normalized spectrum $S(\omega)$ of gaseous Xe particles density fluctuations (dashed curve) vs frequency ω . Cold surface coverage: $\theta \approx 10^4$; temperatures of cold and hot surfaces: $T_1 = 78$ K and $T_2 = 280$ K, respectively; mean pressure: $\bar{p} = 2.5 \cdot 10^{-3}$ Torr

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АНОМАЛЬНЫЕ ФЛУКТУАЦИИ ПЛОТНОСТИ В НЕРАВНОВЕСНОЙ СИСТЕМЕ
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