

Anomalous density fluctuations in a nonequilibrium gas-adsorbate system

V. D. Borman, D. G. Starodub, D. I. Talyzin, V. N. Tronin, and V. I. Troyan
Moscow Engineering-Physics Institute, 115409 Moscow, Russia

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The results of an experimental study of the dynamics of the fluctuations in the number of particles in a nonequilibrium gas-adsorbate system are presented. The adsorbate was a multilayer xenon adsorbate. Fluctuations in the Xe pressure, which are anomalously large in comparison with equilibrium values, were observed. The spectrum of these fluctuations is of the nature of a $1/f$ noise, but it has a peak at the frequency $\omega = 3.3 \times 10^{-2} \text{ s}^{-1}$. The reason for the observed anomalies may lie in the dynamics of the formation of the rough adsorbate surface.

The growth of rough surfaces under nonequilibrium conditions is attracting considerable interest.¹⁻⁷ The usual approach is to study the time evolution of the average width of the interface, $\langle (h - \langle h \rangle)^2 \rangle^{1/2}$, where h is a function of the spatial coordinates X . Theoretically, the growth of a rough surface has been studied only on the basis of macroscopic phenomenological models of the KPZ type.^{1,4} There has been no previous experimental study of the dynamics of fluctuations at an interface during the growth of a rough surface, despite the obvious importance of this topic for reaching an understanding of some points which remain unclear: the microscopic mechanisms for the development of rough surfaces and the particular way in which this development proceeds. Spatial irregularities at a surface are usually discussed as fluctuations in the height of the interface. Below we treat them instead as fluctuations in the number density of particles on a surface.

In this letter we are reporting preliminary results on the dynamics of fluctuations in the number density of particles on a surface in a closed, nonequilibrium, steady-state system consisting of gaseous xenon and a xenon adsorbate. Since the total number of particles in such a system remains constant, we might expect that fluctuations in the number of particles in the adsorbate would lead to pressure fluctuations in the gas phase. Indeed, we observed pressure fluctuations, anomalously large in comparison with equilibrium fluctuations, at degrees of surface coverage by the xenon greater than a critical value $\Theta_c \approx 1$, when the flux of Xe molecules to the cold surface satisfies $j > j_p$, where j_p is the equilibrium flux. Some structural features were observed on Xe and Ar adsorption isotherms at $T \approx 60 \text{ K}$ in Refs. 8 and 9 and attributed to a roughening transition (a transition from a power-law isotherm to a monotonic one). In contrast with those previous studies, we are reporting here results on the dynamics of fluctuations of the surface of the Xe adsorbate under nonequilibrium conditions over the broad ranges $\Theta = 10^{-1} - 10^4$ and $j = (1 - 1.30)j_p$. The fluctuation spectral density reconstructed from the results is of the nature of a $1/f$ noise, but it has a peak at a frequency $\omega \approx 3.3 \times 10^{-2} \text{ s}^{-1}$.

The system studied here consists of a Knudsen gas of Xe in a gap between a cold plate (at a temperature $T_1=78$ K) and a hot one ($T_2=78-280$ K), with the xenon adsorbate on the cold surface. The extent to which the system deviates from equilibrium is determined by the deviation of the flux of molecules incident on the cold surface from its equilibrium value:

$$(j-j_p)/j_p = (\sqrt{T_2} - \sqrt{T_1}) / (\sqrt{T_1} + \sqrt{T_2}). \quad (1)$$

In an experiment with the temperatures $T_1=78$ K and $T_2=280$ K, this value reached ≈ 0.3 . To arrange these conditions we used a sensitive heat-flux sensor with plane geometry.¹⁰ Its key element is a heated mica plate with dimensions of $5.0 \times 6.0 \times 0.01$ cm, on which a layer of gold has been deposited (the gold serves as the temperature-sensitive element). This plate is in a gap between two stainless-steel plates (these are cold plates), which are also coated with a layer of Au. The distance between each of the cold plates and the mica plate is 0.12 cm. The sensor is in a stainless-steel chamber with a volume of 300 cm³. The temperature of the thermal element (T_2) was varied over the range 78–280 K. The cold plates were cooled with liquid nitrogen; their temperature (T_1) was 78 K.

The pressure was measured with a similar gauge and also by a thermocouple gauge and an ionization gauge. These instruments were capable of detecting pressure fluctuations in the range $\delta p \approx 10^{-4}-10^{-8}$ torr at an average pressure $\langle p \rangle = 10^{-2}-10^{-5}$ torr. The pressure gauges which were used had response times ranging from 0.1 to 10 s. The noise of the measurement circuit did not exceed a few percent of the amplitude of the signal being detected (which corresponded to fluctuations in the pressure in the gas phase). The residual pressure in the system was no greater than 10^{-8} torr. The rate of inleakage and outgasing did not exceed 10^{-6} torr/h.

Figure 1 shows a fragment of an experimental time evolution of the pressure, $\delta p(t) = p(t) - \langle p \rangle$, for $\Theta \approx 10^4$ and various temperatures. The average pressure was $\langle p \rangle = 2.5 \times 10^{-3}$ torr. The xenon adsorbate was in a solid state. We see in Fig. 1 that a lowering of the temperature of the hot surface, T_2 , from 280 to 140 K reduces the amplitude of the fluctuations by an order of magnitude. The very slight fluctuations in Fig. 1c correspond to the equilibrium ($T_1=T_2$) gas-adsorbate system and are a consequence of noise of the measurement apparatus. Estimates of the magnitude of the equilibrium fluctuations yield $|\delta p| \approx 10^{-10}$ torr. It was established that with $T_1=78$ K and $T_2=280$ K the pressure fluctuations are anomalously large, with a degree of coverage $\Theta > \Theta_c \approx 1$. At $\Theta > \Theta_c$, the average size of the pressure fluctuations, $\langle |\delta p(t)| \rangle$, is independent of Θ and falls off by two orders of magnitude at $\Theta < \Theta_c$. In this case the $\delta p(t)$ dependence is like that shown in Fig. 1c, regardless of the value of T_2 over the range 78–280 K.

The autocorrelation function $S(t) = \langle \delta p(0) \delta p(t) \rangle$ of the pressure fluctuations for $t = n\tau$ (where n is an integer) was calculated from the formula

$$S(n\tau) = \frac{1}{N+1} \sum_{k=0}^{N-n} \delta p(k\tau) \delta p[(k+n)\tau]. \quad (2)$$

The value of τ (≈ 1 s) was shorter than the time scale of the fastest pressure fluctuations. The duration of an experiment, $T = N\tau$ ($\sim 7 \times 10^3$ s), was greater than the time

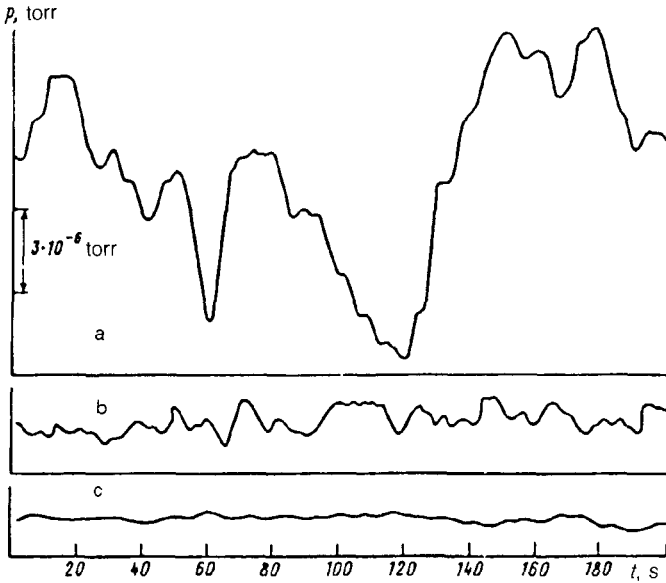


FIG. 1. Time evolution of the fluctuations in the pressure p . a— $T_1=78$ K, $T_2=280$ K; b—78, 140; c— $T_1=T_2=78$ K.

scale of the observed slow fluctuations. A further increase in the duration of an experiment did not result in changes in the time evolution $S(t)$. Figure 2 shows the Fourier transform $S(\omega)$ (the spectral density of the fluctuations) of the correlation function of $S(t)$. We see in this figure that a $1/f$ -noise behavior of the spectral density is observed in the frequency region $\omega \approx 5 \times 10^{-3} - 2 \times 10^{-2} \text{ s}^{-1}$. At $\omega_c \approx 3.3 \times 10^{-2} \text{ s}^{-1}$ we observe a peak in $S(\omega)$.

Since the system is closed ($n_g + n_a = \text{const}$), the observed fluctuations in the number density of particles in the gas phase (δn_g) can be linked with fluctuations in the number of adatoms, δn_a ($\delta n_g = -\delta n_a$). The change in free energy due to the transition of particles from the adsorbate into the gas phase is given by

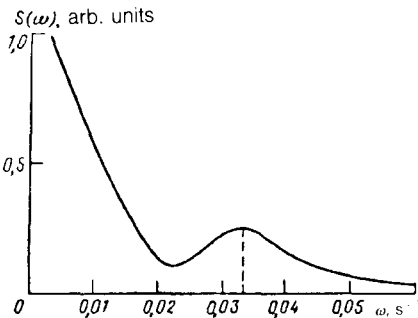


FIG. 2. Spectral density of the fluctuations, $S(\omega)$, calculated for $\Theta \approx 10^4$, $\langle p \rangle = 2.5 \times 10^{-3}$ torr, $T_1 = 78$ K, and $T_2 = 280$ K.

$$\delta F = \mu_a \delta n_a + \mu_g \delta n_g = (\mu_a - \mu_g) \delta n_a \equiv -\Delta\mu \delta n_a. \quad (3a)$$

At the same time, the escape of particles into the gas phase creates vacancies in the adsorbate; i.e., we have $\delta n_v = -\delta n_a$, where δn_v is the fluctuation in the number of vacancies. Consequently, the change in free energy in this case can be written

$$\delta F = \mu_v \delta n_v = -\mu_v \delta n_a, \quad (3b)$$

where μ_v is the chemical potential of the vacancy subsystem. As a result, we find

$$\mu_v = \Delta\mu. \quad (4)$$

Upon a deviation of the system from equilibrium ($T_1 \neq T_2$) the value of $\Delta\mu$ is

$$\Delta\mu = kT_1 \ln [j/j_p]. \quad (5)$$

According to (1), the value of $\Delta\mu$ depends on the surface temperatures T_1 and T_2 ,

$$\Delta\mu/kT_1 = \ln \frac{2\sqrt{T_2}}{\sqrt{T_1} + \sqrt{T_2}}, \quad (6)$$

and under the experimental conditions ($T_1 = 78$ K, $T_2 = 280$ K) it was not zero ($\Delta\mu/kT_1 = 0.27$). Accordingly, by virtue of (4), the chemical potential of the vacancies is nonzero, and the number of vacancies in the system is higher than the equilibrium value. This circumstance leads to a change in the number of nearest neighbors of the adatoms. Because of the interatomic interaction, it also leads to a change in the depths of the adsorption potential wells (E) and thus to some distribution D of the well depths E . Since the lifetime (τ) of the adsorbed atoms on the surface is an exponential function of E , the spectrum of fluctuations of the particles in the adsorbate is described by the lifetime distribution $P(\tau)$:

$$P(\tau) = \frac{kT}{\tau} D(E). \quad (7)$$

A calculation in the approximation of a self-consistent field of the vacancies shows that $D(E)$ is a Gaussian distribution, for which, according to Ref. 11 and distribution (7), the fluctuations in the system are of the nature of a $1/f^\alpha$ noise [$\alpha \approx 1$, $S(\omega) \sim \omega^{-\alpha}$]. A spectral density of fluctuations of this sort is observed in the experiments at low frequencies ($5 \times 10^{-3} - 2 \times 10^{-2}$ s $^{-1}$).

Another important consequence of a change in the number of vacancies might be a transition of the adsorbate into a spatially nonuniform state, with vacancy voids in the upper layer of the adsorbate. The formation of vacancy voids in a monolayer of inert gas was studied theoretically in Ref. 12. A spatially nonuniform state of an adsorbate due to a critical slowing of diffusion¹³ can be characterized by the existence of clusters of adatoms with an average size r_c [$D(r \rightarrow r_c) \rightarrow 0$]. Under such conditions, a rapid desorption of particles from dense clusters results in a reduction of the size of the latter ($r < r_c$). Consequently, the time scale of the fluctuations in the flux of desorbed particles (and thus that of the pressure fluctuations in the gas) is determined by the subsequent diffusive decay [$D(r < r_c) \neq 0$] of such clusters. Estimates show that, for the potential describing the interaction of Xe atoms, the critical cluster size is $r_c \approx 7$ Å. At a critical Xe surface coverage, $n_c \approx 4 \times 10^{14}$ cm $^{-2}$ ($\Theta \approx 1$), the character-

istic cluster decay frequency is $\omega = D(2\pi/r_c)^2 \simeq 10^{-2} \text{ s}^{-1}$. At this frequency the experiments reveal a peak in the spectral density of fluctuations of Xe (Fig. 2).

The much larger nonequilibrium fluctuations (by a factor $\sim 10^2$) compared with the equilibrium fluctuations can be attributed to an exponential dependence of the spectral density on the activation energy. The value of this energy is strongly determined by the interaction of adatoms. The broadening of the peak on the $S(\omega)$ curve can furnish information on the distribution of diffusive-decay times of the adsorbate clusters.

In conclusion we should point out that the system which we have been discussing here is a good model for studying the dynamics of the formation of rough surfaces and for clarifying the microscopic mechanism for this formation process. The reasons are the small value of the binding energy of the atoms in the molecular crystal (Xe) and the novel nature of the experimental method: measuring fluctuations in the gas phase.

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¹M. Kardar *et al.*, Phys. Rev. Lett. **56**, 889 (1986).

²G. S. Bales *et al.*, Phys. Rev. Lett. **62**, 776 (1989).

³C.-H. Lam and L. M. Sander, Phys. Rev. Lett. **69**, 3338 (1992).

⁴K. Sneppen, Phys. Rev. Lett. **69**, 3539 (1992).

⁵V. S. L'vov and I. Procaccia, Phys. Rev. Lett. **69**, 3543 (1992).

⁶A. Maritan *et al.*, Phys. Rev. Lett. **69**, 3193 (1992).

⁷L. M. Galathara *et al.*, Phys. Rev. Lett. **68**, 3741 (1992).

⁸R. Miranda *et al.*, Phys. Rev. Lett. **51**, 782 (1983).

⁹H. S. Youn and G. B. Hess, Phys. Rev. Lett. **64**, 918 (1990).

¹⁰V. D. Borman *et al.*, Prib. Tekh. Eksp., No. 5, 179 (1986).

¹¹Sh. M. Kogan, Usp. Fiz. Nauk **145**, 285 (1985) [Sov. Phys. Usp. **28**, 170 (1985)].

¹²M. S. Veshunov, Poverkhnost', No. 5, 5 (1991).

¹³Yu. N. Devyatko and V. N. Trunin, Zh. Eksp. Teor. Fiz. **98**, 1570 (1990) [Sov. Phys. JETP **71**, 880 (1990)].

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