Abnormal surface diffusion of particles under the action of an external time-periodic force

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Abstract. This paper delves into the abnormal surface diffusion of particles in an external time-periodic field. The relationship is studied of the surface diffusion enhancement as a function of the amplitude and frequency of external fields. It is shown that the diffusion coefficient can be significantly increased (by several orders of magnitude) by applying external time-periodic fields. The diffusion gain ratio strongly depends on the surface temperature and on the external field amplitude and frequency.

1. Introduction
The progress in nanophysics and the intensive studies in the field of development of microsystems with prescribed properties stimulated a keen interest in the investigation of the ordered motion of particles on the surface of a solid body [1-2]. The transfer of atoms and clusters exposed to the external force caused by magnetic and electric fields, laser radiation, external voltage, etc. requires careful studies of the diffusion processes in systems with a periodic potential.

As a rule, the surface diffusion is characterized by low values of the activation barriers and a low friction coefficient [3,4]. Previous research conducted by different authors showed that special diffusion modes, the so-called subdiffusion and hyperdiffusion [5,6] can arise in systems that are characterized by a low kinetic-energy dissipation level. The ordinary diffusion is characterized by a linear relation of the root-mean-square time deviation \( \langle x^2 \rangle \sim t \). In the case when special diffusion modes take place, this relationship is changed \( \langle x^2 \rangle \sim t^n \). At \( n < 1 \) we speak of subdiffusion, at \( 1 < n < 2 \), of superdiffusion, and at \( n > 2 \), of hyperdiffusion. At \( n = 2 \), the special case of ballistic diffusion is realized. These abnormal modes are observed in a certain time domain defined by the temperature and the system’s properties. The stationary state is established after a certain period of time and the spatial dispersion of the particles distribution is described by the standard expression \( \langle x^2 \rangle \sim t \). However, the time limitation of the transport processes may result in the particle motion occurring under conditions of a strong non-equilibrium state characterized by abnormal diffusion modes [7]. Special diffusion modes can be “preserved” through the exposure of the system to periodic fields. It has been shown earlier in [8] that abnormal diffusion enhancement is possible by a

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decrease in the ambient temperature. A possibility of enhancing the surface diffusion along a selected direction without increasing the temperature is of great practical importance, because it allows for the creation of surface structures consisting of clusters of a required shape, size and density. However, the dependence of this phenomenon on the effective force amplitude and frequency has not been studied. The purpose of this scientific paper is to study in detail these relationships using computer simulation methods.

2. Simulation details
The surface motion of particles can be described using the following Langevin equation [9]:

$$m \ddot{x}_i = - \frac{\partial}{\partial x} U(x_1, x_2) - \gamma \dot{x}_i + F_i + \xi_i(t),$$  

(1)

where $x_i$ are the Cartesian coordinates components for the particle in the plane, $t$ is the time, $m$ is the particle mass, $F_i$ are the components of the constant force to which the particle is exposed, $U(x_1, x_2)$ is the potential energy of the particle in the plane, and $\gamma$ is the friction coefficient. The dots denote differentiation with respect to time. The thermal fluctuations $\xi_i(t)$ represent uncorrelated white noises that obey the relationship

$$\langle \xi_i(t) \xi_j(t') \rangle = 2kT \delta(t - t') \delta_{ij},$$  

(2)

where $k$ is the Boltzmann constant, $T$ is the temperature.

Hereinafter, a “particle” will imply an adatom or a cluster consisting of many atoms that can move in the periodic potential. The potential energy of the particle on the crystal surface is defined by the surface symmetry and its atomic composition. In the simplest case of a monoatomic material and a simple rectangular surface lattice, the potential energy can be written as follows [9]:

$$U = - \frac{U_0}{2} \left[ \cos\left(\frac{2\pi}{a} x_1\right) + \cos\left(\frac{2\pi}{b} x_2\right) \right],$$  

(3)

where $a$ and $b$ are the lattice constants along the $x_1$ and $x_2$ axes, and $U_0$ is the activation barrier value.

It has been shown earlier in [10] that in this case the variables $x$ and $y$ are weakly related and the particle motion kinetics is defined by the component of the force acting along this direction. To simplify the computations we can refer to the case of one-dimensional particle motion in a periodic field $U(x)$.

In order to demonstrate the main physical results we studied the case of one-dimensional diffusion. Studying this case allows us to draw general conclusions that represent the main physical findings of this paper.

A moving particle is subjected to the action of the force $F^{Lat}$ produced by a lattice:

$$F^{Lat} = - \frac{\partial U}{\partial x} = F_{cr} \sin\left(\frac{2\pi}{a} x\right),$$  

(4)

Hereinafter the value of $F_{cr} = \frac{\pi}{a} U_0$ will be referred to as the critical force [9]. The time-periodic external field is described by the following expression:
where $\omega$ is the angular frequency of the external force and $F_0$ is its amplitude.

The stochastic equations (1)-(2) are solved numerically using a Verlet-type algorithm with a time step of $\Delta t \approx 0.1$ fs, which is less than 1/100 of the period of oscillation. The statistic averaging is performed over an ensemble consisting of $N = 4 \cdot 10^4$ particles. To verify the model’s consistency, some computations are performed at $N = 4 \cdot 10^5$. The initial conditions are specified in the following way: a particle is placed at the coordinate system origin and is randomly given a velocity with a Maxwellian temperature distribution. The system is then subjected to thermalization during $10^4$ time steps. Afterwards the particle moves at the acquired velocity to the first unit cell.

The diffusion coefficient was calculated using the traditional approach:

$$D = \lim_{t \to \infty} \lim_{t' \to \infty} \frac{\langle x(t) - \langle x(t) \rangle \rangle^2}{2t},$$

where the angle brackets $\langle \ldots \rangle$ denote ensemble averaging.

While analyzing the modelling results, it is reasonable to write the equation in terms of scaled dimensionless variables, namely, time $\tau$, distance $\chi'$ and temperature $T'$ [4]:

$$\tau = \frac{1}{\gamma} \sqrt{\frac{mU_0}{a}}; \quad \chi' = \frac{x}{a}; \quad T' = \frac{kT}{U_0}.$$

The dimensionless friction coefficient is

$$\gamma' = \frac{\gamma a}{(mU_0)^{1/2}},$$

and is set at 0.2 in the present calculations. This value corresponds to the value observed in the experiment carried out to study hydrogen diffusion on a platinum surface [11].

In order to demonstrate the suitability of using dimensionless values, we performed computations for the diffusion of atoms of different elements. Figure 1 gives the temporal dependences of the diffusion coefficients for Pt, C, H and the appropriate dimensionless coefficients $D(\tau)$ for a temperature $T' = 0.5$.

It is seen that after appropriate scaling transformations the diffusion coefficients $D(t)$ fall onto one diffusion curve $D(\tau)$. In order to study the transport processes of particles exposed to an external force, it is sufficient to derive a solution for the particle of one type only. The relationships $D(t)$ for

![Figure 1. Dependences of the diffusion coefficient $D(t)$ for Pt, C, H on the time $t$ and scaled dependence $D(\tau)$ on the dimensionless time $\tau$. The dotted line denotes H; the dashed line, C; and the solid line, Pt. $T' = 0.13$, $\gamma' = 0.2$, $F = 0.15F_{cr}$.](image-url)
particles of another mass can be obtained through scaling transformations. Therefore, we studied the case of hydrogen only.

The activation barrier value is 80 meV, which is a typical value for the diffusion of adatoms across the closely-packed surfaces of metals with a face-centered cubic structure and a hexagonal closely-packed structure. The lattice constant \( a \) was selected to be equal to 2 Å.

Under the action of a constant force \( (\omega = 0) \), different modes of particle motion (figure 2) are realized depending on the relationship between \( F \) and \( F'_{cr} \) (\( F' = F_0 / F_{cr} \)). The results obtained are in a good agreement with the data obtained by other authors [6, 9]. The plot gives the dimensionless values of the mean-square displacements \( \sigma^2 = \langle x'(t) - <x'(t)> \rangle^2 \) on a logarithmic scale.

The modes of superdiffusion and hyperdiffusion in different time domains can be well seen in figure 2.

3. Results and discussion

The external periodic field applied leads to a time limitation of the diffusion processes. As a result, modes of abnormal diffusion are realized that are characteristic for a time period equal to the period of the external field oscillations.

Figure 3 shows the change in the diffusion coefficient behavior as a function of the applied field frequency for different values of the force amplitude \( F_0 \) at a constant temperature. The dashed line denotes the level corresponding to the surface diffusion at \( F_0 = 0 \).

The figure shows that the action of an external periodic field results in a considerable diffusion enhancement in comparison with the equilibrium case. The amplification ratio depends on the frequency and force amplitude of the field applied. Increasing \( F_0' \) to the value of 0.10 (curves 1-3) is accompanied by diffusion enhancement as the force increases in the entire frequency range studied. However, the value of \( D' \) change slightly at low frequencies of the external field. As the force continues to increase (curves 4-5), the shape of the curves changes – they display a low-frequency maximum. Its value exceeds considerably the maximum at frequency \( \omega = \omega_0 \) corresponding to the frequency of self-oscillations of a particle. For all plots given in figure 3, a higher value of \( D' \) corresponds to a higher value of \( F_0' \) in the high-frequency range. However, at low frequencies and for \( F_0' < 0.10 \), a
more intensive diffusion corresponds to a lower force value. An increase in the force amplitude results in a shift of the maximum $D'_{mx}$ to the higher frequencies.

Let us now consider the effect of the temperature on the diffusion frequency dependence. Figure 4 presents the plots of these relationships at a fixed value of $F_0' = 0.15$ for different temperatures. All frequency curves have a maximum at low frequencies; the lower the temperature, the higher the $D'_{mx}$ value. Such an abnormal behavior of the diffusion as a function of the temperature has a different nature in comparison with that of the particle diffusion exposed to a permanent force [8] discussed above. At a constant force, an exponential increase in $D'$ with a drop in the temperature is brought about by the infinite increase in the relaxation time. However, in the case of action of a time-periodic force, we have a natural time limitation defined by the oscillation period of the external field. The abnormal temperature dependence of the enhanced diffusion is related to the existence of time-limited hyperdiffusion modes. The diffusion enhancement can reach many orders of magnitude.

Figure 4 shows that at $T = 120K$ the diffusion is enhanced by more than seven orders of magnitude. The temperature drop results in a shift of the maximum to the low frequencies domain.

4. Conclusions
This paper presents studies on abnormal diffusion enhancement with the temperature drop in an external periodic field. It is shown that the diffusion enhancement depends strongly on the field amplitude and frequency.

The research reported opens new prospects for the creation of surface microstructures with required properties. This becomes especially important for low temperature methods sensitive to heat exposure. BLARG is an example of such a technique [12].

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