Effects of microwave electric fields on the translational diffusion of dipolar molecules in surface potential: A simulation study

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ABSTRACT

Variations of effective diffusion coefficient of polar molecules exposed to microwave electric fields in a surface potential are studied by solving coupled stochastic differential equations of motion with a deterministic component of the surface force. Being an essential tool for the simulation interpretation, a theoretical approach to effective diffusion in surface potential is first developed. The effective diffusion coefficient is represented as the product of the normal diffusion coefficient and potential-dependent correction function, whose temperature dependence is close to the Arrhenius form. The analytically found zero-diffusion condition defines the state of thermal equilibrium at the surface. The diffusion of a water-like dipole molecule in the potential of graphite surface is simulated in the field-free conditions and in the presence of the alternating electric fields of various magnitude intensities and frequencies. Temperature dependence of the correction function exhibits field-induced variations of the effective Lennard-Jones energy parameter. It demonstrates maximum departure from the zero-field value at certain frequencies and intensities, which is associated with variations in the rotational dynamics. A concept of the *amplitude–frequency resonance* put forward to interpret the simulation results is explained using a heuristic reasoning and is corroborated by semi-quantitative considerations in terms of the Dissado–Hill cluster theory of dielectric relaxation.

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1. Introduction

Diffusion in the bulk is a common limitation in interfacial chemical kinetics [1–3] controlled by slow adsorption [4,5] or desorption [5,6]. Chemical processes limited by adsorption and/or desorption of reactant and product molecules include, for example, reactions of toxic exhaust gases (NO_x and CO) on noble metals and oxide catalysts [7–11], catalytic combustion of volatile organic compounds [12], conversion of alcohols [13] in fuel cells, and thiophene desulfurization on zeolites [14]. Diffusion control of adsorption and desorption is essential in a wide range of other applications, for many of which understanding kinetics of surfactant transport near interfaces [15–17] is important. These applications include the self-assembly of monolayers [18–21], design of surface-based biosensors [22], peptide covering [23], engineering of foam-bed chemical reactors [24], preparation of heterogeneous catalysts [25], recovery and separation of minerals [26], capture of combustible gases on zeolites [27], controlled drug release [28–31], controlled desorption of volatile organic compounds in chemical analysis and for dampening concentration fluctuations in biofilters and oxidizers [32–37], and thermal diode development [38]. Controlled adsorption and desorption [39,40], as well as the reactions on heterogeneous catalysts, can be tuned by temperature variation, but alternative techniques, such as the electromagnetic (EM) irradiation of surface, are rapidly progressing [34–36,41,42].

It is worthwhile to note that the EM effects obtained in experiments cannot be explained only in terms of the temperature increase [34,43]. Moreover, specific nonthermal microwave (MW) influence was observed also in catalysis on metal oxide surfaces [44–46]. Though the existence of the specific microwave effects in condensed media is often questioned or denied [47], they have been found in molecular dynamics simulation studies of water in strong MW fields [48,49] and in 3D dipolar lattice in the fields of moderate amplitude intensity [50]. Yet, the origin of the nonthermal MW effects on the physicochemical processes at interfaces is unclear. In the simulations reported in the present work, we concentrate on detecting the nonthermal influence of MW fields on the effective energy barrier affecting the diffusion in the surface potential.

To date, a universal theory of diffusion in an arbitrary potential is not known, but some theoretical approaches for special potentials have been developed. In particular, the effective diffusion coefficients were obtained in closed form for harmonic [51] and rough [52,53] potentials. Furthermore, diffusion in periodic (washboard) potential was considered in several works [54–60], and studies of this type of diffusion were

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extended to the case of oscillating barriers [61,62]. A number of works were focused on diffusion in tilted periodic [63–69], tilted disordered [70–75], oscillating [62,72,76,77] and disordered [57,58,78,79] potentials, which can support giant acceleration of diffusion over surface and separation of different species of Brownian particles. In the simulation of diffusion in these potentials, anomalous diffusion regimes were detected [57,58,68].

Random potentials proved to be useful also for trapping of ultracold atoms as demonstrated in Ref. [80], in which this trapping was modeled and compared with the published experimental results. The Anderson localization effect was shown in [80] to emerge in some conditions. Some microtraps and microsized atom guides are designed and modeled in [81] with taking into account the Casimir–Polder effect destroying trapping of ultracold atoms near conductors of microtraps.

The anomalous diffusion differs from the normal Einsteinian one in the nonlinear growth of mean squared displacement $\langle r^2 \rangle$ with time [82–84]: $\langle r^2 \rangle \sim t^\alpha$. This situation is realized when the distribution of diffusion steps declines from the Gaussian or when the time intervals between diffusion events do not form an exponential distribution. The infinite mean of the waiting time distribution corresponds to subdiffusion ($\alpha < 1$), and the absence of a finite mean travel length is the signature of superdiffusion ($\alpha > 1$). On sufficiently long timescales, however, the diffusion ultimately becomes normal [57,58,85,86].

In this work, we study diffusion of dipolar molecules in the potential well of a graphite surface in zero and nonzero microwave electric fields with the normally distributed random walk steps ($\alpha = 1$) in the direction perpendicular to this surface. The aims of our study are finding nonthermal effects of MW electric fields of different frequencies and magnitude intensities on diffusion of this molecule in the surface potential well and explaining the maximum efficiency of particular frequencies and intensities.

The paper is organized as follows. In Section 2, an analytical approach to diffusion in a potential well in zero electric field is presented and both the exact and approximate relationships for the effective diffusion coefficient are derived as the groundwork for further results. Section 3 is focused on the model, method, and details of the simulation, whereas the derivation of the semi-infinitesimal dipole image charge potential used in the model is presented in Appendix A. The simulation results are reported and discussed in Section 4. Section 5 concludes the paper.

2. Theoretical background

2.1. The Smoluchowski equation and the Boltzmann distribution assumption

Surface diffusion represents an example of combined action of local surface potential and random thermal influence on an adsorbed particle forcing its tangential random walk over the surface [87]. The tangential displacement is commonly defined as the surface diffusion, and it is described by appropriate equations of normal or anomalous diffusion. In the similar manner, the displacement in the normal direction (x) is supposed to obey the Smoluchowski equation [88,89]

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D^\circ \frac{\partial C}{\partial x} + \frac{C}{\zeta}\frac{\partial U}{\partial x} \right) \tag{1}$$

where C is the concentration of the molecular species on surface, D° is the normal diffusion coefficient, U is the surface potential, and ζ is the drag coefficient equal to the inverse mobility. In general, the drag coefficient in a potential is a function of distance. Equivalently, the probability distribution function instead of C can be used in (1). The true diffusion in the x direction is assumed of the normal Einsteinian type, which implies Gaussian distribution of random walk steps.

The surface potential function has a minimum at the equilibrium position of the adsorbed molecule (Fig. 1). It includes the relevant Coulomb and van der Waals contributions in its attractive and repulsive branches.
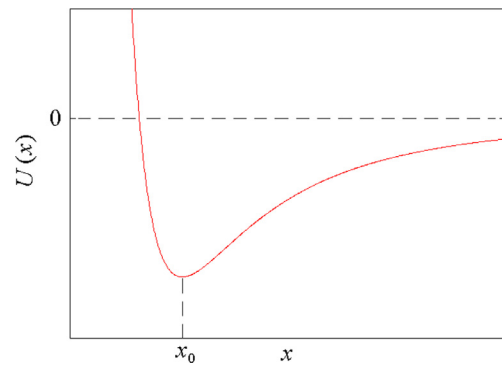

Fig. 1. Surface potential energy of an adsorbed molecule as a function of the coordinate x in the normal direction to the surface. The minimum at x_0 corresponds to the equilibrium position of the molecule.
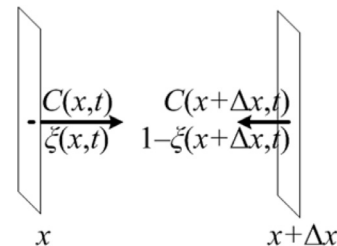

Fig. 2. Quantities related to one-dimensional diffusion in surface potential. The arrows denote the directed transfer of fractions $\xi(x)$ and $1 - \xi(x + \Delta x)$.

If the diffusing molecules have already relaxed to microscopic equilibrium with the environment, which is typically observed in the case of their overdamped motion (on the timescale of 10^{-13} s for ordinary liquids), the Boltzmann distribution can be used to define their concentration as a function of x:

$$C = C_0 \exp\left\{ \left[U(x_0) - U(x) \right]/(k_B T) \right\} \tag{2}$$

where C_0 is the concentration in the potential minimum at x_0.

From (2) one obtains:

$$\partial U / \partial x = -\left(k_B T / C \right)(\partial C / \partial x). \tag{3}$$

The substitution of (3) into (1) results in

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left[\left(D^\circ(x) - \frac{k_B T}{\zeta(x)} \right) \frac{\partial C}{\partial x} \right]. \tag{4}$$

Eq. (4) has an appearance of Fick's second law of diffusion, with the terms in parentheses making up the effective diffusion coefficient D:

$$D(x) = D^\circ(x) - k_B T / \zeta(x), \tag{5}$$

which is introduced to treat the problem of the effective diffusion in the surface potential in terms of the Fickian diffusion formalism, as shown below. The nonlinearity of the potential and the out-of-equilibrium state indicate [90] that in general, the Einstein relation does not hold in this case: $D^\circ(x) \neq k_B T / \zeta(x)$. For molecular analogs of the short-range potentials (such as the Lennard-Jones and Exp-6 potentials) between gas molecules, similar effective diffusion coefficients have been determined as nonlinear functions of temperature [91,92].

2.2. One-dimensional model of effective diffusion in surface potential

Consider the flux of adsorbate in between x and $x + \Delta x$ across a unit area (Fig. 2). If the concentration and fraction of molecules diffusing along x-direction are $C(x, t)$ and $\xi(x)$ at coordinate x, and those at $x + \Delta x$ are $C(x + \Delta x, t)$ and $\xi(x + \Delta x)$, respectively, then the flux is

$$J(x) = (\Delta x / \Delta t)\{C(x,t)\xi(x) - C(x + \Delta x, t)[1 - \xi(x + \Delta x)]\}. \tag{6}$$