

Coverage dependence of the surface diffusion length of an adsorbed molecule

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흡착분자 표면확산거리의 피복률 의존성

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Abstract We discuss the surface diffusion process of an adsorbed gas molecules by the method of Markoff probability process and give a relationship between the surface diffusion length and the surface coverage of an adsorbed molecule.

요 약 고체표면에 흡착된 기체분자의 표면확산과정을 Markoff 확률과정 방법을 이용하여 논의한다. 흡착분자의 표면확산거리와 표면피복률간의 관계식을 유도한다.

In recent years, many researches are concentrated on surface [1]. The fields under very rigorous study include the subject such as surface diffusions [2-5], inelastic collision and the trapping of gas atoms on crystal surface [6-9], adsorption and desorption [10], crystallogrowth phenomena, surface phase transition [11] etc. Our interest here is on the surface diffusion of the adsorbed gas molecule on a solid surface.

When a solid is exposed to a gas, particles constituting the surface of the solid may interact with molecules in the gas. Some of the gas molecules are adsorbed on the surface. The fate of those adsorbed molecules may be categorized into two cases: 1) some of them may be eventually chemisorbed and solidified, 2) others may be wandering around on the surface and finally go back to the gas phase. In this paper, we will discuss the surface diffusion process of adsorbed gas molecules by the method of Markoff probability process and give a relationship between the surface diffusion length and the surface coverage of an adsorbed molecule.

We assume that the surface of the solid may be regarded as constituting a cell structure, and also that an adsorption of the gas molecules occur at an unoccupied site in the cell. A cell is assumed to be limited to accommodate only one molecule and

adsorption of a molecule is assumed to be taking place on a monolayer. We now suppose that each adsorbed molecule fluctuates thermally with constant intervals of time τ on the surface. And we suppose that the molecule adsorbed has four cases of probabilities for each fluctuation [12]. These probabilities are probability P_s of being solidified on the surface adsorbed, probability P_e of evaporating to the gas phase from the surface adsorbed, probability P_h of lateral hopping on the surface, and probability P_d which it has no actions such as solidification, evaporating, or hopping etc. till next fluctuation of time τ after. The probabilities P_s , P_e , P_h , and P_d satisfy

$$P_s + P_e + P_h + P_d = 1. \quad (1)$$

The fluctuations of the adsorbed molecule continue until it evaporate or become solidified. Thus we can write the probability that a molecule adsorbed on the surface passes on to another site at the first site visited is

$$P_{1 \rightarrow 2} = P_h + P_d P_h + P_d^2 P_h + \dots \\ = \frac{P_h}{1 - P_d}. \quad (2)$$

The corresponding probability for the second site visited is

$$P_{1 \rightarrow 2 \rightarrow 3} = P_h P_{1 \rightarrow 2} + P_d P_h P_{1 \rightarrow 2} + P_d^2 P_h P_{1 \rightarrow 2} + \dots \\ = P_{1 \rightarrow 2}^2 \quad (3)$$

By succession of this probability process, the corresponding probability for the Sth site visited is

$$P(S) = P_{1 \rightarrow 2 \rightarrow \dots \rightarrow S \rightarrow S+1} = P_{1 \rightarrow 2}^S \quad (4)$$

The expectation value $\langle S \rangle$ of the number of hopping steps which an adsorbed molecule wanders around on the surface before it evaporate or is solidified can be written as, using the probability $P(S)$ of Eq. (4),

$$\langle S \rangle = \frac{\sum_{S=0}^{\infty} S P(S)}{\sum_{S=0}^{\infty} P(S)} \\ = \frac{P_{1 \rightarrow 2}}{1 - P_{1 \rightarrow 2}} \quad (5)$$

in which $\sum_{S=0}^{\infty} P(S)$ is a normalizing factor and we assumed $P_{1 \rightarrow 2} < 1$ and $P_{1 \rightarrow 2}^{\infty} = 0$. Then the total diffusion time of an adsorbed molecule is written by

$$\tau_d = \frac{\langle S \rangle}{n} \quad (6)$$

where n is the number of hopping steps which the adsorbed molecule suffers in unit time and given by (see appendix)

$$n = \frac{1 - P_d}{\tau} \quad (7)$$

We can assume that all the hopping steps being taken occur in random directions, therefore the surface diffusion length X is given by [13], for large values of $\langle S \rangle$,

$$X^2 = l^2 \langle S \rangle = n l^2 \tau_d \quad (8)$$

where l is the hopping length.

In the great majority of cases, solidifying process of a molecule adsorbed on a surface depends on, largely, the depth of the potential well of the surface, the kinetic energy of the molecule and electronic bonding structure between the molecule and the surface. Thus we shall ignore the coverage dependence of the probability P_s . In fact, for a certain energy range and for an inactive molecules, we may ignore the solidifying process itself without making a serious error, and can concentrate only on

a problem of physisorption.

We can speak that the length of a hopping step l corresponds to the mean free path, which is inversely proportional to a number density, in the kinetic theory of gas. Thus we here let l be inverse to the surface coverage θ :

$$l = \frac{\alpha}{\theta + a} + \beta \quad (9)$$

where α , β and a are constants. The constant a prevents l to diverge when $\theta = 0$. Letting l be l_0 for the clean surface of $\theta = 0$, the constants α and β are, respectively,

$$\alpha = l_0 a (1 + a) \quad \text{and} \quad \beta = -l_0 a \quad (10)$$

As the occupancy θ (vacancy $(1 - \theta)$) of molecules adsorbed on surface increases, a chance that an adsorbed molecule delays (hops) is higher than moves to next place (delays on the site). These are caused by that lateral motion of an adsorbed molecule is restricted (prompted) by increase (decrease) of a collision with environmental molecules or decrease (increase) of a place to occupy etc. Therefore we will assume that the delaying probability P_d or the hopping probability P_h is proportional to the occupancy θ and the vacancy $(1 - \theta)$ of the surface, respectively:

$$P_d = \xi \theta + \eta \quad (11)$$

and

$$P_h = \zeta (1 - \theta) + \gamma \quad (12)$$

Letting the delaying probability P_d be d_1 for the saturated surface of $\theta = 1$ and d_0 for the clean surface of $\theta = 0$, the constants ξ and η in Eq. (11) are, respectively,

$$\xi = d_1 - d_0 \quad \text{and} \quad \eta = d_0 \quad (13)$$

The constants ζ and γ in Eq. (12) are, respectively,

$$\zeta = h_0 \quad \text{and} \quad \gamma = 0 \quad (14)$$

where h_0 denotes the lateral hopping probability on the clean surface. In driving Eqs. (10) and (14), we assumed that the molecule adsorbed can not diffuse on the surface of which coverage is saturated.

From Eqs. (2), (5), (6), and (8)-(14), we obtain the surface diffusion length as a function of the surface coverage:

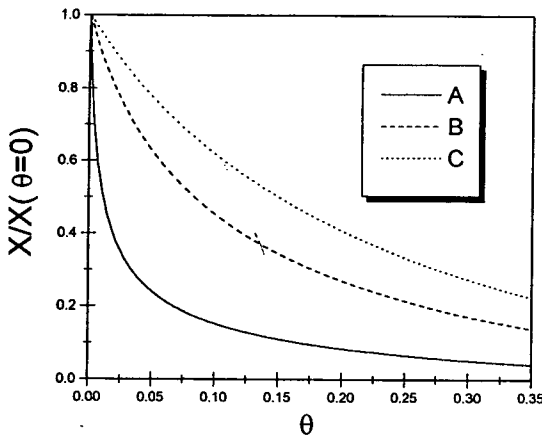


Fig. 1. Normalized surface diffusion length $X/X(\theta=0)$ as a function of coverage θ for various values of h_0 is plotted. For examples, $h_0 =$ (A) 0.995, (B) 0.950, (C) 0.850; $d_0 = 0.001$, $d_1 = 0.005$, and $a = 1$.

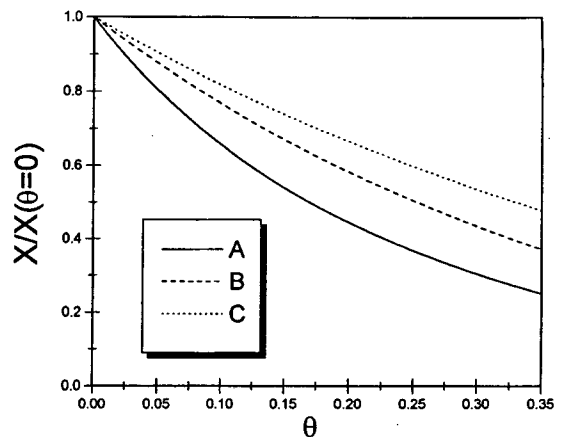


Fig. 2. Normalized surface diffusion length $X/X(\theta=0)$ as a function of coverage θ for various values of d_0 is plotted. For examples, $d_0 =$ (A) 0.998, (B) 0.995, (C) 0.805; $h_0 = 0.001$, $d_1 = 0.995$, and $a = 1$.

$$X = l_0 a \left(\frac{1+a}{\theta+a} - 1 \right) \left[\frac{1 - (d_1 - d_0)\theta - d_0}{h_0(1-\theta)} - 1 \right]^{-1/2} \quad (15)$$

This equation is effective for the range of low coverage. How long the surface diffusion length of the adsorbed molecule on the surface is depends on various factors. We considered here only about the coverage of the surface. From Eq. (1), we know that Eq. (15) is implicit function of P_s and P_c . As mentioned above, the constants l_0 , h_0 , d_0 are the length of hopping step, the lateral hopping probability, and the delaying probability for the clean surface, respectively. The constant d_1 is the delaying probability for the saturated surface. From Eqs. (9), (10), we know that the constant a is explicit function of θ and l . It is expected that the constants, l_0 , h_0 , d_0 , and d_1 are dependent on an interaction between the adsorbed molecule and the surface directly. Validity of our theory and physically reasonable values of the constants l_0 , h_0 , d_0 , d_1 , and a shall be determined by an experimental data, which is not yet found. Eq. (15) shows that as the constant h_0 becomes larger, surface diffusion length X increases and also that as the constant d_0 becomes larger, X decreases under a certain coverage value. In Figs. 1-2, normalized surface diffusion length $X/X(\theta=0)$ as a function of coverage θ for various values of h_0 and d_0 are plotted.

The probability of hopping at j th fluctuation ($j=1, 2, \dots$) on the arbitrary site visited is

$$Q_j = P_d^{j-1} P_h \quad (16)$$

In diffusion process, average number of fluctuations to be required to take a hopping step can be written as, using Eq. (16),

$$\begin{aligned} \langle F \rangle &= \frac{\sum_{j=1}^{\infty} j Q_j}{\sum_{j=1}^{\infty} Q_j} \\ &= \frac{1}{1 - P_d} \end{aligned} \quad (17)$$

where we assumed $P_d < 1$ and $P_d^{\infty} = 0$. The value n of Eq. (7) is given by inverse of $\langle F \rangle \tau$ which means the time being required to take a hopping step.

References

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Appendix: Derivation of Eq. (7)

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