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A Possibility of Macroscopically Asymmetric Diffusion on Stepped Surfaces

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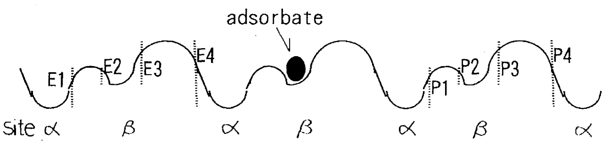
We studied the macroscopic-scale surface diffusion of adsorbates under strong adsorbate–adsorbate lateral interactions (A–A potential) on a surface with periodically repeated asymmetric potential curves, such as a well-ordered stepped surface. By considering a potential curve made of adsorbate–substrate (A–S) and A–A potentials in a random-walk model, we found an asymmetry in a migration probability of an adsorbate in opposite directions. On this basis, we derived and predicted the existence of macroscopically asymmetric diffusion. A Monte-Carlo calculation of the random walk of adsorbates with a certain strong repulsive A–A potential on fcc (112) or bcc (013) caused the adsorbates to diffuse more in a direction of jumping the minimum A–S activation energy, and a difference in flux of the adsorbates in opposite directions greatly depended on the concentration.

Analyzing the macroscopic diffusion of molecules is important for understanding or developing surface chemical reactions, diffusion, and separation processes. The macroscopic aspects of surface diffusion have been steadily brought to light along with the development of an instrument for determining surface diffusion. In many cases the diffusion coefficient is not constant, but depends on the concentration. One of the reasons for this is an adsorbate–adsorbate interaction. Examples of them include O/W(110)[1,2] by the method of contact potential difference, CO/Ni (100)[3] and D/Pt (111)[4] by laser-induced thermal desorption, and K/Pd (111)[5,6] by photoemission electron microscopy. The concentration dependency of the diffusion coefficient was derived from the adsorbate–adsorbate lateral interaction (A–A potential).[7] The basic idea[7,9] is that in a random-walk model a potential barrier which an adsorbate must overcome in order to move to a neighbor site is the height of a mountain of the potential made by summing the adsorbate–substrate interaction (A–S potential) and the A–A potential.

If adsorbates with a strong lateral interaction, such as an alkali metal, are on stepped surfaces, such as Ni (112), what sort of macroscopic diffusion will occur? Well-ordered stepped surfaces where the step and the terrace are alternatively arranged have a periodically repeating asymmetric potential normal to the step. The potential energies on the terrace and on the edge differ from each other concerning not only the bond energy, but also the saddle potential.[9—12] It has been indicated that two kinds of diffusion of a metal adsorbate, descending and ascending a step of an island, have unique and different behaviors and velocities on the microscopic scale.[28—30] The simplest potential curves on well-ordered stepped surfaces have been given in the case of fcc (112), such as CO/Ni (112),[9] and in the case of bcc (013), such as Pd /W (013).[13,14] A typical potential-energy diagram is shown in Fig. 1(a). We found that the potential made by summing a very strong A–A potential and an A–S potential at a well-ordered stepped surface can yield an asymmetry of macroscopic diffusion in opposite directions.

So far, it has been supposed that the diffusion of adsorbates on periodic surfaces, such as fcc (100) and (112), is macro-

(a) low concentration



(b) high concentration

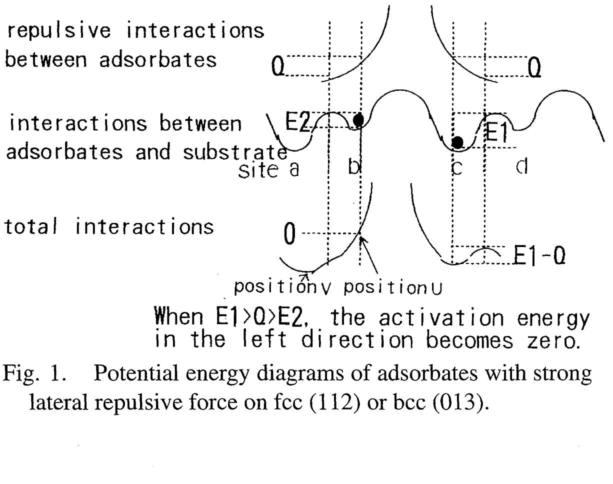


Fig. 1. Potential energy diagrams of adsorbates with strong lateral repulsive force on fcc (112) or bcc (013).

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scopically symmetric; that is, it has equal fluxes in the right and left directions based on the Nernst–Einstein rule that the flux of diffusion is proportional to the gradient of the chemical potential, because the chemical potential, a macroscopic quantity, is equal at any portion of such surfaces. So far, the diffusion coefficients of adsorbates with a not very strong lateral interaction, such as CO, Pd, Ag on stepped surfaces, has been measured.[13—19] All of them have been successfully treated as symmetric ones, although some researchers had sought exceptions, asymmetric ones.[31,32] In contrast, in an experiment involving changing the chemical potential by using an external electric field, macroscopically asymmetric diffusion has been found, of which a typical example is the electromigration of In on Si (111).[33]

While considering the potential on the atomic scale we theoretically studied the diffusion of adsorbates with strong lateral interactions on stepped surfaces which had not been measured. In this paper we report on the existence of the condition that asymmetric diffusion can occur without any external fields. The diffusion perpendicular to the steps is described below.

Theory and Method of Calculation

Rough Basis. We consider the case of the simplest potential pattern involving two different repeated potential mountains, such as fcc (112) or bcc (013), which is shown in Fig. 1. We treat the case of a strong repulsion, where the gradient of the repulsive A–A potential at the nearest-neighbor sites is comparable to the gradient of the A–S potential. When adsorbates are separated from each other by a large distance, the activation energy for a one-site hop of the adsorbate is regulated by the A–S potential only. In Fig. 1(a) this is represented by energies E_1 and E_3 for migration to the right, and by energies E_2 and E_4 for migration to the left (where $E_4 > E_3$, $E_1 > E_2$). A hop model where an adsorbate moves by hopping to the nearest-neighbor sites is consistent with many experimental results, such as for hydrogen on Ni (100).[13] When the adsorbate moves to a site next to another adsorbate, a strong repulsive force is generated, and the potential curve for a one-site hop becomes the sum of the A–S and the A–A potentials. It is the symplest model expressing the short-range properties of the actual lateral A–A potential.[7]

The difference in the A–A potential between the bond site (bottom of ravine) and the neighboring saddle point (mountaintop) is shown as Q in Fig. 1(b). We consider the case where two adsorbates are at the positions shown in Fig. 1(b). When E_1, E_2, E_3, and E_4 are larger than Q, the activation energy for a one-site hop of the two adsorbates is E_1-Q to the right and E_2-Q to the left, respectively. The activation energies for migrations in both directions decrease, and the decrease in migration probabilities in both directions is the same percentage. When $E_1 > Q > E_2$, however, the activation enery is E_1-Q to the right, while *to the left it is zero due to the negative value of* E_2-Q. The negative value of E_2-Q indicates that there is no activation energy, but a monotonous slope of the potential. This phenomenon can occur when the right adsorbate overcomes the positive activation barrier and migrates from site d to site c, the nearest-neighbor site of the left adsorbate in Fig. 1(b). According to the conventional collision rate theory, all of the collisions with energies over a certain value cause a reaction to occur. Random-walk theory of surface diffusion, based on the conventional collision-rate theory, indicates that no thermal energy is needed for an adsorbate having overcome a potential barrier between two bond sites to attain a stable position within the site. Therefore, at a very low temperature the velocity of the movement of the left adsorbate from the unstable place, position u, to the stable place, position v, is much higher than that of migration with a certain potential barrier, even when the potential barrier or the slope between positions u and v is small. For the overall velocity of diffusion we may count the velocities of migrations with only activation barriers. Bcause the leftward diffusion only includes the above case of an extinguishment of a factor of E_2 in the activation energy, the balance of the leftward and the rightward diffusions breaks. We roughly found the principle that in Fig. 1(b) due to the extinguishment of "a mountain of potential" in one direction (left), the diffusion probability in the direction (left) becomes larger than that in another direction (right). The detailed process of inducing the result follows.

Induction of Random-Walk Probability (the Effect of Lateral Repulsive Interaction). By examining the behavior of the average position of adsorbates in a hopping process we judged whether macroscopic diffusion is asymmetric or not. We expressed the hop dependency of the average position of adsorbates as a function of each hopping probability, while it is difficult to analytically induce its time dependency as a function of each hopping rate.[25] In Fig. 1(a) $P_i = \nu\exp(-E_i/RT)$ (i = 1, 2, 3, or 4) is the hopping rate with A–S activation energy; E_i. ν, R, and T are the pre-exponential factor, gas constant, and temperature, respectively. For example, in the case of no A–A interactions, the hopping probabilities of an adsorbate from a β site to the right-neighbor site and to the left-neighbor site are $P_3/(P_2+P_3)$ and $P_2/(P_2+P_3)$, respectively.

When the adsorbates are fully apart from each other, there is only the A–S potential (no lateral interaction). In this case, the α or β site in Fig. 1(a) each has a certain potential energy. The respective certain probability, ρ_α or ρ_β, of the adsorbate at the α or β site has the relation of $(P_1+P_4)\rho_\alpha = (P_3+P_2)\rho_\beta$ according to the conventional principle of no accumulations of adsorbates in diffusion.[16,26,27] From $P_1P_3 = P_2P_4$, we obtain.

$$\rho_\beta/\rho_\alpha = P_1/P_2 = \exp[(E_2-E_1)/RT]. \tag{1}$$

We take the simple model that the A–A potential is zero more than 2-site distance. We consider every case of two hops of two adsorbates with a distance of just two sites, of which the initial probabilities are known in Eq. 1. The sum of "the displacement in the plus direction (right) × the probability" is counted, where a displacement of $+n$ means an n-site movement of the adsorbate to the right in Fig. 1. Table 1 or Table 2 shows the results of the probability obtained in the case of the two adsorbate at the α or β site, respectively. A difference in the repulsive potential between the 1-site distance and the 1.5-site distance of the two adsorbates is taken to be Q, as shown in the section of Rough Basis. The total activation energy for a hop from the position with the 2-site distance to the position with the 1-site distance is a sum, E_i+Q, of the A–S activation energy (E_i), and the A–A potential difference (Q). When we take $q = \nu\exp(-Q/RT)$, the probability of the hop is $\nu\exp[-(E_i+Q)/RT] = qP_i$. The total activation energy for a hop from a position with the 1-site distance to a position with the 2-site distance is $\nu\exp[-(E_i-Q)/RT] = P_i/q$, where q is given in Tables 1 and 2.

In the case of $Q \leqq E_2$ ($q \geqq P_2$), the expectation value of the displacement to the right ($\sum$(displacement × probability)) from an α site or a β site is $2(P_1-P_4)/(P_1+P_2+P_3+P_4)$ or $2(P_3-P_2)/(P_1+P_2+P_3+P_4)$, respectively. The ratio of the probabilities of the adsorbate at α and β sites is P_2/P_1 by Eq. 1. The total expectation value of a displacement to the right from every site is counted as follows:

Table 1. Probability of Two Hops of the Two Adsorbates with 2-Site Distance from α Site

Hops		Displacement	Probability	
1st	2nd		Case of $q \geqq P_2$	Case of $q < P_2$
A,R	A,R	+2	0	0
A,R	A,L	0	$qP_1/W \times P_2/q/Y$	0
A,R	B,R	+2	$qP_1/W \times P_1/q/Y$	0
A,R	B,L	0	0	0
A,L	A,R	0	$P_4/W \times P_3/Z$	$P_4/W \times P_3/Z$
A,L	A,L	−2	$P_4/W \times P_2/Z$	$P_4/W \times P_2/Z$
A,L	B,R	0	$P_4/W \times P_1/Z$	$P_4/W \times P_1/Z$
A,L	B,L	−2	$P_4/W \times P_4/Z$	$P_4/W \times P_4/Z$
B,R	A,R	+2	$P_1/W \times P_1/Z$	$P_1/W \times P_1/Z$
B,R	A,L	0	$P_1/W \times P_4/Z$	$P_1/W \times P_4/Z$
B,R	B,R	+2	$P_1/W \times P_3/Z$	$P_1/W \times P_3/Z$
B,R	B,L	0	$P_1/W \times P_2/Z$	$P_1/W \times P_2/Z$
B,L	A,R	0	0	0
B,L	A,L	−2	$qP_4/W \times P_4/q/S$	$qP_4/W \times P_4/q/S$
B,L	B,R	0	$qP_4/W \times P_3/q/S$	$qP_4/W \times P_3/q/S$
B,L	B,L	−2	0	0
Expectation value of displacement ($\sum$(displacement × probability))			$2(P_1-P_4)/Z$	$2(P_1-P_4)/Z-2qP_1^2/(q+1)/(P_1+P_2)/(P_1+P_4)$

A and B: adsorbates. R and L: moving to the right and the left. Displacement: adsorbate's displacement on the x axis (the number of site) during the two hops. $W \equiv P_4+qP_1+qP_4+P_1$. $Y \equiv P_2/q+P_1/q$. $Z \equiv P_1+P_2+P_3+P_4$. $S \equiv P_4/q+P_3/q$.

Table 2. Probability of Two Hops of the Two Adsorbates with 2-Site Distance from β Site

Hops		Displacement	Probability	
1st	2nd		Case of $q \geqq P_2$	Case of $q < P_2$
A,R	A,R	+2	0	0
A,R	A,L	0	$qP_3/G \times P_4/q/S$	$qP_3/G \times P_4/q/S$
A,R	B,R	+2	$qP_3/G \times P_3/q/S$	$qP_3/G \times P_3/q/S$
A,R	B,L	0	0	0
A,L	A,R	0	$P_2/G \times P_1/Z$	$P_2/G \times P_1/Z$
A,L	A,L	−2	$P_2/G \times P_4/Z$	$P_2/G \times P_4/Z$
A,L	B,R	0	$P_2/G \times P_3/Z$	$P_2/G \times P_3/Z$
A,L	B,L	−2	$P_2/G \times P_2/Z$	$P_2/G \times P_2/Z$
B,R	A,R	+2	$P_3/G \times P_3/Z$	$P_3/G \times P_3/Z$
B,R	A,L	0	$P_3/G \times P_2/Z$	$P_3/G \times P_2/Z$
B,R	B,R	+2	$P_3/G \times P_1/Z$	$P_3/G \times P_1/Z$
B,R	B,L	0	$P_3/G \times P_4/Z$	$P_3/G \times P_4/Z$
B,L	A,R	0	0	0
B,L	A,L	−2	$qP_2/G \times P_2/q/Y$	$qP_2/G \times 1/(1+P_1/q)$
B,L	B,R	0	$qP_2/G \times P_1/q/Y$	$qP_2/G \times P_1/q/Y$
B,L	B,L	−2	0	0
Expectation value of displacement ($\sum$(displacement × probability))			$2(P_3-P_2)/Z$	$2(P_3-P_2)/Z+2qP_1P_2(P_2-q)/(q+1)/(P_1+q)/(P_1+P_2)/(P_2+P_3)$

A, B, R, L, and the displacement are explained in Table 1. $G \equiv P_2+qP_3+qP_2+P_3$. $Y \equiv P_2/q+P_1/q$. $Z \equiv P_1+P_2+P_3+P_4$. $S \equiv P_4/q+P_3/q$.

$$P_2 \times 2(P_1-P_4)/(P_1+P_2+P_3+P_4) \\ +P_1 \times 2(P_3-P_2)/(P_1+P_2+P_3+P_4) = 0. \tag{2}$$

Therefore, the total movement of the average position is zero under a repulsive interaction with the relation $Q \leqq E_i$ (i = 1, 2, 3, and 4).

In the case of $E_1 > Q > E_2$ ($P_1 < q < P_2$), that is, in the case of "the extinguishment of a mountain of potential," the expectation value of a displacement to the right from an α or β site is $2(P_1-P_4)/(P_1+P_2+P_3+P_4)-2qP_1^2/(q+1)/(P_1+P_2)/(P_1+P_4)$ or $2(P_3-P_2)/(P_1+P_2+P_3+P_4)+2qP_1P_2(P_2-q)/(q+1)/(P_1+q)/(P_1+P_2)/(P_2+P_3)$, respectively from Table 1 or Table 2. The total expectation value of a displacement to the right from every site is as follows:

$$P_2 \times [2(P_1-P_4)/(P_1+P_2+P_3+P_4) \\ -2qP_1^2/(q+1)/(P_1+P_2)/(P_1+P_4)] \\ +P_1 \times [2(P_3-P_2)/(P_1+P_2+P_3+P_4) \\ +2qP_1P_2(P_2-q)/(q+1)/(P_1+q)/(P_1+P_2)/(P_2+P_3)] \\ = -2q^2P_1^2/(q+1)/(q+P_1)/(P_1+P_4) \neq 0. \tag{3}$$

This indicates that the average position of the adsorbates is not constant, but moves in the direction of hopping the minimum A–S activation energy under a repulsive interaction with the relation $E_1 > Q > E_2$. Of course, in the case of no A–A interaction or a very low concentration of adsorbates (A–A interactions are negligible), the conventional rule of the constant average position stands, because the total expectation value of a hop is $\rho_\alpha(P_1-P_4)/(P_1+P_4)+\rho_\beta(P_3-P_2)/(P_2+P_3)=0$.

Monte Carlo Calculation. By a Monte-Carlo calculation in a one-dimensional array, we examined whether the theory worked. For the calculation we simply took the potential curve as a triangle, which is shown in Fig. 2. $E_1=2RT$, $E_2=1RT$, $E_3=2RT$, $E_4=3RT$, and $Q=1.5RT$ were taken as typical values. The A–A potential was generated only when adsorbates were very near. The height of the A–A potential was $3RT$ at the 1-site distance, $1.5RT$ at the 1.5-site distance, and 0 at and more than the 2-site distance (Fig. 2(a)). A random walk of 101 adsorbates on the surface with these potentials was repeatedly conducted. The restricted conditions follow: (1) The adsorbate hops just one site. No jump of more than one site one time occurs. (2) The adsorbate does not hop onto a site occupied by another adsorbate. 101 adsorbates are in turn named from the left, No. 1—101. The generator of random numbers of 0—1 is started. When the random number (R) follows the condition $0 \leqq R \leqq \exp(-E/RT)$, a hop is conducted. E is the synthesized activation energy, that is, the height of the potential "mountain" made by summing the A–S potential (Fig. 2(b)) and the A–A potential (Fig. 2(a)). The various values of E under various conditions are listed in Tables 3 and 4. We simply took the pre-exponential factor of the hopping rate as being 1. Here, we did not consider an absolute value of time. An example of determining the value of the activation energy by summing the two potentials follows. When adsorbate A at $x=0$ hops to the right, influenced by another adsorbate (B) at the right next–next site ($x=2$), the activation energy (E) is $E_3+Q=2RT+1.5RT=3.5RT$. E for hopping to the left is $E_2=1RT$, not including Q, because during the hop the distance between the two adsorbates is more than 2 sites. Notably, when A at $x=-1$ is influenced by B at the right next–next site ($x=1$), the activation energy for a migration of A to the right becomes ∞ due to an extinguishment of the potential mountain between $x=-1$—0. In other words, the potential of A forms a monotonous slope going up to the right within $x=-1$—0.5. Moreover, when B hops from $x=2$ (β site) to the left α site, coming near A at $x=0$, A loses the potential mountain between $x=-1$—0, losing the activation barrier for hop to the left. We examined whether the potential of A forms the shape of the slope within $x=-1$—0.5 no matter where B is within $x=1$—1.5 just after overcoming the activation barrier at $x=1.5$—2. The result is noted in the next section.

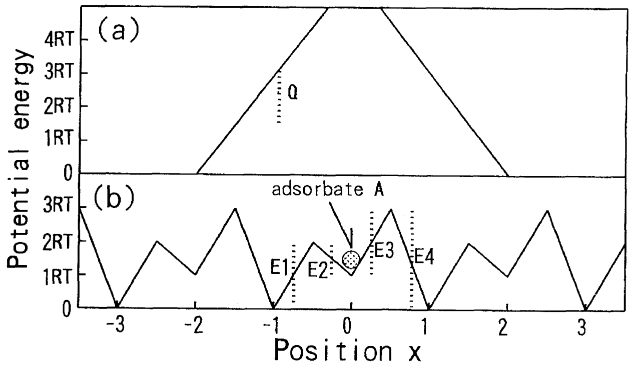

Fig. 2. Symple potential diagrams for Monte Carlo calculation. (a) the dependence of A–A potential at $x=0$ on the position of another adsorbate. (b) the positional dependency of A–S potential of the adsorbate A. A–S activation energies $E_1=2RT$, $E_2=1RT$, $E_3=2RT$, and $E_4=3RT$. The repulsive potential difference $Q=1.5RT$.

Table 3. Activation Energy for Hopping of an Adsorbate A at α Site ($x=\cdots, -3, -1, 1, 3, \cdots$) Synthesized in Fig. 2

Distance of A and the left nearest adsorbate	Distance of A and the right nearest adsorbate		
	Over 2 sites	Just 2 sites	Just 1 site
Over 2 sites	$2RT$ $3RT$	∞ $3RT$	∞ $1.5RT$
Just 2 sites	$2RT$ $4.5RT$	∞ $4.5RT$	∞ $3RT$
Just 1 site	$0.5RT$ ∞	$2RT$ ∞	∞ ∞

Upper: E_R, activation energy for hopping to the right. Lower: E_L, activation energy for hopping to the left.

Table 4. Activation Energy for Hopping of an Adsorbate A at β Site ($x=\cdots, -2, 0, 2, \cdots$) Synthesized in Fig. 2

Distance of A and the left nearest adsorbate	Distance of A and the right nearest adsorbate		
	Over 2 sites	Just 2 sites	Just 1 site
Over 2 sites	$2RT$ $1RT$	$3.5RT$ $1RT$	∞ 0
Just 2 sites	$2RT$ $2.5RT$	$3.5RT$ $2.5RT$	∞ $1RT$
Just 1 site	$0.5RT$ ∞	$2RT$ ∞	∞ ∞

The upper and the lower are explained in Table 3.

Random numbers were generated for all 101 adsorbates. Scans were conducted not only from the left adsorbate to the right adsorbate, but also from the right to the left, and the average was taken so as to minimize any anomalous effects. The concentration was determined by dividing 10 by the length of each region where each bunch of 10 adsorbates existed. The coverage is the ratio of the number of adsorbates and the number of bond sites.

Results of Calculation and Discussion

Figure 3 shows the synthesized shapes of the "A–S and A–A" potentials of A and B in the case that B moves from the site at $x=2$ (β site) to the site at $x=1$ (α site) when A stays at the β site near $x=0$. Although different positions of A give different potential shapes of B, all of the potential shapes of B at $x=1.5$—2.5 form potential wells, which indicates that no matter where A is within $x=-0.5$—0.5, B requires a collision energy in order to move to the left α site. The activation energy of B is $1RT$—$2RT$. The most probable value is $2RT$, which is given when A is at $x=0.0$. The potential shape of A at $x=-1$—0.5 is greatly changed by a change in the position of B within $x=1.0$—2.0. When B is at $x=1.7$—2.0, the potential of A maintains a potential well

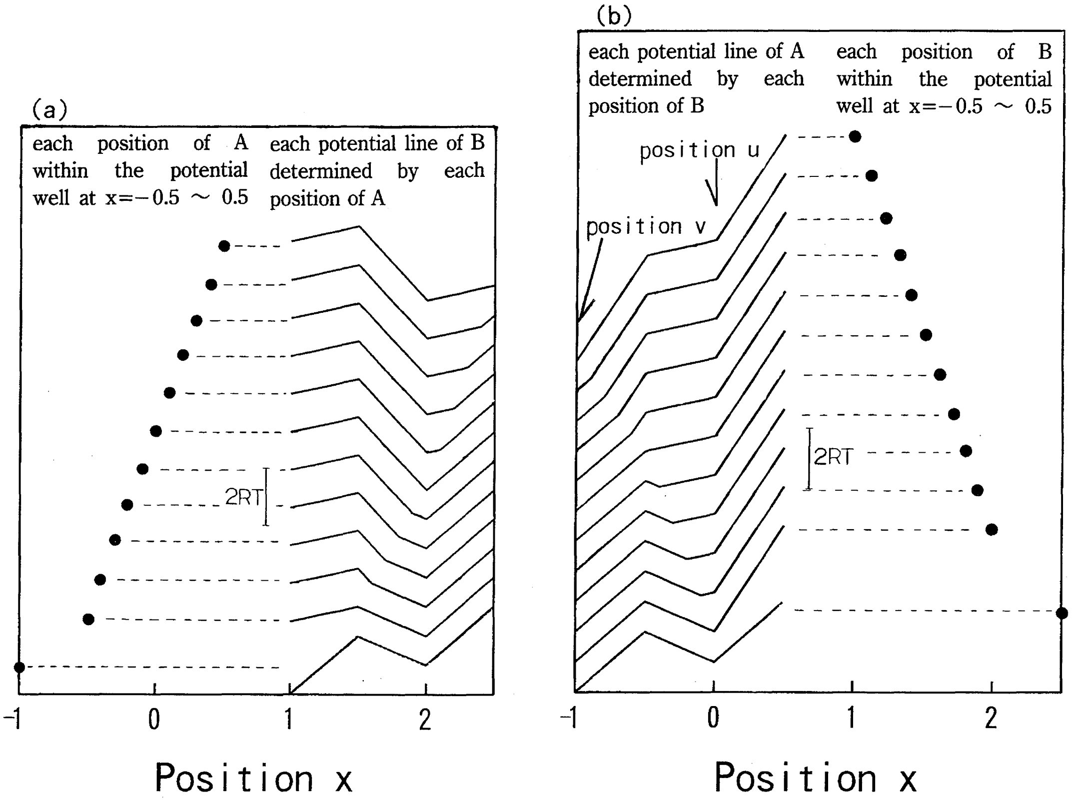

Fig. 3. The synthesized shapes of the "A–S and A–A" potentials of A and B. (a): the potential of B influenced by the position of A. (b): the potential of A influenced by the position of B.

at $x = -0.5$—0.5, of which the leftward barrier is 0.1*RT*—1.0*RT*. In contrast, when B is at $x = 1.0$—1.6, the potential shapes of A are not wells, but slopes going down in the left side. This indicates that when B migrates from $x = 2$ (α site) to $x = 1$ (β site) by overcoming the above-mentioned certain activation barrier, A at $x = 0$ (α site) loses the potential well and descends the new slope, finally attaining a β site ($x = -0.1$).

Figure 4 shows the time course of the coverage at $Q = 1.5RT$ (the case of the extinguishment of potential mountain) and at $Q = 0$ (the case of no lateral interaction). At the initial stage, the coverage of a region with 101 adsorbates at $x = -50$—50 is 100%. In Fig. 4, t, the index of time, is the value of the generating times of random numbers divided by the number of adsorbates. In the case of $Q = 0$, the diffusion significantly proceeds with increasing t from 0 to 100000, and the amount of diffusion in a plus region is almost the same as that in a minus region. Actually, the numbers of adsorbates in the plus ($x > 0$) and minus ($x < 0$) regions are 50, 50 at $t = 0$, 50, 50 at $t = 20000$, and 52, 49 at $t = 100000$, respectively. In contrast, in the case of $Q = 1.5RT$, adsorbates diffuse more in a minus region than in a plus region. The ac-

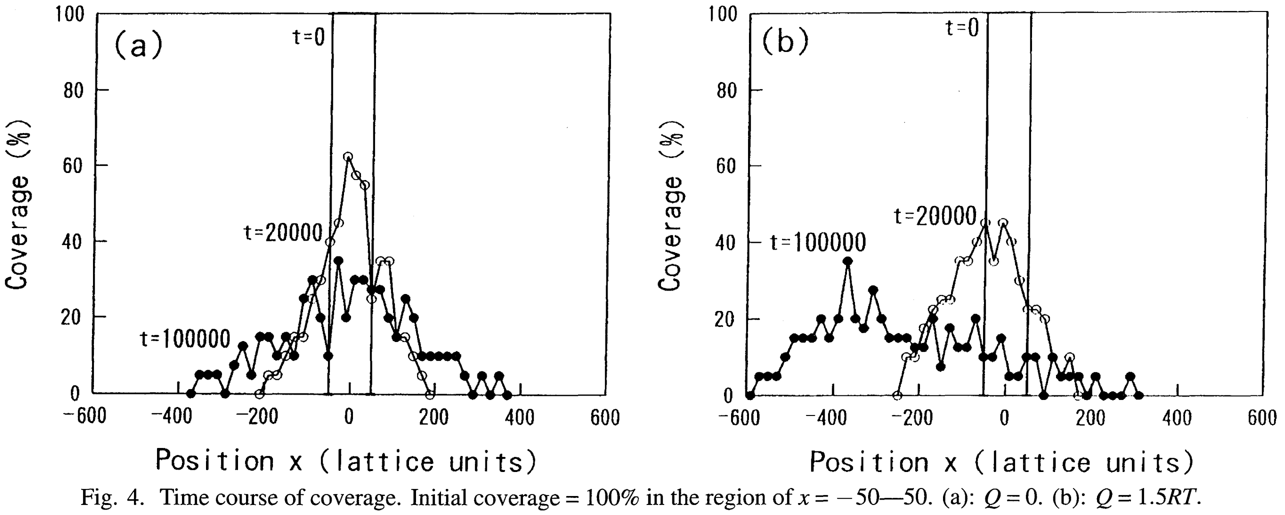

Fig. 4. Time course of coverage. Initial coverage = 100% in the region of $x = -50$—50. (a): $Q = 0$. (b): $Q = 1.5RT$.

tual numbers of adsorbates in the plus and minus regions are 32, 69 at $t = 20000$, and 13, 88 at $t = 100000$, respectively. We conducted more calculations to ascertain the asymmetric diffusion in Fig. 4(b). The conditions are case (a) $E_1 = 1.7RT$, $E_2 = 0.7RT$, $E_3 = 2.4RT$, $E_4 = 3.4RT$, and $Q = 1.5RT$, case (b) $E_1 = 2.2RT$, $E_2 = 1.2RT$, $E_3 = 1.7RT$, $E_4 = 2.7RT$, and $Q = 1.5RT$, case (c) $E_1 = 1.7RT$, $E_2 = 0.7RT$, $E_3 = 2.4RT$, $E_4 = 3.4RT$, and $Q = 0$, case (d) $E_1 = 2.2RT$, $E_2 = 1.2RT$, $E_3 = 1.7RT$, $E_4 = 2.7RT$, and $Q = 0$, respectivey. Cases (a) and (b) yield "an extinguishment of potential mountain", and cases (c) and (d) do not. The results are noted as the average position of the adsorbates (x_{av}) and the standard deviation of the distribution (σ) at $t = 20000$. (x_{av}, σ) in the cases of (a), (b), (c), and (d), were (−24.6, 78.3), (−49.2, 93.3), (3.0, 64.8), and (−0.3, 81.7), respectively. The average errors of x_{av} and σ were ± 4.3 and ± 3.4, respectively. These results also revealed that adsorbates with a strong lateral interaction move on the average in the minus direction, while those with no interaction are symmetric within the error, as can be seen in Fig. 4. Further, for a comparison, we conducted a calculation under the conditions that adsorbates are confined within $x = -50$—50. A random walk was conducted under the same conditions as those in Fig. 4(b) other than the A–S potential $= \infty$ at $x = -50.5$ and 50.5, and an initial coverage of 50%. The result was a constant coverage of 50% at any region within $x = -50$—50 at both $t = 20000$ and 100000. Thus, it was ascertained that no flux of adsorbates is generated in a closed system having no gradient of concentration at the edges of the region with adsorbates. The above results indicate that a driving force of the macroscopic diffusion in Fig. 4(b) is the gradient of the concentration, being the same as that of conventional diffusion. The theoretically discovered macroscopic asymmetry means that two fluxes in directions of ascending and descending the steps are different in the case of equal gradients of concentration. (x_{av}, σ) in Figs. 4(b) and 4(a) were (−45.7, 89.8) and (−1.2, 75.3), respectively. The distribution width of the adsorbates at $Q = 1.5RT$ was larger than that at $Q = 0$ due to that lateral repulsion accelerates diffusion at $Q = 1.5RT$. The difference was not large at both $t = 20000$ and 100000. The reason may be explained as follows. The actual repulsion between adsorbates, such as alkali metals on surfaces, is proportional to r^{-3} (r: a distance between two adsorbates).[8] In our calculations, we took the simple condition that the repulsive force is zero at and more than 2 sites. Thus, the repulsion's contribution to the diffusion is not large at a coverage of less than 50% (average adsorbate–adsorbate distance more than 2 sites). Another reason is probably that our hopping number of less than 10^5 is smaller than that at which the repulsion much influences the distribution width.

Figure 5 shows how the average position of each bunch of 10 adsorbates moves with time. The initial coverage of 101 adsorbates is 33.3% in the region $x = -150$—150. The two bunches at both edges diffuse outside during $T = 0$—30000; 8 bunches between both edges diffuse toward the minus region. The flux of the adsorbates is yielded. Asymmetric flow is not clearly seen in a region near to an edge with very low concentration. The difference means that the asymmetric flow depends on the concentration. The asymmetric flow is toward the minus direction, which is that of jumping the mountains of the A–S activation energy, E_2 and E_4. The direction coincides with that derived in the section Theory and Method of Calculation.

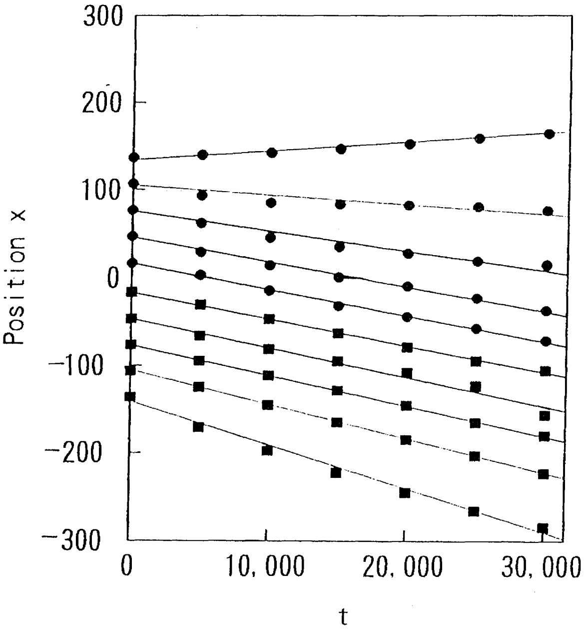

Fig. 5. Time course of the average position of each bunch. A bunch contains 10 adsorbates. The initial coverage of 101 adsorbates = 33.3% in the region of $x = -150$—150.

We examined the concentration dependency of asymmetric flow. We determined the average flux, $\Delta x/\Delta t$, of the middle 6 bunches at each initial coverage = 0.5—100% from the displacement of the average position of the bunches during $t = 0$—10000. The result is shown in Fig. 6. With increasing the coverage from 0.5% to about 30% the flux increases. With further increasing the coverage to more than about 30%, the flux decreases reversely. The flux has a maximum at about 30%, and greatly depends on the coverage. This suggests that there exists an average distance between the adsorbates at which the probability of the extinguishment of potential mountain becomes very large.

The adsorbates of which the diffusion have been examined on stepped surfaces so far[13—19] are those with no strong lateral interaction, such as CO, Pd, and Ag. These dipole moments are less than 1 D, leading to less than 1 kcal mol^{-1} at an adsorbate–adsorbate distance of 1 Å by a calculation of the dipole–dipole interaction. The activation energy for the diffusion of adsorbates on a transition metal is usually in the range of 1—50 kcal mol^{-1}. Therefore, these A–A and A–S potentials do not overlap. In the present theory, the overlap of the two values under restricted conditions leads to "a rupture of the activation energy in only one direction", yielding asymmetric diffusion. Alkali metals, alkali earth metals, or cyanide groups have strong effective charges or strong dipole moments on the surface.[8,20,21] Usually, an alkali metal on a transition metal has not covalent, but an ionic

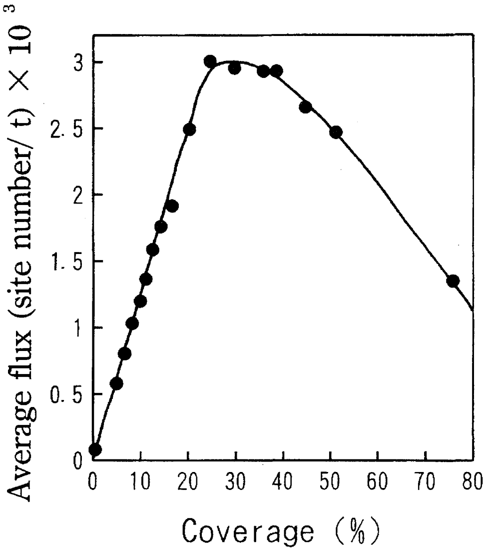

Fig. 6. Coverage dependency of the asymmetric flux. Average flux: a value of average displacement of the 6 bunches during t = 0—10000 divided by 10000.

character in a region of relatively low coverage, of which typical cases are Na and K/Ni (100).[22] The lateral potential energy at a distance of 1 Å on the surface is 330 kcal mol^{-1} at an effective ionic charge = 100%, 82 kcal mol^{-1} at 50%, and 3.3 kcal mol^{-1} at 10%, respectively. These values completely overlap the A–S activation energy for diffusion. In fact, in the diffusion of K on Pd (111) very rapid diffusion was recently observed,[5] which is considered due to a large effect of the lateral potential. So far, experiments concerning the diffusion of alkali metals on stepped surfaces have hardly been conducted. Experimental findings are greatly expected with a help of useful technique of surface-diffusion measurements.[23,24] Preparations for high concentrations of alkali metals on stepped surfaces in the experiments are not difficult: (1) exposure of a beam of alkali metal vapor on a part of the cleaned surface at low temperature through a pipe by heating a reservoir in a UHV system;[5,6,8] (2) the rise in temperature and a measurement of the diffusion at constant temperature. In our calculations we disregarded the following phenomena so as to concentrate on the subject of macroscopic asymmetry: (1) the compensation effect[3,24] between the activation energy and the pre-exponential factor of the surface diffusion coefficient; (2) the case of a variable A–S potential originating from the covalent properties[22] of alkali metal adsorbates on transition metals at much high concentrations. The theory can be applied to adsorbates on not only stepped surfaces, but also on walls of oriented materials, including an attractive A–A potential.

Finally, we discuss the physical basis and meaning of the phenomenon of asymmetry. At first, we discuss the principle that the potential controlling surface diffusion is the sum of the A–S and A–A potentials. The A–S potential acts on a bond of adsorbate and substrate, while the A–A potential usually acts on all parts of the adsorbate. Thus, the principle stands in the case that the conformation in an adsorbate is not changed at any coverage. It is effective for monoatomic adsorbates, such as alkali metals, transition metals, hydrogen, and sulfur. In the case of a strong repulsion on stepped surfaces, summing the A–S and A–A potentials results extinguishing the potential mountain in only one direction, because the slopes of the A–S potential mountains in the two right and left directions are not equal, due to a difference in the image force,[34] coordination number,[8] or other. The obtained diffusion system consists of a mixture of hops over potential mountains in two directions and the movement of sliding down the potential slopes without a mountain in only one direction. The former is the Arrhenius-type diffusion induced by a heat and reversible on the atomic scale. The latter is a non-thermal movement induced by an electrostatic force, and is irreversible. The reason for macroscopic asymmetry is that such an irreversible movement occurs in only one direction. The momentum of the asymmetrically diffused adsorbates is not conserved, because their average positions move in one direction. However, the entire momentum of the diffused adsorbates and the substrate is conserved as the adsorbates interact with the substrate.

Conclusions

Using random-walk model, we found an asymmetry of the migration probability of an adsorbate in opposite directions on ordered surfaces under no external fields. This is because "a rupture of the activation energy" can occur in only one direction in the case of adsorbates with a strong A–A potential on a surface with periodically repeated asymmetric A–S potential curves. By conducting a Monte-Carlo calculation of the random walk of adsorbates with a certain strong repulsive A–A potential on fcc (112) or bcc (013) model surface, we observed that the adsorbates diffuse more in a direction of jumping the minimum A–S activation energy, and the difference in flux of adsorbates in opposite directions greatly depends on the concentration.

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