

= Surface diffusion =

Surface diffusion is a general process involving the motion of adatoms, molecules, and atomic clusters (adparticles) at solid material surfaces. The process can generally be thought of in terms of particles jumping between adjacent adsorption sites on a surface, as in figure 1. Just as in bulk diffusion, this motion is typically a thermally promoted process with rates increasing with increasing temperature. Many systems display diffusion behavior that deviates from the conventional model of nearest neighbor jumps. Tunneling diffusion is a particularly interesting example of an unconventional mechanism wherein hydrogen has been shown to diffuse on clean metal surfaces via the quantum tunneling effect.

Various analytical tools may be used to elucidate surface diffusion mechanisms and rates, the most important of which are field ion microscopy and scanning tunneling microscopy. While in principle the process can occur on a variety of materials, most experiments are performed on crystalline metal surfaces. Due to experimental constraints most studies of surface diffusion are limited to well below the melting point of the substrate, and much has yet to be discovered regarding how these processes take place at higher temperatures.

Surface diffusion rates and mechanisms are affected by a variety of factors including the strength of the surface adparticle bond, orientation of the surface lattice, attraction and repulsion between surface species and chemical potential gradients. It is an important concept in surface phase formation, epitaxial growth, heterogeneous catalysis, and other topics in surface science. As such, the principles of surface diffusion are critical for the chemical production and semiconductor industries. Real world applications relying heavily on these phenomena include catalytic converters, integrated circuits used in electronic devices, and silver halide salts used in photographic film.

= = Kinetics = =

Surface diffusion kinetics can be thought of in terms of adatoms residing at adsorption sites on a 2D lattice, moving between adjacent (nearest neighbor) adsorption sites by a jumping process. The jump rate is characterized by an attempt frequency and a thermodynamic factor that dictates the probability of an attempt resulting in a successful jump. The attempt frequency ν is typically taken to be simply the vibrational frequency of the adatom, while the thermodynamic factor is a Boltzmann factor dependent on temperature and E_{diff} , the potential energy barrier to diffusion. Equation 1 describes the relationship:

<formula>

Where ν and E_{diff} are as described above, Γ is the jump or hopping rate, T is temperature, and k_B is the Boltzmann constant. E_{diff} must be smaller than the energy of desorption for diffusion to occur, otherwise desorption processes would dominate. Importantly, equation 1 tells us how very strongly the jump rate varies with temperature. The manner in which diffusion takes place is dependent on the relationship between E_{diff} and $k_B T$ as is given in the thermodynamic factor: when $E_{diff} < k_B T$ the thermodynamic factor approaches unity and E_{diff} ceases to be a meaningful barrier to diffusion. This case, known as mobile diffusion, is relatively uncommon and has only been observed in a few systems. For the phenomena described throughout this article, it is assumed that $E_{diff} \gg k_B T$ and therefore $\Gamma \ll \nu$. In the case of Fickian diffusion it is possible to extract both the ν and E_{diff} from an Arrhenius plot of the logarithm of the diffusion coefficient, D , versus $1/T$. For cases where more than one diffusion mechanism is present (see below), there may be more than one E_{diff} such that the relative distribution between the different processes would change with temperature.

Random walk statistics describe the mean squared displacement of diffusing species in terms of the number of jumps N and the distance per jump a . The number of successful jumps is simply Γ multiplied by the time allowed for diffusion, t . In the most basic model only nearest neighbor jumps are considered and a corresponds to the spacing between nearest neighbor adsorption sites. The root mean squared displacement goes as <formula> (eq. 2). The diffusion coefficient is

given as D
 $= \frac{a^2}{z}$ (eq . 3) , where $z =$