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⁶G. Bluman and S. Kumei, *J. Math. Phys.* **21**, 1019 (1980).⁷Equation (6) shows that the extensible distance coordinate $\hat{x} = \hat{x}(x, t)$ is an analog of a Lagrange coordinate in fluid dynamics [see, e.g., W. F. Ames, *Nonlinear Partial Differential Equations in Engineering* (Academic, New York, 1965), pp. 126-133].

Classical Stochastic Diffusion Theory for Desorption of Atoms and Molecules from Solid Surfaces

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A theory of desorption of atoms and molecules from solid surfaces based on a classical stochastic diffusion formulation is presented. A simple rate expression is obtained which has the form $R = (\Omega_0/2\pi) f(T) \exp(-D_e/kT)$, where Ω_0 is the surface-adsorbate vibrational frequency, $f(T) = 1$ for atoms, and for molecules $f(T)$ depends on the parameters for the frustrated rotations at the surface. This theory has been applied to the desorption of both atoms and molecules and excellent agreement with experiment is obtained.

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It is well established experimentally that the rate of first-order desorption of atoms and molecules from surfaces can be described by an Arrhenius expression $R = A \exp(-E/kT)$, where E is assumed to be closely related to the bond enthalpy. Such an expression is obtained from simple thermodynamic arguments applied to the transition state; however, it is difficult to quantify this theory since the transition complex for desorption is not easily identifiable. Although there is considerable disagreement between the experimentally derived preexponential factors for desorption of molecules,¹ most experimental results lead to preexponential factors much larger than expected from transition-state theory.

One would like to obtain the rate expression in terms of the microscopic properties (e.g., vibrational frequencies, bond energy, etc.) and dynamics of the adsorbate-surface system. Unfortunately, despite recent theoretical progress,² there is not as yet a theory capable of reproducing the experimental rates of desorption for atoms and molecules.

In the present paper we report such a theory based on a classical stochastic diffusion equation using a general form for the adsorbate-surface interaction. The result is the simple expression

$$R = (\Omega_0/2\pi) f(T) \exp(-D_e/kT), \quad (1a)$$

where Ω_0 is the characteristic frequency of the

adsorbate-surface interaction potential. D_e is the well depth of this interaction and $f(T)$ is given by

$$f_{\text{atom}}(T) = 1, \quad f_{\text{mol}}(T) = \frac{2\mu l^2 \Omega_\tau^2 \mathcal{S}_0^2}{\pi k T}. \quad (1b)$$

for atoms and molecules desorbing from the surface, respectively, where the quantities μ , l , Ω_τ , and \mathcal{S}_0 are related to the frustrated rotational motion at the surface (*vide infra*). The evaluation of this expression is straightforward, requiring only the basic parameters of the interaction potential between the adsorbed species and the surface. Equation (1) is valid for low coverages, where there is no interaction between the adparticles.

To obtain Eq. (1) consider first the motion of an adatom in the direction perpendicular to the surface and (following Adelman *et al.*³ and Tully⁴) define on the surface a set of primary zone atoms that are strongly interacting with the adatom. Without loss of generality, this primary zone can be considered to contain one surface atom, leading to a generalized Langevin equation of motion,

$$m_s \ddot{x}_s = - \frac{\partial V(x_{\text{ad}} - x_s)}{\partial x_s} - m_s \omega_0^2 x_s + m_s \int_0^t \Theta(t - \tau) x_s(\tau) d\tau + F(t). \quad (2)$$

Here x_{ad} and x_s are the coordinates of the adatom and surface atom, respectively, $V(x_{ad} - x_s)$ is the interaction potential between the adatom and the surface, $\Theta(t)$ is a memory kernel, and $F(t)$ is a random force. The last three terms in Eq. (2) represent the coupling between the surface atom and the rest of the crystal, which acts as a heat bath. The equation of motion for the adatom is

$$m_{ad} \ddot{x}_{ad} = \partial V(x_{ad} - x_s) / \partial x_{ad} . \quad (3)$$

We next take the Markovian limit of Eq. (2) and solve it formally (using the Laplace transform method^{3,4}) for x_s and substitute the result into Eq. (3). To do this we represent $V(x_{ad} - x_s)$ by a set of parabolic splines in which the value of the function and its first derivative are matched at the boundaries of the different intervals. After substituting x_s into Eq. (3) we take the Markovian limit to obtain a Langevin equation of motion for x_{ad} ,

$$m_{ad} \ddot{x}_{ad} = - \frac{\partial V(x_{ad})}{\partial x_{ad}} \left(1 - \frac{C}{m_s \Omega^2} \right) - m_{ad} \beta \dot{x}_{ad} + \bar{F}(t) , \quad (4)$$

in which both the friction coefficient and the effective frequency are functions of the distance from the surface. To calculate them we used the Debye model for the solid, leading to $\beta = C^2 \beta_{Debye} / m_{ad} m_s \Omega^4$ and $\Omega^2 = \Omega_{Debye}^2 + C / m_s$, where C is the curvature of the potential at the point where β and Ω are calculated. The friction coefficient β_{Debye} and the frequency Ω_{Debye} are given in terms of the Debye temperature of the substrate.^{3,4}

Following Kramers⁵ but generalizing to a potential appropriate for describing desorption, we solve for $W(x, u)$, the probability of finding the atom at a distance x with a velocity u , such that W is Maxwell-Boltzmann at the bottom of the well and goes to zero as $x \rightarrow \infty$. We then calculate the diffusion current density crossing a plane parallel to the surface at a distance x_0 from it, given by

$$j(x_0) = \int_{u_0}^{\infty} W(x_0, u) u du . \quad (5)$$

Care must be taken that the diffusion current at x_0 only includes those particles whose kinetic energy is large enough so that they can actually desorb. Thus, u_0 must satisfy the following relationship:

$$D_e = \bar{V}(x_0) + \frac{1}{2} m_{ad} u_0^2 , \quad (6)$$

where \bar{V} is the effective potential between the

adparticle and the surface modified by the motion of the surface atom [cf. the first term of Eq. (4)]. The rate of desorption is obtained by dividing $j(x_0)$ by the number of particles at the surface.⁵ This leads to Eq. (1) with $f(T) = 1$ for all values of β , Ω , and T which are of physical interest. Equation (6) implies that the expression for the rate of desorption is independent of x_0 .

In Fig. 1 we compare our results with the experimental values and with the calculations of De *et al.*² for the systems Xe (physisorption) and K (chemisorption) on W(111). For both systems we used the same parameters as De *et al.* As can be seen in Figs. 1(a) and 1(b) the agreement be-

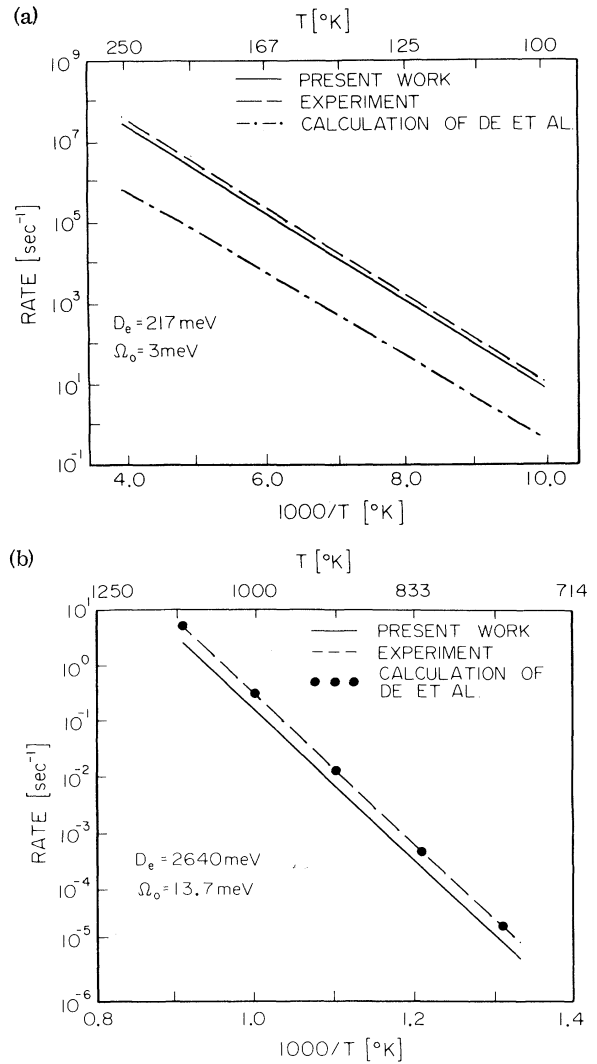


FIG. 1. (a) Rate of desorption of Xe on W(111). (b) Rate of desorption of K on W(111). The values of D_e and Ω_0 are the experimental values used by De *et al.* (Ref. 2).

tween our results and the experimental values is excellent for both systems.

In order to generalize the formalism to the case of molecular desorption we assume that the molecule can transform energy from the degrees of freedom corresponding to frustrated motions at the surface into translational kinetic energy. For definiteness we shall consider CO on Ni surfaces.¹ For this system the most important frustrated motion corresponds to the bending mode of the O atom about the Ni-C bond. To include this extra degree of freedom we followed the procedure outlined above for the case of atoms, but with W now a function of x , u , ϑ , and $\dot{\vartheta}$, where ϑ is the Ni-C-O angle, and $\dot{\vartheta} = d\vartheta/dt$. Equation (6) then takes the form

$$D_e = \frac{1}{2} \mu \Omega_r^2 l^2 \vartheta^2 + \frac{1}{2} \mu l^2 \dot{\vartheta}^2 + \bar{V}(x_0) + \frac{1}{2} m_{ad} u_0^2. \quad (7)$$

where μ is the reduced mass for the bending mode, Ω_r the vibrational frequency and l the corresponding distance (so that $\mu l^2 \Omega_r^2$ is the force constant of the frustrated rotation). This leads to Eq. (1) with the form of $f(T)$ described in (1b); ϑ_0 corresponds to the maximum angle of rotation (which we took to be equal to $\pi/2$).

Figure 2 compares our calculated results with the experimental values of Helms and Madix¹ for CO desorbing from Ni(110). We also show the rate of desorption that one obtains using Eq. (1) with $f(T) = 1$. The values of the parameters Ω_r , l , D_e , and Ω_0 were taken from Refs. 1 and 6.

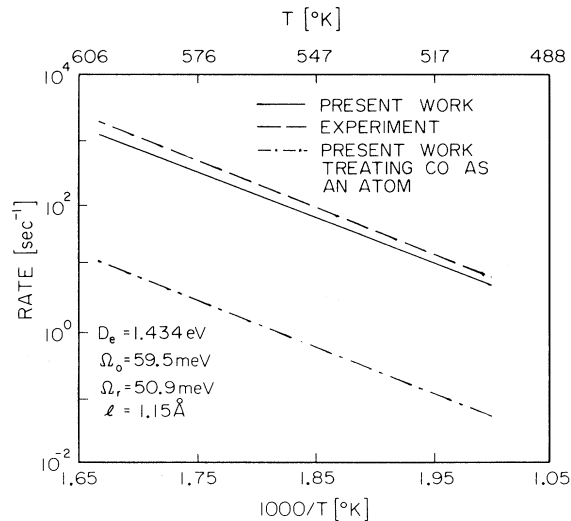


FIG. 2. Rate of desorption of CO on Ni(110). The experimental results are those of Helms and Madix (Ref. 1). The values of the parameters were taken from Refs. 1 and 6.

The excellent agreement between our results and the experimental data provides very strong evidence that the frustrated rotations of molecules at the surface are responsible for the large value of the preexponential factor ($\sim 10^{15}$) observed experimentally.

According to transition-state theory⁷ the preexponential factor is given by

$$A = (kT/h) f^*/f_{ad}, \quad (8)$$

where f^* and f_{ad} are the partition functions of the transition state and the adsorbate layer, respectively. In the case of atomic desorption f^*/f_{ad} is usually taken as 1, leading to a preexponential factor which is proportional to kT . In the present work the corresponding preexponential factor, $\Omega_0/2\pi$, is directly related to the interaction between the atom and the surface. The experimental preexponential factors differ by about an order of magnitude between chemisorbed and physisorbed atoms. This reflects the fact that Ω_0 changes by an order of magnitude also. Equation (8) fits the observed rates because the experimental temperature ranges also increase by an order of magnitude between the physisorbed and chemisorbed atomic systems. For the case of molecules Pinür *et al.*¹ give an expression for f^*/f_{ad} assuming that the molecule is immobile at the surface and that it is a free rotor in the transition state. Their expression for the preexponential factor leads to a different temperature dependence than the $1/kT$ that we find.

To our knowledge this is the first theoretical calculation that presents a consistent explanation of the rates of desorption of atoms and molecules from surfaces. We believe that it provides a very useful tool for the prediction of rates of desorption of atoms and molecules since it involves only microscopic parameters which can be experimentally determined.

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Evidence for Coupling of Velocity and Composition Fluctuations in a Binary Liquid Mixture

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A critical mixture of isobutyric acid and water was quenched from the one-phase region into the two-phase region and, after the spinodal ring was well developed, a reverse quench returned the system to the one-phase region. Light-scattering measurements for this process exhibit a clearly nondiffusive relaxation which, at least for early times after the quench reversal, is in good agreement with Ruiz's scheme for the coupling of velocity and composition fluctuations.

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In a recent series of papers Ruiz and Nelson^{1,2} have discussed the properties of "active" turbulent mixing of two fluids; i.e., mixing which is observably affected by coupling between velocity and composition fluctuations. As a simple special case of velocity-composition coupling, Ruiz³ has performed an approximate calculation for the behavior of the relaxation of very large composition fluctuations under conditions where the mass diffusion coefficient, D , becomes sufficiently small that active coupling to the velocity field can compete with diffusive relaxation.

In this Letter we report the results of an experiment designed to look for active coupling effects near the critical point in a binary fluid mixture. In each measurement a critical mixture of isobutyric acid and water, initially at equilibrium at temperature T_1 in the one-phase region, was quenched to temperature T_2 in the two-phase region (at time $t = -t_0$), allowed to remain at T_2 until the spinodal light scattering maximum reached a wave number $k_m \sim 2000 \text{ cm}^{-1}$, and then abruptly returned to T_1 (at time $t = 0$). Under these circumstances, Ruiz's primary prediction³ is that

$$\ln k_m(t) = \frac{1}{2} \ln \frac{A}{2D} + \frac{\alpha}{2D\nu} C_{\text{tot}}(t), \quad (1)$$

where $k_m(t)$ is the time-dependent wave number of the maximum in the light-scattering angular distribution, A is a constant of the motion, $t = 0$ is the time of return to the one-phase region, ν is the kinematic viscosity, and α is the coefficient of the composition-gradient-squared term in the Landau-Ginzburg Hamiltonian. $C_{\text{tot}}(t)$ is the global strength of the concentration fluctuations, $\psi_{\vec{k}}(t)$; i.e.,

$$C_{\text{tot}}(t) \equiv \frac{1}{2} \int \frac{d^3k}{(2\pi)^3} \langle |\psi_{\vec{k}}(t)|^2 \rangle.$$

A quantitative test of Ruiz's prediction requires a good estimate of the parameter $R \equiv \alpha C_{\text{tot}}(t=0) / 2D\nu$. One renormalization-group calculation,⁴ which uses an Ornstein-Zernike form for the susceptibility of the order parameter, gives $R = B(\epsilon_2/\epsilon_1)^{2\beta}$ where B is of order unity, $\epsilon_2 = (T_c - T_2)/T_c$, $\epsilon_1 = (T_1 - T_c)/T_c$, and $\beta \approx \frac{2}{3}$. This result is readily obtained on use of $\alpha = \epsilon^2/\chi\rho$, where ρ is the mass density and χ is the order-parameter susceptibility. Taking $\chi \approx \epsilon^{-\gamma}/k_B T$, $D(T_1) = k_B T / 6\pi\nu\rho \xi(T_1)$ [where the correlation length $\xi(T) = (3.57 \text{ \AA}) \epsilon^{-0.613}$ for isobutyric acid + water],⁵ $C_{\text{tot}}(t=0) \approx \epsilon_2^{2\beta}$, and $\nu = 2\beta$ gives $B = 3\pi$. An alternative renormalization-group calculation⁶ of R yields a result which is similar in temperature dependence and in order of magnitude,