

## Kinetic lattice-gas model: Time-dependent generalization of the grand-canonical ensemble

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The kinetic lattice-gas model for an open system of adsorbed particles is used to derive a hierarchy of coupled equations that represent a time-dependent generalization of the grand-canonical ensemble. This formulation is particularly useful to describe adsorption, desorption, and diffusion in inhomogeneous systems, such as adsorbates with attractive lateral interactions within the coexistence regime.

### I. INTRODUCTION

Adsorbates with attractive lateral interactions exhibit coexistence of dilute and dense phases below the critical point. Such systems can be described by an adaptation of the lattice-gas model to adsorption phenomena in which one assumes that adsorption of gas particles on the surface of a solid takes place at localized adsorption sites. One assigns occupation numbers  $n_i = 1$  or 0 depending on whether a particle is adsorbed on site  $i$  or not. For systems in which nearest-neighbor interactions dominate, the Hamiltonian is given by<sup>1</sup>

$$H = E_s \sum_i n_i + \frac{1}{2} V_2 \sum_{i,j} n_i n_j . \quad (1)$$

To arrive at this Hamiltonian, one must average over the degrees of freedom associated with the motion of the adsorbed particle in its surface-potential well. One can then identify the single-particle energy in (1) as<sup>2</sup>

$$E_s = -V_0 - k_B T \ln(q_s q_{\text{int}}) . \quad (2)$$

Here  $-V_0$  is the depth of the surface potential;  $q_s$  is the single-particle partition function for the center of mass of an adsorbed particle, i.e.,

$$q_s = q_z q_{xy} , \quad (3)$$

where

$$q_z = \exp(h v_z / 2k_B T) / [\exp(h v_z / k_B T) - 1] \quad (4)$$

is its component for the motion perpendicular to the surface. Likewise,  $q_{xy}$  is the partition function for the motion parallel to the surface, and  $q_{\text{int}}$  accounts for the internal degrees of freedom of a molecule, i.e., for its vibrations and frustrated rotations.

Although we are primarily concerned in this paper with the time evolution in such systems, it is worthwhile to briefly discuss the approaches for the calculation of their equilibrium properties, as related problems will show up in their nonequilibrium statistical mechanics. To evaluate the equilibrium properties of a system controlled by (1), we can employ the canonical ensemble by imposing the condition that the number of particles in the adsorbate is fixed, i.e., that

$$\sum_i n_i = N . \quad (5)$$

Thus the first term in (1) does not depend on the microstates, yet it should not be dropped, as its  $T$  dependence is important for thermodynamic properties. The canonical partition function is given as usual by

$$Z_N = \sum_{\mathbf{n}(N)} \exp\{-H[\mathbf{n}(N)]/k_B T\} , \quad (6)$$

where the sum extends over all microstates  $\mathbf{n}(N) = (n_1, n_2, \dots, n_s)$  satisfying (5). The chemical potential is calculated from the Helmholtz free energy

$$F(T, N, N_s) = -k_B T \ln Z_N \quad (7)$$

as

$$\mu_a = \left[ \frac{\partial F}{\partial N} \right]_{T, N_s} . \quad (8)$$

To get the isotherms or isobars we then observe that in equilibrium the chemical potential of the adsorbate must be equal to that of the gas phase above the surface given by

$$\exp(\mu_g / k_B T) = \lambda_{\text{th}}^3 (P / k_B T) Z_{\text{int}}^{-1} , \quad (9)$$

where

$$\lambda_{\text{th}} = h / (2\pi m k_B T)^{1/2} \quad (10)$$

and  $Z_{\text{int}}$  is the internal partition function for vibrations and rotations if the particles under consideration are molecules. As long as the partition function is evaluated exactly, it does not matter in which ensemble one works. However, if approximations are invoked, such as mean-field theory, the inherent assumption of homogeneity introduces unphysical features in the canonical ensemble such as van der Waals loops in the isotherms of adsorbates with attractive interactions. This is discussed at length by Hill,<sup>3</sup> who also points out that, to avoid such artifacts, it is better to work in the grand-canonical ensemble. Before we enter into that discussion, we would like to point out that the van der Waals loop can be the starting point of a model of metastability, albeit rather a crude one due to the fact that mean-field theory does not give a satisfactory description of critical phenomena. One has therefore resorted to the construction of restricted ensembles, valid around the local minima of the metastable states, in which one defines, e.g., clusters of parti-

cles, restricting each cluster to a maximum size.<sup>4</sup>

The grand-canonical partition function is given by

$$\Xi = \sum_{\mathbf{n}} \exp \left[ - \left[ H(\mathbf{n}) - \mu \sum_i n_i \right] / k_B T \right], \quad (11)$$

where the sum is taken over all microstates  $\mathbf{n}$ . Note that (11) can also be written in the familiar form as

$$\Xi = \sum_{N=0}^{N_s} \lambda^N \sum_{\mathbf{n}(N)} \exp[-H(\mathbf{n})/k_B T] = \sum_{N=0}^{N_s} Z_N \lambda^N, \quad (12)$$

where

$$\lambda = \exp(\mu/k_B T) \quad (13)$$

is the fugacity. We can then calculate the average coverage as

$$\theta = \bar{N}/N_s = k_B T N_s^{-1} \partial \ln \Xi / \partial \mu = N_s^{-1} \sum_N N P_0(N), \quad (14)$$

where

$$P_0(N) = \lambda^N \sum_{\mathbf{n}(N)} \exp[-H(\mathbf{n})/k_B T] / \Xi \quad (15)$$

is the probability that a system of  $N$  particles is realized at a given temperature and pressure. We note that within the coexistence region of an adsorbate with attractive interactions,  $P_0(N)$  will exhibit two peaks characterizing the densities of the coexisting dilute and dense phases even if  $Z_N$  is evaluated in some approximation, such as mean field. It is therefore suggestive that a generalization of (15) to a time-dependent probability function is a good starting point for a kinetic theory of adsorption, desorption, and diffusion on surfaces, in particular for inhomogeneous adsorbates, e.g., in the two-phase regime. In this paper we will follow this approach.

In the next section we will start with formulating the master equation that controls adsorption, desorption, and diffusion, and then discuss earlier attempts at solving it either by straightforward Monte Carlo techniques or by deriving, and suitably truncating, a hierarchy of equations of motion for correlation functions. In Sec. III we

will then advance our approach based on a nonequilibrium generalization of the grand-canonical ensemble, which is followed in Sec. IV by a discussion of possible approximation schemes. In Sec. V we summarize our discussion and point out the work ahead.

## II. MASTER EQUATION

To set up a theory of time-dependent phenomena on surfaces, we assume that the relevant processes, such as adsorption, desorption, and diffusion, are Markovian. We define the probability  $P(\mathbf{n}; t)$  that the microstate  $\mathbf{n}$  is realized at time  $t$ . It satisfies a master equation<sup>5-7</sup>

$$dP(\mathbf{n}; t)/dt = \sum_{\mathbf{n}'} [W(\mathbf{n}; \mathbf{n}')P(\mathbf{n}'; t) - W(\mathbf{n}'; \mathbf{n})P(\mathbf{n}; t)], \quad (16)$$

where  $W(\mathbf{n}'; \mathbf{n})$  is the probability per unit time that the system undergoes a transition from a microstate  $\mathbf{n}$  to  $\mathbf{n}'$ . In principle, it should be calculated from a Hamiltonian that includes, in addition to the terms in (1), the coupling of adsorbed particles to the vibrational and electronic degrees of freedom of the substrate. This has been done for phonon-mediated adsorption and desorption of physisorbed particles.<sup>8</sup> Following a heuristic approach, we have recently examined a number of choices<sup>2</sup> for  $W(\mathbf{n}'; \mathbf{n})$ , all subject to the demands of detailed balance:

$$W(\mathbf{n}; \mathbf{n}')P_0(\mathbf{n}') = W(\mathbf{n}'; \mathbf{n})P_0(\mathbf{n}). \quad (17)$$

Assuming that the residence time of an adsorbed particle in an adsorption site is much longer than the transition time into or out of that site, we can write  $W(\mathbf{n}'; \mathbf{n})$  as a sum of terms accounting for individual processes of adsorption, desorption, and diffusion, i.e.,

$$W(\mathbf{n}'; \mathbf{n}) = W_{a-d}(\mathbf{n}'; \mathbf{n}) + W_{\text{dif}}(\mathbf{n}'; \mathbf{n}). \quad (18)$$

The simplest choice is what we have termed Langmuir kinetics,<sup>2</sup> for which we assume that adsorption into a site  $i$  takes place provided that site is empty, irrespective of whether neighboring sites are occupied. We then get

$$W_{a-d}(\mathbf{n}'; \mathbf{n}) = W_0 \sum_i \left[ 1 - n_i + C_0 n_i \left( 1 + C_1 \sum_a n_{i+a} + C_2 \sum_{a,a'} n_{i+a} n_{i+a'} + \dots \right) \right] \delta(n'_i, 1 - n_i) \prod_{l \neq i} \delta(n'_l, n_l), \quad (19)$$

where  $a$  and  $a'$  enumerate the neighbors of site  $i$ . Similarly, we write for diffusion

$$W_{\text{dig}}(\mathbf{n}'; \mathbf{n}) = J_0 \sum_{i,a} n_i (1 - n_{i+a}) \left[ 1 + C_1 \sum_{b \neq a} n_{i+b} + \dots \right] \delta(n'_i, 1 - n_i) \delta(n'_{i+a}, 1 - n_{i+a}) \prod_{l \neq i, i+a} \delta(n'_l, n_l), \quad (20)$$

where

$$C_0 = \exp(E_s/k_B T), \quad (21)$$

$$C_r = [\exp(V_2/k_B T) - 1]^r. \quad (22)$$

Langmuir kinetics, in particular, results in a sticking coefficient

$$S(\theta) = S_0(1 - \theta). \quad (23)$$

Other choices and their physical or unphysical implications have been discussed in Ref. 2. As long as the master equation (16) is used in Monte Carlo simulations solely to determine the equilibrium properties of the system, it does not matter what choices are made for the transition probabilities  $W(\mathbf{n}'; \mathbf{n})$  as long as they satisfy detailed balance (17). However, if we are interested in the adsorption, desorption, and diffusion kinetics of a particular physical system, the choice of transition probabilities

$W(\mathbf{n}';\mathbf{n})$  is rather narrowed as discussed in Ref. 2. We adopt the choices (19)–(22) in the subsequent discussion, leaving the specification of the rate constants  $W_0$  and  $J_0$  till later.

To solve the master equation (16), Monte Carlo techniques have been invoked as reviewed in Refs. 9–11. The renormalization group has also been used successfully.<sup>12,13</sup> Likewise, one can derive a hierarchy of coupled equations of motion for average occupations and correlation functions.<sup>2,5,14–17</sup> To this end we define

$$\langle n_i \rangle = \sum_{\mathbf{n}} n_i P(\mathbf{n}; t), \quad (24)$$

$$\langle n_i n_j \rangle = \sum_{\mathbf{n}} n_i n_j P(\mathbf{n}; t), \quad (25)$$

$$\langle n_i n_j \cdots n_m \rangle = \langle n_i n_j \rangle \langle n_j n_k \rangle \cdots \langle n_i n_m \rangle / \langle n_i \rangle \langle n_j \rangle \langle n_k \rangle \cdots \langle n_m \rangle, \quad (27)$$

or similar closures at the level of triple or higher correlations. This leaves us with  $N_s$  equations for the average occupation functions and yet more equations for correlation functions. To reduce this set further, one then assumes homogeneity in the adsorbate, so that the average occupation functions are all equal to the coverage, i.e.,

$$\langle n_i \rangle = \theta \quad (28)$$

for all sites  $i$ . In the simplest (Kirkwood) approximation, one thus is left with two coupled equations for  $\theta$  and for the average correlation function

$$\psi = \langle n_i n_{i+a} \rangle. \quad (29)$$

They read for a square lattice

$$d\theta/dt = W_0[1 - \theta - C_0\theta(1 + C_1\psi/\theta)^4], \quad (30)$$

$$d\psi/dt = 2W_0[\theta - \psi - C_0(C_1 + 1)\psi(1 + C_1\psi/\theta)^3] - 2J_0(1 + C_1\psi/\theta)^2[3(C_1 + 1)\psi(1 - \psi/\theta) + (\psi^2/\theta - \theta^2)(1 + C_1\psi/\theta) - 2\theta^2 + 2(1 - C_1)\psi^2/\theta + 2C_1\psi^4/\theta^4] \quad (31)$$

We note that the equilibrium solution of these equations yields, at least in the absence of the diffusional terms, the quasichemical approximation to the isotherms, i.e., a van der Waals loop in the coexistence region. This is not surprising because the assumption of homogeneity is clearly not justified here. In a similar vein, the time-dependent equations give a reasonable description of adsorption and desorption phenomena for repulsive interactions and above the critical point for attractive interactions.

We stress again that for systems with attractive lateral interactions that exhibit coexistence of two phases below the critical point, the set of equations of motion for correlation functions (26), etc., is not very practical because the inhomogeneity of such systems forces one to consider the site dependence of these functions, preempting the use of the simplifying assumption of homogeneity. One way out of this difficulty is to define physical clusters of particles and derive equations of motion for their time evolution; e.g., we can define the probability to find single-particle clusters on the surface at time  $t$  as

$$p_1(t) = N_s^{-1} \sum_i \sum_{\mathbf{n}} n_i \prod_a (1 - n_{i+a}) P(\mathbf{n}; t), \quad (32)$$

and the probability to find dimers as

and obtained from (16)

$$d\langle n_i \rangle / dt = W_0(1 - \langle n_i \rangle) - W_0 C_0 \left[ \langle n_i \rangle + C_1 \sum_a \langle n_i n_{i+a} \rangle + \cdots \right], \quad (26)$$

and similar equations for the higher-order correlation functions. This hierarchy is obviously exact. To solve it, approximations must be invoked; in particular, the hierarchy must be truncated, e.g., by invoking the Kirkwood closure approximation, which states that

$$p_2(t) = N_s^{-1} \sum_{i,a} \sum_{\mathbf{n}} n_i n_{i+a} \prod_{a' (\neq a)} (1 - n_{i+a'}) \times (1 - n_{i+a-a'}) P(\mathbf{n}; t). \quad (33)$$

Obviously it becomes increasingly more difficult to define probability functions for clusters of many particles due to the fact that an exact theory should also take their shapes into account. Such a theory is very much akin to cluster theories of nucleation;<sup>4,11,18,19</sup> see, e.g., Zinsmeister's adaptation<sup>20,21</sup> of the Becker-Döring theory<sup>22</sup> to surface kinetics.<sup>23–26</sup>

### III. TIME-DEPENDENT GRAND-CANONICAL ENSEMBLE

To describe time-dependent phenomena in two-phase adsorbates, we now reformulate the theory in terms of the time-dependent generalization of (15). It is obtained as

$$P(N;t) = \sum_{\mathbf{n}(N)} P(\mathbf{n}; t), \quad (34)$$

where the sum is again over all microstates  $\mathbf{n}$  satisfying (5). Its equation of motion is obtained from (16). In the

absence of interactions, i.e.,  $V_2=0$ , it reads for  $N=0,1,\dots,N_s$

$$dP(N;t)/dt = g(N-1)P(N-1;t) - r_0(N)P(N;t) - g(N)P(N;t) + r_0(N+1)P(N+1;t), \quad (35)$$

where

$$g(N) = W_0(N_s - N), \quad (36)$$

$$r_0(N) = W_0 C_0 N, \quad (37)$$

$$g(-1) = g(N_s) = r_0(0) = r_0(N_s + 1) = 0. \quad (38)$$

This is the master equation for a "birth and death" or linear one-step process, as discussed at length by van Kampen.<sup>7</sup> To interpret this set of equations we adopt Landau's picture of the grand-canonical ensemble to the present situation of the time evolution of an adsorbate. We imagine that the surface of the solid is subdivided into a large number of subsystems, each of which is still of macroscopic size.  $P(N;t)$  then gives the probability that at time  $t$  one of these subsystems has  $N$  particles. Alternately, we can interpret  $P(N;t)$  as the fraction of the surface with a homogeneous coverage  $N/N_s$ . The probability of finding a system with  $N$  particles then increases in time according to (35) because a particle adsorbs into a system with  $N-1$  particles (first term) or

desorbs from a system with  $N+1$  particles (fourth term). The probability to find  $N$  particles in a subsystem decreases because a particle desorbs (second term) or adsorbs (third term).

We note that the equilibrium solution of (35), properly normalized, is given by

$$P_0(N) = C_0^{-N} \frac{N_s!}{N!(N_s - N)!} (1 + C_0^{-1})^{-N_s}, \quad (39)$$

in agreement with (15).

To obtain the rate equation for the coverage, we multiply (35) with  $N/N_s$  and sum over all  $N$  to get

$$d\theta/dt = W_0(1 - \theta + C_0\theta). \quad (40)$$

This allows us the identification<sup>2</sup>

$$W_0 = S_0 a_s P(2\pi m k_B T)^{-1/2}, \quad (41)$$

where  $S_0$  is the sticking coefficient at zero coverage,  $a_s$  is the area of an adsorption cell, and  $P$  is the pressure of the gas phase above the surface at temperature  $T$ . With (21) we thus get the desorption rate constant

$$W_0 C_0 = S_0 a_s (k_B T / h \lambda_{th}^2) q_s^{-1} \times (Z_{int} / q_{int}) \exp(-V_0 / k_B T). \quad (42)$$

In the presence of nearest-neighbor interactions, the transition probabilities (19) and (20) lead to a modification of the equations (35), namely

$$dP(N;t)/dt = g(N-1)P(N-1;t) - W_0 C_0 [NP(N;t) + C_1 P_{2n}(N;t) + C_2 P_{3n}(N;t) + \dots] - g(N)P(N;t) + W_0 C_0 [(N+1)P(N+1;t) + C_1 P_{2n}(N+1;t) + C_2 P_{3n}(N+1;t) + \dots], \quad (43)$$

where we defined correlation functions

$$P_{2n}(N;t) = \sum_{i,a} \sum_{n(N)} n_i n_{i+a} P(\mathbf{n};t), \quad (44)$$

$$P_{3n}(N;t) = \sum_{i,a} \sum_{a'(\neq a)} \sum_{n(N)} n_i n_{i+a} n_{i+a'} P(\mathbf{n};t). \quad (45)$$

These functions are subject to equations similar to (43), generating an exact hierarchy, equivalent in its contents to (26), etc.; e.g., we get

$$dP_{2n}(N;t)/dt = S_a(N-1) - S_d(N) - S'_d(N) + S'_d(N+1) + S_{dir}(N), \quad (46)$$

where the adsorption terms are given by

$$S_a(N-1) = W_0 [2c(N-1)P(N-1;t) + (N_s - N - 1)P_{2n}(N-1;t)], \quad (47)$$

$$S'_d(N) = W_0(N_s - N)P_{2n}(N;t),$$

with  $c$  being the coordination number of the two-dimensional lattice. For the desorption terms we get

$$S_d(N) = W_0 C_0 \left[ NP_{2n}(N;t) + C_1 \sum_{n(N)} \sum_{i,a} n_i n_{i+a} \sum_{j,b} n_j n_{j+b} P(\mathbf{n};t) + \dots \right], \quad (48)$$

$$S'_d(N+1) = W_0 C_0 \left[ (N-1)P_{2n}(N+1;t) - 2C_1 P_{3n}(N+1;t) - 2C_1 P_{2n}(N+1;t) + C_1 \sum_{n(N+1)} \sum_{i,a} n_i n_{i+a} \sum_{j,b} n_j n_{j+b} P(\mathbf{n};t) + \dots \right],$$

and for the diffusion term

$$S_{\text{dif}}(N) = 2J_0 [cN(N-1)P(N;t) - N_s(C_1+1)P_{2n}(N;t) + \dots], \quad (49)$$

where terms involving higher-order correlations have been omitted. Note that the diffusional part of the transition probabilities (20) does not appear in (43) because hopping across the surface does not change the coverage. Diffusion, however, affects the correlation functions.

In closing, we note that in equilibrium there is a simple relation for the nearest-neighbor correlation function, namely

$$P_{2n}^0(N) = -2k_B T \partial \ln(Z_N) / \partial V_2. \quad (50)$$

Such relations might be useful in finding truncation schemes for the hierarchy of equations. In particular, for noninteracting particles in equilibrium we get

$$P_{2n}^0 = c [N(N-1)/N_s] P_0(N), \quad (51)$$

where  $c$  is the number of nearest neighbors.

#### IV. APPROXIMATIONS

To use the equations of motion for  $P(N;t)$  and the correlation functions, we need a truncation scheme expressing higher-order correlations in terms of lower ones, similar to Eq. (27). In our first such attempt we will reduce the theory to involve  $P(N;t)$  only. This is most easily done by starting at the very beginning, i.e., with the conditions of detailed balance (17). In such a procedure we have to specify an approximation equilibrium distribution, which we take for simplicity to be given by the Bragg-Williams (BW) or mean-field approximation, i.e.,<sup>3</sup>

$$P_0(N) = A \binom{N_s}{N} C_0^{-N} \exp(-cV_2 N^2 / 2k_B T N_s), \quad (52)$$

where

$$A^{-1} = \sum_N \binom{N_s}{N} C_0^{-N} \exp(-cV_2 N^2 / 2k_B T N_s). \quad (53)$$

Inserted into (17) and assuming that adsorption proceeds with a constant sticking coefficient, the adsorption term is given by the constant (41), i.e.,

$$W_{\text{ad}}(N+1, N) = W_0, \quad (54)$$

and the desorption term reads

$$W_{\text{des}}(N-1, N) = W_0 C_0 N / (N_s - N + 1) \times \exp[(N - \frac{1}{2})cV_2 / k_B T N_s]. \quad (55)$$

We have made the assumption of a constant sticking coefficient, rather than one linearly decreasing as in (23), because of its appropriateness for many adsorption systems, such as metals on metals, for which it is also known experimentally that desorption is a zeroth-order process within the coexistence region,<sup>27-29</sup> a point to which we will return shortly.

The master equation now reads

$$dP(N;t)/dt = W_0 P(N-1;t) - r^{\text{BW}}(N) P(N;t) - W_0 P(N;t) + r^{\text{BW}}(N+1) P(N+1;t), \quad (56)$$

where

$$r^{\text{BW}}(N) = W_0 C_0 N / (N_s - N + 1) \times \exp[-(N - \frac{1}{2})cV_2 / k_B T N_s]. \quad (57)$$

A similar set of equations has been used for the discussion of the kinetics of magnetic phase transitions within the mean-field theory of Weiss.<sup>5,30</sup>

Before we present numerical examples, we would like to briefly discuss the relevance of (56). It can certainly serve as a model for the kinetics of systems that undergo phase transitions. However, its physical significance is rather limited due to the fact that diffusion has completely dropped out of the theory. We know, however, that in most adsorption systems diffusion rates are typically much faster than desorption rates; i.e., if we write the diffusion rate constant in the Arrhenius form

$$J_0 = v_{\text{dif}} \exp(-Q/k_B T), \quad (58)$$

then one typically finds that the activation barrier for diffusion  $Q$  is about a fifth of the surface binding energy  $V_0$  with prefactors being comparable. Exceptions are weakly bound physisorbed systems such as the lighter rare gases on metals, where diffusion and desorption occur on similar time scales at desorption temperatures. Another class of systems where diffusion might in fact be totally inoperative due to steric hindrance are monolayer films of large organic molecules.

We have used (56) to study desorption kinetics. Thus we assume that initially an adsorbate is present with coverage  $\theta_0 = \theta(t=0)$  maintained at temperature  $T$ . For times  $t > 0$  we drop the adsorption terms in (56) by reducing the pressure significantly by rapid pumping, and calculate the isothermal desorption rate as

$$d\theta/dt = - \sum_N r(N) P(N;t). \quad (59)$$

We have evaluated (59) for a typical system for temperatures below critical starting from various initial coverages above and within the coexistence region. In Fig. 1 we plot the isothermal desorption rate as a function of the remaining coverage. It should not be surprising that the rate depends strongly on the initial coverage because, in the absence of diffusion, desorption evolves far from local equilibrium. This is also demonstrated in Figs. 2 and 3, where we plot the time evolution of  $P(N;t)$ , depicted not as a function of time, but of the coverage  $\theta(t)$  remaining at time  $t$ . Note that we have excluded  $P(N=0;t)$  from these plots, as this function increases in a trivial way by accumulating all desorbing particles. Starting in Fig. 2 from an initial coverage of 0.5,  $P(N;t=0)$  exhibits the two-peak structure typical for the coexistence region. As time evolves, particles desorb first from the dense phase. In addition, some particles from the dense phase are also

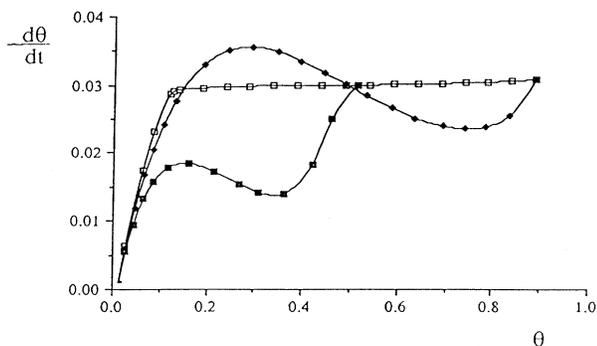


FIG. 1. Isothermal desorption for a system with parameters  $V_0 = 3200$  K,  $cV_2 = -375$  K,  $v_z = v_x = v_y = 10^{12}$  s $^{-1}$ ,  $S_0 = 1.0$ . Open squares calculated for the mean-field model, (59) and (56). Closed squares for the quasiequilibrium model (64) for two different initial coverages.

transferred to the dilute phase, as evidenced by the fact that the peak for small  $N$  initially increases. This, however, does not persist for all coverages in the coexistence region. Rather, the dilute phase desorbs quickly with the remaining coverage (all in the dense phase) following more slowly along the diagonal ridge in Fig. 2. Starting from a higher initial coverage, Fig. 3, these features are dramatized even more. These examples are for a surface with  $N_s = 200$  adsorption sites. For larger  $N_s$  all features become narrower.

In closing the discussion of (56) we note that we can approximate this set of coupled equations by a Fokker-Planck equation of diffusion type as discussed at length for one-step processes in van Kampen's book.<sup>7</sup> For this purpose we identify  $N_s$  as van Kampen's large parameter and get in the variable  $x = N/N_s$

$$\frac{\partial}{\partial t} P(x; t) = \frac{\partial}{\partial x} \left[ U'(x)P(x; t) + \frac{1}{2} \frac{\partial}{\partial x} [D(x)P(x; t)] \right], \quad (60)$$

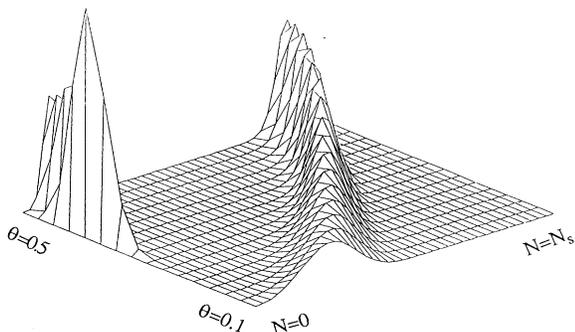


FIG. 2. Time evolution of  $P(N; t)$  from (56) under isothermal desorption conditions starting from an initial coverage  $\theta(t=0) = 0.5$ . Parameters as in Fig. 1.

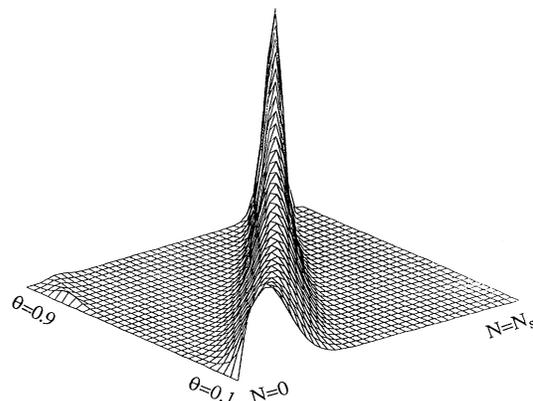


FIG. 3. Same as Fig. 2 but for initial coverage  $\theta(t=0) = 0.9$ .

where

$$U'(x) = -r(x) + g(x) \quad (61)$$

is the derivative of the bistable external potential in which particles "diffuse," i.e., in  $x$  space and not along the surface, with a density-dependent "diffusion" coefficient

$$D(x) = r(x) + g(x) \quad (62)$$

expressed in terms of the generation and reduction functions

$$g(x) = W_0, \quad (63)$$

$$r(x) = W_0 C_0 [x/(1-x)] \exp(xcV_2/2k_B T).$$

Looking, e.g., at the equilibrium solution by setting the expression inside the large parentheses in (60) equal to zero, one sees easily that for sufficiently large values of  $cV_2/2k_B T$ ,  $P_{\text{eq}}(x)$  will have two peaks, as is appropriate inside the coexistence region.

As we remarked earlier, surface diffusion cannot be neglected in almost all adsorption systems. Rather, diffusion may be so fast that quasiequilibrium is maintained throughout desorption, i.e., the distribution functions  $P(N; t)$  in (59) are given by the equilibrium expression (52) for the remaining coverage  $\theta(t)$ . Under these conditions, (59) reads

$$d\theta/dt = - \sum_N r(N) P_0(N; \theta(t)). \quad (64)$$

Using (52) we can rewrite this equation as

$$d\theta/dt = - (S_0 a_s k_B T / h \lambda_{\text{th}}^2) \exp(\mu/k_B T). \quad (65)$$

This standard result of surface reaction kinetics, obtainable within the framework of nonequilibrium thermodynamics<sup>31</sup> in particular, implies that within the coexistence region of a two-phase adsorbate, desorption proceeds with zero order due to the fact that the chemical potential remains constant, as demonstrated in Fig. 1. In Fig. 4 we give the time evolution of the distribution function  $P_0(N)$  as it appears in (64) to contrast it with

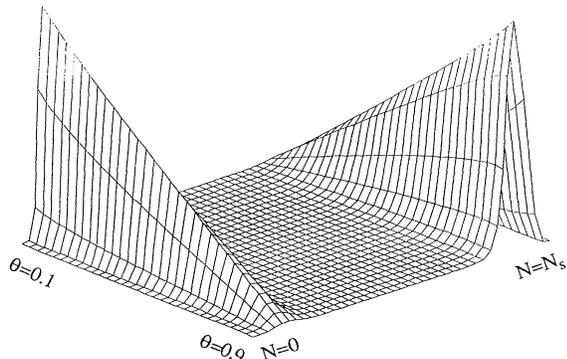


FIG. 4. Time evolution of  $P(N;t)$  from (56) but with the adsorbate maintained in quasiequilibrium as for the open squares in Fig. 1.

Figs. 2 and 3, which were obtained from the master equation (56), valid in the absence of diffusion.

To study the influence of diffusion on the adsorption-desorption kinetics, neither of the two approximation

schemes above is useful. Rather, one must return to the hierarchy of equations for  $P(N;t)$  and the correlation functions (43)–(48). To make it the basis for a study of surface kinetics, we must devise a truncation scheme, e.g., one similar to the Kirkwood approximation (27) at the level of two-particle correlation functions, which leaves one with two sets of coupled equations for  $P(N;t)$  and  $P_{2n}(N;t)$ . To make connection with what was said between Eqs. (27) and (31), we note that

$$\sum_N P_{2n}(N;t) = cN_s \psi(t). \quad (66)$$

In the spirit of (27) we are thus led to the following closure:

$$P_{3n}(N;t) = \frac{1}{2} \frac{c-1}{c} [P_{2n}(N;t)]^2 / NN_s P(N;t), \quad (67)$$

and similar expressions for the higher-order correlation functions. Equation (43) then reads

$$\begin{aligned} dP(N;t)/dt = & g(N-1)P(N-1;t) - W_0 C_0 N P(N;t) \left\{ 1 + C_1 P_{2n}(N;t) / NN_s P(N;t) \right. \\ & \left. + \frac{1}{2} \frac{c-1}{c} [C_1 P_{2n}(N;t) / NN_s P(N;t)]^2 + \dots \right\} - g(N)P(N;t) \\ & + W_0 C_0 (N+1)P(N+1;t) \left\{ 1 + C_1 P_{2n}(N+1;t) / N_s (N+1)P(N+1;t) \right. \\ & \left. + \frac{1}{2} \frac{c-1}{c} [C_1 P_{2n}(N+1;t) / N_s (N+1)P(N+1;t)]^2 + \dots \right\}. \quad (68) \end{aligned}$$

Similarly we obtain from (46)

$$\begin{aligned} dP_{2n}(N;t)/dt = & W_0 [2c(N-1)P(N-1;t) + (N_s - N - 1)P_{2n}(N-1;t) - (N_s - N)P_{2n}(N;t)] \\ & + W_0 C_0 \left\{ \left[ N(C_1 + 1)P_{2n}(N;t) + \frac{1}{2} \frac{(c-1)^2}{c} C_1 (C_1 + 1) [P_{2n}(N;t)]^2 / NN_s P(N;t) + \dots \right] \right. \\ & \left. - [(N-1)P_{2n}(N+1;t) + \dots] \right\} + 2J_0 [cN(N-1)P(N;t) - N_s (C_1 + 1)P_{2n}(N;t) + \dots]. \quad (69) \end{aligned}$$

This set of  $2N_s$  coupled equations for  $P(N;t)$  and  $P_{2n}(N;t)$  then describes the time evolution of the adsorbate even if the density is inhomogeneous, as in the two-phase regime. Although still at the level of a mean-field theory, the closure approximation (67) is the simplest realistic scheme for the description of adsorption, desorption, and diffusion in an inhomogeneous adsorbate. We see in particular that for fast diffusion, i.e., large  $J_0$ , the last term in (69) ensures that  $P_{2n}(N;t)$  and  $P(N;t)$  remain in equilibrium at the remaining coverage, as anticipated in the derivation of (64). On the other hand, in the absence of diffusion and under desorption conditions,

$P_{2n}(N;t)$  develops according to the second term in (69) independently of  $P(N;t)$  but obviously affecting the evolution of the latter in (68). If desorption and diffusion proceed on comparable time scales, the set of equations (68) and (69) must be studied numerically, which we will do in a future paper for particular systems, such as rare gases on metals and metals on metals.

## V. OUTLOOK

Guided by the desire to develop an analytical theory of the adsorption, desorption, and diffusion kinetics in inho-

ogeneous adsorbates, we have reexamined the kinetic lattice-gas model. We have proposed a time-dependent generalization of the grand-canonical ensemble that leads to a new hierarchy of coupled equations of motion for probability functions (43)–(48). A simple closure approximation (67) leads to two sets of equations (68) and (69) that can be regarded as a generalization of the Becker-Döring droplet model. The limited usefulness of a mean-field model (56) for surface kinetics is discussed.

It remains to study (68) and (69) numerically for particular systems, and to investigate better closure approximations than the one contained in (67). Furthermore, it might be interesting to derive a set of coupled Fokker-Planck equations from (68) and (69) to see whether one

can define an effective (external) potential and a diffusion coefficient, in analogy to (61) and (62), both most likely time or state dependent.

It is known that next-nearest-neighbor and trio interactions are important in most adsorbates.<sup>27</sup> Furthermore, for attractive interactions, second and third adsorption layers start to grow before a monolayer is complete.<sup>27–29</sup> Such effects can be incorporated in the kinetic lattice-gas model and should also be studied in this approach.

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