PHYSICAL REVIEW B VOLUME 62, NUMBER 7 15 AUGUST 2000-I

Analysis of direct correlation measurements from adsorbed atom fluctuations

Z. Chvoj,[1] E. H. Conrad,[2] and M. C. Tringides[3]
[1]Institute of Physics, Academy of Sciences of the Czech Republic Cukrovarnicka 10, 162 53 Prague 6, Czech Republic
[2]School of Physics, Georgia Institute of Technology, Atlanta, Georgia 30332
[3]Ames Laboratory, Department of Physics and Astronomy, Iowa State University, Ames, Iowa 50011

(Received 16 December 1999)

Despite its importance in theoretical studies of surface diffusion there has been limited experimental progress in developing methods to measure the dynamic structure factor $S(\mathbf{q},t)$. In this work we study gases adsorbed on single-crystal surfaces and show that their equilibrium dynamics is measurable in a diffraction experiment through density fluctuations described by the dynamic correlation function $\langle S(\mathbf{q},t)S(\mathbf{q},0)\rangle$. Using a lattice-gas model with nearest-neighbor repulsive interaction, we demonstrate how to separate out the microscopic dynamics caused by diffusion and adsorption-desorption from the form of $\langle S(\mathbf{q},t)S(\mathbf{q},0)\rangle$. Our analytical results show that $\langle S(\mathbf{q},t)S(\mathbf{q},0)\rangle$ decays as an exponential with a time constant $\tau(q)$. Significant deviations from the hydrodynamic dependence of $1/\tau(q)=D_c q^2$ are found with and without desorption. These deviations have important consequences in extracting diffusion constants from experiments.

I. INTRODUCTION

The use of atomic imaging techniques (i.e., Scanning Tunneling Microscopy (STM) and Field Electron Microscopy (FEM) has demonstrated how information about surface adatom mobility can be obtained by following in detail the diffusive path of a few adatoms in well defined configurations (single atoms, dimmers, etc.).[1] This information includes the determination of the energy barrier, diffusion mechanism, etc., of the configuration under investigation. However, these experiments are limited to regimes of either low adsorbate coverage or in conditions far from equilibrium (i.e., low temperatures). The reason for this is that the time scale set by the experiment selects processes with the fastest rate while other microscopic processes corresponding to the slower rates ''freeze'' out. Because of these limits, the dynamics of these systems are parametrized by the so-called tracer diffusion coefficient, D_t. In the opposite limit of finite coverage (high particle densities) and/or at high temperatures (when many microscopic processes are operating), collective effects become more relevant (e.g., formation of ordered phases, long-range correlations in the atom motion, etc.). In these limits the system's dynamics require a different description of the diffusion process that is based on the collective or chemical diffusion coefficient, D_c. At a finite coverage, Θ, the degree of mass transport in the system depends on the differences in energy costs when an atom occupies various sites (i.e., chemical potential differences). These differences arise from both interactions between the adsorbate atoms and/or the substrate atoms and thus also depend on the local adsorbate distribution. Measurements of the collective diffusion coefficient reveal important information not only about the adatom-substrate interactions but also about adatom-adatom interactions. Methods for measuring $D_c(\Theta)$, however, are much more difficult to implement than methods for measuring D_t.

To measure D_c, one must be able to detect small-amplitude, thermally produced concentration fluctuations in the adsorbate under equilibrium conditions. So far, attempts to make these measurements have been based on electron emission techniques [FEM and STM (Refs. 2 and 3)]. The high spatial amplification of the electron emission process (a result of the exponential dependence of emission on changes in the local adatom concentration) provides the necessary gain to magnify the small equilibrium density fluctuations. These techniques measure density fluctuations over a variable diameter of 30–300 Å depending on the magnification factor in the emission geometry. A serious problem with these methods is that the electron emission process requires the presence of a high electric field (typically 0.5 V/Å). Depending on the system under study, field effects can modify the diffusive motion of the atom. If the diffusing atom has a sufficiently high polarizability or permanent dipole moment, the electric field can change normal diffusion to a biased random walk.[3] In addition, depending on temperature density fluctuations can be extremely fast (much faster than seconds) so that processes faster than the integration time constant in the electronics cannot be followed (typically video rates).

Despite the success of these methods in measuring surface diffusion coefficients in numerous systems, there are motivations to use a reciprocal space method (i.e., surface diffraction) to measure the density fluctuations. Besides the electric field and the limited time resolution problems mentioned above, there is an impetus to developing temporal diffraction methods because they measure quantities more intimately related to those derived by theoretical analysis of adsorbate dynamics in surface diffusion.

In a diffraction experiment, the quantity measured is the structure factor, $I(\mathbf{q},t)$. For an adsorbate with N possible adsorption sites, of which ΘN are occupied, the structure factor from the adsorbate is defined as

$$I(\mathbf{q},t)=\frac{1}{(N\Theta)^2}\int \rho(\mathbf{r}',t)\rho(\mathbf{r}'+\mathbf{r},t)\exp(-i\mathbf{q}\cdot\mathbf{r})d\mathbf{r}'d\mathbf{r}, \tag{1}$$

where $\rho(\mathbf{r},t)$ is the local adsorbate concentration at position $\mathbf{r}$ and time t, and $\mathbf{q}$ is the momentum transfer vector. Fluctuations about the time-averaged mean value of $I(\mathbf{q},t)$,

$\langle I(\mathbf{q})\rangle_t$, are measured as a function of time and are used to construct the autocorrelation function,

$$C(\mathbf{q},t)=\langle[I(\mathbf{q},t)-\langle I(\mathbf{q})\rangle_t][I(\mathbf{q},0)-\langle I(\mathbf{q})\rangle_t]\rangle. \tag{2}$$

The averaging process $\langle\ \rangle$ means an ensemble average over different configurations of the system but in practice it is carried out as a time average since systems in equilibrium are ergodic and the two averaging processes are equivalent.

As we will show in the next section, a measurement of $C(\mathbf{q},t)$ is equivalent to a measurement of the dynamic structure factor, $S(\mathbf{q},t)$, defined as

$$S(\mathbf{q},t)=\frac{1}{(N\Theta)^2}\int\delta\rho(\mathbf{r}',0)\,\delta\rho(\mathbf{r}'+\mathbf{r},t)\exp(-i\mathbf{q}\cdot\mathbf{r})d\mathbf{r}'d\mathbf{r}, \tag{3}$$

where $\delta\rho(\mathbf{r},t)=\rho(\mathbf{r},t)-\langle\rho\rangle$. The average adsorbate concentration (averaged over space and time) is $\langle\rho\rangle=\Theta$.

Theoretical progress in recent years has developed expressions that relate the collective diffusion coefficient to equilibrium thermodynamic quantities such as the average jump rate, Γ, and a thermodynamic factor analogous to the Darken equation relating $D_c(\Theta)$ to the tracer diffusion coefficient D_t:[2,4]

$$D_c(\Theta)=D_t\frac{\partial(\mu/kT)}{\partial\ln\Theta}, \tag{4}$$

where μ is the chemical potential, k is Boltzmann's constant, a is the lattice constant, and T is the temperature.

The reason a measurement of $S(\mathbf{q},t)$ is so desirable is because the thermodynamic factor is related to the dynamic structure factor in the limit that both t and q go to zero,[1]

$$\left(\frac{\partial(\mu/kT)}{\partial\ln\Theta}\right)^{-1}=\langle S(0,0)\rangle. \tag{5}$$

If it is possible to measure the full decay of the structure factor $S(\mathbf{q},t)$, then the collective diffusion coefficient can be extracted from the expression for $S(\mathbf{q},t)$ in the hydrodynamic regime $(q\rightarrow 0)$: $S(\mathbf{q},t)\underset{t\rightarrow 0}{\approx}S(\mathbf{q},0)(1-D_cq^2t)$.[1]

Despite the importance of the dynamic structure factor in theoretical studies of surface diffusion and the development of different methods for its calculation, there is limited progress in developing experimental methods to measure $S(\mathbf{q},t)$. In part this is because the small-amplitude density fluctuations give rise to correspondingly small variation in $I(\mathbf{q},t)$, making them difficult to detect. However, this problem has been overcome recently,[5,6] making the possibility of measuring $D_c(\Theta)$ a reality.

A direct measurement of $S(\mathbf{q},t)$ can be carried out with a diffraction technique if two experimental conditions are realized: first the instrument should have high q resolution so measurements can be carried out at well-defined wave vectors $\mathbf{q}$, and second the acquisition speed should be sufficiently fast compared to the time constant of the physical process under investigation. The first restriction is required because integration over a finite window in reciprocal space $\Delta\mathbf{q}$, can average out the time structure. This follows from the fact that fluctuations with different wave vectors within the resolution window are not in general correlated. The second restriction prevents sampling time broadening of the true time constant.

As demonstrated recently (e.g., Refs. 5 and 6) both conditions are met with a high-resolution low-energy-electron-diffraction (HRLEED) diffractometer (with resolution better than 0.001 Å^{-1}). Since signal acquisition in HRLEED is based on pulse counting using a high gain Channeltron detector, the sampling gate time can in principle be as low as 0.1 μs (limited only by the pulse width in the Channeltron). However, the diffracted count rate may place a practical limit of $\sim$1–10 μs on the gate time. The successful use of high-resolution LEED to measure temporal fluctuations has been shown in recent experiments that monitored thermal equilibrium step fluctuations on a high-index stepped W(430) surfaces in the temperature range $T=700$–900 K.[5] $I(\mathbf{q},t)$ was measured at different diffraction conditions by varying the normal component of the momentum transfer, q_z. Strong fluctuations were observed at the out-of-phase condition, $q_z=(2l+1)\pi/d$, where d is the step height and l is an integer. At this q_z, $I(\mathbf{q},t)$ is maximally sensitive to the step position because neighboring steps scatter destructively. No fluctuations were observed at the in-phase-condition, $q_z=2l\pi/d$, where $I(\mathbf{q},t)$ is insensitive to step position (i.e., neighboring steps scatter constructively).

For the case of step fluctuations, the form of $I(\mathbf{q},t)$ has been derived from a continuum model for different step kinetics. These calculations predict strong differences in the time structure of the diffraction signal depending on which physical process dominates the kinetics. It is possible to have more than one microscopic process present in a system with the resulting fluctuations originating from competing processes. An example would be low-temperature inert gas adsorption on a surface where both the desorption and diffusion barriers are sufficiently low (several millivolts) so that both processes contribute to the adsorbed atom density fluctuations.[7,8] In this example, dynamic equilibrium exists between the rate of adsorption of gas-phase atoms from the incident flux and the rate of desorption of atoms in the surface lattice gas. In addition to these dynamics, it is possible for the adsorbed atoms, during their residence time on the surface, to diffuse to different sites, nucleate islands, and generate domains of the ordered phase as a result of their mutual interactions. Atoms desorbing from the two-dimensional (2D) ordered phase back to the lattice-gas phase give rise to density fluctuations with different dynamics compared to the adsorption-desorption process.

Under these conditions, when two microscopic processes operate with possibly different time constants, what determines the fluctuations in $S(\mathbf{q},t)$? Stated another way, what is the form of the measured autocorrelation from fluctuations of $I(\mathbf{q},t)$ due to different combinations of diffusion and adsorption-desorption rates? We would like to answer this question as well as to be able to extract the physical significance of the measured time constant of $C(\mathbf{q},t)$ for different combinations of desorption versus diffusion rates. To be able to do this, as shown in the next section, we need to calculate $S(\mathbf{q},t)$ for both processes. These calculations show that the $\mathbf{q}$ dependence is markedly different depending on which process is involved in the kinetics. Therefore, by comparing the measured $S(\mathbf{q},t)$ from a diffraction experiment with the results of our calculations, not only can the dominant process be identified, but it should be possible to deduce energetics parameters such as activation energies for diffusion and desorption as well as adatom-adatom interactions.

Our analysis is based on a lattice-gas model with repulsive nearest-neighbor interactions. Depending on the local environment of the atom, the interactions will affect the single-atom rate for both desorption and diffusion and lead to rates that are coverage-dependent.

II. RELATIONSHIP OF THE DIFFRACTION AUTOCORRELATION FUNCTION TO $S(\mathbf{q},t)$

Although we will derive the relation between the measured quantity, $C(\mathbf{q},t)$, and the theoretically more relevant quantity, $\langle S(\mathbf{q},t)\rangle$, within the lattice-gas approximation, the derivation that follows is general enough to be applicable to the continuum case. The expression for $C(\mathbf{q},t)$ in Eq. (2) can be rewritten as

$$C(\mathbf{q},t)=\langle I(\mathbf{q},0)I(\mathbf{q},t)\rangle-\langle I(\mathbf{q})\rangle^2=C_0(\mathbf{q},t)-\langle I(\mathbf{q})\rangle^2. \tag{6}$$

Clearly the first term in this expression fully determines the time dependence of the autocorrelation function. The last term ensures that the correlation function will decay to zero. The expression for $C_0(\mathbf{q},t)$ in Eq. (6) can be rewritten in terms of site-occupation variables using the definition of $I(\mathbf{q},t)$ in Eq. (1).

Before continuing, note that we neglected explicitly the bulk contribution to the structure factor in Eq. (1). However, if we assume that the adsorbed overlayer is ordered, commensurate, and forms a nonprimitive superstructure compared to the substrate, we can ignore the substrate contribution to $I(\mathbf{q},t)$ if we choose $\mathbf{q}$ properly. Specifically, this type of discrete lattice gas will produces a structure factor with nonzero intensity at wave vectors parallel to the surface of $\mathbf{q}_\parallel=\mathbf{b}n/2$ (n an integer). Here $\mathbf{b}$ is a reciprocal-lattice vector of the substrate surface lattice, and $\mathbf{b}=h(2\pi/a_x)\hat{x}+k(2\pi/a_y)\hat{y}$ (h and k integers). For n odd, the intensity at these $\mathbf{q}$'s only has a contribution from the adsorbate atoms and not the substrate atoms. Generalization to the case when both adatom and substrate atoms contribute to the structure factor (as would be the case for n even) is straightforward.

For a discrete lattice gas, $\rho(\mathbf{r},t)$ can be written in terms of the occupation variables, $p_{\boldsymbol{l}}$, for each point on the lattice ($p_{\boldsymbol{l}}=1$ if the site is occupied and $p_{\boldsymbol{l}}=0$ if the site is empty),

$$\rho(\mathbf{r},t)=\sum_{\boldsymbol{l}}^{N} p_{\boldsymbol{l}}(t)\,\delta(\mathbf{r}-\boldsymbol{l}), \tag{7a}$$

where $\boldsymbol{l}$ is the position vector of an adsorption site on the surface, $\boldsymbol{l}=n\mathbf{a}_x+m\mathbf{a}_y$ with n and m integers. The corresponding Fourier transform of $\rho(\mathbf{r},t)$ is

$$\tilde{\rho}(\mathbf{q},t)=\sum_{\boldsymbol{l}}^{N} p_{\boldsymbol{l}}(t)\exp(-i\mathbf{q}\cdot\boldsymbol{l}), \tag{7b}$$

$$\delta\tilde{\rho}(\mathbf{q},t)=\sum_{\boldsymbol{l}}^{N}[p_{\boldsymbol{l}}(t)-\Theta]\exp(-i\mathbf{q}\cdot\boldsymbol{l}). \tag{7c}$$

Substitution of Eq. (7a) for the adsorbate concentration into Eq. (1) and using Eq. (6) gives an expression for $C_0(\mathbf{q},t)$ in terms of the discrete occupation variables:

$$C_0(\mathbf{q},t)=\frac{1}{(n\Theta)^4}\sum_{\boldsymbol{l}_1,\boldsymbol{l}_2,\boldsymbol{l}_3,\boldsymbol{l}_4}\langle p_{\boldsymbol{l}_1}(0)P_{\boldsymbol{l}_3}(0)p_{\boldsymbol{l}_2}(t)p_{\boldsymbol{l}_4}(t)\rangle \times\exp[-i\mathbf{q}\cdot(\boldsymbol{l}_2-\boldsymbol{l}_1+\boldsymbol{l}_4-\boldsymbol{l}_3)]. \tag{8}$$

One clearly sees the difficulty in writing an analytic expression for $C_0(\mathbf{q},t)$ since we must derive expressions for the four-point correlation functions that depend both on space and time. To do this, we must know the conditional probabilities to occupy sites $p_{\boldsymbol{l}_2}$ and $p_{\boldsymbol{l}_4}$ at time t given the occupation of sites $p_{\boldsymbol{l}_1}$ and $p_{\boldsymbol{l}_3}$ at an earlier time $t=0$ when these sites are separated by a distance $\boldsymbol{l}_1-\boldsymbol{l}_3$ and $\boldsymbol{l}_2-\boldsymbol{l}_4$, respectively. This conditional probability, and thus $C_0(\mathbf{q},t)$, will depend on the extent that correlations develop in the system as a result of the interactions between the adatoms and will be a strong function of temperature.

It is a general result in statistics that higher-order correlation functions can be expressed in terms of lower-order correlation functions by employing the cumulant expansion.[9] If at a temperature T the distribution $P\{p_{\boldsymbol{l}}(t)\}$ is a normal distribution [where $\{\}$ denotes specific configurations of the system's occupation variables $p_{\boldsymbol{l}}(t)$], then there is a well-defined expression for the four-point correlation functions as a combination of three- and two-point correlation functions and the averages of $p_{\boldsymbol{l}}(t)$.[9] Similarly, the three-point correlation functions can be expressed in terms of two-point correlation functions and the averages. Details of the calculation will be given elsewhere[10] but the reduction process is straightforward and gives

$$C(\mathbf{q},t)=\langle S(\mathbf{q},t)\rangle^2[1+F^2(2\mathbf{q}-\mathbf{b})]+2\langle S(\mathbf{q},t)\rangle J(\mathbf{q}-\mathbf{b}) \times[1+F(2\mathbf{q}-\mathbf{b})], \tag{9a}$$

$$J(\mathbf{q}-\mathbf{b})=\frac{1}{N^2}\sum_{\boldsymbol{l}_1,\boldsymbol{l}_2}^{N}\exp[-i2\mathbf{q}\cdot(\boldsymbol{l}_1-\boldsymbol{l}_2)], \tag{9b}$$

$$F(2\mathbf{q}-\mathbf{b})=\frac{1}{N}\sum_{\boldsymbol{l}_1}^{N}\exp[-2\mathbf{q}\cdot\boldsymbol{l}_1]. \tag{9c}$$

The function J and F have simple analytical expressions[11] but are essentially δ functions in $\mathbf{q}=\mathbf{b}$ and $2\mathbf{q}=\mathbf{b}$, respectively. They simply reflect the fact that, at any time, atoms are found only on lattice sites.

Equation (9a) shows that the measured autocorrelation function in a diffraction measurement is determined by the dynamic structure factor. In the next section, we derive $\langle S(\mathbf{q},t)\rangle$ for the case of an adsorbate where both diffusion and adsorption-desorption cause local fluctuations in the adsorbate density.

III. DETERMINATION OF THE DYNAMIC STRUCTURE FACTOR $\langle S(\mathbf{q},t)\rangle$

For simplicity, we will assume that the adsorbate rests on a square lattice and that the overlayer has a nonprimitive unit cell [e.g., a $c(2\times2)$ structure, where $\Theta=0.5$]. It is easily shown that interference between the substrate and the overlayer adds an additional term to Eq. (9a) proportional to $\sim (f_B/f_A)^2\langle S(\mathbf{q},t)\rangle \delta(\mathbf{q}-\mathbf{b})$ (where f_B and f_A are the atomic structure factors of the substrate and adsorbate atoms, respectively). Since the main objective in the current paper is to determine both the $\mathbf{q}$ and t dependence of $S(\mathbf{q},t)$ for different microscopic processes, we will ignore the substrate contribution in further discussions.

In the limit of no evaporation or adsorption, atoms can hop to nearest-neighbor sites at a rate $w(T,\Theta)$. In the absence of interactions, and at zero coverage, the hopping rate is simply $w(T,\Theta=0)\equiv W_0(T)=D_t(T,0)/a^2$, where $D_t(T,0)$ is the tracer diffusion coefficient when $\Theta=0$. In the presence of interactions, the hopping rate will be modified by the local adatom concentration. In the subsequent discussion, we allow only nearest-neighbor interactions with a strength δE ($\delta E>0$ for repulsive interaction). Even with this simple interaction, the transition dynamics become sufficiently complicated because they cause long-range correlations between atoms to develop, especially at low temperatures. With a nearest-neighbor approximation in mind, the rate $w_{\mathbf{l},\mathbf{l}+\mathbf{s}_A}$ to jump from a site $\mathbf{l}$ to a nearest-neighbor site $\mathbf{l}+\mathbf{s}_A$ is influenced, at finite coverage, by the occupation of the four nearest-neighbor sites at positions $\mathbf{l}+\mathbf{s}_i$ as well as the occupation of the site $\mathbf{l}+\mathbf{s}_A$,

$$w_{\mathbf{l},\mathbf{l}+\mathbf{s}_A}(p_{\mathbf{l}})=W_0(1-p_{\mathbf{l}+\mathbf{s}_A})\exp\left(\frac{\delta E}{kT}\sum_{i=1}^{4} p_{\mathbf{l}+\mathbf{s}_i}\right). \tag{10}$$

We are implicitly assuming that the diffusion energy barrier is changed by δE if an adjacent site is occupied and that the total interaction is a simple additive sum of interactions from all occupied adjacent sites.

In the opposite limit, when diffusion is zero, the dynamics of the overlayer is described by adatom adsorption-desorption. In this limit, when the coverage is zero, the system is parameterized by the rates of desorption, W^D, and adsorption, W^A. The two rates W^D and W^A are not independent but are related by a detailed balance because in equilibrium the average coverage is constant.[10] As for diffusion alone, we use the same dependence on the local environment of the atom (i.e., nearest neighbors) and repulsive interactions to describe the adsorption-desorption rates at finite coverage,

$$w^D_{\mathbf{l}}(p_{\mathbf{l}})=W^D\exp\left(\frac{\delta E}{kT}\sum_{i=1}^{4} p_{\mathbf{l}+\mathbf{s}_i}\right), \tag{11}$$

$$w^A_{\mathbf{l}}(p_{\mathbf{l}})=W^A\exp\left(-\frac{\delta E}{kT}\sum_{i=1}^{4} p_{\mathbf{l}+\mathbf{s}_i}\right). \tag{12}$$

In general, we will have contributions from both adsorption-desorption and diffusion. This mixed dynamics situation will be parametrized by W_0, the ratio W^D/W_0 (i.e., the ratio of desorption to diffusion), the ratio $\delta E/kT$, and the coverage Θ. We can define a dynamic operator, L, that governs the equation of motion of the occupation variables $p_{\mathbf{l}}$ at site $\mathbf{l}$ due to all three processes:

$$Lp_{\mathbf{l}}\equiv\frac{dp_{\mathbf{l}}}{dt}=\sum_{\mathbf{s}_i}^{\mathrm{NN}}\{p_{\mathbf{l}+\mathbf{s}_i}w_{\mathbf{l}+\mathbf{s}_i,\mathbf{l}}(p_{\mathbf{l}})-p_{\mathbf{l}}w_{\mathbf{l},\mathbf{l}+\mathbf{s}_i}(p_{\mathbf{l}})\} \\ +(1-p_{\mathbf{l}})w^A_{\mathbf{l}}(p_{\mathbf{l}})-p_{\mathbf{l}}w^D_{\mathbf{l}}(p_{\mathbf{l}}), \tag{13}$$

where NN denotes the summation over four nearest-neighbor positions, $\mathbf{s}_i$. The first term in Eq. (13) describes the probability of an atom already present at one of the four neighboring sites $\mathbf{l}+\mathbf{s}_i$ to hop to site $\mathbf{l}$. The second term describes the probability of an atom already at site $\mathbf{l}$ to hop to one of the four nearest-neighbor sites. The third term describes the probability of an atom in the gas phase to adsorb into an empty site $\mathbf{l}$ and the last term describes the probability of an atom at site $\mathbf{l}$ to desorb back into the gas phase.

The local jumps described by Eq. (13) will change the instantaneous occupation of any site $\mathbf{l}$ at time t. Since the occupation of the sites $\mathbf{l}$ determines the global quantity $S(\mathbf{q},t)$ according to Eqs. (3) and (7), fluctuations in the local occupation variables will generate fluctuations in $S(\mathbf{q},t)$. There is a standard method (described elsewhere[12]) that can be used to write an equation of motion for $S(\mathbf{q},t)$. To do this, we start by using Mori's projection operator method to write the equation of motion for the Fourier coefficients of the local concentration $\delta\tilde{\rho}(\mathbf{q},t)$ given by Eq. (7c):

$$\frac{\partial\delta\tilde{\rho}(\mathbf{q},t)}{\partial t}=\frac{\langle\delta\tilde{\rho}(-\mathbf{q},0)L\,\delta\tilde{\rho}(\mathbf{q},0)\rangle}{\langle\delta\tilde{\rho}(-\mathbf{q},0)\,\delta\tilde{\rho}(\mathbf{q},0)\rangle}\delta\tilde{\rho}(\mathbf{q},t) \\ -\int_0^t\delta\tilde{\rho}(\mathbf{q},t-t_1)M(\mathbf{q},t_1)dt_1+B(\mathbf{q},t). \tag{14}$$

$B(\mathbf{q},t)$ are the Fourier coefficients of some stochastic driving force that lead to fluctuations in $\delta\tilde{\rho}(\mathbf{q},t)$. Note that the residual forces, $B(\mathbf{q},t)$, are perpendicular to $\delta\tilde{\rho}(\mathbf{q},t)$ and therefore do not contribute to $\langle S(\mathbf{q},t)\rangle$. $M(\mathbf{q},t)$ is referred to as the "memory" term and contains information about how the jump of an atom at time t depends on all previous jumps. In other words, it describes correlations between past and future jumps. These correlations develop either because of adatom-adatom interactions or because of the slow equilibration time to the substrate phonon bath. Because of these memory effects, the assumption of statistically independent successive jumps is never strictly valid.

Equation (14) is derived from the Liouville equation and is completely general in that it applies to all forms of the dynamic operator and not just the L derived from our model. By using standard Laplace transform techniques (see Ref. 12), the Laplace transform $\langle S(\mathbf{q},z)\rangle$ of $\langle S(\mathbf{q},t)\rangle$ can be written

$$\langle S(\mathbf{q},z)\rangle=\frac{\langle S(\mathbf{q},0)\rangle}{z+\Omega(\mathbf{q})+M(\mathbf{q},z)}. \tag{15}$$

The term $\Omega(\mathbf{q})$ is the frequency matrix that depends on the dynamic operator L [defined in Eq. (13)]:

$$\Omega(\mathbf{q})=-\frac{\langle\tilde{\rho}(-\mathbf{q},0)L\tilde{\rho}(\mathbf{q},0)\rangle}{(N\Theta)^2\langle S(\mathbf{q},0)\rangle}. \tag{16}$$

In order to proceed towards finding an expression for $\langle S(\mathbf{q},t)\rangle$, we must make a simplifying assumption to Eq. (15). We will follow the ''standard'' approximation and neglect the memory effect and assume that successive jumps are statistically independent (i.e., a Markovian diffusion process). Inclusion of memory effects remains an important unsolved problem in diffusion. Within the standard assumption, the expression for $\langle S(\mathbf{q},z)\rangle$ is easily transformed back into the time domain since $\Omega(\mathbf{q})$ is not a function of z. The result is an exponentially decaying function of time,

$$\langle S(\mathbf{q},t)\rangle = \langle S(\mathbf{q},0)\rangle e^{-\Omega(\mathbf{q})t}, \tag{17}$$

where the characteristic decay time of a fluctuation in $\langle S(\mathbf{q},t)\rangle$ is given by the inverse of the frequency matrix.

It is important to notice that by neglecting memory effects, the decay of the structure factor $\langle S(\mathbf{q},t)\rangle$ from an equilibrium fluctuation is *always* exponential in time regardless of whether or not these fluctuations are due to diffusion, adsorption-desorption, or a combination of the two. The initial magnitude of the fluctuation at $t=0$ is given by the static structure factor or wave-vector-dependent ''compressibility,'' $\langle S(\mathbf{q},0)\rangle$. Because $\langle S(\mathbf{q},t)\rangle$ decays as an exponential, it follows from Eq. (9a) that the diffraction autocorrelation function $C(\mathbf{q},t)$ also decays as an exponential for $\mathbf{q}=(2n+1)\mathbf{b}/2$ (or the sum of two exponentials for $\mathbf{q}=n\mathbf{b}$).

It is obvious from Eq. (13) that L is a simple linear operator and therefore $\Omega(\mathbf{q})$ will be a sum of two terms, one from diffusion kinetics and one from adsorption-desorption kinetics. Since L depends on each microscopic process, $\Omega(\mathbf{q})$ will in turn depend on which process is operating, specifically through its q dependence. Therefore, an experimental measurement of the q dependence of $\Omega(\mathbf{q})$ should allow the active dynamic process to be identified. This will be demonstrated in Sec. IV.

To evaluate Eq. (16), we begin by defining the parameter $\sigma_{\pm}\equiv\exp(\pm\delta E/kT)-1$, which will allow us to rewrite the exponential terms in Eqs. (10)–(12) as the product of combinations of the occupation variables $p_{\boldsymbol{l}}$. The dynamic operator L can also be written in terms of these combinations. Since the p's are discrete variables (0 or 1), we can write

$$\exp\left(\pm\frac{\delta E}{kT}\sum_{\mathbf{s}} p_{\boldsymbol{l}+\mathbf{s}}\right)=\prod_{\mathbf{s}}(\sigma_{\pm}p_{\boldsymbol{l}+\mathbf{s}}+1). \tag{18}$$

With this identity, $\Omega(\mathbf{q})$ can be rewritten as a series of multiterm correlation functions since the correlation function $\langle\tilde{\rho}(-\mathbf{q},0)L\tilde{\rho}(\mathbf{q},0)\rangle$ is a sum of terms of the form $\langle p_{\mathbf{k}}Lp_{\boldsymbol{l}}\rangle$. For example, the second term in Eq. (13) would lead to a term in $\Omega(\mathbf{q})$ proportional to

$$\Omega(\mathbf{q})\propto\cdots+W_0\left\langle p_{\boldsymbol{l}}p_{\mathbf{k}}(1-p_{\boldsymbol{l}+\mathbf{s}})\prod_{\mathbf{s}'\neq\mathbf{s}}(\sigma_{+}p_{\boldsymbol{l}+\mathbf{s}'}+1)\right\rangle+\cdots. \tag{19}$$

Therefore, the evaluation of the frequency matrix, $\Omega(\mathbf{q})$, requires one to calculate correlations between simultaneous occupation of positions in clusters containing up to six sites. The largest clusters require the evaluation of six-point correlation functions of the form $\langle p_{\mathbf{j}}p_{\boldsymbol{l}}p_{\boldsymbol{l}+\mathbf{s}_1}p_{\boldsymbol{l}+\mathbf{s}_2}p_{\boldsymbol{l}+\mathbf{s}_3}p_{\boldsymbol{l}+\mathbf{s}_4}\rangle$, where $\mathbf{j},\boldsymbol{l}$ range over the entire lattice. The $p_{\boldsymbol{l}+\mathbf{s}_1}$ term is the ending site of the jump and the other three $p_{\boldsymbol{l}+\mathbf{s}_1}$ are the neighboring sites that interact with it. There are no exact expressions for these correlation functions. However, as described in Sec. II, we can again use a cumulant expansion to reduce the problem to one of solving only two-point correlation functions, $\langle p_{\boldsymbol{l}}p_{\mathbf{j}}\rangle$, and averages [with the assumption that deviations from the most probable configuration of $\{p_{\boldsymbol{l}}(t)\}$ are normal]. What then remains is a method for evaluating these two-point correlations.

Without loss of generality [as far as the relation between the different microscopic processes and the shape of $S(\mathbf{q},t)$ is concerned], we examine the dynamics of an adsorbate for the case $\Theta=0.5$ [e.g., the coverage for an ideal $c(2\times2)$ overlayer]. The static analysis of this problem is completely defined from the well-known solution of the Ising model and we will make use of some of those results.[13] The exact solution of the 2D Ising model dynamics, however, and the calculation of the time-dependent correlation functions is still an open question. To proceed with our problem of finding an expression for $\Omega(q)$, we must introduce some approximation for the functional decay of $\langle p_{\boldsymbol{l}}p_{\mathbf{j}}\rangle$ on the separation distance $|\boldsymbol{l}-\mathbf{j}|$. Whatever the approximate form for the two-point correlation we use, its validity will depend on the correlation length, $\xi(T)$, in the adsorbed film. For example, at temperatures where $\xi(T)$ is small, longer-range correlations will be unimportant and a short-range approximation to $\langle p_{\boldsymbol{l}}p_{\mathbf{j}}\rangle$ will be adequate.

As a first drastic approximation to simplify the algebra, we have carried out the summation in Eq. (16) within the quasichemical approximation to the Ising model.[14] In this approximation the two-point correlations become

$$\langle p_{\boldsymbol{l}}p_{\mathbf{j}}\rangle=\left\{\begin{array}{cc}\Theta, & \boldsymbol{l}=\mathbf{j}\\ \Theta-\dfrac{2\Theta(1-\Theta)}{\sqrt{1+4\sigma_{-}\Theta(1-\Theta)}+1}, & \boldsymbol{l},\mathbf{j}\ \text{are NN}\\ \Theta^2 & \text{otherwise,}\end{array}\right\} \tag{20}$$

where σ_{-} is defined before Eq. (18). Equation (20) expresses the statistical independence of sites that are further away than nearest neighbors. We point out that such a drastic approximation suppresses long-range correlations (especially when $T/T_c<1$) and can underestimate some of the observed effects discussed in the next section.

Within the quasichemical approximation, the decay constant $\Omega(\mathbf{q})$ is fully determined by the static equilibrium two-point correlation functions. This result is fully legitimate because the system is in an equilibrium configuration. Although a closed-form solution to Eq. (16) can be developed in this approximation, the final expression is cumbersome and will not be reported here. For the purposes of our discussion, we will instead simply display results for $\Omega(q)$ that were calculated based on the outline given above. The reader is referred to Ref. 10 for details of these calculations.

IV. RESULTS

Since the decay of $\langle S(\mathbf{q},t)\rangle$ is always exponential when memory effects are neglected, the distinction between which microscopic mechanism is operating in a system cannot be

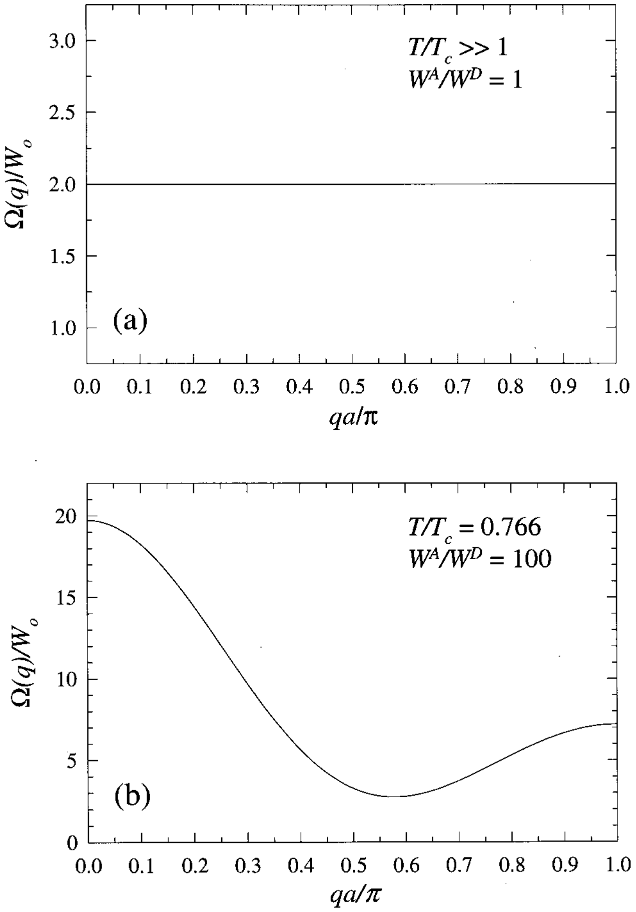

FIG. 1. The q dependence of Ω for $\Theta = 0.5$ in the limit of a pure adsorption-desorption. The wave vector is in the q_x direction ($q_y = 0$). (a) No interactions with $W^A/W^D = 1$; (b) strong interaction ($T/T_c = 0.766$) with $W^A/W^D = 100$. Note the minimum at $qa = \pi/2$.

determined from the time dependence of $C(\mathbf{q},t)$ alone. This is in contrast to the kinetics of steps where the time dependence of $C(\mathbf{q},t)$ was directly related to the microscopic mechanism responsible for step fluctuations.[15] However, in an adsorbate system, the microscopic kinetics leading to density fluctuations in the film can be distinguished by the **q** dependence of $\Omega(\mathbf{q})$. To illustrate this point, we calculate $\Omega(\mathbf{q})$ (with repulsive interactions) for several limiting cases of diffusion and adsorption-desorption.

A. Adsorption-desorption: $W_0 = 0$

We begin by looking at the case of pure adsorption-desorption (no diffusion, $W_0 = 0$). The ordered phase of the adsorbate will have a critical temperature, T_c, that we will use to define the relative strength of the adatom interactions [for the Ising model $\delta E = 1.76kT_c$ (Ref. 13)]. Figure 1 shows $\Omega(q)$ versus q for the case of pure adsorption-desorption in two limits: (a) no interactions (which is parametrized by the limit $T/T_c \rightarrow \infty$) and (b) for temperatures below the critical temperature of the ordered phase formation $T/T_c = 0.766$. Note that q lies along the x axis defining one side of the $c(2\times2)$ unit cell.

For the case of no interactions, $\Omega(q)$ is independent of the wave vector over the whole Brillouin zone [see Fig. 1(a)]. This is because the probability to desorb from, or adsorb at, any site on the lattice is constant, independent of the local environment of the atom. With interactions this is no longer true. In Fig. 1(b), when interactions have been included, we see a strong q dependence in $\Omega(q)$: a maximum at $q = 0$ and a minimum near $q \approx \pi/2a$.

This change in the q dependence of $\Omega(q)$ with interactions is related to the formation of the $c(2\times2)$ structure. Since both desorption and diffusion are local processes, the local energy barrier is affected by the occupation of neighboring sites according to Eqs. (11) and (12). For long-wavelength fluctuations ($q \rightarrow 0$), changes in site occupation relative to equilibrium values are far apart. Therefore, for these types of fluctuations, nearest-neighbor sites remain occupied, thus maximizing the effect of the repulsive interaction and increasing the difference between desorption and adsorption rates. This in turn minimizes the relaxation time of the fluctuation [or makes $\Omega(q)$ a maximum]. Such effects are expected to be more pronounced at even lower temperatures. The largest change in nearest-neighbor concentration occurs for fluctuations with wavelengths between $\lambda \approx 3a \rightarrow 4a$ (or $qa/\pi \approx \frac{1}{2} \rightarrow \frac{2}{3}$). This will produce many empty neighboring sites leading to a subsequent decrease in the repulsive interaction for this wavelength disturbance. This in turn increases the adsorption rate and decreases the desorption rates, thus increasing the relaxation time of the fluctuation. Since $\Omega(q)$ is the inverse of the relaxation time, it must be a minimum near $qa/\pi \approx 0.5 \rightarrow 0.7$.

B. Diffusion: $W^D = W^A = 0$

In the limit of pure diffusion ($W^D = W^A = 0$), the q dependence of $\Omega(q)$ is very different. This is because, unlike for adsorption-desorption, there is a conservation law for the occupancy of sites (i.e., the hop to a neighboring site can occur only if the site is empty). In the absence of interactions, Eq. (16) can be solved without any approximations:

$$\Omega(\mathbf{q}) = 2W_0\{2 - \cos(q_x a) - \cos(q_y a)\}. \tag{21}$$

This result is plotted in Fig. 2(a). For fluctuations with wavelength $\lambda/2 = a$ ($qa = \pi$), the relaxation time is a minimum [$\Omega(q)$ maximum] because diffusion need only proceed through neighboring sites. Long-wavelength fluctuations ($q \rightarrow 0$) take forever to decay [$\Omega(q) = 0$] because the atoms in a chain $2\pi/q$ long must all diffuse in a correlated fashion. For small values of q, Eq. (21) has the approximate form $\Omega(\mathbf{q})_{\lim q\rightarrow 0} \approx W_0(\mathbf{q}\cdot\mathbf{a})^2$. This is the expected q dependence, characteristic of diffusion in the long-wavelength hydrodynamic regime,[16]

$$\Omega(\mathbf{q})_{\lim q\rightarrow 0} \approx D_c q^2. \tag{22}$$

In other words, the collective diffusion coefficient is defined as the curvature of the Ω versus q curve. Equation (22) is plotted as the dashed line in Figs. 2(a) and 2(b). Thus the curvature in Fig. 2(a) defines $D_c(\Theta)$ for the noninteracting model: $D_c(\Theta) = D_t$ as expected.

If we allow interactions in the pure diffusion limit, the Ω versus q curve (near $q = 0$) becomes steeper as shown by the dashed curve in Fig. 2(b). Since the curvature of Ω versus q is proportional to the collective diffusion coefficient [Eq.

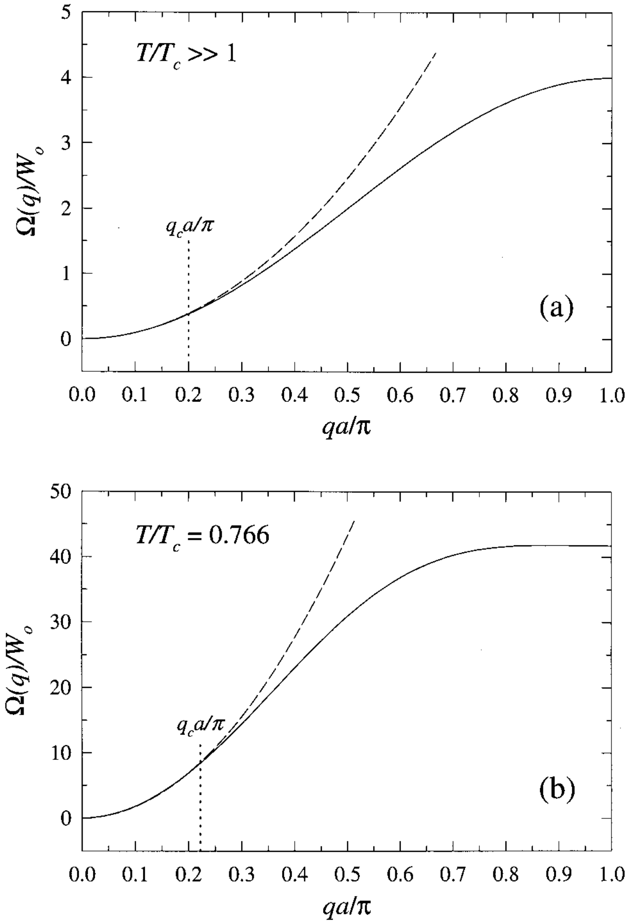

FIG. 2. The q dependence of Ω for $\Theta = 0.5$ in the limit of a pure diffusion ($W^A = W^D = 0$). The wave vector is in the q_x direction ($q_y = 0$). (a) No interactions. The parabolic dependence $\Omega(q) \sim D_c q^2$ (dashed curve with $D_c = D_t$) typical of the hydrodynamic regime is observed up to a wave vector $q_c \sim \pi/5a$. (b) Strong interaction ($T/T_c = 0.766$). Again the parabolic dependence is observed up to $q_c \sim \pi/5a$ (dashed curve) but $D_C = 16.8 D_t$ (16.8 times the diffusion constant in the noninteracting limit).

(22)], repulsive interactions have increased D_c as expected. From the curvature near $q = 0$, a value of $D_c = 17 D_t$ is found (i.e., 17 times greater than in the noninteracting limit). This increase is consistent with Monte Carlo simulations results.[17]

It is worth emphasizing that, although $\Omega(q)$ shows the expected q^2 behavior, the parabolic form is not valid over the entire Brillouin zone. Instead, it is a reasonable approximation only up to some characteristic wave vector q_c. As seen in Figs. 2(a) and 2(b), $\Omega(q)$ deviates from the expected parabolic q dependence for q_c above $\pi/5a$.

The similar values of q_c observed for the two temperatures ($T/T_c = \infty$ and 0.766) are a result of the approximation we have used for $\langle p_l p_{\mathbf{j}} \rangle$. A more accurate expression would include correlations beyond nearest neighbors that decayed as a function of $|\boldsymbol{l} - \mathbf{j}|$ on a length scale given by a temperature-dependent correlation length, $\xi(T)$. The correlation length would reflect changes in the system configuration (e.g., the formation of ordered structures for $T/T_c < 1$). We expect that a more accurate representation of $\langle p_l p_{\mathbf{j}} \rangle$ would produce a smaller value of q_c at lower temperatures.

We would like to briefly side track from the main discussion and emphasise that the parameter q_c is relevant in the interpretation of surface diffusion coefficients measured from different experimental methods. In other words, we can ask when is the long-wavelength hydrodynamic limit a valid approximation for interpreting diffusion data? Each experimental method has a characteristic diffusion length scale, R, over which the density fluctuations relax. In FEM or STM fluctuation measurements it is the probe area; in quasielastic helium scattering experiments it is the inverse of the momentum transfer $(\Delta q)^{-1}$; in optical diffraction experiments it is the diffraction grating period, etc. If the long-wavelength limit is to be valid, then R must be greater than $1/q_c$, otherwise the extracted diffusion coefficient will be inaccurate.

To see this, consider Fig. 2(a). Suppose the region $q < q_c$ is not accessible experimentally. Measuring $\Omega(q)$ for $q > q_c$ and assuming that it obeys the limiting form ($D_c q^2$) causes the measured D_c to be lower than the actual value. In the case of Fig. 2(b), the measured D_c/D_t would be 6 if $\Omega(q)$ were measured at $qa/\pi = 0.8$ (instead of the actual value of 17). This difference will be more pronounced if a more accurate expression for the pair correlation function $\langle p_l p_{\mathbf{j}} \rangle$ were used because q_c would move to lower values as the temperature is decreased. The error associated with measuring D_c when $q > q_c$ is very relevant to recent literature results that show large differences in the diffusion coefficients measured experimentally[18] or found in Monte Carlo simulations.[19,20]

C. Mixed diffusion and adsorption-desorption

Figure 3(a) shows the case of a mixed process with diffusion and adsorption-desorption in the limit of no interactions ($T/T_c \rightarrow \infty$). For $\Theta = 0.5$, one expects from a detailed balance that $W^A = W^D$ [we have chosen W^D to be the same as the rate of diffusion W_0 in Fig. 3(a)]. As can be seen in Fig. 3(a), $\Omega(q)$ does not go to zero at $q = 0$. This is a result of the linearity of the operator L that makes the contributions from the two microscopic processes additive: $\Omega(0) = (W^A + W^D) + D_c q^2$. One can easily invert an experimental measurement of $\Omega(q)$ around $q = 0$ and still deduce in a unique way the diffusion coefficient and the rate of desorption-adsorption from the curvature and background, respectively.

Figure 3(b) shows the case for mixed processes at a finite temperature $T/T_c = 0.766$ with $W^D = 0.03 W_0$ and $\Theta = 0.5$. In this case a detailed balance requires $W^A = 100 W^D$. Physically, W^A must be larger than W^D to maintain equilibrium by compensating for the higher probability of an atom to desorb rather than to adsorb when repulsive interactions are present. The shape of Ω versus q in Fig. 3(b) looks similar to the curve shown in Fig. 2(b). However, the wave vector q_c, where deviations from a parabolic q dependence begin, is found to shift to a smaller value, $aq_c \sim \pi/6$.

We have intentionally chosen the desorption rate to be relatively low in Fig. 3(b) because higher desorption rates will cause a more dramatic change in the slope of $\Omega(q)$ near $q = 0$. In fact, for a sufficiently large adsorption-desorption term we expect the curvature of $\Omega(q)$ to become negative at $q = 0$, $d^2\Omega/dq^2 < 0$ [as is the case in Fig. 1(b)]. Under these conditions, the parabolic q dependence of $\Omega(q)$ completely breaks down resulting in $\Omega(q)$ having a minimum away from zero. In most systems the desorption energy is usually larger than the diffusion energy (implying $W_0 \gg W^D$), so it is

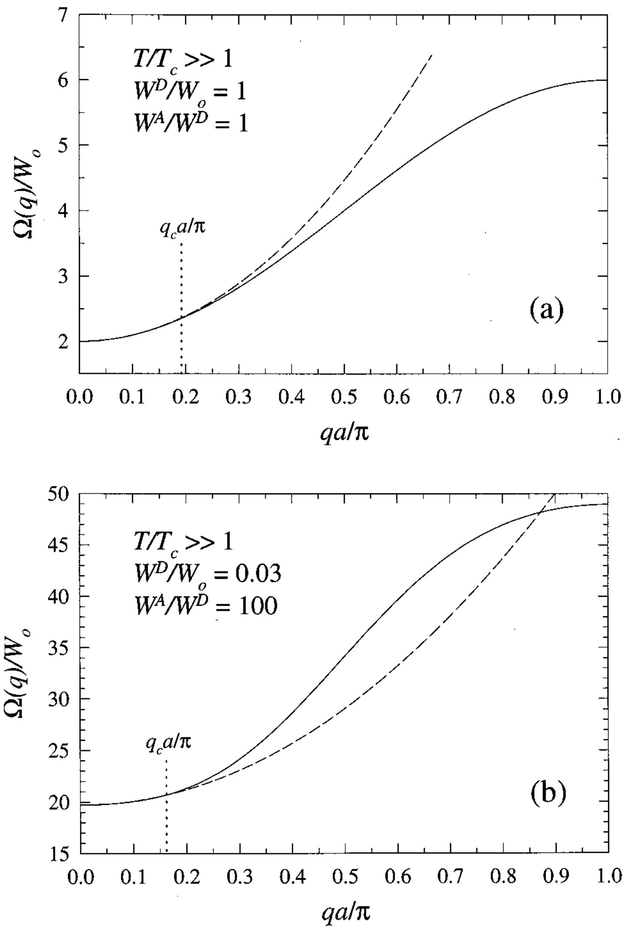

FIG. 3. The q dependence of Ω for $\Theta=0.5$ for mixed diffusion and adsorption-desorption. The wave vector is in the q_x direction $(q_y=0)$. (a) No interactions with $W^D/W_0=1$ and $W^A/W^D=1$. The dashed curve is the hydrodynamic limit with $D_c=D_t$. (b) Strong interaction with $W^D/W_0=0.03$ and $W^A/W^D=100$. The hydrodynamic limit (dashed curve) gives a curvature $D_c=4D_t$. Note the shift of q_c to a lower value when interactions are increased.

unlikely that a negative curvature in $\Omega(q)$ at $q=0$ could be observable, especially at low temperatures. If this situation is to be seen at all, it is most likely to occur at higher temperatures when the desorption rate is closer to the diffusion rate. Of course, if systems and temperatures were found that give rise to a negative curvature in $\Omega(q)$ at $q=0$, it becomes difficult to uniquely determine how much of the curvature is due to diffusion and how much is due to adsorption-desorption. In these cases more information about the system would be necessary (i.e., type of interactions) before the individual contribution from diffusion and adsorption-desorption could be disentangled. Presumably such additional information would be determined from a different experiment.

V. SUMMARY

We have studied the dependence of the dynamic structure factor $\langle S(\mathbf{q},t)\rangle$ on the wave vector $\mathbf{q}$ for different microscopic processes present in an adsorbed surface film (i.e., either diffusion or adsorption-desorption, or both). No matter what the dynamic process is, the structure factor and its autocorrelation function decay as a simple exponential with decay constant $\tau(q)=1/\Omega(q)$ when memory effects are ignored. The q dependence of τ is found to be characteristic of the dynamics. For the case of pure diffusion, we observe the characteristic long-wavelength hydrodynamic limit for τ, $\tau \approx 1/D_c q^2$. When diffusion is replaced by an adsorption-desorption process, strong deviations from the parabolic q dependence are observed as expected (especially at high temperatures).

These results are relevant for the interpretation of equilibrium diffraction intensity fluctuation measurement using HR-LEED. The results of this paper show how information on diffusion rates, adsorption-desorption rates, and adsorbate-adsorbate interaction energies can be extracted from commensurate adsorbate systems on single-crystal surfaces. The results also demonstrate that limiting the range of q to values near the zone boundary causes serious errors in extracting the collective diffusion coefficient.

All of the results presented here have assumed that memory effects are absent and that the quasichemical approximation gives a fair representation of the pair correlation function. The latter approximation is particularly poor when $T<T_c$ and leads to a pair correlation function that is weakly dependent on temperature. Future work will use improved temperature- and spatial-dependent pair-correlation functions to calculate $\Omega(q)$. These calculations will provide a better picture of how $S(q,t)$ depends on different microscopic processes.

ACKNOWLEDGMENTS

This work was supported in part by the Academy of Sciences of the Czech Republic under Grant No. A1010718 (Z.C.), by the NSF under Grant No. DMR-9211249 (E.C.), and by the Director for Energy Research Office of Basic Energy Sciences (M.T.). Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82.

---

[1] *Surface Diffusion: Atomistic and Collective Processes*, edited by M. C. Tringides (Plenum, New York, 1997).

[2] R. Gomer, Surf. Sci. **38**, 373 (1973).

[3] M. C. Tringides, M. Gupalo, Q. Li, and X. Wang, in *Anomalous Diffusion from Basics to Applications*, edited by A. Pekalski, R. Kutner, and K. Sznajd-Weron (Springer, Berlin, 1999); M. Lozano and M. C. Tringides, Europhys. Lett. **30**, 537 (1995).

[4] A. G. Naumovets and Y. S. Vedula, Surf. Sci. Rep. **4**, 365 (1985).

[5] E. H. Conrad, A. Menzel, S. Kiriukhin, and M. C. Tringides, Phys. Rev. Lett. **81**, 3175 (1998).

[6] M. C. Tringides, M. I. Larsson, H. Pfnür, H. Frischat, K. Budde, and M. Henzler, J. Appl. Phys. **82**, 1507 (1997).

[7] J. Ellis, A. P. Graham, and J. P. Toennis, Phys. Rev. Lett. **82**, 5072 (1999).

[8] G. A. Reider, V. Hofer, and T. F. Heinz, Phys. Rev. Lett. **66**, 1994 (1991).

[9] C. W. Gardiner, *Handbook of Stochastic Methods for Physics, Chemistry and the Natural Sciences* (Springer-Verlag, Berlin, 1985).

[10] Z. Chvoj, E. H. Conrad, and M. C. Tringides (unpublished).

[11] J. M. Cowley, *Diffraction Physics* (North-Holland, Amsterdam, 1984), p. 36.

[12] E. Fick and G. Sauermann, *The Quantum Statistics of Dynamic Processes* (Springer-Verlag, Berlin, 1990).

[13] R. Kubo, M. Toda, and N. Hashitsume, *Statistical Physics II* (Springer-Verlag, Berlin, 1991).

[14] R. M. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, New York, 1939), p. 430.

[15] A. Menzel, K. Wiesenfeld, E. H. Conrad, and M. C. Tringides, Phys. Rev. B **61**, 2997 (2000).

[16] E. M. Lifshicz and L. P. Pitaevkiy, *Statistical Physics II* (Nauka, Moscow, 1978).

[17] D. A. Reed and G. Ehrlich, Surf. Sci. **102**, 588 (1981).

[18] A. P. Graham, W. Silvestri, and J. P. Toennis, in *Surface Diffusion: Atomistic and Collective Processes*, edited by M. C. Tringides (Plenum, New York, 1997).

[19] Q. Li and M. C. Tringides, Surf. Sci. **365**, 495 (1996).

[20] C. Uebing and R. Gomer, Surf. Sci. **381**, 33 (1997).