KINETIC LATTICE GAS MODEL FOR ADSORPTION, DESORPTION AND DIFFUSION: AN INVESTIGATION OF TRUNCATION SCHEMES

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Abstract

The lattice gas model of an adsorbate, which assigns adsorbed particles to a regular array of sites of a substrate, permits a succinct description of the equilibrium properties of the adsorbate. To rigorously describe its evolution, specifically adsorption from and desorption to its gas phase and surface diffusion, in the presence of lateral interactions, a kinetic lattice gas model is set up. From the master equation a hierarchy of equations of motion is derived for the coverage and the higher-order particle correlators. A manageable set of evolution equations is derived by examining different methods of truncation of this hierarchy and factorizations of the correlators. These equations are developed with a set of computer codes.

From these we calculate the equilibrium correlators of a gas adsorbed on a square-latticed substrate. These, as well as thermodynamic quantities of interest (isosteric heat of adsorption, chemical potential), are compared with quasi-exact results obtained using the transfer matrix method and with existing analytic approximation methods. We explore thermal desorption under quasi-equilibrium and nonequilibrium conditions induced by limited surface diffusion. We show that a five-correlator basis on a square lattice gives very good results. The extension of the basis to fifteen functions improves the quality even further. The latter is now the best available analytic approximation for a description of the evolution of a lattice gas with interactions. The approach can be generalized to multi-component adsorbates and other surface processes.

List of Abbreviations and Symbols

a_s Adsorption surface area per particle

a Heating rate

A_i Adsorption coefficients

c Site coordination number

E_s Single adparticle free energy

F Helmholtz free energy

h Planck's constant

q_{int} Adparticle internal partition function

J_0 Diffusion coefficient

K Interaction parameter

K_c Critical interaction parameter

k_B Boltzmanns constant

L Landau potential

m Adparticle mass

ML Monolayer

Ns Number of adsorption sites

$\mathbf{n}$ Vector describing the microstate of the system

P Pressure of the gas phase

$\overline{P}$ Equilibrium gas phase pressure

$P_0(\mathbf{n})$ Equilibrium probability for the state $\mathbf{n}$

Q Diffusion activation barrier

Q_{iso} Isosteric heat of adsorption

QCA Quasichemical approximation

R_d Rate of desorption

S_0 Sticking coefficient at vanishing coverage

t Time

T Temperature

T_c Critical temperature

TM Transfer Matrix

TPD Temperature programmed desorption

V_0 Depth of the surface potential

V_1 Nearest neighbor adparticle interaction

$W(\mathbf{n}'; \mathbf{n})$ Transition probability

Z Partition function

α QCA parameter

β Inverse temperature $\beta = 1/k_B T$

δ Kronecker delta symbol

λ Matrix eigenvalue

λ_{th} Thermal de Broglie wavelength

μ Chemical potential of a 2-D system

μ_a Chemical potential of the adsorbate

μ_g Chemical potential of the gas phase

ν_x, ν_y, ν_z Frequencies of adparticle vibrations

ν_{diff} Hopping frequency for diffusion

θ Surface coverage

Ξ Grand partition function

$\langle ij \rangle$ Nearest neighbors

$\langle ij' \rangle$ Next nearest neighbors

$\Big\langle \bullet \Big\rangle$ Lowest order correlator, equivalent to the surface coverage

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Chapter 1

Introduction

Surface reactions play an important role in current technology [1]. Almost all of the chemicals produced today use catalytic processes where the reactions occur on the surface of a catalyst. Integrated circuits are made by depositing films on the surface of a semiconductor. Surface reactions also play a key role in the production of fuels, the disposal of noxious chemicals, the corrosion and passivation of metals, the processing of ceramics, the production of photographic film and friction and lubrication. Surface interactions are crucial in regulating the behavior of biological membranes. As modern technology progresses and physical devices become smaller and smaller, entering into the realm of nanotechnology, the need for understanding the nature of the interactions of solid surfaces with other solids, fluids and gases becomes more and more important.

The new environmental pollution standards will soon require the use of catalytic converters on each transportation vehicle, and this makes the study and modeling of the adsorption, desorption and diffusion processes of atoms or molecules on metallic surfaces even more timely. In particular, theory must develop and expand frameworks in which not only simple processes, such as one species adsorbing on just one preferred surface site, can be modeled but also complex systems such as competing adsorption and subsequent reaction of several species on different sites. What kind of theory is appropriate depends on the systems to be studied and also on the level of understanding that one wants to achieve. Before we survey such theories we will discuss in general terms the basic physics involved in surface processes.

We start, following [2], by considering the statics of a gas phase in contact with the surface of a solid. The gas particles will be subjected to surface forces arising from the solid whose potential is of the general form depicted in Fig.1.1. Such a potential can be viewed as arising from a sum of long-ranged attractive and short-ranged repulsive forces. At separation distances, typically, more than $5\mathring{A}$ the atomic structure of the surface is smeared out and the interaction potential V_s, between the particle and the surface becomes a function only of the distance, z , from the surface. If the gas particle is charged it is attracted to the surface by its image charge. Even if the incoming particle is neutral, it experiences a long-ranged attractive dispersion or van der Waals force. The latter is the result of virtual electron-hole pairs excited in the metal by spontaneous fluctuations in the charge cloud of the gas particle. Such fluctuating dipoles and higher multipoles, as derived in [3], induce their images in the solid leading to an overall attractive force, whose potential energy is given in the dipole approximation by the van der Waals interaction:

$$V(z) = -C/z^3 \tag{1.1}$$

When the particle approaches within a few angstroms of the solid, details of the atomic structure become important and quantum mechanics must be invoked to account for the short range interactions. For closed shell atoms and molecules such as rare gases, methane etc., the van der Waals interaction is still a major contribution, even at short distances. In such situations, i.e. when the electronic configuration of the adsorbing particle remains more or less intact except for fluctuating dipoles, one speaks of physical adsorption or physisorption.

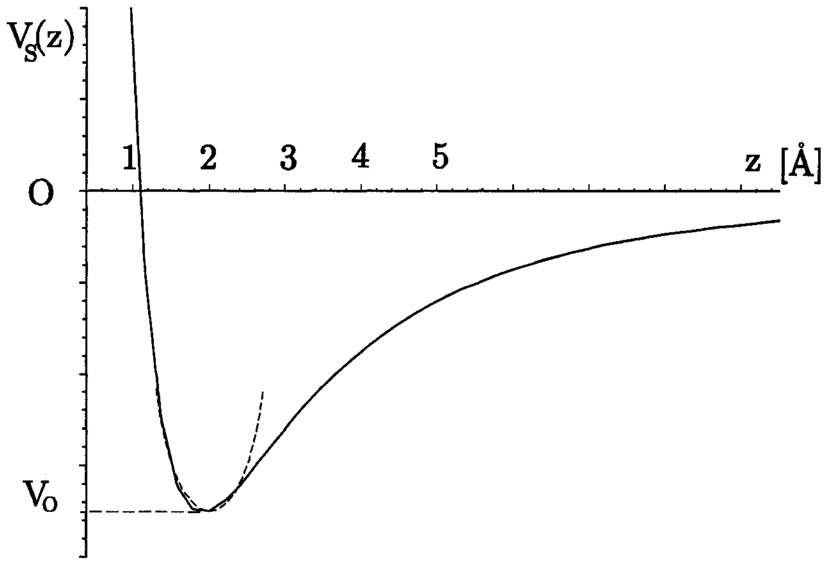


Figure 1.1: Representative surface potential as a function of the distance above the surface, z, (solid line) and its parabolic approximation (dashed)

For reactive atoms and molecules, such as O, CO, etc., see for instance [4], a substantial rearrangement of electronic orbitals of the adparticle occurs as it approaches the surface, i.e. chemical bonds are established. In this situation one speaks of chemisorption. The strength of the chemisorption surface bond is proportional to the wave function overlap of valence electrons on the adparticle and metal electrons near the Fermi level. Because these wave functions decay exponentially, the attraction resulting from bond formation is also exponential as a function of distance from the surface.

As the adparticle approaches even closer to the surface Coulomb repulsion and Pauli exclusion produce strong repulsion. The precise form of the surface potential can only be obtained from quantum mechanical calculations. These days most such calculations are based on density functional theory, as generally implemented in quantum chemistry. Not surprisingly one finds that adparticles can bind to different

Figure 1.2: Surface potential along the surface (solid line) and its parabolic fit (dashed)

symmetry sites on a surface such as in an ontop position above a metal atom, in bridge positions between two atoms, or in three- or fourfold hollow sites.

All particles trapped in the surface potential make up the adsorbate. The potential minimum to the vacuum level is defined as the binding energy ($-V_0$, with V_0 positive). This binding energy for physisorption is typically less than 0.5eV and around a few eV for chemisorption.

For a perfect substrate (i.e. one without defects) this potential minimum will change periodically along any direction on the substrate, going between peaks and valleys, as shown on Fig.1.2. This surface corrugation is described by the dependence of the surface potential, $V_s(\overrightarrow{R}, z)$, on a two-dimensional vector $\overrightarrow{R}$ along the surface, in addition to the distance z above the surface. Thus the adsorbed particle is, in general, not free to move laterally on the surface. To do so it has to jump over potential barriers that separate the potential minima. If the temperature is sufficiently low the adparticle can only vibrate around its equilibrium position, at the bottom of the potential well at a particular site of the lattice structure. Increasing the temperature makes the hops from one potential minimum to another more probable, accounting for the surface diffusion. In the extreme case, when the potential barrier parallel to the surface is much less than k_BT, the corrugation is negligible and the surface becomes flat for the adparticle. Then the adsorbate can be treated as a two-dimensional gas.

So far we have only looked at a single gas particle close to the surface of a solid. When more particles arrive from the gas phase one must also account for their mutual interactions. These lateral interactions can also be extracted from quantum mechanical calculations. Once this is done we have complete knowledge of the many-body Hamiltonian of the adsorbate and thus are in a position to calculate its equilibrium properties such as phase diagrams, adsorption isotherms etc. by minimizing its Helmholtz free energy in the canonical ensemble or the Landau potential in the grand canonical ensemble.

In practice for the calculation of these equilibrium properties, via equilibrium statistical mechanics, the form of the Hamiltonian is usually simplified to that of a "lattice gas". Here the corrugated surface potential is represented by its potential minima alone i.e. each adparticle may reside only at the vertices of a lattice with a characteristic binding energy, $-V_o$. As well, the adparticle interactions, whether direct or via the substrate, are transformed to a set of effective interactions between particles residing at these vertices, or adsorption sites.

Because the ultimate aim is to understand surface processes we have to go beyond equilibrium statistical mechanics and identify the microscopic energy transfer processes that lead to adsorption, desorption, diffusion and surface reactions. The relevant time scales of these govern the time evolution of a gas-solid system. When a gas particle approaches the surface of a solid it either bounces back elastically or, if it gets rid of enough energy within the attractive region of the surface potential, it is trapped. However, even if it descends all the way to the bottom of the surface potential well, it will eventually evaporate again; thus absolute trapping does not exist, there always exists a possibility for the particle to evaporate. For times t_0 (usually $10^{-13}s$) required for a particle to traverse the potential well, it will remain close to the top of the well within an energy of k_BT. In this time there is a fair chance that the particle escapes again. On the other hand, the particle might loose energy when colliding with the surface in an inelastic scattering process in which it excites either phonons or electron-hole pairs in the solid. As a consequence the particle will begin its descent to the bottom of the potential well. In a quantum picture this descent corresponds to a cascade of transitions between the bound states of the surface potential, each downward transition accompanied by emission of phonons or electron-hole pairs into the solid and each upward transition with the absorption of phonons or electron-hole pairs. This adsorption process, characterized by a time scale t_a is more likely at low temperatures. Accommodation of a gas particle in the surface potential for times longer than an order of magnitude of the oscillation time is viewed as surface adsorption.

The adparticle will oscillate around the minimum of the surface potential. By excitation or phonon absorption from the surface it might acquire energy to climb up the surface potential. It will eventually succeed in doing so after a desorption time t_d. If t_a is much shorter than t_d, then the adsorption and desorption are statistically independent, and the processes of sticking, energy accommodation (i.e. thermalization) and desorption can be separated in different terms. This is most likely the case if the thermal energy $k_B T$ is much less than the depth of the surface potential well.

Another process of importance in an adsorbate is surface diffusion. It is the result of the adparticles hopping from one surface potential minimum, i.e. adsorption site, to another one close by. If the time scale of diffusion, t_{diff}, is short compared to the time scale of adsorption (desorption) the adsorbate will arrange itself in a state of quasi-equilibrium during adsorption (desorption). By this we mean that the geometric structure and the energetics of the adsorbate is the same as if the adsorbate were in equilibrium at the instantaneous coverage with all particle correlators assuming their equilibrium values.

The theory of adsorption-desorption kinetics under conditions of quasi-equilibrium has been advanced more than fifteen years ago within the framework of non-equilibrium thermodynamics, [5], [6], [7], [8],[9] and is now capable of describing complex gas-solid systems with different kinds of molecules adsorbing on several adsorption sites and undergoing surface reactions.

Most mesoscopic theories of adsorption and desorption are based on the lattice gas model. It is constructed for a periodic single crystal surface without defects. The states are characterized by site occupation numbers and their energetics enter a Hamiltonian via surface binding energies and lateral interactions. The statistical mechanics of the lattice gas model allows the calculation of phase diagrams, adsorption isotherms and other equilibrium properties. Methods employed fall into camps of analytical approximations (Bragg-Williams [10], quasichemical approximation [11],[12], [13] and Kikuchi-Hill [14] cluster approximations), and quasi-exact Monte Carlo simulations and Transfer matrix methods. A couple of these methods are discussed in Chapter 2.

To study the kinetics of adsorption-desorption and diffusion within the context of the lattice gas model one introduces a function that gives the probability of finding the adsorbate in a given microstate at time t. This probability evolves according to a Markovian master equation with transition probabilities describing adsorption, desorption and diffusion and satisfying detailed balance. The time independent solution of this master equation yields yet another approach to the equilibrium properties of the adsorbate.

This master equation can be solved by kinetic Monte Carlo simulation,[15],[16],[17], [18], with well defined transition probabilities to produce the kinetics. The main disadvantage of the Monte Carlo approach is that the statistical fluctuations inherent in the method impair a systematic and fast assessment of the quantities of interest, as a function of different input parameters. Likewise, extensive run-times may be required to evolve to the equilibrium state. Although very useful, Monte Carlo methods are not a substitute for a formal statistical theory in which one first derives a small set of kinetic equations from which observable quantities and relationships are derived. This will be the approach followed in this work. However, it is generally believed that for studies of systems with many binding sites or long range interactions Monte Carlo simulations are more economic.

In a one-dimensional adsorbate system exact results have been worked out, [19], [20], that have served as a guide for simple approximations in two-dimensional systems, [21], [22]. The main aim of this thesis is to advance the kinetic lattice gas model for a two-dimensional system further, by developing a rigorous and unique approximation scheme in which convergence is guaranteed in the sense that each higher level approximation will yield a better result for the overall equilibrium properties and the kinetics of a particular gas-solid system.

The thesis is structured as follows: in the next chapter we formulate, after a brief summary of the basic thermodynamics and kinetics, the lattice gas model by first specifying its Hamiltonian. We then survey known results from statistical mechanics of a non-interacting adsorbate and show how lateral interactions can be qualitatively described within the quasichemical approximation. After that we describe the transfer matrix method, which has been developed into an efficient tool to obtain the equilibrium properties "exactly".

In Chapter 3 we turn to the kinetic lattice gas model, which is based on the master equation for a Markovian process. From this equation we derive a hierarchy of equations of motion for the coverage and many particle correlators, mathematically equivalent (and thus unsolvable) to the original master equation. The main challenge and result of this thesis is to find a systematic closure approximation that truncates this hierarchy at a manageable level. We will show that retaining the equations for correlators involving from 1 to 4 neighboring sites on a square lattice gives very good results which is assessed by retaining on the next level all correlators up to 15. To actually derive these equations with hundreds of terms on their right hand sides we have developed a series of algebra codes, examples of which are given in Appendices.

In Chapter 4 we calculate the equilibrium properties of a gas adsorbed on a surface with a square lattice of adsorption sites using our approach and compare the outcome with the cluster variation methods and transfer matrix results. Chapter 5 is then devoted to results on the adsorption-desorption kinetics with emphasis on the role of limited surface diffusion. In Chapter 6 we give a brief summary and an outlook on what can now be done for more complicated adsorbate systems using our approach.

Chapter 2

Lattice Gas Model

We begin this section with a short review of the basic thermodynamics and some kinetics to set the stage for the proper formulation of models that will be the basis on which the statistical mechanics for the equilibrium and non-equilibrium properties of adsorbates will be developed.

2.1 Thermodynamics and kinetic preliminaries

2.1.1 Thermodynamics

In ordinary three-dimensional thermodynamics, in the energy representation, the internal energy U is expressed as a function of the entropy S, the volume V and the number of particles N_i of each of species present. The fundamental thermodynamic relation is written as

$$dU = TdS - PdV + \sum \mu_i dN_i \tag{2.1}$$

or, after integrating when holding all intensive variables T, P, μ_i constant

$$U = TS - PV + \sum \mu_i N_i \tag{2.2}$$

We consider now an adsorbate-substrate system which contains N_{sub} particles of the substrate and N_{ad} adparticles in equilibrium with the gas phase. The fundamental thermodynamic relation Eqn.(2.1) must then be extended to read,

$$dU = TdS - PdV + \mu_{sub} dN_{sub} + \mu_a dN_{ad} \tag{2.3}$$

On the other hand for the pure substrate substance it has the form

$$dU_0 = TdS_0 - PdV_0 + \mu_0 dN_{sub} \tag{2.4}$$

Subtracting Eqn.(2.4) from Eqn.(2.3), and defining excess quantities

$$U_s = U - U_0, V_s = V - V_0, S_s = S - S_o, \varphi = \mu_0 - \mu_{sub} \tag{2.5}$$

we get for the differential energy for the adsorbate,

$$dU_s = TdS_s - PdV_s - \varphi dN_{sub} + \mu_a dN_{ad} \tag{2.6}$$

In the special case when the substrate molecules are inert, U_s becomes just the energy of N_{ad} adsorbed particles in the potential field of the inert adsorbent and the energy of the adsorbent subtracts out, except for the interaction energy between the adsorbent and the the adsorbate. As for S_s and V_s, they are additive extensive quantities describing the adsorbate. N_{sub} is proportional to the surface area, so that φ is proportional to the spreading pressure.

One usually takes N_{sub} to be the total number of lattice sites, N_s, in the surface and Eqn.(2.6) becomes

$$dU_s = TdS_s - PdV_s - \varphi dN_s + \mu_a dN_{ad} \tag{2.7}$$

Equation (2.7) has exactly the same form as that for the three dimensional thermodynamics except for the extra term $-\varphi dN_s$, [24]. If the gas phase is in equilibrium with the adsorbed gas particles then the chemical potentials must be equal

$$\mu_a(\theta, T) = \mu_g(P, T) \tag{2.8}$$

where μ_g is the chemical potential of the gas phase as a function of temperature and pressure. Likewise μ_a is the chemical potential of the adsorbate as a function of the coverage $\theta = N_{ad}/N_s$ and of temperature. From their equality we get the adsorption isotherms

$$\theta = \theta(T, P) \tag{2.9}$$

and the isosteric heat of adsorption per particle

$$Q_{iso} = k_B T^2 \frac{\partial \ln P}{\partial T}|_\theta \tag{2.10}$$

The latter is a measure of the energy released upon adsorption under isosteric conditions. Furthermore one can show [24] that the spreading pressure of the adsorbate is given by

$$\varphi = RT \int_0^P \theta(T, P')d(\ln P') \tag{2.11}$$

The entropy per particle of the adsorbate is then given by

$$s_s = S_s/N_{ad} = -k_B T \frac{\partial \ln P}{\partial T}|_\varphi + s_G \tag{2.12}$$

where s_G is the entropy per particle in the gas phase and $P = P(T, \varphi)$ can be obtained by inverting Eqn.(2.11).

Thus we say that all the equilibrium properties of the adsorbate can be obtained once we have calculated the chemical potential, using methods of statistical mechanics. We will see in the next section that the desorption kinetics is also determined by the chemical potential for adsorbates in which quasi-equilibrium is maintained by fast surface diffusion.

2.1.2 Adsorption and desorption kinetics

To set the stage for the study of adsorption-desorption kinetics in later chapters we consider here the most frequent situation of an adsorbate where surface diffusion is so fast (on the time scale of desorption) that the adsorbate is maintained in quasi-equilibrium throughout the desorption process. That is to say, at the coverage $\theta(t)$, at some particular time t during adsorption or desorption, at temperature $T(t)$, the adsorbate can be completely characterized by its chemical potential, $\mu_a(\theta(t), T(t))$ as a function of coverage and temperature.

To derive an explicit expression of the adsorption and desorption rates we consider the simplest adsorbates, i.e. no dissociation on the surface, one molecular component and submonolayer adsorbates. The more general case has been considered elsewhere (for further references see [25]). We look at a situation where the gas phase pressure P, is different from its value, $\overline{P}$, which maintains an adsorbate at coverage θ. There is then an excess flux to re-establish equilibrium between gas phase and adsorbate so that we can write

$$d\theta/dt = S(\theta, T)\left(P - \overline{P}\right)\frac{a_s\lambda_{th}}{h} \tag{2.13}$$

where

$$\lambda_{th} = h/\sqrt{2\pi m k_B T} \tag{2.14}$$

is the thermal wavelength of a particle with mass m, and a_s is the adsorption surface area per particle [25].

Next we express the equilibrium pressure in terms of the gas phase chemical potential, $\mu_g(P,T)$,

$$\overline{P} = \frac{k_B T}{\lambda_{th}^3} Z_{int} \exp(\mu_g / k_B T) \tag{2.15}$$

Here Z_{int} is the intramolecular partition function accounting for rotations and vibrations. However, in equilibrium, the chemical potential in the gas phase is equal to that in the adsorbate, $\mu_a(\theta,T)$, so that we can write the desorption rate in Eqn.(2.13) as

$$R_d = S(\theta,T) \frac{a_s^2}{\lambda_{th}} \frac{k_B T}{h} Z_{int} \exp(\mu_a / k_B T) \tag{2.16}$$

This is the principal result for the rate of desorption from an adsorbate that remains in quasi-equilibrium throughout desorption ("quasi" in the sense that there is an equilibrium on the surface, but there is no equilibrium between the particles in the three-dimensional gas and those on the surface). Noteworthy is the clear separation into a dynamic factor, the sticking coefficient $S(\theta,T)$, and a thermodynamic factor involving single particle partition functions and the chemical potential of the adsorbate. The coefficient, $S(\theta,T)$, is defined as the ratio of the rate of adsorption of gas to the rate of collision with the surface i.e. simply the probability that an incoming particle sticks. It is a measure for the efficiency of energy transfer in adsorption. Since energy supply from the substrate is required for desorption, the sticking coefficient, albeit usually at a higher temperature, must appear in the desorption rate by the detailed balance argument. The sticking coefficient cannot be obtained from thermodynamic arguments but must be calculated from a microscopic or mesoscopic theory or be postulated in a phenomenological approach, based on experimental evidence for a particular system or some simple arguments.

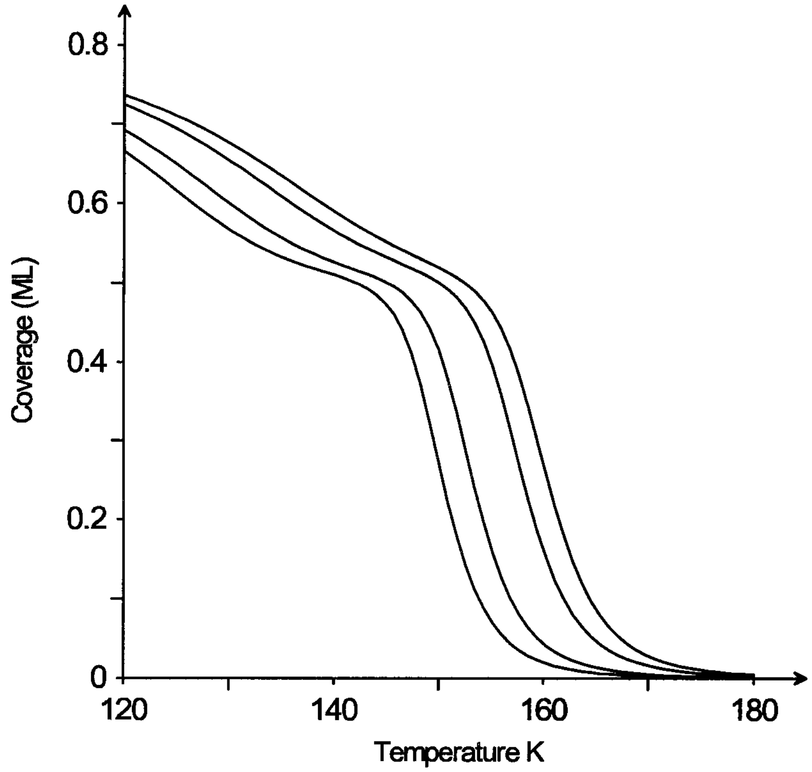


Figure 2.1: Coverage isobars for N_2 on Ni(110) at pressures (bottom to top at $T = 140K$) P =5.0x10^{-6}, 1.0x10^{-5}, 4.0x10^{-5}, 8.5x10^{-5} Pa.

Eqns. (2.13,2.15,2.16) show that to determine the equilibrium properties of an adsorbate and also the adsorption-desorption (and dissociation) kinetics under quasi-equilibrium conditions we need to calculate the chemical potential as a function of coverage and temperature. To do this we need a model of the adsorbate which will be introduced shortly.

2.1.3 Experimental preliminaries

The experimental study of adsorption-desorption processes falls into two broad classes: (i) experiments in which the adsorbate is in equilibrium with the gas phase above it and (ii) experiments in which the rates of adsorption and desorption are not equal and the surface coverage changes with time. This may happen quickly, on the time scale of surface diffusion, in which case the adsorbate is not in equilibrium during the experiment either. The latter case is less commonly explored.

In equilibrium usually the external pressure of the gas and the temperature of the surface are kept constant. An obvious and important experiment is to observe how the coverage changes with respect to these external parameters. If the equilibrium coverage is plotted as a function of substrate temperature for constant pressure, one speaks of isobars. If the temperature is constant, the respective curves are referred to as isotherms.

A typical example of isobaric plots is shown on Fig.2.1. The isobars are labelled by the equilibrium gas pressure of N_2 above the Ni(110) surface [26], [27].

Differentiating these isotherms with respect to the temperature one acquires Q_{iso}. For this system it is given on Fig.2.2. The drop at 1/2 ML in this case implies a change in the binding of the adsorbate.

A common and direct way to explore the kinetics of the adsorbate is to use the technique of Temperature-Programed Desorption (TPD). Gas is first adsorbed onto a cold surface, then the surface is heated in a controlled way (usually in a linear fashion) and a mass spectrometer is used to measure the rate at which products desorb. By varying the initial exposure, a set of desorption traces (TPD spectra) is generated, from which one can also estimate the binding to the surface and the effects of adsorbate interactions [40]. A typical example of such spectra is given on Fig.2.3. It shows the rate of desorption of N_2 from the same Ni surface. As the initial coverage is increased the desorption peaks increase in area. For coverages above 1/2 ML a

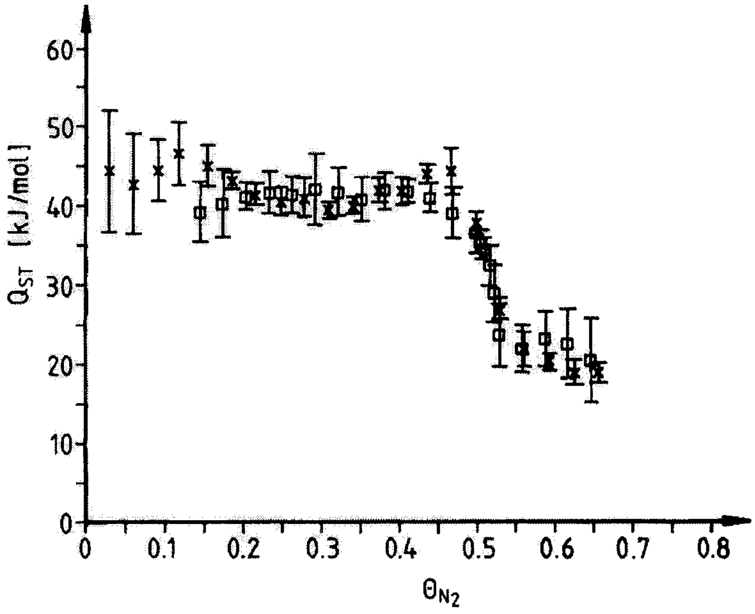


Figure 2.2: Isosteric heat of adsorption Q_{iso} as a function of surface coverage for N_2 on Ni(110)

second low-temperature appears at $120K$ correlated, of course, with the behavior of the isobars.

Another example of TPD is the desorption of Ni from a tungsten surface [28] is shown on Fig.2.4. In this case even for coverages above 1/2 ML only one peak is observed and all peaks are displaced to higher temperature with increasing coverage, unlike the previous example.

The characteristic features of these data are those which a theoretical model should explain.

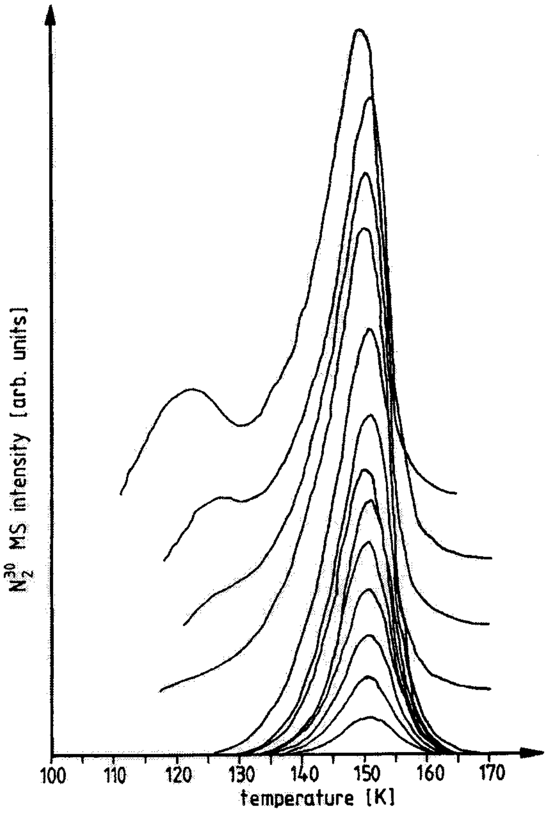


Figure 2.3: Temperature programmed desorption with a heating rate of $1.5Ks^{-1}$of N_2 on Ni(110). Initial coverages up to $\theta = 0.65$ ML. Some peaks displaced for clarity.

2.2 Hamiltonian

Most microscopic theories of adsorption and desorption are based on the lattice gas model. It is constructed for a periodic single crystal surface without defects. In general, the unit cell of such a surface has many adsorption sites, in particular for higher index planes, but even for low index planes adsorption can take place on several different types of sites. To outline the derivation of the lattice gas model we simplify the task and only take into account the most strongly bound adsorption site which, on a square lattice, we take to be the ontop site. We also assume that adsorption is

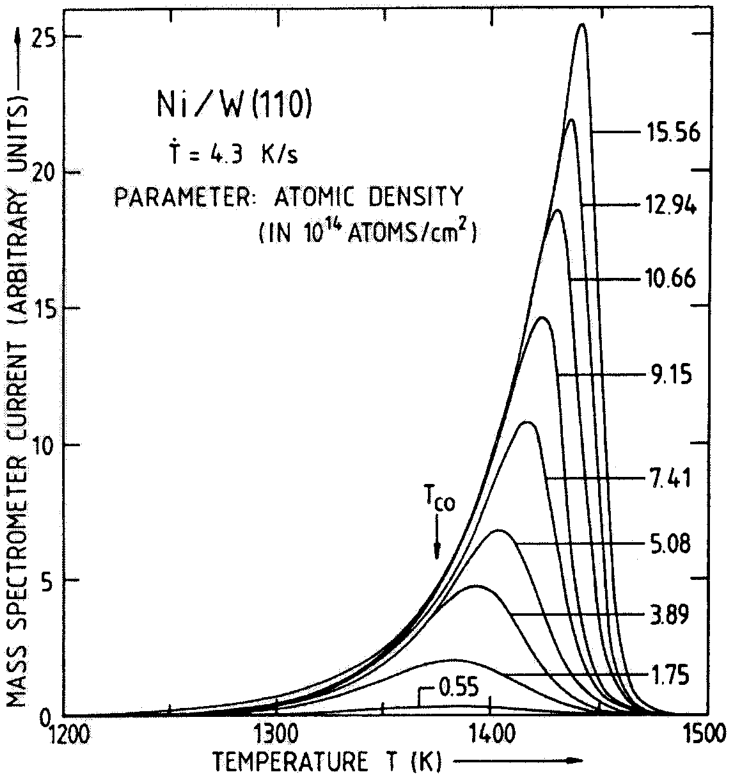


Figure 2.4: Temperature programed desorption spectra of Ni on W(110). Heating rate 4.3 Ks^{-1}, parameter is the initial Ni density in 10^{14} atoms/cm^2.

restricted to the submonolayer regime and consider only gas-solid systems in which the surface structure and the adsorption sites do not change as a function of coverage. We label the unit cells by an index i, running from 1 to the total number of sites, Ns. Each cell can be either occupied or empty. This is accounted for by a microscopic occupation number, n_i, which takes the value 1 if the cell is occupied and 0 if it is not. A microstate of the system is then given by a vector $\mathbf{n} = (n_1...n_i...n_{N_s})$; thus there are 2^{N_s} microstates, i.e. all possible sequences of zeroes and ones.

The dynamics of the system are introduced by a model Hamiltonian which, for the simplest system of a one component adsorbate with one adsorption site per unit cell, is

$$H = E_s \sum_i n_i + V_1 \sum_{\langle ij \rangle} n_i n_j + V_2 \sum_{\langle ij' \rangle} n_i n_{j'} + \ldots \tag{2.17}$$

Here E_s is a single particle free energy and V_1 and V_2 are the two-particle interactions between nearest neighbors $\langle ij \rangle$ and next nearest neighbors $\langle ij' \rangle$, respectively. As long as the number of particles in the adsorbate does not change, the first term in (2.17) can be dropped from further consideration. However if we want to study adsorption-desorption kinetics the number of adparticles changes as a function of time and all variables introduced in the phenomenological hamiltonian must be considered carefully. This is particularly true for the single particle energy E_s which is the primary energy responsible for the localization of the adsorbate. It is the result of the interactions of a gas phase particle with the substrate, and causes, at least at low coverages, the adsorbate to be in registry with the surface lattice. At higher coverages, the interactions between adsorbed particles might become strong enough to create its own periodicity of intrinsic localization, not necessarily commensurate with the substrate. We will be concerned only with external localization. Neglecting band structure effects, the energy spectrum of E_s consists of localized bound states. We label these energies of the surface potential by ϵ_i. The partition function for a particle trapped in the surface potential is given by

$$Z = \sum_i \exp((\epsilon_i + V_0)/k_B T) \tag{2.18}$$

where V_0 is the depth of this potential. Thus the partition function per site is

$$Z = q_3 q_{int} \exp(V_0/k_B T) \tag{2.19}$$

where q_{int} is the internal partition function for vibrations and (frustrated) rotations of the adsorbed particle. If we approximate the surface potential at each site by independent harmonic oscillators of frequency ν_x, ν_y and ν_z we get,

$$q_3 = q_z q_y q_z \tag{2.20}$$

Then the vibrational partition function of an adsorbed particle in the z direction (respectively for the x and y direction) is,

$$q_z = exp\left(h\nu_z/2k_BT\right) / \left[exp\left(h\nu_z/k_BT\right) - 1\right] \tag{2.21}$$

On the other hand, if the adsorbate is mobile, we can approximate it by a gas in two dimensions, and get

$$q_3 = q_z(\lambda_{th}^2/a_s) \tag{2.22}$$

From Eqn. (2.19) we get the Helmholtz free energy,

$$F = -V_0 - k_BT\ln\left(q_3 q_{int}\right) \tag{2.23}$$

We note that we get the same free energy per particle from the lattice gas hamiltonian (without accounting for the lateral interactions) (2.17), if we identify

$$E_s = F \tag{2.24}$$

Because the lattice gas model does not describe the dynamics of motion of an adsorbed particle in cell i, the respective degrees of freedom can only enter the model as thermal averages via q_3 and q_{int}. This concludes the proper specification of the lattice hamiltonian.

To proceed to the equilibrium statistical mechanics of the lattice gas model we can work in the canonical ensemble at fixed temperature and number of adsorbed particles (and of course at fixed area or number of lattice sites) and get the Helmholtz free energy from

$$F(T,N,N_s) = -k_B T \ln[Z(T,N,N_s)] \tag{2.25}$$

with the partition function

$$Z(T,N,N_s) = \sum_{n_1,n_2,...=0}^{1} \exp\left[-\beta H(n_1,n_2,...)\right] \tag{2.26}$$

from which we get the chemical potential by differentiation

$$\mu_a = \frac{\partial F}{\partial N}|_{T,N_s} \tag{2.27}$$

On the other hand we can also start from the grand canonical ensemble at fixed chemical potential with the Landau potential

$$L(T,N_s,\mu_a) = -k_B T \ln(\Xi) \tag{2.28}$$

where

$$\Xi(T,N_s,\mu_a) = \sum_{\mathbf{n}} \exp\left[-(H(\mathbf{n}) - \mu_a N(\mathbf{n}))/k_B T\right] \tag{2.29}$$

$$N(\mathbf{n}) = \sum_{i=1}^{N_s} n_i \tag{2.30}$$

In this case the coverage, the average site occupancy, is obtained by differentiation with respect to μ_a,

$$\theta = \frac{\langle N \rangle}{N_s} = \frac{k_B T}{N_s} \frac{\partial \ln \Xi}{\partial \mu_a} \tag{2.31}$$

The internal energy and other ensemble averages also follow directly by differentiation of the partition function with respect to the independent variables.

2.2.1 Non-interacting adsorbate

We start with a non-interacting molecular adsorbate for which the chemical potential is given by

$$\mu_a(\theta, T) = -V_0 + k_B T[\ln(\theta/(1-\theta)) - \ln(q_3 q_{int})] \tag{2.32}$$

This follows by retaining only the first term in Eqn.(2.17) and calculating subsequent expressions to arrive at Eqn.(2.27). Inserted in Eqn.(2.15) this gives the Langmuir isotherm

$$\overline{P} = \frac{k_B T}{\lambda_{th}^3} Z_{int} \exp(\mu_a/k_B T) = \frac{k_B T}{\lambda_{th}^3} \frac{Z_{int}}{q_3 q_{int}} \exp(-V_0/k_B T) \frac{\theta}{1-\theta} \tag{2.33}$$

from which we get the isosteric heat of adsorption

$$Q_{iso}(\theta, T) = k_B T^2 \frac{\partial \ln \overline{P}}{\partial T}|_\theta = V_0 + \frac{5}{2} k_B T - k_B T^2 \frac{\partial}{\partial T} \ln(q_3 q_{int}/Z_{int}) \tag{2.34}$$

a coverage independent quantity. Substituting Eqn.2.32 in Eqn.2.16 we obtain the desorption rate

$$R_d = S(\theta, T) \frac{\theta}{1-\theta} \frac{a_s}{\lambda_{th}^2} \frac{k_B T}{h} \frac{Z_{int}}{q_3 q_{int}} \exp(-V_0/k_B T) \tag{2.35}$$

The case when the sticking probability is simply determined by site-exclusion, $S(\theta, T) = S_0(T)(1-\theta)$ is called "Langmuir kinetics". In this case the desorption rate R_d is that of a first order "reaction" at low coverage. This simple picture breaks down when either the sticking coefficient depends differently on the coverage, as it does for instance for precursor-mediated adsorption or when lateral interactions become important.

In all calculations we have assumed Langmuir kinetics, but we will revisit the case of non-Langmuir kinetics in a separate section.

2.2.2 Lateral interactions in the quasichemical approximation

To gain some qualitative insight into the effect of lateral interactions it is useful to employ simple analytical approximations in the calculation of the chemical potential of which the quasichemical approximation is the best suited. We split the chemical potential into a non-interacting part, Eqn.(2.32) , and a term due to lateral interactions, $\mu_a = \mu_a^{(ni)} + \mu_a^{(lat),}$ and get for the latter, for c nearest neighbor interactions,

$$\mu_a^{(lat)}(\theta, T) = cV_{1n} + \frac{1}{2}ck_BT \ln \left[\frac{\alpha - 1 + 2\theta}{\alpha + 1 - 2\theta} \frac{1 - \theta}{\theta} \right] \tag{2.36}$$

where

$$\alpha^2 = 1 - 4\theta(1 - \theta) \left[1 - \exp(-V_1/k_BT)\right] \tag{2.37}$$

The interaction adds to the isosteric heat which now reads

$$Q_{iso}(\theta, T) = Q_{iso}(0, T) + \frac{1}{2}cV_1 \left[(1 - \alpha - 2\theta)/\alpha\right] \tag{2.38}$$

For a large repulsive interaction, $V_1/k_BT \gg 1$, for example, Q_{iso} exhibits two distinct and essentially constant values for $\theta \lessgtr 1/2$ because, for $\theta < 1/2$, adsorbed particles are essentially isolated from each other by the mutual repulsion on nearest neighbor sites, whereas, for $\theta > 1/2$, those particles that have c neighbors have their binding energy reduced by cV_{1n}. The consequence of this energetics on desorption is that in temperature programmed desorption, one observes one desorption peak for initial coverages $\theta < 1/2$, essentially that of a noninteracting adsorbate, and, for initial coverages $\theta > 1/2$, an additional peak at lower temperature for desorption out of a local environment of c neighbors.

To go beyond the quasichemical approximation cluster variational methods have been developed. Other methods of determining the equilibrium properties and kinetics of adsorbates exist, within the lattice gas model, [23].

In the Kikuchi [29] cluster variation methods [30], [31] the actual lattice is replaced with sets of representative assemblies or arrays. The properties of these simpler arrays are considered to mirror the lattice properties, and by increasing the complexity of these arrays, the properties of the lattice are approximated to a desired degree.

2.3 Transfer Matrix method

The equilibrium properties of a lattice gas model can be obtained "exactly" employing the transfer matrix method. Because we will use it later extensively for comparative studies we outline its main features, following a recent review article [25].

To introduce the transfer matrix method we repeat some well-known facts for a 1-D lattice gas of N_s sites with nearest neighbor interactions, V_1, and cyclical boundary conditions [32]. Substituting the 1-dimensional hamiltonian of type (2.17) into the grand partition function Ξ, Eqn.(2.29), we get

$$\begin{aligned} \Xi &= \sum_{\mathbf{n}} \prod_{i=1}^{N_s} T(n_i, n_{i+1}) && (2.39) \\ &= \sum_{\mathbf{n}} T(n_1, n_2) T(n_2, n_3) \ldots . T(n_{N_s}, n_1) && (2.40) \\ T(n_i, n_{i+1}) &= \exp\left[\frac{\varepsilon}{2}(n_i + n_{i+1}) - v n_i n_{i+1}\right] && (2.41) \end{aligned}$$

with $\varepsilon = (\mu_a - E_s)/k_BT$ and $v = V_1/k_BT$. If the factors $T(n_i, n_{i+1})$ are regarded as the elements of a 2x2 matrix in the (occupation number) basis $\{|0\rangle, |1\rangle\}$ for each site we have, ($z = \exp(\varepsilon)$; $y = \exp(-v)$)

$$\mathbf{T} = \begin{bmatrix} T(0,0) & T(0,1) \\ T(1,0) & T(1,1) \end{bmatrix} = \begin{bmatrix} 1 & z^{1/2} \\ z^{1/2} & zy \end{bmatrix} \tag{2.42}$$

The summation over states in Eqn.(2.39) is equivalent to matrix multiplication, e.g.

$$\sum_{n_2=0,1} T(n_1, n_2)T(n_2, n_3) = T^2(n_1, n_3) \tag{2.43}$$

where $T^2(n_1, n_3)$ is an element of the matrix $\mathbf{T}^2$. Summing over all intermediate states gives, with the cyclic condition $n_{N_s+1} = n_1$,

$$\begin{aligned} \Xi &= \sum_{n_1=0,1} T^{N_s}(n_1, n_1) = Tr[\mathbf{T}^{N_s}] \\ &= \lambda_1^{N_s} + \lambda_2^{N_s} \end{aligned} \tag{2.44}$$

where $\lambda_{1,2}$ are the eigenvalues of the transfer matrix $\mathbf{T}$. With $\lambda_2 < \lambda_1$ the second term becomes insignificant for large N_s so that all thermodynamic information about the system is contained in the largest eigenvalue of the transfer matrix.

One gets the coverage as ($\beta = 1/k_BT$)

$$\begin{aligned} \theta(T, \mu_a) &= \frac{\langle N \rangle}{N_s} = \frac{1}{N_s} \frac{\partial \ln \Xi}{\partial(\beta\mu_a)}|_{T,N_s} \\ &= \frac{\partial \ln(\lambda_1)}{\partial(\beta\mu_a)}|_{T,N_s} \end{aligned} \tag{2.45}$$

To avoid explicit differentiation one uses the fact that an eigenvalue can be expressed as $\lambda_1 = \mathbf{v}_1^L \mathbf{T} \mathbf{v}_1^R$ where $\mathbf{v}_1^{L,R}$ are the corresponding normalized left and right eigenvectors. Differentiation of the eigenvalue with respect to any parameter is then equivalent to the differentiation of the transfer matrix, and one finds

$$\theta(T, \mu_a) = \frac{z}{\lambda_1} \mathbf{v}^L \frac{\partial \mathbf{T}}{\partial z} |_{T,N_s} \mathbf{v}^R \tag{2.46}$$

$$= \sum_{k=1,2} p_k v_{1k}^2 \tag{2.47}$$

where $\mathbf{v}_1^L = (\mathbf{v}_1^R)^T = \mathbf{v}_1 = (v_{11}, v_{12})$ in the basis in which the first and second components are the empty ($p_1 = 0$) and occupied ($p_2 = 1$) sites, respectively. Thus the problem of finding the coverage as a function of temperature and chemical potential is reduced to the determination of the (largest) eigenvalue and corresponding eigenvector of a matrix of Boltzmann factors. Other information can be readily extracted in the same way, for instance, the (average) nearest neighbor correlation function is given by

$$\begin{aligned} \langle n_i n_{i+1} \rangle &= \frac{1}{N_s \Xi} \sum_{\mathbf{n}} \sum_{i=1}^{N_s} n_i n_{i+1} \exp\left[-(H(\mathbf{n}) - \mu_a N(\mathbf{n}))/k_B T\right] \\ &= -\frac{1}{N_s} \frac{\partial \ln \Xi}{\partial (\beta V_{1n})} |_{T,N_s} = \frac{y}{\lambda_1} \mathbf{v}^L \frac{\partial \mathbf{T}}{\partial y} |_{T,N_s} \mathbf{v}^R \end{aligned} \tag{2.48}$$

The transfer matrix method extends rather straightforwardly to more than one dimension, systems with multiple interactions, more than one adsorption site per unit cell and more than one species by enlarging the basis in which the transfer matrix is defined.

For the extension to two dimensions we consider a square lattice with nearest neighbor interactions on a strip with N_s sites in one direction and M sites in the second so that, with cyclic boundary conditions in the second dimension as well, we get a toroidal lattice with of 2^{N_s+M} microstates. The occupation numbers n_i at site i in the 1-D case now become a set $\mathbf{n}_i = (n_{i1}, n_{i2}, ..., n_{iM})$ of occupation numbers of M sites along the second dimension and the transfer matrix elements are generalized to

$$T(\mathbf{n}_i, \mathbf{n}_{i+1}) = \exp\left[\frac{1}{2}(\varepsilon(\mathbf{n}_i) + \varepsilon(\mathbf{n}_{i+1})) - \mathbf{v}(\mathbf{n}_i, \mathbf{n}_{i+1})\right] \tag{2.49}$$

$$\varepsilon(\mathbf{n}_i) = \varepsilon \sum_{j=1}^{M} n_{ij} - v \sum_{j=1}^{M} n_{ij} n_{i,j+1} \tag{2.50}$$

$$\mathbf{v}(\mathbf{n}_i, \mathbf{n}_{i+1}) = v \sum_{j=1}^{M} n_{ij} n_{i+1,j} \tag{2.51}$$

Thus $\varepsilon(\mathbf{n}_i)$ is the energy of the row of M sites and $\mathbf{v}(\mathbf{n}_i, \mathbf{n}_{i+1})$ is the interaction energy of two adjacent rows. The partition function is then given in terms of the 2^M eigenvalues of this matrix as

$$\Xi(T, N_s, M, \mu_a) = \sum_{j=1}^{2^M} \lambda_j^{N_s} \tag{2.52}$$

For large N_s this sum is again dominated by the first eigenvalue, λ_1, which will now depend on M. For practical calculations M is restricted by computer memory. However, the symmetry of the hamiltonian allows a block diagonalization of the transfer matrix, and it can be shown that λ_1 occurs in its totally symmetric subblock, $\mathbf{T}_s$[33]. This significantly reduces the size of the matrix to be handled. This reduced matrix $\mathbf{T}_s$ is constructed by:[34, 33]

(i) Identifying equivalence classes, labeled α, of $\mathbf{n}_i$ states which can be transformed into each other by rotations and/or reflections among the M sites in one row (ring).

(ii) Constructing the matrix elements

$$(\mathbf{T}_s)_{\alpha\beta} = \sum_{\mathbf{n}_{i+1} \in \beta} T(\mathbf{n}_i \in \alpha, \mathbf{n}_{i+1}) \tag{2.53}$$

Here $\mathbf{n}_i$ is any one member of the equivalence class α and the sum is over all the members of β, i.e. across columns of Boltzmann factors in $\mathbf{T}$.

As an example, for $M = 4$, we list the six equivalence classes of the four sites in terms of their occupation numbers

	1	2	3	4	5	6
α	(0000)	(0001)	(0011)	(0101)	(0111)	(1111)
		(0010)	(0110)	(1010)	(1110)	
		(0100)	(1100)		(1101)	
		(1000)	(1001)		(1011)	
p_α	0	1	2	2	3	4
d_α	1	4	4	2	4	1
m_α	1	2	6	10	14	30

We have also given the number of particles, p_α, and the degeneracy, d_α, associated with each equivalence class and the base-10 equivalent, m_α, of the binary number associated with state α. Because m_α uniquely determines the occupancies in α a mere (cyclic) bitshifting generates all equivalent states. This results in a reduced transfer matrix $\mathbf{T}_s$ of the form

$$\begin{bmatrix} 1 & 4z^{1/2} & 4zy & 2z & 4z^{3/2}y^2 & z^2y^4 \\ z^{1/2} & z(3+y) & z^{3/2}y(3+y) & z^{3/2}(1+y) & z^2y^2(3+y) & z^{5/2}y^5 \\ 2y & 2z^{3/2}y^2(1+y) & z^2y^2(1+y)^2 & 2z^2y^2 & 2z^{5/2}y^4(1+y) & z^3y^7 \\ z & 2z^{3/2}(1+y) & 4z^2y^2 & z^2(1+y^2) & 2z^{5/2}y^3(1+y) & z^3y^6 \\ z^{3/2}y^2 & z^2y^2(1+3y) & 2z^{5/2}y^4(1+y) & z^{5/2}y^3(1+y) & z^3y^6(1+3y) & z^{7/2}y^9 \\ z^2y^4 & 4z^{5/2}y^5 & 4z^3y^7 & 2z^3y^6 & 4z^{7/2}y^9 & z^4y^{12} \end{bmatrix} \tag{2.54}$$

Terms in this matrix have the form $z^{(p_\alpha+p_\beta)/2}y^{c_{\alpha\beta}}$ where $c_{\alpha\beta}$ is the total number of nearest neighbor pairs within and between states α and β. The determination of the latter is a straightforward procedure in binary operations. For example, to get the number of nearest neighbor bonds in state α one performs a cyclic bitshift by one lattice site, followed by a binary AND of the two states, and counts the number of bits. Because the coverage and the correlation functions are obtained as derivatives of $\mathbf{T}_s$ with respect to z or y this simply brings down the powers of z and y, i.e. the terms in the derivative matrix become simple multiples of those in $\mathbf{T}_s$ itself. In terms of its eigenvectors the coverage can be written as

$$\theta = \frac{1}{M}\sum_\alpha p_\alpha v_{1\alpha}^L v_{1\alpha}^R \tag{2.55}$$

If $\mathbf{T}$ is symmetric then $v_{1\alpha}^L = d_\alpha v_{1\alpha}^R$ and only one eigenvector calculation is required. Multi-site and longer-ranged correlators are obtained by appropriate bond counting, without the explicit introduction of the corresponding interactions into the Hamiltonian.

The TM method is convenient and computationally efficient way to calculate equilibrium quantities. To mimic the effect of a 2-d lattice one should let the strip width,

M, increase to infinity. In practice, this is unnecessary and calculated quantities converge quickly for small strips e.g. $M = 8$ will do for a 5 digit precision. In making comparisons with the results of Chapter 3 we choose a strip width of 4 to correspond to the typical size of our correlators.

Chapter 3

Kinetic Lattice Gas Model

So far we have only considered equilibrium adsorption and desorption under quasi-equilibrium. If surface diffusion is not fast on the time scale of adsorption-desorption the nonequilibrium effects will show up in the desorption and diffusion must be accounted for in the kinetic equations. This will be done in the framework of the Kinetic Lattice Gas model.

3.1 Master equation

In the following derivations of the equations of motion all the relevant processes like adsorption, desorption and diffusion are assumed Markovian, i.e. they do not depend on the past history of the system so that there is no hysteresis. Then a function $P(\mathbf{n};t)$ can be introduced, which gives the probability that a given microscopic configuration $\mathbf{n}$ is realized at time t. The time evolution of the system is controlled by a master equation [2],

$$\frac{dP(\mathbf{n};t)}{dt} = \sum_{\mathbf{n}'} [W(\mathbf{n};\mathbf{n}')P(\mathbf{n}') - W(\mathbf{n}';\mathbf{n})P(\mathbf{n})] \tag{3.1}$$

where $W(\mathbf{n}';\mathbf{n})$ is the transition probability that a microstate $\mathbf{n}$ changes into $\mathbf{n}'$ per unit time. The master equation simply states that the rate of change of the probability of a certain microstate is the sum of the probabilities of all the other microstates to transform to this state minus the probability to transform out of this microstate, to these others.

If the system is isolated, it evolves towards equilibrium in the long time limit. Then the right hand side of Eqn.(3.1) is zero. In addition, detailed balance demands that each term in the sum is zero implying that every microscopic reaction is balanced in equilibrium by its reverse

$$W(\mathbf{n}';\mathbf{n})P_0(\mathbf{n}) = W(\mathbf{n};\mathbf{n}')P_0(\mathbf{n}') \tag{3.2}$$

where

$$P_0(\mathbf{n}) = \frac{1}{\Xi} exp(-(H(\mathbf{n}) - \mu_a N(\mathbf{n}))/k_B T)) \tag{3.3}$$

is the equilibrium probability for the state $\mathbf{n}$ to be realized. Ξ is the grand partition function of the system and μ_g is the chemical potential of the adsorbed gas. In principle the transition probability $W(\mathbf{n}';\mathbf{n})$ must be calculated from the Hamiltonian, that includes in addition to the terms in Eqn.(2.17), coupling terms to the gas phase and the solid that mediate mass and energy exchange. Here we will use an approach initiated by Glauber [37] in which one sets up a kinetic lattice gas model and chooses an appropriate form for $W(\mathbf{n}';\mathbf{n})$, subject to detailed balance.

If the residence time in a given state is much longer than the time needed for a transition to another state, as discussed in the Introduction, the transition probability can be written as a sum of independent transition probabilities for adsorption, desorption and diffusion on different adsorption sites, one at a time

$$W(\mathbf{n}';\mathbf{n}) = W_{ads}(\mathbf{n}';\mathbf{n}) + W_{des}(\mathbf{n}';\mathbf{n}) + W_{diff}(\mathbf{n}';\mathbf{n}) \tag{3.4}$$

Various choices for the adsorption term have been proposed, [22]. In the case of Langmuir kinetics adsorption at site n_i is impossible when the site is occupied but otherwise it is independent of the local environment of that site. The adsorption term then has the form

$$W_{ads}(\mathbf{n}';\mathbf{n}) = W_0 \sum_i (1-n_i)\delta(n_i', 1-n_i) \prod_{l\neq i} \delta(n_l', n_l) \tag{3.5}$$

The sum runs over all cells i. The Kronecker deltas specify that the adsorption event can occur only on the desired site i that will lead to microstate $\mathbf{n}'$.

The desorption term with only nearest neighbor interactions (enumerated by the labels α and α') is

$$\begin{aligned} W_{des}(\mathbf{n}';\mathbf{n}) &= W_0 C_0 \sum_i n_i (1 + C_1 \sum_\alpha n_{i+\alpha} + C_2 \sum_\alpha \sum_{\alpha'} n_{i+\alpha} n_{i+\alpha'} \\ &+ C_3 \sum_\alpha \sum_{\alpha'} \sum_{\alpha''} n_{i+\alpha} n_{i+\alpha'} n_{i+\alpha''} + \ldots) \delta(n_i', 1-n_i) \prod_{l\neq i} \delta(n_l', n_l) \end{aligned} \tag{3.6}$$

i.e. desorption from a site can occur only if that site is already occupied by a particle, with the condition that all remaining particles don't move from their sites.

Substituting Eqn.(3.5) and Eqn.(3.6) into the detailed balance equations (3.2) gives the values of the coefficients, namely

$$C_0 = exp(E_s/k_B T) \tag{3.7}$$

and for the higher order interaction coefficients, with $r = 1, 2..c$, the nearest-neighbor coordination of the site,

$$C_r = (exp(V_1/k_BT) - 1)^r \tag{3.8}$$

The diffusion term in Eqn.(3.4) is written as,

$$\begin{aligned} W_{diff}(\mathbf{n}';\mathbf{n}) = \; & J_0 \sum_{i,\alpha} n_i(1 + C_1 \sum_{\beta \neq \alpha} n_{i+\beta} + ...) \\ & \delta(n_i', 1 - n_i)\delta(n_{i+\alpha}', 1 - n_{i+\alpha}) \prod_{l \neq i, i+\alpha} \delta(n_l', n_l) \end{aligned} \tag{3.9}$$

A particle can jump only to a neighboring site if it is unoccupied. The summations are over all adsorption sites and all neighboring sites for the site from which the particle jumps.

For most adsorption systems the masses of the adsorbed atoms and molecules are so heavy that in the entire temperature range of interest, the motion can be treated classically, [38]. As with all thermally activated processes, an Arrhenius form separating the rate into a prefactor and an exponential of the form is usually employed to analyze the temperature dependence,

$$J_0 = \nu_{diff} \exp(-Q/k_BT) \tag{3.10}$$

Average occupation numbers of a site can be defined as

$$\overline{\mathrm{n_i}}(t) = \sum_{\mathbf{n}} n_i P(\mathbf{n};t) \tag{3.11}$$

with the sum running over all microstates $\mathbf{n}$ with each $n_i = 0$ and 1. The coverage is then given by

$$\theta(t) = \frac{1}{N_s} \sum_i \overline{n_i}(t) \tag{3.12}$$

3.2 Equations of motion

The time evolution of the average occupation numbers is obtained from Eqn.(3.1)

$$\begin{aligned} \frac{d\overline{n_i}(t)}{dt} &= \sum_{\mathbf{n}} n_i \frac{dP(\mathbf{n};t)}{dt} \\ &= \sum_{\mathbf{n},\mathbf{n}'} n_i [W(\mathbf{n};\mathbf{n}')P(\mathbf{n}',t) - W(\mathbf{n}';\mathbf{n})P(\mathbf{n},t)] \end{aligned} \tag{3.13}$$

Exchanging $\mathbf{n}$ and $\mathbf{n}'$ in the first term of the sum, we get

$$\frac{d\overline{n_i}(t)}{dt} = \sum_{\mathbf{n},\mathbf{n}'} (n_i' - n_i) W(\mathbf{n}',\mathbf{n}) P(\mathbf{n},t) \tag{3.14}$$

In terms of the coverage the equation reads

$$\frac{d\theta}{dt} = \frac{1}{N_s} \sum_i \sum_{\mathbf{n},\mathbf{n}'} (n_i' - n_i) W(\mathbf{n}';\mathbf{n}) P(\mathbf{n},t) \tag{3.15}$$

For a homogeneous substrate multi-site correlations functions are not site specific and can be defined as averages,

$$\left\langle \bullet \right\rangle = < n_i > = \theta \tag{3.16}$$

$$\left\langle \bullet\bullet \right\rangle = < n_i n_{i+a} > \tag{3.17}$$

$$\left\langle \bullet \overset{\bullet}{\bullet} \right\rangle = < n_i n_{i+a} n_{i+a'} > \tag{3.18}$$

$$\langle \circ \rangle = <(1-n_i)> = 1-\theta \tag{3.19}$$

where, for instance the nearest neighbor correlator, $\langle \bullet\bullet \rangle$, is

$$\langle \bullet\bullet \rangle = \frac{1}{N_s}\sum_i \sum_{\mathbf{n}} n_i n_{i+a} P(\mathbf{n}, t) \tag{3.20}$$

This 2-site correlator in the quasichemical approximation (section 2.2.2) is given by the function,

$$\langle \bullet\bullet \rangle_{QCA} = \theta\left(1 - 2\frac{1-\theta}{1+\alpha}\right) \tag{3.21}$$

Not all of the above correlators are independent, e.g.,

$$\langle \circ \rangle = 1 - \langle \bullet \rangle \tag{3.22}$$

$$\langle \bullet\circ \rangle = \langle \bullet \rangle - \langle \bullet\bullet \rangle \tag{3.23}$$

These correlators are also subject to their own equations of motion each one coupling to yet larger correlators. If we restrict the lateral interactions to nearest neighbors only, the equation for the n-site correlator involves correlators involving up to $n+4$ additional sites on a square lattice.

On a square lattice the first two correlation functions have the following equations for desorption:

$$\begin{aligned}\frac{d\langle \bullet \rangle}{dt}\Big|_{des} = -W_0C_0\Big[&\langle \bullet \rangle + 4C_1\langle \bullet\bullet \rangle + 4C_2\left\langle \begin{smallmatrix} & \bullet \\ \bullet & \bullet \end{smallmatrix} \right\rangle + 2C_2\langle \bullet\bullet\bullet \rangle \\ &+ 4C_3\left\langle \begin{smallmatrix} & \bullet & \\ \bullet & \bullet & \bullet \end{smallmatrix} \right\rangle + C_4\left\langle \begin{smallmatrix} & \bullet & \\ \bullet & \bullet & \bullet \\ & \bullet & \end{smallmatrix} \right\rangle\Big]\end{aligned} \tag{3.24}$$

$$\begin{aligned}\frac{d\langle \bullet\bullet \rangle}{dt}\Big|_{des} = -W_0C_0[&\langle \bullet\bullet \rangle + 2C_1\langle \bullet\bullet \rangle + 2C_1\langle \bullet\bullet\bullet \rangle + 4C_1\left\langle \begin{smallmatrix} & \bullet \\ \bullet & \bullet \end{smallmatrix} \right\rangle \\ &+ 2C_2\langle \bullet\bullet\bullet \rangle + 4C_2\left\langle \begin{smallmatrix} & \bullet \\ \bullet & \bullet \end{smallmatrix} \right\rangle + 6C_2\left\langle \begin{smallmatrix} & \bullet & \\ \bullet & \bullet & \bullet \end{smallmatrix} \right\rangle \\ &+ 2C_3\left\langle \begin{smallmatrix} & \bullet & \\ \bullet & \bullet & \bullet \\ & \bullet & \end{smallmatrix} \right\rangle + 2C_4\left\langle \begin{smallmatrix} & \bullet & \\ \bullet & \bullet & \bullet \\ & \bullet & \end{smallmatrix} \right\rangle] \end{aligned} \tag{3.25}$$

In the case of Langmuir kinetics the adsorbing particle does not see its prospective neighbors and the adsorption evolves simply as

$$\frac{d\langle \bullet \rangle}{dt}\Big|_{ads} = W_0\langle \circ \rangle = W_0(1-\theta) \tag{3.26}$$

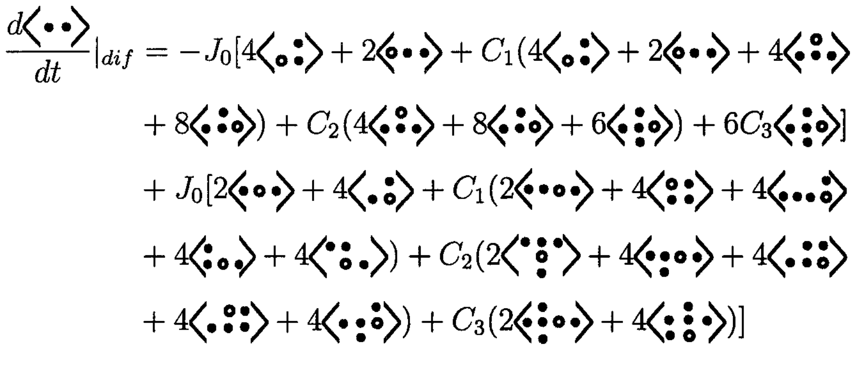
$$\frac{d\langle \bullet\bullet \rangle}{dt}\Big|_{ads} = 2W_0\langle \bullet\circ \rangle = 2W_0(\langle \bullet \rangle - \langle \bullet\bullet \rangle) \tag{3.27}$$

Equations for the three-site correlators are given in Appendix A. Comparing Eqn.(3.26) (see [40]) with the phenomenological adsorption rate in Eqn.(2.13) shows that the sticking coefficient varies as $(1-\theta)$ and that W_0 has the value

$$W_0 = \frac{S_0 a_s P \lambda_{th}}{h} \tag{3.28}$$

Thus W_0 is just the flux of gas particles, per unit adsorption cell, hitting the surface. a_s is again the area of one adsorption site and S_0 is the sticking coefficient of the adsorbing species at vanishing coverage. Thus the sticking coefficient as a function of temperature and coverage is $S(\theta) = S_0(T)(1-\theta)$, i.e. sticking is limited by site exclusion only. More complicated adsorption kinetics lead to a nonlinear θ-dependence.

The diffusion on the surface does not change the total coverage and thus does not contribute to the first equation of the time evolution hierarchy. The nearest neighbor correlator evolves according to,



(3.29)

The equations of motion for higher correlation functions are given in appendix A. This hierarchy of equations extends all the way to the N_s-particle correlator at which level it is exactly equivalent to the original master equation (apart from the assumption of homogeneity). It is our next task to find a factorization or closure scheme that will truncate this hierarchy at a manageable level. This is done in the next section.

3.3 Closure approximation

Because in the equation of motion for an n-particle correlator there appear, on the right side, terms involving higher order correlators on a square lattice with up to 4 additional sites or particles, we must find a scheme to factorize these higher order correlators in terms of those for which we want to keep the equations of motion. We call this set of correlators the basis set of correlators. How large this set has to be depends on the accuracy with which we intend to describe the system. Our strategy is to start at the lowest level and proceed with larger basis sets until some form of convergence has been reached. We will also, in the section on numerical results, show comparisons of results obtained in equilibrium at these different levels of complexity with the "exact" results obtainable with the transfer matrix method.

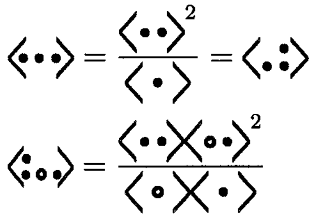
To introduce the approach to closure we start with the simplest possible scenario, namely by only including the coverage itself in the basis set in which case we are dealing with just one equation of motion, (3.24). For all correlators on the right hand side the correlators are then just powers of θ and we get

$$\frac{d\theta}{dt}|_{des} = -W_0 C_0 \theta [1 + 4C_1\theta + 6C_2\theta^2 + 4C_3\theta^3 + C_4\theta^4] \tag{3.30}$$

In this approximation diffusion is completely neglected because all correlators are those appropriate for a random adsorbate.

3.3.1 1-particle overlap: 2-correlator basis set

To include diffusion we keep, at the next level of sophistication, θ and $\langle \bullet\bullet \rangle$ in our basis set. The only factorization scheme possible in this case is 1-particle overlap, e.g.


(3.31)

(3.32)

This scheme is unique and factorizing Eqn.(3.24) and Eqn.(3.25) leads to two coupled equations of motion. The first example is an exact result in 1-D [20]. It corresponds to the Kirkwood approximation to the 3-particle distribution function in the theory of multi-particle distributions. As such, it is independent of the system dimension.

$$\begin{aligned}\frac{d\langle\bullet\rangle}{dt}|_{des} &= -W_0C_0[\langle\bullet\rangle + 4C_1\langle\bullet\bullet\rangle + 6C_2\langle\bullet\bullet\rangle^2/\langle\bullet\rangle \\ &+ 4C_3\langle\bullet\bullet\rangle^3/\langle\bullet\rangle^2 + C_4\langle\bullet\bullet\rangle^4/\langle\bullet\rangle^3] \qquad (3.33)\\ \frac{d\langle\bullet\bullet\rangle}{dt}|_{des} &= -W_0C_0[\langle\bullet\bullet\rangle + 2C_1\langle\bullet\bullet\rangle + 6C_1\langle\bullet\bullet\rangle^2/\langle\bullet\rangle \\ &+ 6C_2\langle\bullet\bullet\rangle^2/\langle\bullet\rangle + 6C_2\langle\bullet\bullet\rangle^3/\langle\bullet\rangle^2 \\ &+ 2C_3\langle\bullet\bullet\rangle^4/\langle\bullet\rangle^3 + 2C_4\langle\bullet\bullet\rangle^4/\langle\bullet\rangle^3] \qquad (3.34)\end{aligned}$$

There is another fundamental aspect that affects our choice of the basis set and that is the simple observation that in equilibrium detailed balance must hold. This implies that adsorption must balance desorption

$$\begin{aligned}&0 = \frac{d\langle\bullet\rangle}{dt} = \frac{d\langle\bullet\rangle}{dt}|_{ad} + \frac{d\langle\bullet\rangle}{dt}|_{des} = \\ &W_0(1-\langle\bullet\rangle) - W_0C_0(\langle\bullet\rangle + 4C_1\langle\bullet\bullet\rangle + 6C_2\langle\bullet\bullet\rangle^3/\langle\bullet\rangle^2) \\ &+ 4C_3\langle\bullet\bullet\rangle^3/\langle\bullet\rangle^2 + C_4\langle\bullet\bullet\rangle^4/\langle\bullet\rangle^3) \qquad (3.35)\\ &0 = \frac{d\langle\bullet\bullet\rangle}{dt} = \frac{d\langle\bullet\bullet\rangle}{dt}|_{ad} + \frac{d\langle\bullet\bullet\rangle}{dt}|_{des} \\ &2W_0(\langle\bullet\rangle - \langle\bullet\bullet\rangle) - W_0C_0[\langle\bullet\bullet\rangle + 2C_1\langle\bullet\bullet\rangle \\ &+ 6C_1\langle\bullet\bullet\rangle^2/\langle\bullet\rangle + 6C_2\langle\bullet\bullet\rangle^2/\langle\bullet\rangle + 6C_2\langle\bullet\bullet\rangle^3/\langle\bullet\rangle^2 \\ &+ 2C_3\langle\bullet\bullet\rangle^4/\langle\bullet\rangle^3 + 2C_4\langle\bullet\bullet\rangle^4/\langle\bullet\rangle^3] \qquad (3.36)\end{aligned}$$

Between these two equations we can eliminate the constant C_0 (and of course W_0) and thus get a solution for the 2-site correlator as a function of the coverage and also of temperature through the coefficients C_r, involving the lateral interactions. It can be shown that the equilibrium solution of the adsorption-desorption term is equivalent to the quasichemical approximation, which provides a qualitatively acceptable description for such properties as adsorption isotherms and phase diagrams as long as only nearest neighbor interactions are important. This is clear from the fact that in Eqn.(3.31) the triangular correlator and the linear trio correlator are equated to each other.

On the other hand detailed balance demands that the diffusional term, by itself, also vanishes giving a second equation for the determination of the 2-site correlator, namely

$$
\begin{aligned}
0 =& \frac{d\langle\bullet\bullet\rangle}{dt}\Big|_{dif} = \\
&- J_0[6\langle\bullet\circ\rangle\langle\bullet\bullet\rangle/\langle\bullet\rangle + C_1(6\langle\bullet\circ\rangle\langle\bullet\bullet\rangle/\langle\bullet\rangle + 12\langle\bullet\circ\rangle\langle\bullet\bullet\rangle^2/\langle\bullet\rangle^2) \\
&+ C_2(12\langle\bullet\circ\rangle\langle\bullet\bullet\rangle/\langle\bullet\rangle + 6\langle\bullet\circ\rangle\langle\bullet\bullet\rangle^3/\langle\bullet\rangle^3) + 6C_3\langle\bullet\circ\rangle\langle\bullet\bullet\rangle^3/\langle\bullet\rangle^3] \\
&+ J_0[6\langle\bullet\circ\rangle^2/\langle\circ\rangle + C_1(2\langle\bullet\bullet\rangle\langle\bullet\circ\rangle^2/(\langle\circ\rangle\langle\bullet\rangle) \\
&+ 4\langle\bullet\bullet\rangle^2\langle\bullet\circ\rangle^2/(\langle\circ\rangle\langle\bullet\rangle^3) + 4\langle\bullet\bullet\rangle^2\langle\bullet\circ\rangle^2/(\langle\circ\rangle\langle\bullet\rangle^2) \\
&+ 8\langle\bullet\bullet\rangle\langle\bullet\circ\rangle^2/(\langle\circ\rangle\langle\bullet\rangle)) + C_2(6\langle\bullet\bullet\rangle^2\langle\bullet\circ\rangle^2/(\langle\circ\rangle\langle\bullet\rangle^2) \\
&+ 8\langle\bullet\bullet\rangle^3\langle\bullet\circ\rangle^2/(\langle\circ\rangle\langle\bullet\rangle^4) + 4\langle\bullet\bullet\rangle^2\langle\bullet\circ\rangle^2/(\langle\circ\rangle\langle\bullet\rangle^2) \\
&+ C_3(2\langle\bullet\bullet\rangle^3\langle\bullet\circ\rangle^2/(\langle\circ\rangle\langle\bullet\rangle^3) + 4\langle\bullet\bullet\rangle^4\langle\bullet\circ\rangle^2/(\langle\circ\rangle\langle\bullet\rangle^4))]
\end{aligned}
\tag{3.37}
$$

This is obviously an overdetermination of the correlator. The choice of the basis set must be such that these two solutions are "close" to each other over the complete coverage range. We stress that this problem of two solutions cannot be overcome by setting the right hand sides of the two equations of motion equal to zero, because this would be in contradiction to the principle of detailed balance, and as a result would make the equilibrium solution dependant on the ratio of the kinetic coefficients.

3.3.2 2-particle overlap: 5-correlator basis set

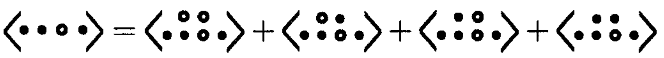
At the next level of sophistication we take

(3.38)

as our basis set and must now do the factorization with two-particle overlap. One may be tempted to include other 3- and 4-particle correlators such as  and  in the basis set. We tried this but it turns out that keeping only the compact clusters in the basis set leads (i) to a unique factorization scheme and (ii) to better converging results. This will be shown in the numerical examples. The argument about compact clusters is also behind the inclusion of the triple cluster containing a hole, instead of  . Essentially one has to account for cluster interior holes as well.

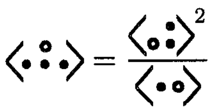
In the present factorization scheme the correlators containing several sites on a row are expressed as a sum,

(3.39)

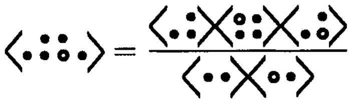


(3.40)

The correlators are then factorized in 2-site overlap,



(3.41)



(3.42)

Next the holes on the periphery of the cluster are reduced by subtraction,

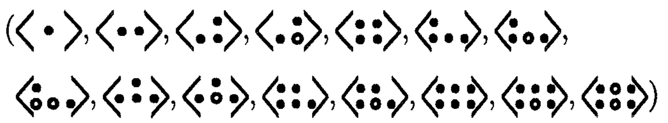
(3.43)

(3.44)

Whereas the equations of motion and the factorization can be derived by hand for 1-site overlap this is no longer economical for larger basis sets. We have therefore written two Fortran programmes. One programme, given in Appendix C, lists all correlators with their coefficients on the right hand side of the equation of motion of a given correlator. A second programme then factorizes every correlator on the right hand side in terms of a prescribed basis set. The equations of motion including all factorized correlators in the 5-site basis set are given in Appendix B.

3.3.3 4-particle overlap: 15-correlator basis set

We will see in the numerical examples that the 5-correlator basis set with two-particle overlap provides excellent results for equilibrium properties obtained from the diffusional solution, but not quite the same level from the adsorption-desorption terms. We have therefore extended the basis set to include 15 correlators



(3.45)

and derived, with the Fortran programme analogous to the one for diffusion given in Appendix C, the equations of motion for adsorption-desorption kinetics. These equations contain more than 750 terms which we cannot list in this dissertation but are available as supplementary material.

Chapter 4

Equilibrium Properties

In this chapter we will present results of the equilibrium properties of an adsorbate, for the various truncation schemes, and compare these to the transfer matrix (TM) method and the quasichemical approximation (QCA). As mentioned above in equilibrium the TM gives essentially exact solutions for all correlators, for sufficiently large strip width.

The properties of a system in equilibrium are described by the values of all correlators, as a function of coverage and temperature. In practice this amounts to finding the zeroes of the right hand side of the adsorption-desorption or the diffusion terms of the equations in Appendix A. For a given level of truncation there will be as many equations to solve as there are correlators in the basis set. Because of the factorizations involved, these equations become highly nonlinear, e.g. of order 4 even for the trivial 1-site overlap. As a result, there can be more than one solution for each set of correlators. It becomes tricky to keep track of the physical solution in which all correlators are positive and bounded by unity. This becomes even more evident at high coverages, where all higher order correlators approach unity. Many of the factorized correlators contain differences of correlators, each close to unity, in their denominators and even small deviations in the guesses of the numerical nonlinear equation solver lead to divergence of solutions. Even when using numerical continuation and polynomial guesses for a subsequent solution, these guesses must sometimes be extremely close to the exact solution for the system to become solvable. To overcome these numerical difficulties we have adopted the strategy of solving the equations, not as a function of coverage for a fixed interaction, but as function of increasing interaction for a fixed coverage, starting from the noninteracting case with subsequent extrapolation to the desired high interaction. This approach leads to longer running times for the programs, but does not diverge and gives the physical solutions. The average running time for the higher order factorizations on a RISC 6000 is about an hour.

4.1 Adparticle repulsion

4.1.1 Equilibrium correlators

The strength of nearest neighbor repulsions V_1 can be represented by the unitless parameter $K = V_1/2k_BT$. For instance $K = 0.5$ represents a system of moderate repulsion, where the interaction (in Kelvins) is equal to the temperature, while $K \gtrsim 3$ can be considered a very strong repulsion for many adsorbate systems.

We begin our discussion of equilibrium results with the noninteracting case, $K = 0$. All factorizations schemes, in their noninteracting limit, have the same behavior of their correlators, represented in Fig.4.1. In this case the positions of the particles on the surface are uncorrelated, all adparticles are distributed randomly and the correlators are just polynomial functions of the power of the coverage, e.g. $\langle \overset{\bullet}{\bullet\,\circ} \rangle = \theta^2(1-\theta)$. The 3-site correlator is always smaller than the 2-site correlator because the probability of encountering three adjacent adparticles is always smaller than that of finding

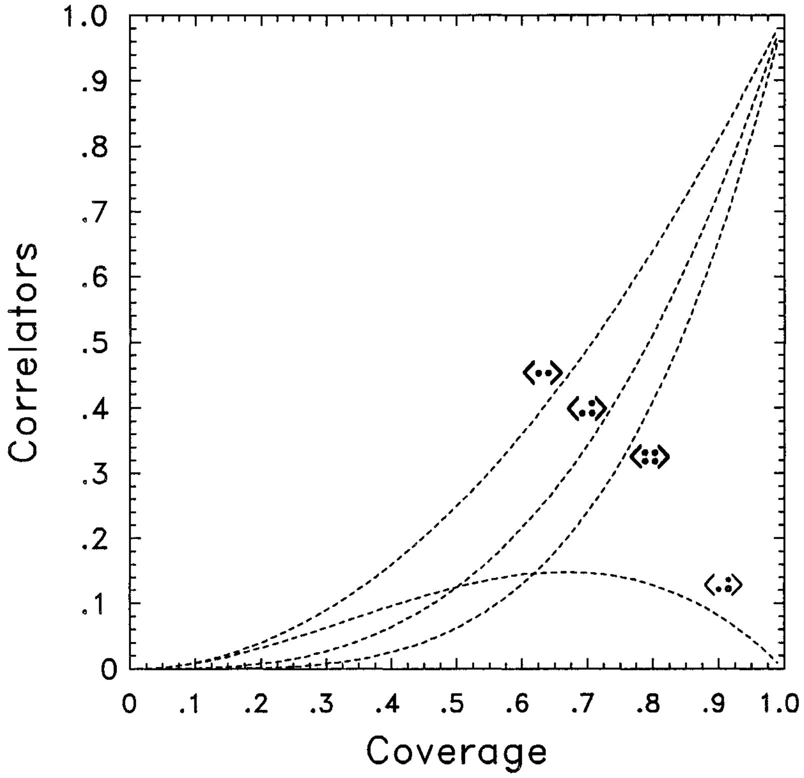


Figure 4.1: Equilibrium correlation functions as a function of coverage for no nearest-neighbor interactions. Correlators (top to bottom at $\theta = 0.9$) $\langle \bullet\bullet \rangle$, $\langle \bullet \genfrac{}{}{0pt}{}{\bullet}{\bullet} \rangle$, $\langle \genfrac{}{}{0pt}{}{\bullet}{\bullet}\genfrac{}{}{0pt}{}{\bullet}{\bullet} \rangle$, $\langle \bullet \genfrac{}{}{0pt}{}{\bullet}{\circ} \rangle$.

two. Only in the noninteracting case is the linear 3-site correlator, $\langle \bullet\bullet\bullet \rangle$, exactly the same as the triangular 3-site correlator $\langle \bullet \genfrac{}{}{0pt}{}{\bullet}{\bullet} \rangle$. In the limit of full coverage all particle correlators approach unity and all correlators containing holes, zero.

The case, when the repulsive interaction is large in comparison to the temperature is shown on Fig.4.2, for $K = 1.5$. The solid lines represents the "exact" solution obtained using the Transfer Matrix method for a strip width of four sites. At coverages lower than half a monolayer (ML), where vacancies predominate on the lattice, the adparticles can avoid being nearest neighbors. There is only a very small probability, of order $\exp(-\beta V_1) = \exp(-2K)$, of finding two of them together; thus $\langle \bullet\bullet \rangle$ is of this

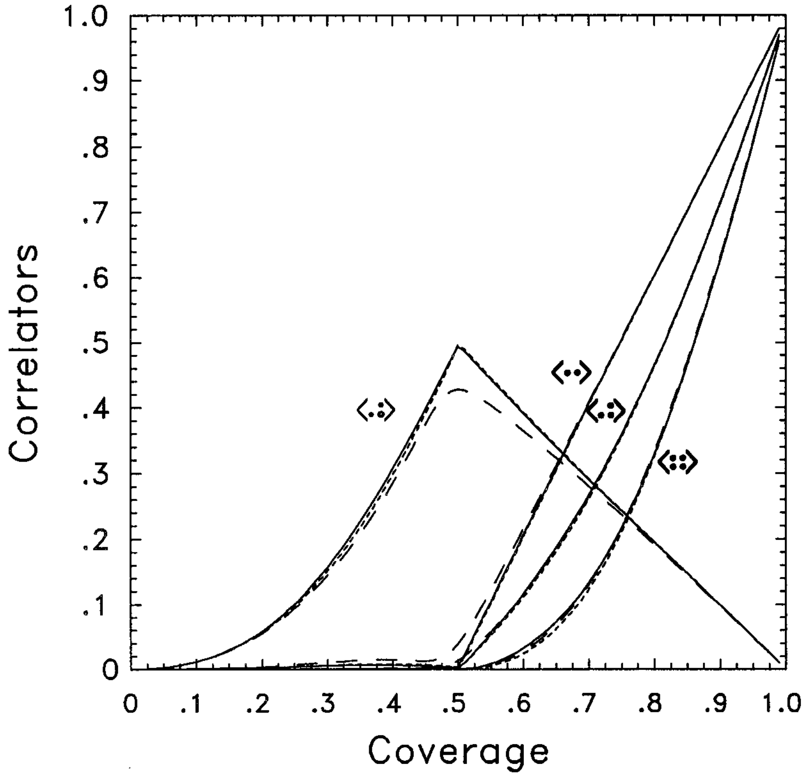


Figure 4.2: Equilibrium correlation functions as a function of coverage for K =1.5. Solid lines TM method, long dashed lines 5-basis set for adsorption-desorption equilibrium, dotted lines 5-basis set for diffusive equilibrium. Correlators (top to bottom at $\theta = 0.9$) $\langle \bullet\bullet \rangle$, $\langle \bullet \substack{\bullet\\ \bullet} \rangle$, $\langle \substack{\bullet\\ \bullet}\substack{\bullet\\ \bullet} \rangle$, $\langle \bullet \substack{\bullet\\ \circ} \rangle$.

order, too. The only significant correlator in this case is $\langle \bullet \substack{\bullet\\ \circ} \rangle$ and it rises roughly quadratically with the coverage. At exactly at 1/2 ML coverage the strong repulsion leads to a checkered, i.e. c(2x2), structure of the lattice gas on the surface. Because the probability for a single site to be occupied is one half and the rest of the surface structure is fixed $\langle \bullet \substack{\bullet\\ \circ} \rangle$ equals one half. Each additional particle added on the surface above 1/2 ML will see four nearest neighbors. This leads to a rise of the 2-site correlator, as a straight line $\langle \bullet\bullet \rangle$ of slope 2θ, to reach unity at full coverage. The hole correlator, concurrently declines linearly, with slope $-\theta$, as each added particle

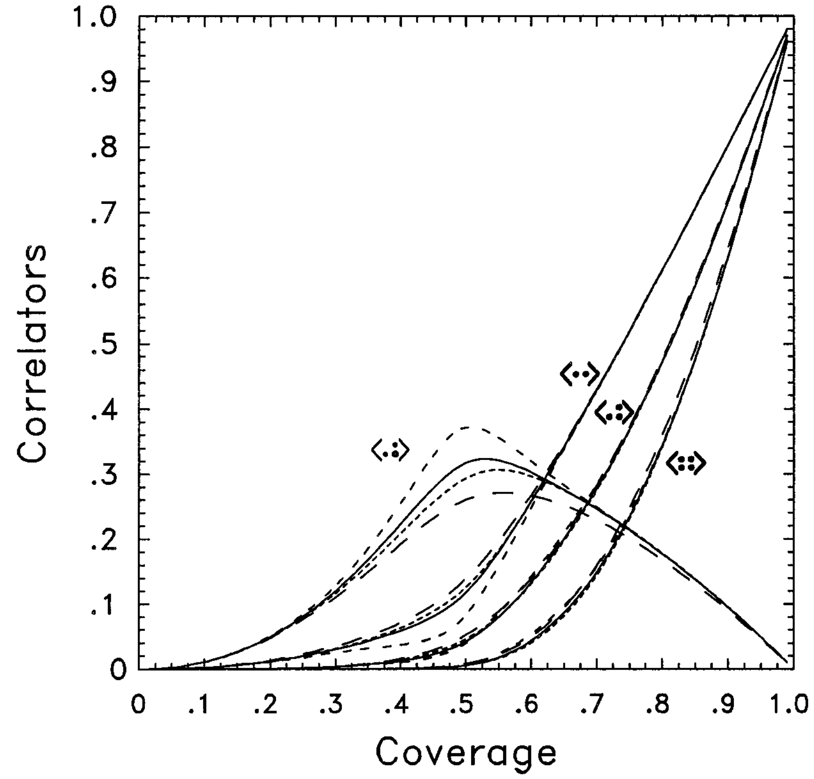


Figure 4.3: Equilibrium correlation functions as a function of coverage for $K = 0.75$. Solid lines TM method, long dashed lines 5-basis set for adsorption-desorption, dotted line 5-basis set for diffusive, short dashed lines 15-basis set adsorption-desorption. Correlators (top to bottom at $\theta = 0.9$) $\langle \bullet\bullet \rangle$, $\langle \bullet {}^{\bullet}_{\bullet} \rangle$, $\langle {}^{\bullet}_{\bullet}{}^{\bullet}_{\bullet} \rangle$, $\langle \bullet {}^{\bullet}_{\circ} \rangle$.

removes exactly one configuration $\langle \bullet {}^{\bullet}_{\circ} \rangle$.

The dotted lines represent the solution obtained from the diffusion equation zeroes in the 2-site overlap or, in other words, the 5-basis set factorization. In this regime this solution is almost as accurate as the TM results. The long-dashed lines give the solution for the adsorption-desorption zeroes. The latter solution is close but not as good as the diffusive solution.

For the intermediate interaction case presented in Fig.4.3 ($K = 0.75$) we compare the TM results with two adsorption-desorption equilibrium solutions: 2-site overlap

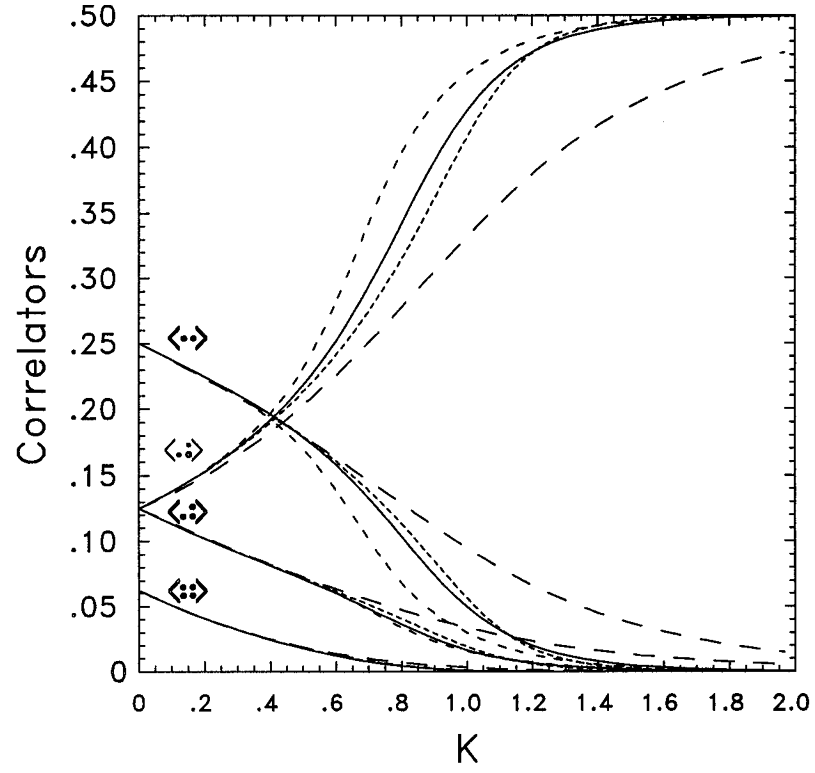


Figure 4.4: Equilibrium correlation functions as a function of K for $\theta = 0.5$. Solid lines TM, long-dashed lines 5-basis set for adsorption-desorption, dotted line 5-basis set for diffusion, short dashed lines 15-basis set adsorption-desorption. Correlators (top to bottom at $K = 0.2$) $\langle \bullet\,\bullet \rangle$, $\langle \bullet\,\overset{\bullet}{\circ} \rangle$, $\langle \bullet\,\overset{\bullet}{\bullet} \rangle$, $\langle \overset{\bullet}{\bullet}\,\overset{\bullet}{\bullet} \rangle$.

containing 5 basis functions, both for adsorption-desorption and diffusion, and the extended basis set containing 15 basis functions for adsorption-desorption. All factorizations approximate well the main features of the TM curves at low and high coverages, with the larger basis set giving slightly better agreement for the higher order correlators. At intermediate coverages all factorizations show discrepancy for the 2-site correlator, and the hole correlator. The 15-basis set overestimates the number of holes, while the 5-basis set underestimates them. The diffusion correlators are closest to the TM solution.

At a fixed surface coverage the values of the correlators will reflect the strength of the interactions, as seen in Fig.4.4. For coverage of 1/2 ML the initial correlators at zero interaction are just powers of θ and $(1 - \theta)$. As the repulsive interaction increases all particle correlators decrease to zero as the c(2x2) structure is formed on the surface.

Although it seems that the 5-basis set deviates significantly from the TM solution, it is much closer to it than the quasichemical approximation. On this graph the 2-site correlator for QCA is almost a straight line from 0.25 for $K = 0$ to about 0.06 for $K = 2$, and the hole correlator is a straight line from 0.125 to 0.38.

The 15-basis set for adsorption-desorption is significantly closer to the TM results than the 5-basis set. The diffusion equations give the best approximation in this case deviating at most by 7%.

For surface coverages higher than one half, for instance $\theta = 0.75$, Fig.4.5 the 5-basis set for adsorption-desorption and diffusion and the 15-basis set give results similar to each other and to those of the TM. In fact the curves from diffusive factorization, on this graph, are nearly indistinguishable from the TM result. For coverages below 1/2 ML, all basis sets give results close to the TM as well.

Generally speaking we expect that around half a monolayer there will be the largest deviation of the different factorization schemes from the TM result for large K because here the particle correlators can change by orders of magnitude.

4.1.2 Chemical potential

To calculate the chemical potential efficiently we fix the coverage and calculate the corresponding value of C_o in the adsorption-desorption equations. This is related to the chemical potential of the 2-D adsorbate system, μ, which can be referenced to the 3-D gas phase by $(\mu_a - E_s)/k_B T \equiv \beta\mu = -\ln(C_0)$.

We begin with the chemical potential as a function of coverage for a range of

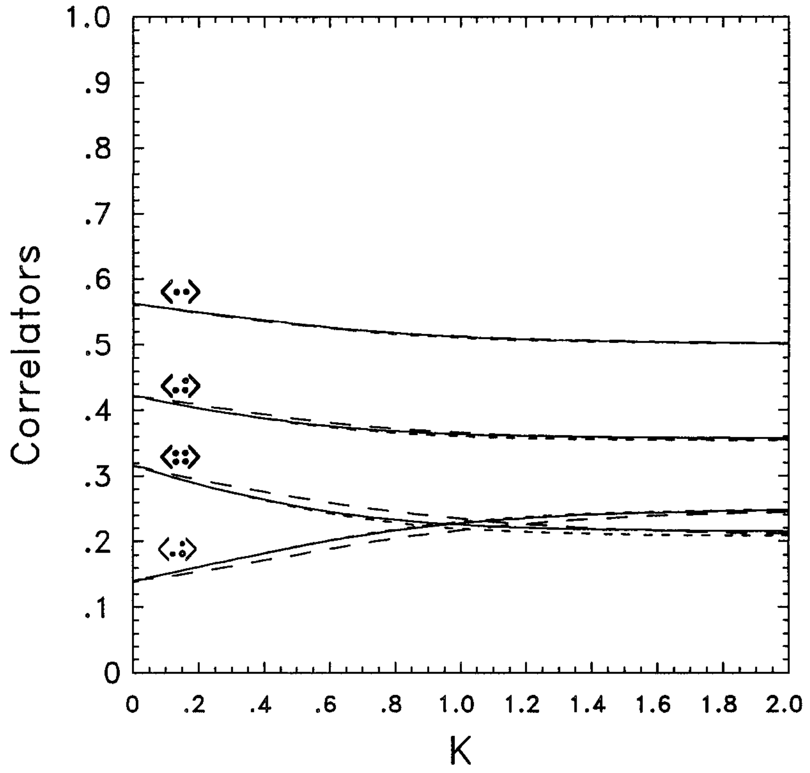


Figure 4.5: Equilibrium correlation functions as a function of K for coverage $\theta = 0.75$. Solid lines TM, long-dashed lines 5-basis set for adsorption-desorption, dotted lines 5-basis set for diffusion, short dashed lines 15-basis set for adsorption-desorption. Correlators (top to bottom at $K = 0.2$) $\langle \bullet\bullet \rangle, \langle \bullet\,{}^{\bullet}_{\bullet} \rangle, \langle {}^{\bullet}_{\bullet}{}^{\bullet}_{\bullet} \rangle, \langle \bullet\,{}^{\bullet}_{\circ} \rangle$.

nearest neighbor interactions. We show in Fig.4.6 the results from the adsorption-desorption terms for the 1-site overlap (equivalent to the quasichemical approximation) and for 2-site overlap with 5 basis correlators for adsorption-desorption in comparison to the results obtained by the Transfer Matrix method. It is obvious that the 2-site overlap is a significant improvement over the 1-site overlap, particularly for coverages below 1/2 ML, even for the strongest repulsions. There is a slight asymmetry of our factorization solutions about 1/2 ML, due to the fact that our factorization scheme is not symmetric with respect to particles and holes.

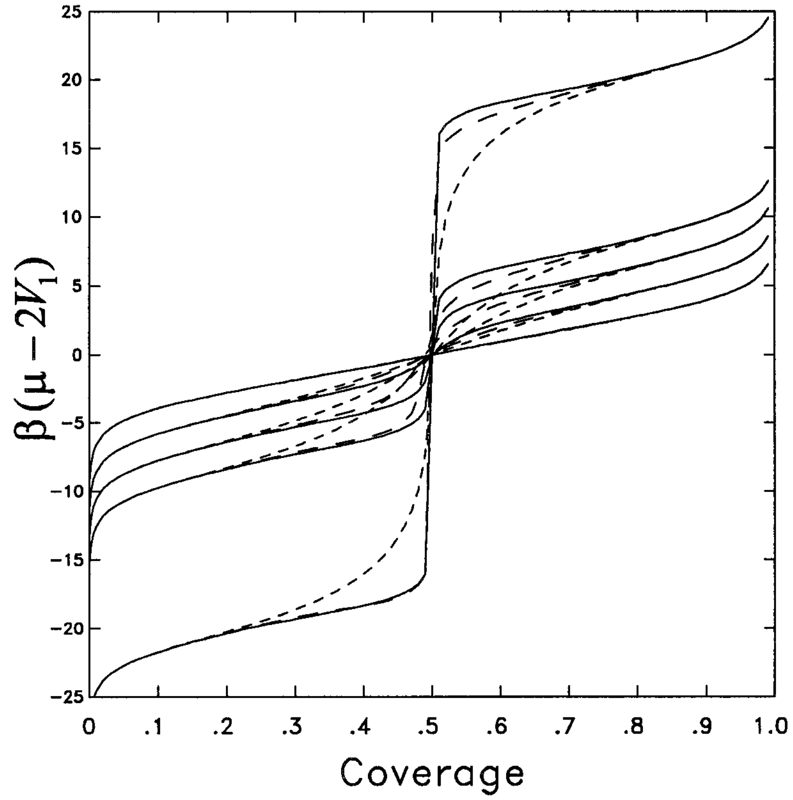


Figure 4.6: Temperature scaled chemical potential, relative to its value at 1/2 ML, as a function of coverage for several repulsive interactions (top to bottom at $\theta = 0.3$) $K = 0.5$, 1, 1.5, 2, 5. Solid lines TM, long-dashed lines 5-basis set for adsorption-desorption, short-dashed lines 1-site overlap (QCA).

Since the chemical potential measures the change of free energy of the system for the last particle added, it exhibits a sharp rise for the largest value of K, around $\theta = 1/2$, by an amount amount close to $4V_1$, because any particle added to the surface above half a monolayer will see four neighbors. At coverages below 1/2 ML there are very few particles next to each other on average, and the adsorbate behaves similarly to a non-interacting gas on a lattice. Each additional adsorption adds a particle in the same environment to produce smooth curve.

Going to the next level of sophistication with a 15-correlator basis set, as seen on

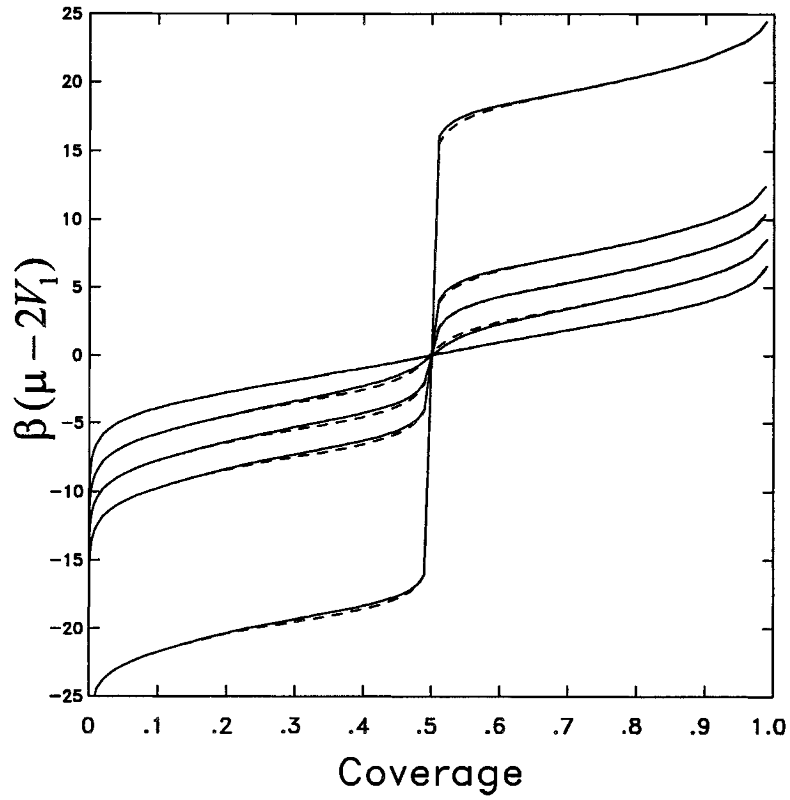


Figure 4.7: Temperature scaled chemical potential, relative to its value at 1/2 ML, as a function of coverage for several repulsive interactions (top to bottom at $\theta = 0.3$) $K = 0.5$, 1, 1.5, 2, 5. Solid lines TM, short dashed lines 15-basis set for adsorption-desorption.

Fig.4.7, the agreement with the transfer matrix results is excellent.

The diffusion zeroes of our equations for the correlators do not produce the chemical potential directly, because particle number is conserved in diffusion. Rather to obtain an effective chemical potential we have substituted the equilibrium values for the basis correlators, obtained by solving the equations for diffusion, into the adsorption-desorption equation for the single correlator Eqn.(3.35). This determines an effective C_o.

$$\begin{aligned}\beta\mu = \ln(1/C_o) = &\ln([\langle \bullet \rangle + 4C_1\langle \bullet\,\bullet \rangle + 4C_2\langle \begin{smallmatrix} & \bullet \\ \bullet & \bullet \end{smallmatrix} \rangle + 2C_2\langle \bullet\,\bullet\,\bullet \rangle + 4C_3\langle \begin{smallmatrix} & \bullet & \\ \bullet & \bullet & \bullet \end{smallmatrix} \rangle \\ &+ C_4\langle \begin{smallmatrix} & \bullet & \\ \bullet & \bullet & \bullet \\ & \bullet & \end{smallmatrix} \rangle]/[1 - \langle \bullet \rangle]) \end{aligned} \tag{4.1}$$

In this specific equation, when using the diffusion correlators, we found the best agreement with the TM results is achieved not with the usual representation of the five site correlator as $\langle \begin{smallmatrix} & \bullet \\ \bullet & \bullet \end{smallmatrix} \rangle^3/\langle \bullet\,\bullet \rangle^2$, but when factorized as

$$\langle \begin{smallmatrix} & \bullet & \\ \bullet & \bullet & \bullet \\ & \bullet & \end{smallmatrix} \rangle = \langle \begin{smallmatrix} & \bullet & \\ \bullet & \bullet & \bullet \end{smallmatrix} \rangle^2/\langle \bullet\,\bullet\,\bullet \rangle \tag{4.2}$$

where the linear trio can expanded and then factorized in the usual way, outlined in section 3.3.2.

The resulting chemical potential, Fig.4.8 is closer to the TM calculation than the chemical potential for adsorption-desorption with the same number of basis functions, and almost as good as the 15-basis set solution on Fig.4.7.

4.2 Adparticle attraction

4.2.1 Equilibrium correlators

Next we turn to attractive interactions between particles. For weak attraction all basis sets give results extremely close to those obtained via TM. Increasing the interaction strength causes the 5-basis set adsorption-desorption equations to fail to solve above $K = -0.25$. Fig.4.9 represents the correlators for the four cases of adsorption-desorption for the 5- and 15-basis set, diffusion for the 5-basis set and TM for attraction parameter $K = -0.5$. All correlators agree within a few percent of each other. The peak of the hole correlators shifts to higher coverages compared to the

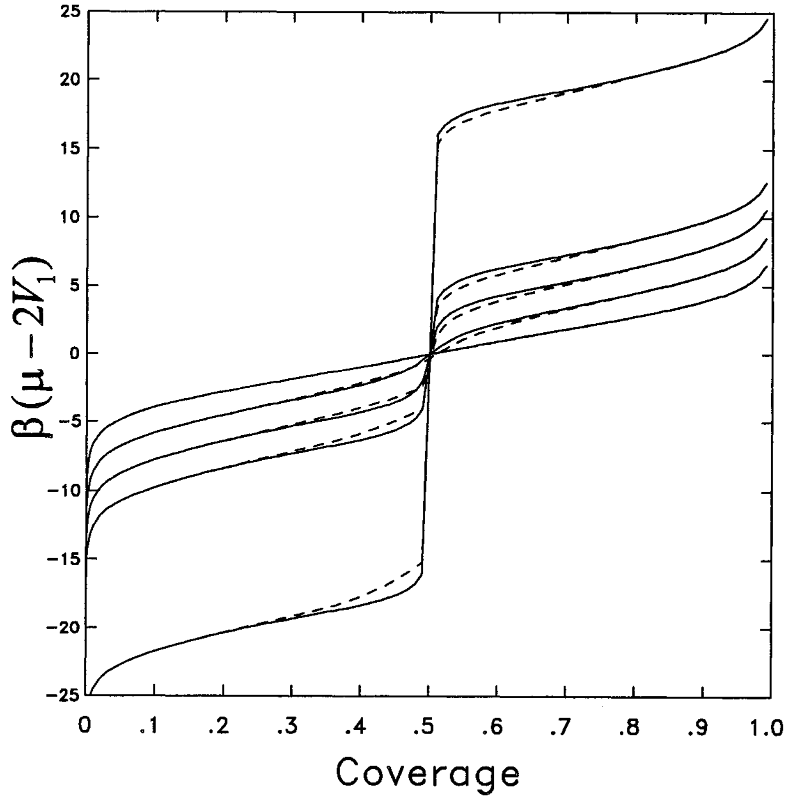


Figure 4.8: Temperature scaled chemical potential, relative to its value at 1/2 ML, via diffusive equilibrium correlators, as a function of coverage for several repulsive interactions (top to bottom at $\theta = 0.3$) $K = 0.5, 1, 1.5, 2, 5$. Solid lines TM, short dashed lines 5-basis set for diffusion.

repulsive case, as a result of the attraction.

The diffusion equations fail to solve above $K = -0.5$ but we still could obtain solutions, e.g. for $K = -0.75$, using the 15-basis set, see Fig.4.10. The higher correlators start to differ from the exact TM solutions, but the important 2-site correlator is still fairly close.

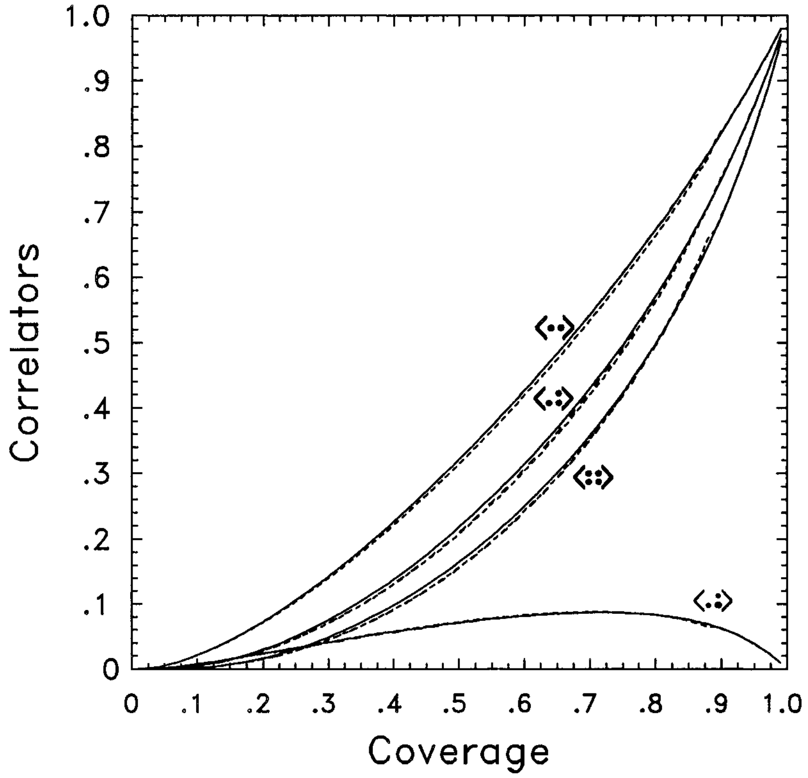


Figure 4.9: Equilibrium correlation functions as a function of coverage with $K = -0.5$. Solid lines TM, long-dashed lines 5-basis set for adsorption-desorption, dotted lines 5-basis set for diffusion, short dashed lines 15-basis set for adsorption-desorption. Top to bottom at $\theta = 0.9$ $\langle \bullet\bullet \rangle$, $\langle \bullet \overset{\bullet}{\bullet} \rangle$, $\langle \overset{\bullet}{\bullet}\overset{\bullet}{\bullet} \rangle$, $\langle \bullet \overset{\bullet}{\circ} \rangle$.

4.2.2 Chemical potential

In the attractive case decreasing the temperature (increasing the interaction) lowers and 'flattens' the chemical potential at intermediate coverages around 1/2 ML, relative to a non-interacting gas. At the critical temperature the chemical potential develops a point of inflexion at this coverage and, for lower temperatures, produces a van der Waals loop in coverage, signalling the phase separation into dilute and condensed lattice gas components. The loop is a consequence of choosing to work

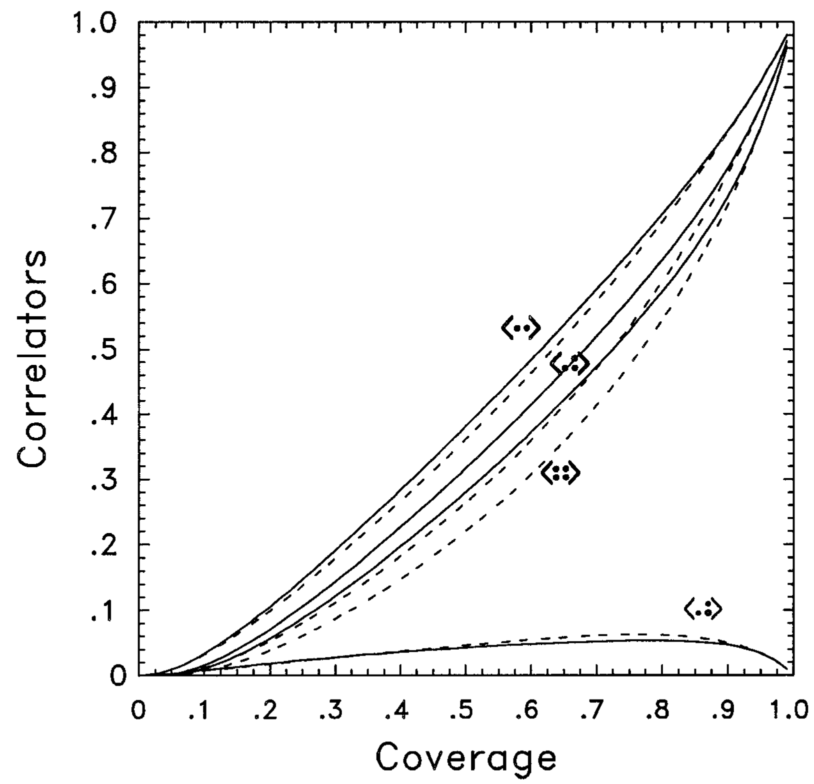


Figure 4.10: Equilibrium correlation functions as a function of coverage with $K = -0.75$. Solid lines TM, short dashed lines 15-basis set for adsorption-desorption. Top to bottom at $\theta = 0.9$ ⟨••⟩, ⟨•:⟩, ⟨::⟩, ⟨•:⟩.

with coverage and temperature as the independent variables. If we chose μ and T instead, i.e. to work in the grand-canonical ensemble, the chemical potential would assume the value $cV_1/2$ in the two-phase region of coverage.

For small interactions, $K = -0.25$, Fig.4.11 all basis sets and the TM give the same chemical potential. For larger attraction, $K = -0.5$, μ from the diffusion zero shows deviations from the TM curve with increasing coverage. At 1/2 ML it does not have the expected value of $2V_1$. This is due to the lack of symmetry in our factorization with respect to particles and holes. Yet the 15-basis set gives very good results. It

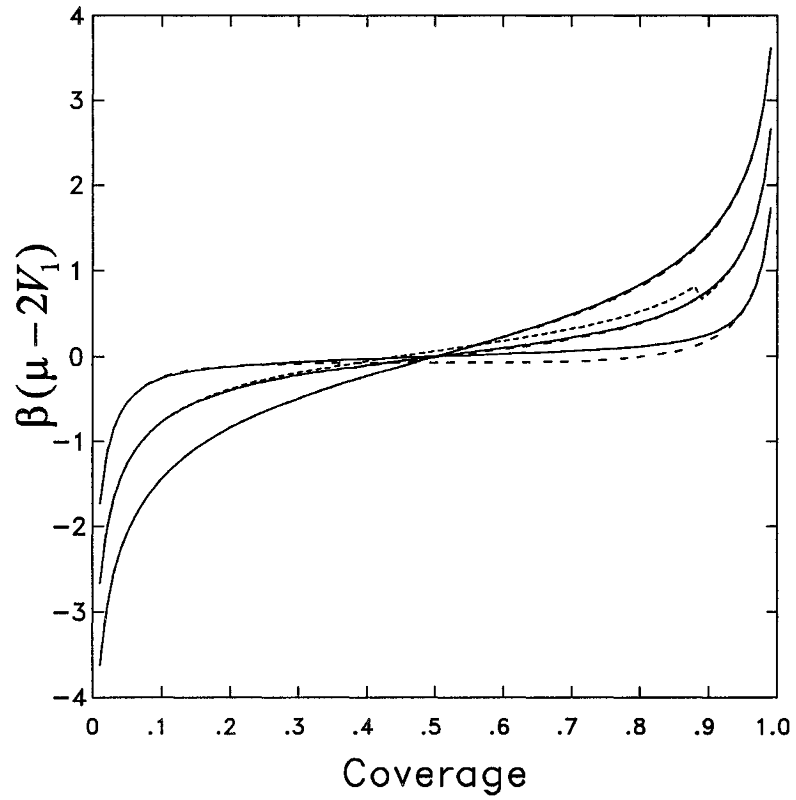


Figure 4.11: Temperature scaled chemical potential, relative to its value at 1/2 ML, as a function of coverage for several attractive interactions (top to bottom at $\theta = 0.3$) K = -0.25,-0.5,-0.75. Solid lines TM, long-dashed lines 5-basis set for adsorption-desorption, dotted lines 5-basis set for diffusion, short-dashed lines 15-basis set for adsorption-desorption.

starts to deviate from the TM solution only at the high interaction of $K = -0.75$. To proceed to even stronger attraction we should allow for the determination of the phase boundary. However, this is an unnecessary complication for our testing of our factorization procedures and will not be pursued.

4.2.3 Isosteric heat of adsorption

As outlined in Chapter 2 we can obtain the isosteric heat of adsorption by taking a temperature derivative of the chemical potential, in effect. For an atomic adsorbate

$$Q_{iso} = \frac{5}{2}k_B T - \frac{\partial(\beta\mu_a(\theta,T))}{\partial\beta}|_\theta \tag{4.3}$$

To isolate the effects of the interacting adsorbate from the single site contribution to Q_{iso}, due to the binding to the surface, which exists for all coverages, we define a reduced quantity,

$$\Delta Q_{iso} = Q_{iso}(\theta,T) - Q_{iso}(0,T) \tag{4.4}$$

For repulsive interactions, on Fig.4.12 we plot the coverage dependence of the reduced isosteric heat, derived from the adsorption-desorption chemical potential calculated in one site overlap, for several interaction strengths. This factorization is equivalent to the quasi-chemical approximation and is given in analytically by

$$\Delta Q_{iso}/4V_1 = -\frac{1}{2}\left[(1-\alpha-2\theta)/\alpha\right] \tag{4.5}$$

There are two distinct plateaus in the graph for large repulsion (small k_BT/V_1). The one below 1/2 ML is due to the fact that the particles on the surface do not see any neighbors and the energy released upon adsorption of a particle is a constant value of the surface binding energy, $Q_{iso}(0,T)$. On the other hand adsorption of a particle onto a surface covered with more than 1/2 ML will always be into a site where the particle will be surrounded by four neighbors. Thus the adsorption energy will be reduced by $4V_1$. Decreasing the interactions, equivalently increasing the temperature, smears the sharp step between these two energy levels. Eventually one recovers the mean-field (Bragg-Williams) result of a linear decrease of Q_{iso} with coverage. At 1/2

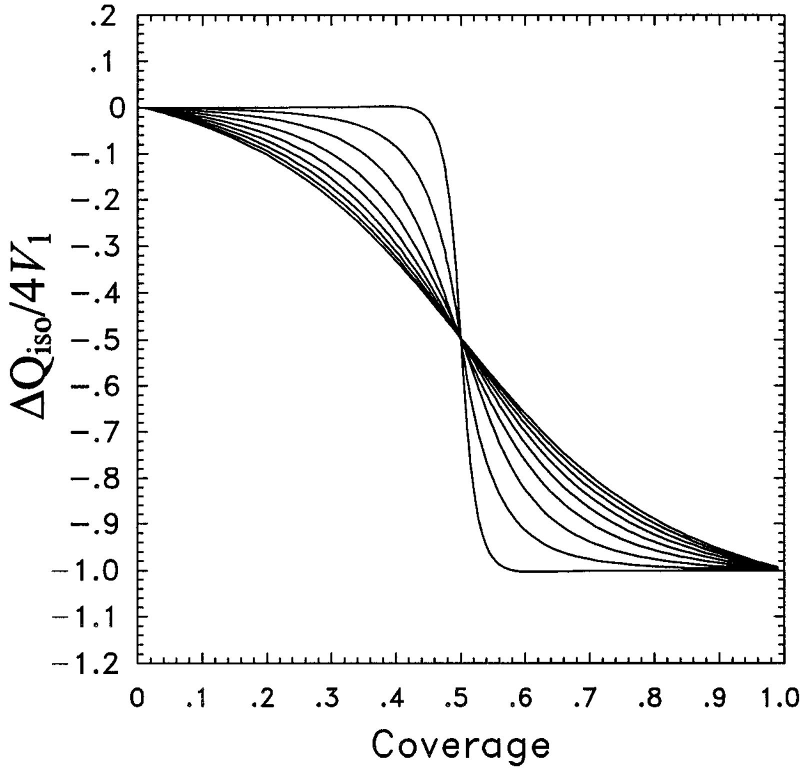


Figure 4.12: Coverage and interaction dependence of the normalized isosteric heat of adsorption for repulsive interactions for quasichemical approximation. The curves correspond to (top to bottom at $\theta = 0.3$) k_BT/V_1 =0.15, 0.25, 0.35, 0.45, 0.55, 0.65, 0.75, 0.85, 0.95.

ML according to Eqn.(4.5), the scaled isosteric heat is $-1/2$. This value will hold true no matter what kind of factorization is used provided particle-hole symmetry exists.

When the factorization is improved, Fig.4.13 to the 2-site overlap, adsorption-desorption 5-basis set, the drop of ΔQ_{iso} at 1/2 ML is even sharper at low T, and a new feature arises, namely an increase in the isosteric heat just below 1/2 ML and an overshoot in the drop above 1/2 ML. Coincidentally, it also turns out that this feature is somewhat exaggerated in the 2-site overlap approximation. We will

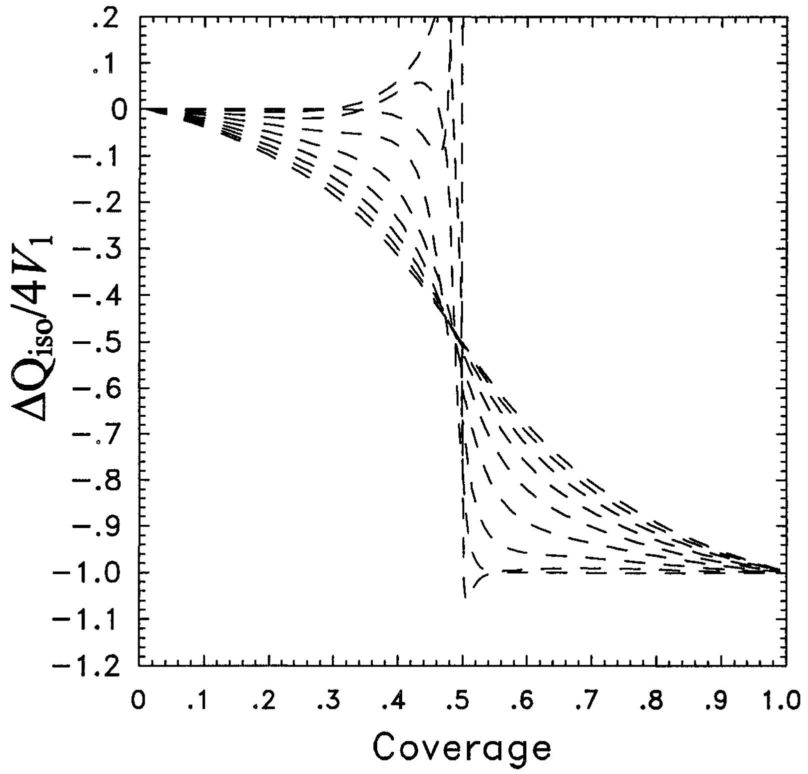


Figure 4.13: Coverage and interaction dependence of the normalized isosteric heat of adsorption for repulsive interactions for 5-basis set for adsorption-desorption. The curves correspond to (top to bottom at $\theta = 0.3$) $k_B T/V_1$ =0.15, 0.25, 0.35, 0.45, 0.55, 0.65, 0.75, 0.85, 0.95.

postpone a discussion of its physical meaning to the end of this section.

Within the 2-site overlap we can construct a hybrid calculation for which we use the equation for C_0 from the adsorption-desorption terms of the equation of motion for the coverage but insert the correlators calculated from the diffusion equilibrium. This is justified by the fact that it is diffusion that maintains the system in quasi-equilibrium during adsorption-desorption in an experiment. It coincidentally also reduces the overshoots to bring the isosteric heat (in this approximation) closer to the TM results. Thus we use the hybrid diffusive chemical potential of Eqn.(4.1) to

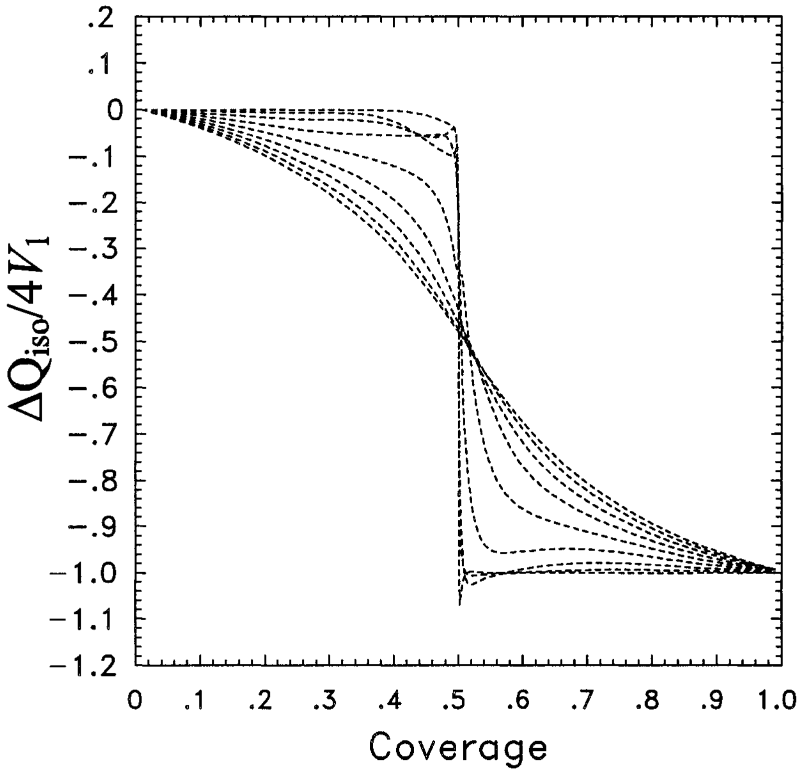


Figure 4.14: Coverage and interaction dependence of the normalized isosteric heat of adsorption for repulsive interactions for 5-basis set for diffusion. The curves correspond to (top to bottom at $\theta = 0.3$) k_BT/V_1 =0.15, 0.25, 0.35, 0.45, 0.55, 0.65, 0.75, 0.85, 0.95.

calculate the effective isosteric heat represented on Fig.4.14.

The best result for the isosteric heat is achieved for the 15-basis set in adsorption-desorption equilibrium, Fig.4.15. The curves calculated within this procedure are very close those calculated with the 4-site infinite strip TM calculation. There are features here intimately related to the ordering of the adsorbate as a consequence of the minimization of its free energy. Below 1/2 ML and at lowest temperature the heat of adsorption is constant and the adparticles stay apart, to form a c(2x2) structure. As the temperature is raised the nearest-neighbor correlator increases and there is an

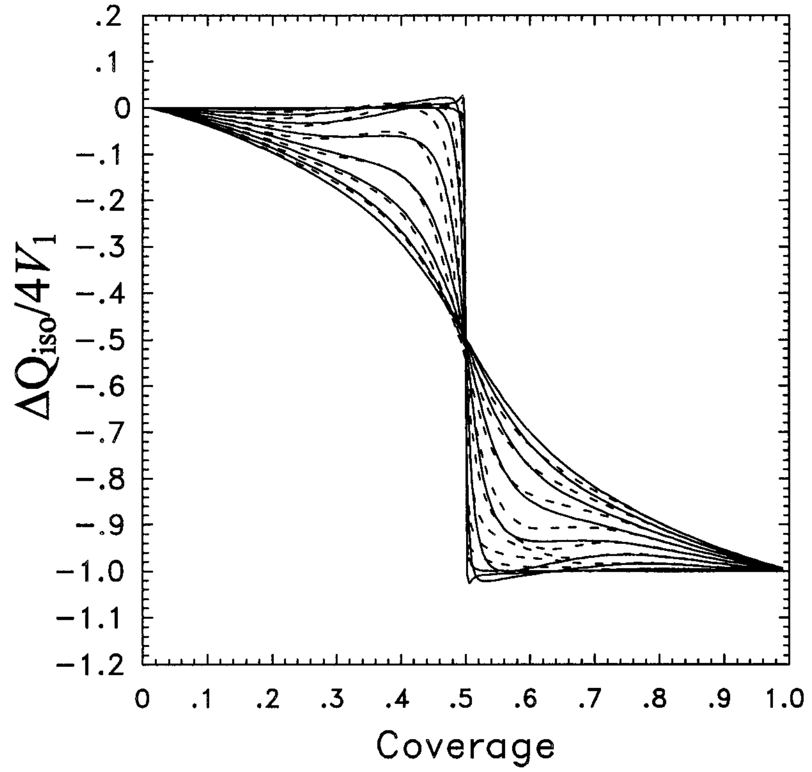


Figure 4.15: Coverage and interaction dependence of the normalized isosteric heat of adsorption for repulsive interactions. Solid lines TM, short dashed line 15-basis set for adsorption-desorption. The curves correspond to (top to bottom at $\theta = 0.3$) k_BT/V_1 =0.15, 0.25, 0.35, 0.45, 0.55, 0.65, 0.75, 0.85, 0.95.

initial decrease in Q_{iso}. As 1/2 ML is approached this correlator decreases and a rise in Q_{iso} occurs, despite the fact that only nearest-neighbor repulsions are present in the Hamiltonian. This ordering of the adsorbate into the checker-board pattern that occurs for $T < T_o = 0.57V_1$, involves a trade-off between the energy of repulsion and the entropy associated with increasing disorder as $\theta \rightarrow 0.5$. On the high temperature side the entropy contribution to the free energy is higher and tends to balance the additional repulsive energy of nearest neighbor pairs, and the characteristic rise and dip disappears. These features are repeated above 1/2 ML and on both sets of curves.

4.3 Sticking coefficient

Everything done so far is based on the Langmuir kinetics implicit in the prescribed transition probabilities for adsorption Eqn.(3.5). The result is that the sticking coefficient is given trivially by $S(\theta) = S_0(1-\theta)$. For many systems this simple form, based on site exclusion only, does not apply. In particular, if precursor states mediate adsorption one expects a sticking coefficient that is initially coverage independent. These states are weakly bound and lowly-populated intermediates to the final chemisorbed state in which the particle moves freely over both the bare substrate and the chemisorbed particles.

One might also argue that the adsorbing particle experiences the local environment in a way analogous to the desorbing particle. In such cases lateral interactions will affect the adsorption probability, e.g. repulsive nearest-neighbor interactions will inhibit adsorption. For such a situation, the so-called interaction kinetics [39] the transition probabilities can be chosen to read,

$$\begin{aligned} W_{ads}(\mathbf{n}';\mathbf{n}) =& W_0 \sum_i (1-n_i)(1 + A_1 \sum_\alpha n_{i+\alpha} + A_2 \sum_\alpha \sum_{\alpha'} n_{i+\alpha} n_{i+\alpha'} \\ & + A_3 \sum_\alpha \sum_{\alpha'} \sum_{\alpha''} n_{i+\alpha} n_{i+\alpha'} n_{i+\alpha''} + \ldots)\delta(n_i', 1-n_i) \prod_{l\neq i} \delta(n_i', n_l) \end{aligned} \tag{4.6}$$

Detailed balance then implies that (for a square lattice),

$$A_1 = \tanh(V_1/2k_BT) \tag{4.7}$$

$$A_2 = \tanh(V_1/k_BT) - 2\tanh(V_1/2k_BT) \tag{4.8}$$

$$A_3 = \tanh(3V_1/2k_BT) - 3\tanh(V_1/k_BT) + 3\tanh(V_1/2k_BT) \tag{4.9}$$

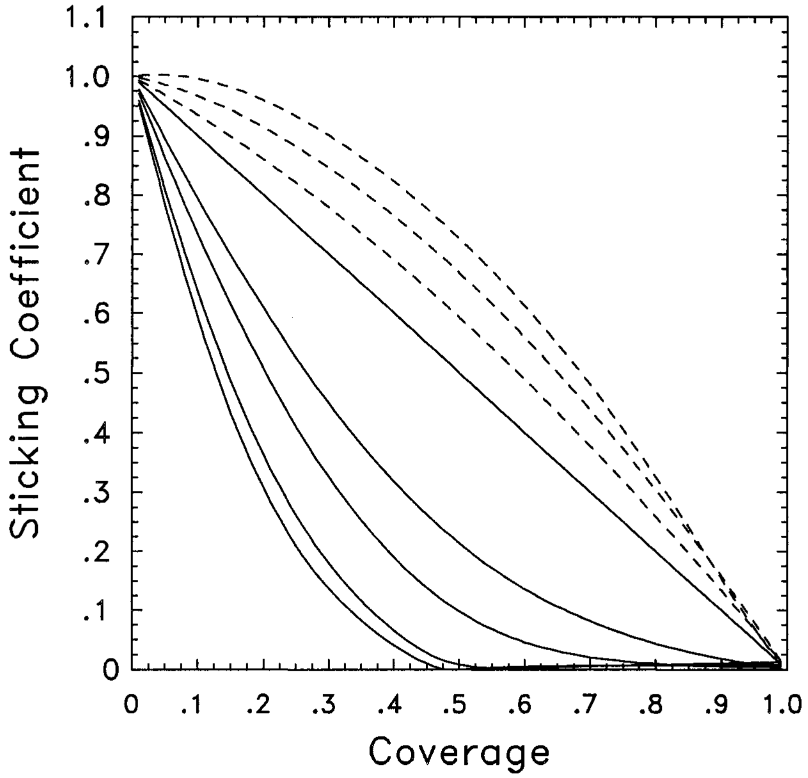


Figure 4.16: Normalized sticking coefficient $S(\theta)/S_0$, in the interaction kinetics for attractive interactions (dashed lines) and repulsive interactions (solid lines). Values of K (top to bottom at $\theta = 0.3$): –0.3, 0.2, -0.1, 0, 0.3, 0.5, 1.0, 1.5.

$$A_4 = \tanh(2V_1/k_BT) - 4\tanh(3V_1/2k_BT) + 6\tanh(V_1/k_BT) - 4\tanh(V_1/k_BT) \quad (4.10)$$

From Eqn.(4.6) an effective coverage-dependent sticking coefficient is derived,

$$S(\theta,T) = S_0(\langle \circ \rangle - 4A_1\langle \bullet\circ \rangle - 4A_2\langle \bullet\overset{\bullet}{\circ} \rangle - 2A_2\langle \bullet\circ\bullet \rangle - 4A_3\langle \bullet\overset{\bullet}{\circ}\bullet \rangle - A_4\langle \bullet\overset{\bullet}{\underset{\bullet}{\circ}}\bullet \rangle) \quad (4.11)$$

The correlation functions here are those in equilibrium if adsorption occurs at temperatures where the adsorbate is mobile. On the other hand, at low coverages this process is a random one so that the correlation functions factorize, for instance $\langle \bullet \circ \rangle = \langle \circ \rangle \langle \bullet \rangle$.

Numerical examples of sticking coefficients for a mobile adsorbate are given in Fig.4.16. For strong repulsive nearest-neighbor interactions the sticking coefficient as a function of coverage falls initially as $S(\theta) = S_0(1-5\theta)$ as the adsorbing site and all four neighboring sites must be empty. Above 1/2 ML the sticking is essentially zero. For attractive interactions the sticking coefficient is always larger than $1-\theta$. However in the limit of very strong attraction the sticking coefficient approaches the limit $1-\theta$ due to the fact that all particle correlators approach the value of θ. Essentially, the adparticles clump together and the empty sites have the same probability as for a non-interacting adsorbate. As mentioned before, the 5-site basis set factorization fails for stronger attractive interactions.

Due to the fact that transition probabilities must satisfy detailed balance in equilibrium, the rather complicated coverage dependence of the sticking coefficient will reflect itself in the desorption kinetics.

4.4 Failed factorization schemes

We have, of course, tried different factorization schemes. A promising, physically accurate and unique way to extend the basis set would seem to include every additional correlator that appears in the time evolution equations. Thus an extension to the two-site basis set ($\langle \bullet \rangle$, $\langle \bullet \bullet \rangle$) is to include both trio correlators $\langle {}_{\bullet} \overset{\bullet}{\bullet} \rangle$, and $\langle \bullet \bullet \bullet \rangle$ In this basis all correlators containing holes can be expressed in terms of particle correlators only, e.g.

$$\langle \bullet\circ\bullet \rangle = \frac{\langle \bullet\circ \rangle^2}{\langle \circ \rangle} = \frac{\left(\langle \bullet \rangle - \langle \bullet\bullet \rangle\right)^2}{1-\langle \bullet \rangle} \tag{4.12}$$

Also all higher order correlators can be expressed uniquely as an average of all possible ways of factorization with correlators containing one less site, applying this rule until the basis set is reached. For instance the correlator $\langle \bullet\overset{\bullet}{\underset{\bullet}{\bullet}}\bullet \rangle$ in the basis set of ($\langle \bullet \rangle$, $\langle \bullet\bullet \rangle$, $\langle \bullet\overset{\bullet}{\bullet} \rangle$, $\langle \bullet\bullet\bullet \rangle$) is factorized as

$$\begin{aligned}\langle \bullet\overset{\bullet}{\underset{\bullet}{\bullet}}\bullet \rangle &= \frac{1}{6}\left(2\frac{\langle \bullet\overset{\bullet}{\bullet}\bullet \rangle^2}{\langle \bullet\bullet\bullet \rangle} + 4\frac{\langle \bullet\overset{\bullet}{\bullet}\bullet \rangle^2}{\langle \bullet\overset{\bullet}{\bullet} \rangle}\right) = \frac{1}{3}\langle \bullet\overset{\bullet}{\bullet}\bullet \rangle^2\left(\frac{1}{\langle \bullet\bullet\bullet \rangle} + \frac{2}{\langle \bullet\overset{\bullet}{\bullet} \rangle}\right) = \\ &= \frac{1}{3}\left(\frac{1}{3}\left(\frac{\langle \bullet\overset{\bullet}{\bullet} \rangle^2}{\langle \bullet\bullet \rangle} + 2\frac{\langle \bullet\overset{\bullet}{\bullet} \rangle\langle \bullet\bullet\bullet \rangle}{\langle \bullet\bullet \rangle}\right)\right)^2\left(\frac{1}{\langle \bullet\bullet\bullet \rangle} + \frac{2}{\langle \bullet\overset{\bullet}{\bullet} \rangle}\right)\end{aligned} \tag{4.13}$$

We encountered great difficulty when solving numerically the system of four equations with such a basis set and this combinatorial factorization. From the TM calculations we know that the equilibrium values of the correlators $\langle \bullet\overset{\bullet}{\bullet} \rangle$,$\langle \bullet\bullet\bullet \rangle$ are not identical but differ only less than one percent. However the time evolution equations for each of these correlators are quite different; they differ both in the number of terms, and their higher-order correlators. Each factorization of every higher order correlator inherently adds errors to the representation of this correlator and this causes the equilibrium values for $\langle \bullet\overset{\bullet}{\bullet} \rangle$ and $\langle \bullet\bullet\bullet \rangle$ to strongly deviate from each other for some coverages.

An added difficulty in this factorization scheme is that the proper counting of all possible factorizations of each correlator is very time consuming when derived by hand and difficult to encode in a routine.

Simply increasing the basis set to include the higher order correlators, for instance the 9-site basis set of ($\langle \bullet \rangle$, $\langle \bullet\bullet \rangle$, $\langle \bullet\overset{\bullet}{\bullet} \rangle$, $\langle \bullet\bullet\bullet \rangle$, $\langle \bullet\bullet\bullet\bullet \rangle$, $\langle \bullet\overset{\bullet}{\overset{\bullet}{\bullet}} \rangle$, $\langle \bullet\overset{\bullet}{\bullet}\bullet \rangle$, $\langle \underset{\bullet}{\bullet}\overset{\bullet}{\bullet} \rangle$, $\langle \overset{\bullet}{\bullet}\overset{\bullet}{\bullet} \rangle$) and using just one type of factorization for the higher-order correlators, does not fare any better. Although the system of nine equations is solvable for some coverages, for others it diverges giving nonphysical solutions.

These difficulties were overcome by expressing the extended correlators in terms of more "compact" ones, for instance,

$$\langle \bullet\bullet\bullet \rangle = \langle \bullet\overset{\bullet}{\bullet}\bullet \rangle + \langle \bullet\overset{\circ}{\bullet}\bullet \rangle \tag{4.14}$$

In this way the above 9-site basis set is reduced to the 4-site basis set, ($\langle \bullet \rangle$, $\langle \bullet\bullet \rangle$, $\langle \bullet\overset{\bullet}{\bullet} \rangle$, $\langle \overset{\bullet}{\bullet}\overset{\bullet}{\bullet} \rangle$). The basis set required to factorize the higher order correlators is smaller and the procedure for this reduction is unique.

We have found that it is not the number of the correlators in the basis set but the size of the overlap that is the leading factor for improving the results. For instance, extending the 4-site basis set ($\langle \bullet \rangle$, $\langle \bullet\bullet \rangle$, $\langle \bullet\overset{\bullet}{\bullet} \rangle$, $\langle \overset{\bullet}{\bullet}\overset{\bullet}{\bullet} \rangle$) to the 5-site basis ($\langle \bullet \rangle$, $\langle \bullet\bullet \rangle$, $\langle \bullet\overset{\bullet}{\bullet} \rangle$, $\langle \overset{\bullet}{\bullet}\overset{\bullet}{\bullet} \rangle$, $\langle \bullet\overset{\bullet}{\underset{\bullet}{\bullet}}\bullet \rangle$) does not improve the quality of the results for the equilibrium correlators. Rather, one has to extend the basis set with correlators of the likes of $\langle \overset{\bullet}{\bullet}\overset{\bullet}{\bullet}\bullet \rangle$ and $\langle \overset{\bullet}{\bullet}\overset{\bullet}{\bullet}\overset{\bullet}{\bullet} \rangle$ and increase the overlap in the factorization to achieve notable improvement.

Going to higher order of overlap necessitates the use of correlators that have empty sites. Because the operations of multiplication and subtraction do not commute when factorizing the higher order correlators the results are not symmetric with respect particles and holes. This explains the particle-hole asymmetry in the chemical potential.

When using the 6-site basis set ($\langle \bullet \rangle$, $\langle \bullet\bullet \rangle$, $\langle \bullet\overset{\bullet}{\bullet} \rangle$, $\langle \bullet\bullet\bullet \rangle$, $\langle \bullet\circ\bullet \rangle$, $\langle \bullet\overset{\bullet}{\circ} \rangle$) and combinatorial factorization we obtain very large deviations between the two hole correlators and, for some coverages, unphysical behavior. The converging results obtained by a basis set ($\langle \bullet \rangle$, $\langle \bullet\bullet \rangle$, $\langle \bullet\overset{\bullet}{\bullet} \rangle$, $\langle \bullet\bullet\bullet \rangle$, $\langle \bullet\overset{\bullet}{} \rangle$) were also unsatisfactory. Whenever the system of equations solved the result was at par with the quality of the quasichemical approximation.

We did try the full combinatorial factorization for a basis set containing the 15 basis functions, ( ) but for some coverages the solutions diverge and are nonphysical.

4.5 Survey of other cluster methods

As far as the equilibrium properties of a lattice gas are concerned, our calculation method is but one of many approximation techniques that have been advanced over the years, based on the calculation of the partition function of the system. Here we give a brief overview of these other methods [41].

The quasichemical approximation mentioned earlier is the simplest example of the cluster variation method. In QCA, [42] the interaction between pairs of occupied sites is counted; then these pairs are treated as independent of each other and an approximate partition function is calculated, by examining the arrangements of such pairs on the lattice, without overcounting of particles i.e. by minimizing the Helmholmtz free energy $U - TS$. However, for such pairs on a square cluster of occupied sites, there is overlap at all corners and one cannot represent the systems configuration accurately, except in the limits of $\theta \rightarrow 0$ or 1, where pairs of particles (holes) vanish. The direct generalization of the basic unit to a square cluster of sites, [43] does not lead to a significant improvement. In particular, for particle repulsion, Fig.4.12 is repeated with some change in the slopes of the curves, only. For attractive interaction the estimate of critical temperature, $K_c = V_1/2T_c$ is barely improved over QCA. Kikuchi, [29], improved the method by using a kink site to represent the building up of the lattice, one site at a time. Consistency conditions for the correct fractional distribution of groups of sites, associated with this kink, then give a set of nonlinear equations from

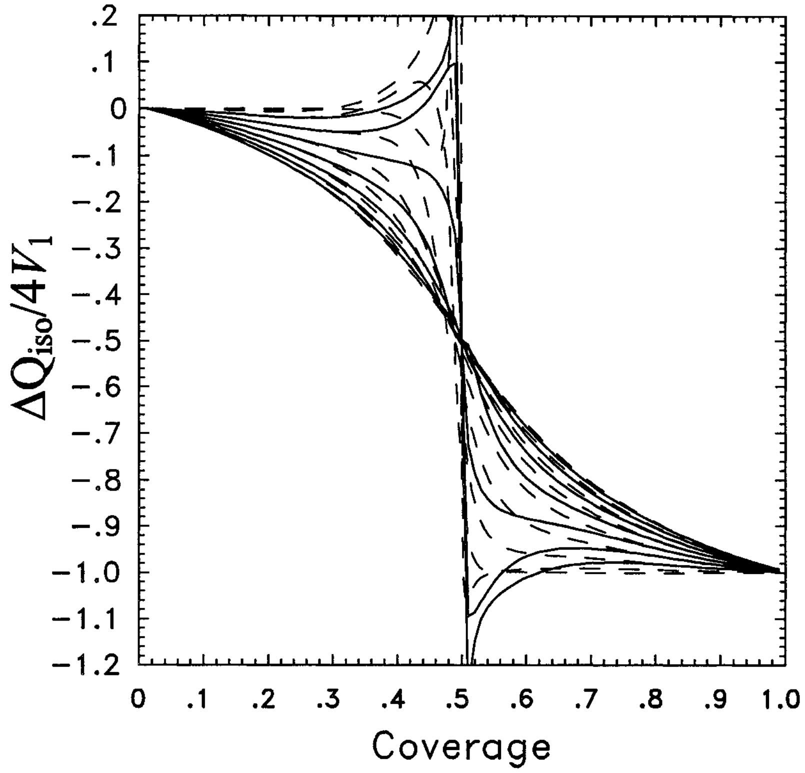


Figure 4.17: Coverage and interaction dependence of the normalized isosteric heat of adsorption for repulsive interactions. Solid lines Honig formulae from [28], dashed line 5-basis set for adsorption-desorption. The curves correspond to (top to bottom at $\theta = 0.3$) k_BT/V =0.15, 0.25, 0.35, 0.45, 0.55, 0.65, 0.75, 0.85, 0.95.

which the equilibrium distributions follow. The estimate of K_c, a common figure of merit of an approximation method, is closer to the exact values obtained by series expansions, for both square and hexagonal lattices, than generalized QCA. Also, the level of approximation can be systematically improved. However, an examination of the method shows that it boils down to the level of factorization with one- or two-site overlap. So it cannot represent a system with repulsive interactions as well as our 15-basis set, for example.

In a series of complicated papers, Hijmans and de Boer [30] generalized and systematized Kikuchi's method for all lattices. They considered the problem of choice of a basic cluster and overlaps between clusters. They concluded, as we do, that the larger the basic cluster the better the level of approximation. Again, however, only attractive interaction was considered. The only attempt to apply their analysis to adsorbates with repulsive interactions is that of Honig [31]. For the square lattice the largest cluster used was the square of our 5-basis, with a total of 9 variables constrained by equilibrium, consistency and normalization conditions. Generally, there is a rapid increase of the number of constraints with the size of the largest cluster and larger than our basis.

On Fig.4.17 we compare our 5-basis set result to a calculation with Honig's equations for the square lattice. Honig's result is symmetric with respect to the point $(0.5, -0.5)$ but, just like our result, it overshoots considerably for coverages slightly less and more than a $1/2$ ML.

Independently of the quality and complexity of the best of these alternate cluster variation methods, they can only represent the equilibrium distributions of clusters. Our solution technique for the correlators, via the kinetic lattice gas model, extends away from equilibrium. A second feature of our technique is that we bypass most of the combinatorial difficulties associated with these methods.

Chapter 5

Thermal Desorption and Nonequilibrium Properties

A common method to experimentally explore the kinetics of an adsorbate is temperature-programmed desorption (TPD). In this technique a gas is adsorbed onto the surface of a cold substrate at temperature T_0. The latter is then heated with a linear temperature ramp, $T(t) = T_0 + at$. As the surface warms up the adsorbate starts to desorb until no adsorbate is left. Typically a mass spectrometer is used to monitor the flux of desorbing particles, which in turn is proportional to the negative of the rate of desorption. The result is a TPD spectrum that is a plot of the desorption rate of the gas, as a function of the sample temperature (if we replace the time axis by temperature).

We have calculated TPD spectra for the model systems discussed in previous chapters, using the kinetic lattice gas model. The desorption rate factor which enters the time evolution of all the correlators, occurs explicitly in Eqn.(3.6) as the factor $W_o C_o$

$$W_oC_o = S_o a_s \frac{k_B T}{h\lambda_{th}} \frac{Z_{int}}{q_3 q_{int}} \exp(-\beta V_o) \tag{5.1}$$

which follows by combining expressions in Eqns.(2.24, 3.7, 3.28). Thus the additional parameters needed to determine the desorption rate are the mass of the desorbing particle ($m = 52amu$), the area of a single adsorption site ($a_s = 7\AA^2$), the site binding energy ($V_0/k_B = 15000K$) and the surface vibrational frequencies ($\nu_z = 10^{13}s^{-1}$, $\nu_x = \nu_y = 10^{12}s^{-1}$). (For simplicity we will assume an atomic adsorbate and dispense with internal degrees of freedom.) All these are typical numbers for desorption of metals or carbon monoxide from metals and, for a typical heating rate of $a = 2Ks^{-1}$, the desorption spectra span a temperature range $300 - 500K$.

We begin with an adsorbate in which diffusion is so fast that it maintains quasi-equilibrium on the surface during desorption. This is the case when the rate of diffusion is at least three orders of magnitude larger than the desorption rate. This implies that at any point in time during desorption all correlators attain their equilibrium values appropriate for the instantaneous coverage at that time.

In our first model adsorbate there is a nearest neighbor repulsion, V_1, large with respect to the thermal energy of desorption. The resulting TPD spectra are shown in Fig.5.1 (dotted lines). Here we have varied the coverage on the substrate at the desorption temperature ($T_o = 200K$). The desorption rate maxima are clearly proportional to the initial coverages, at least for values below 1/2 ML, and the area under a curve measures its initial coverage. As we have seen in the previous chapter the heat of adsorption has two plateaus, below and above half a monolayer. This implies that for initial coverages of less than 1/2 ML the desorbing particles do not have neighbors and the energy required to desorb them is roughly the site binding energy. For initial coverages above 1/2 ML adparticles experience repulsion from their neighbors, which implies that the energy required for desorption is reduced by this repulsion, to

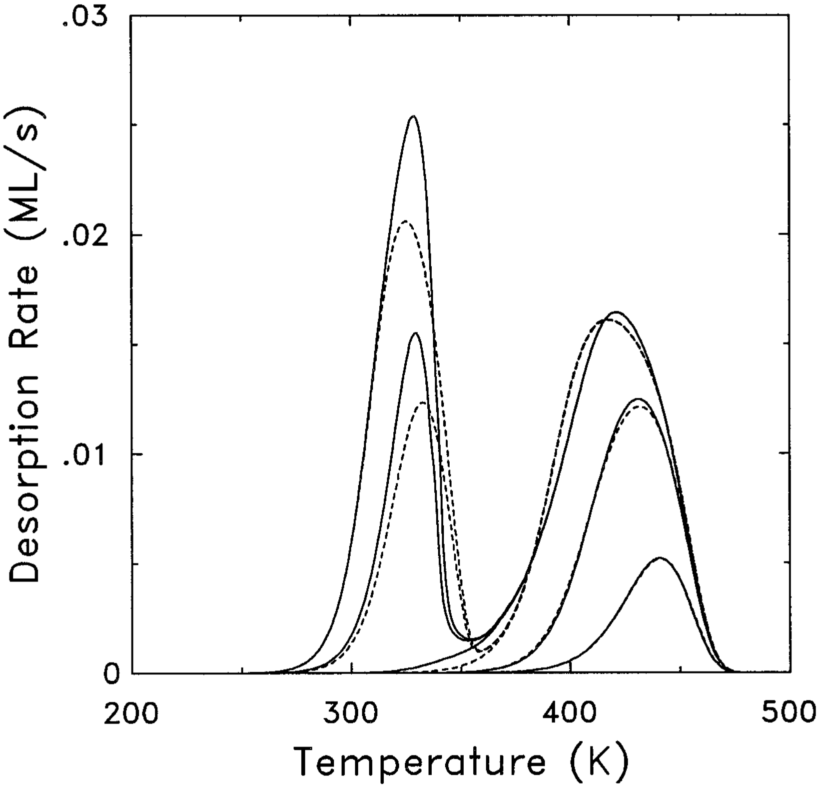


Figure 5.1: Temperature-programmed desorption rate (in units of monolayers per second) for a mobile adsorbate with repulsive interaction $V_1/k_B = 1000K$. Solid lines TM, dotted lines 5-basis set. The curves correspond to initial coverages θ =0.1, 0.3, 0.5, 0.7, 0.9

a maximum of $4V_1$ on a square lattice. The consequence for TPD is that the spectra have two distinct peaks, each corresponding to one of the plateaus in ΔQ_{iso}. This is clearly seen in Fig.5.1 where the TPD traces span initial coverages from 0.1 to 0.9 ML. Obviously the splitting of the peaks is proportional to V_1 and, indeed, it is the understanding of the origin of such features that motivates our modelling of the thermal desorption.

The calculations for Fig.5.1 were done in the 5-basis set. Because this adsorbate was kept by fast diffusion in quasi-equilibrium throughout desorption, we can compare

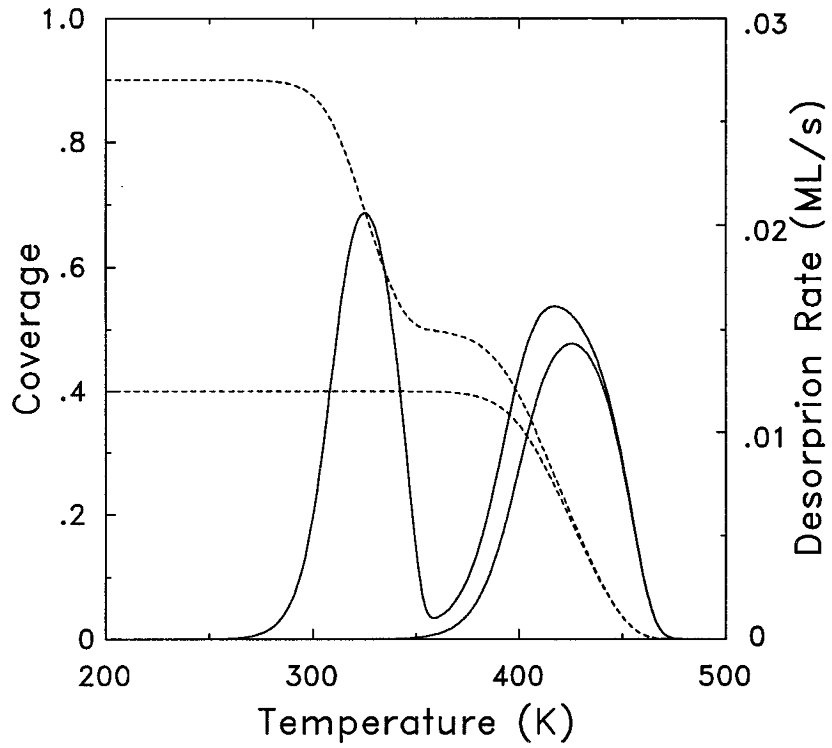


Figure 5.2: TPD rates (solid lines) and the evolution of the corresponding surface coverages (dotted lines) for a mobile adsorbate with repulsive interaction $V_1/k_B = 1000K$ calculated using the 5-basis set. Initial coverages θ =0.4, 0.9

our results with those obtained using Eqn.(2.16) with the chemical potential calculated by the TM method with a 4-site strip width (solid lines). For initial coverages below 1/2 ML the approximation to the kinetic lattice gas model gives TPD spectra essentially identical to those obtained with the quasi-equilibrium TM method. This is to be anticipated as a consequence of the closeness of the equivalent equilibrium solutions. For initial coverages above 1/2 ML some discrepancies show up for the 5-basis set approximation (which are however overcome with 15-basis set).

In Fig.5.2 we show the time evolution of the coverage itself during desorption

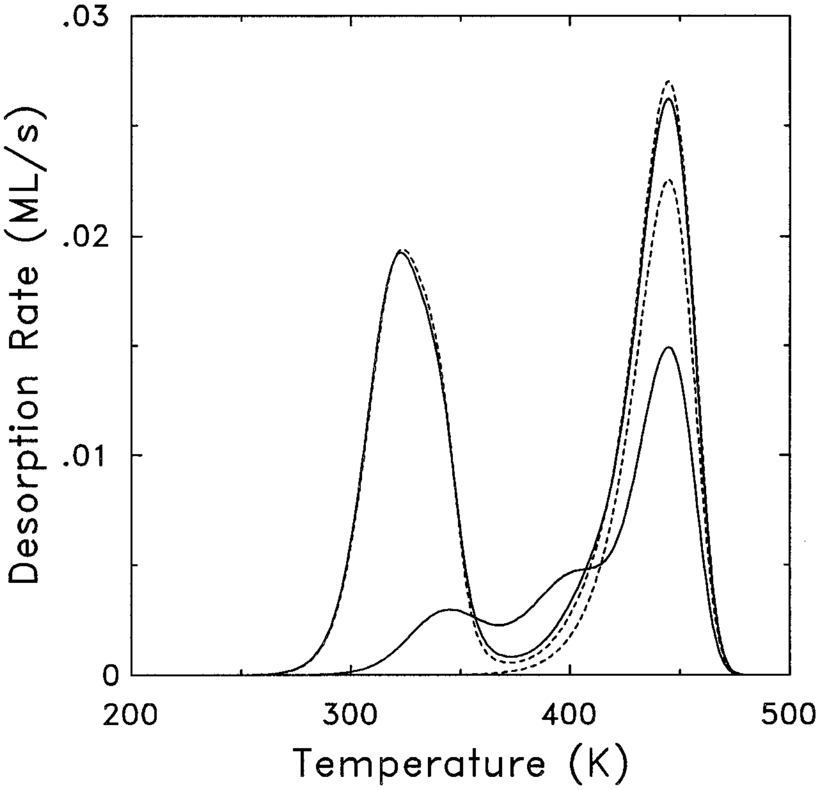


Figure 5.3: Desorption rates for immobile adsorbate with repulsive interaction $V_1/k_B = 1000K$ and initial coverages $\theta = 0.4, 0.9$ calculated using the 5-basis set for random initial correlators (solid lines) and equilibrium initial correlators (dotted lines).

superimposed on the rates for two initial coverages. Remember that temperature changes linearly with time so that the temperature regime from 300 to $500K$ takes $100s$ for a heating rate of $2Ks^{-1}$. Not surprising is the fact that in the valley of the desorption rates the coverage remains more or less constant.

So far we have looked at TPD from an adsorbate with fast diffusion. In our next example we look at the other extreme, namely negligible diffusion, with $J_0 = 0$ in the evolution equations. In such situations it is crucial to know the initial state of the adsorbate. We can envisage two extreme situations: (i) the adsorbate is left at the initial temperature of deposition, T_0, for long enough that surface diffusion, albeit slow, has brought the adsorbate into equilibrium. Thus the correlators that must be specified as initial conditions to solve the time evolution in desorption are those of equilibrium at T_0. (ii) After deposition of the adsorbate at T_0 the heating ramp is started before equilibration is achieved. In this case the initial values of the correlators are those of a random adsorbate, i.e. for an n-particle correlator equal to θ^n.

The TPD spectra Fig.5.3 do not reflect any difference for initial coverages close to a monolayer for these two situations because the initial correlators are all of order one whether the system has equilibrated or is random. However, these different initial conditions affect the TPD spectra significantly for initial coverages below 1/2 ML. In particular, desorption for the first situation onsets at temperatures about $80K$ higher than the second. The reason is that in an initially equilibrated adsorbate there are few nearest neighbor sites occupied for coverages below 1/2 ML. Thus the desorption is essentially that of a non-interacting adsorbate, i.e. one high energy (temperature) peak. On the other hand, for a random adsorbate there is a sufficient number of nearest neighbor sites occupied so that their desorption occurs at lower temperature (due to the reduction of the desorption energy by the nearest neighbor repulsion).

The appearance of an intermediate desorption peak around $400K$ can be traced to the number of neighbors surrounding the desorbing particle. This is obviously quantified by the correlators, whose time evolution and rates are plotted in Fig.5.4 for this case. In the range of the low temperature shoulder around $350K$ in the trace of the coverage we see that the 4- and 3-particle correlators are destroyed, in order, and also the 2-particle correlator diminishes. However the latter has another peak in its rate of change at an intermediate temperature around $400K$. Thus, what is left for desorption at higher temperatures are single particles without neighbors on the

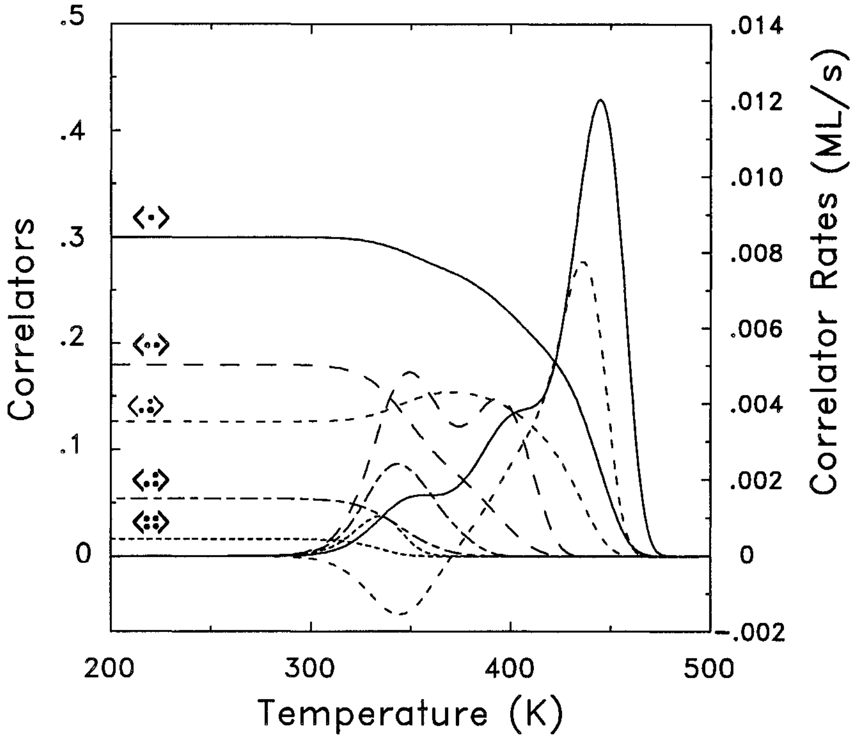


Figure 5.4: Correlators and their rates of change (of same line type) for immobile adsorbate with repulsive interaction $V_1/k_B = 1000K$ for initial coverage of $\theta = 0.3$ calculated using the 5-basis set. Correlatots form top to bottom at $T = 250K$,⟨•⟩,⟨••⟩,⟨.:⟩,⟨.:⟩,⟨::⟩)

surface, i.e. without the effect of lateral repulsion. The rate for the trio correlator with one hole (short-dashed line) becomes negative at first with the increase of the temperature, because the number of such correlators is actually increasing on the surface. It is clear that, even for near-monolayer initial coverage, the two-peaked spectra of Fig.5.1 and Fig.5.3 are distinct. Each peak has an area corresponding to (about) 1/2 ML, but the relative desorption rates at low and high temperature are switched. The origin of this switch will be elucidated below.

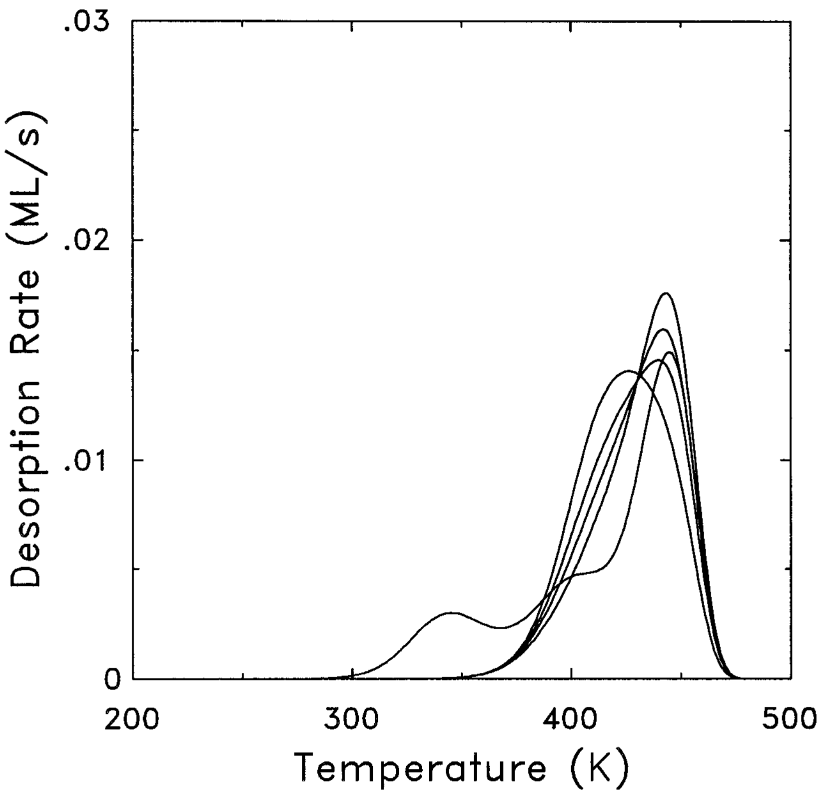


Figure 5.5: Desorption rates for adsorbate with partial surface mobility and repulsive interaction $V_1/k_B = 1000K$ calculated using the 5-basis set and site-site hopping frequency of (top to bottom at $T = 420K$) $J_0 = 10^{-1}$, 10^{-2}, 5.0x10^{-3}, 2.5x10^{-3},0 s^{-1}. Initial coverage of $\theta = 0.4$.

We now examine the qualitative and quantitative changes occurring when diffusion is switched on, from no diffusion to fast diffusion, starting in all cases from random initial conditions at $T_0 = 280K$ and with the barrier for diffusion, Q in Eqn.(3.10), set to zero for simplicity, (this corresponds to no surface corrugation). We first look at the evolution from an initial coverage of 0.4 ML, represented on Fig.5.5. The situation of establishing quasi-equilibrium before desorption starts is achieved with a site-to-site hopping rate J_0 larger than $10^{-1}s^{-1}$. On the other hand, a reduction of J_0 by a factor of 40 is still such that diffusion is fast enough to destroy all 4-

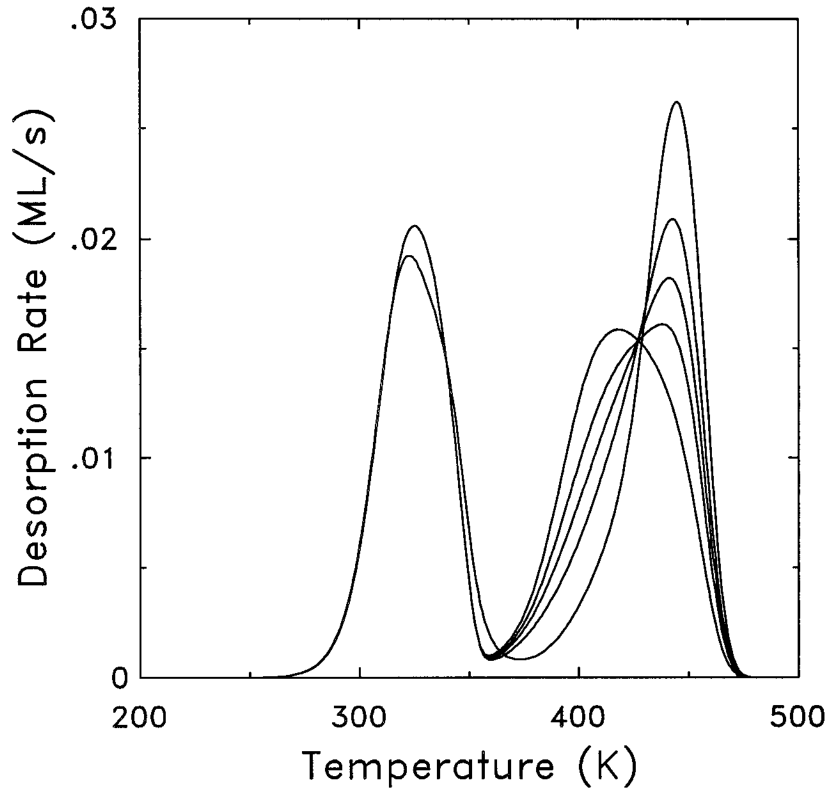


Figure 5.6: Desorption rates for adsorbate with partial surface mobility and repulsive interaction $V_1/k_B = 1000K$ calculated using the 5-basis set and surface hopping frequency (top to bottom $T = 450K$) $J_0 = 0$, 2.5x10^{-3}, 5.0x10^{-3},10^{-2},10^{-1}s^{-1}, initial coverage of $\theta = 0.9$.

and 3-particle clusters which, for no hopping, are responsible for the low temperature peak at $350K$. The remaining modification of the high temperature peak is such that its peak height and width are increased compared to zero diffusion. Increasing the diffusion coefficient towards fast diffusion reduces the peak height, moves it to lower temperature and broadens it.

The physical reason behind this behavior is as follows: for random initial distributions of particles on the surface, there are particles with zero to four neighbors. Those with three or four neighbors will desorb first giving rise to the peak at $350K$;

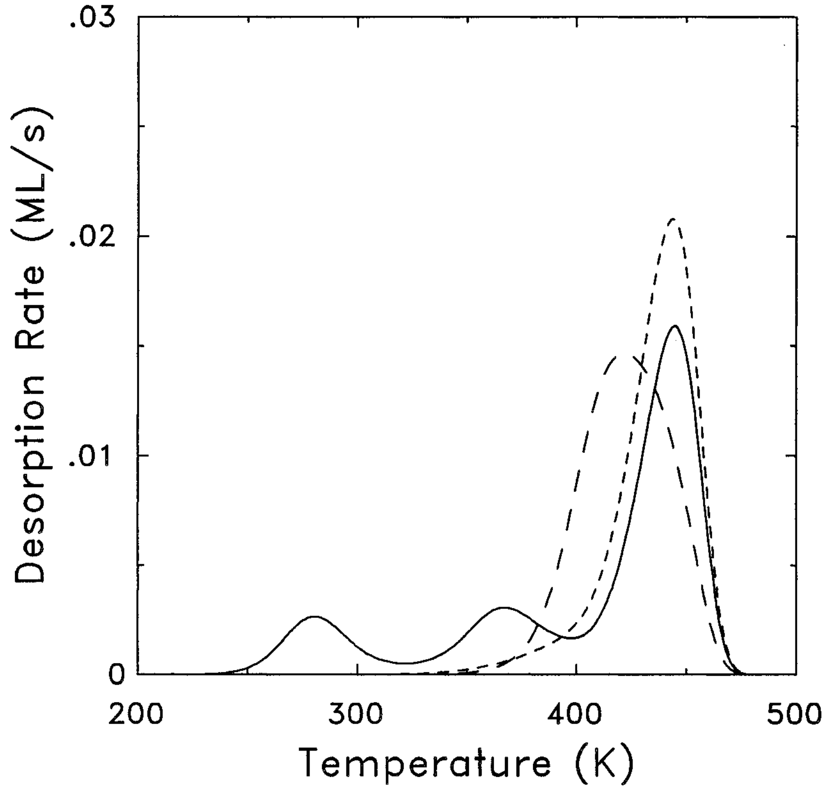


Figure 5.7: Desorption rates for adsorbate with repulsive interaction $V_1/k_B = 1500K$ calculated using the 5-basis set and hopping barrier $Q/k_B = 600K$ and frequency (top to bottom at $T = 450K$) $\nu_{diff} = 10^3$, 0, 10^6 for initial coverage of $\theta = 0.4$. Random initial correlators.

when there is limited diffusion particles are able to move apart, on the time scale of desorption, and thus desorb as if isolated on the surface. This produces the highest peak. However, when the hopping rate increases even more, the probability for a particle with no neighbors to hop to an environment where it has neighbors increases, i.e. in thermal equilibrium at temperatures of the order of the repulsion nearest neighbor sites are occupied. So the particles repel each other more and this shifts the peak to lower temperature. For initial coverage well above 1/2 ML, presented on Fig.5.6, diffusion has a limited effect on the low temperature peak. Due to the

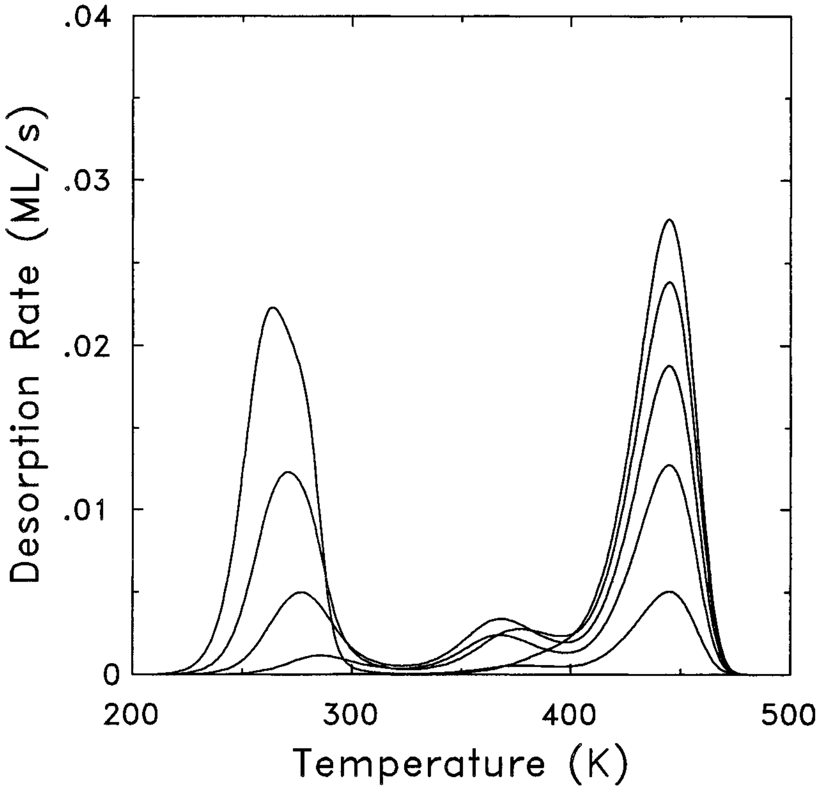


Figure 5.8: TPD rates for immobile adsorbate and repulsive interaction $V_1/k_B = 1500K$. For coverages (bottom to top at $T = 450K$) θ =0.1, 0.3, 0.5, 0.7, 0.9

high coverage, all correlators are of order one. Thus the low temperature peak is only slightly effected. The high temperature peak is again shifting to a lower temperature and getting broader. As mentioned above, the separation of the peaks in the mobile case is a measure of the interaction energy. This is not strictly true for desorption under limited diffusion conditions - one would infer a value of V_1 25% larger than actually exists by measuring this peak separation. Usually experimental TPD spectra are analyzed to deduce the effective binding energy, as a function of coverage, hence the effective interaction [5]. Clearly one has to be aware of limited surface diffusion before attempting such an analysis.

If we use a more physical Arrhenius activation behavior with a barrier of $Q/k_B = 600K$, say, and higher nearest-neighbor repulsion of $V_1/k_B = 1500K$, a surface hopping frequency of $\nu_{diff} = 10^6 s^{-1}$ is required to achieve a mobile case, Fig.5.7. This frequency roughly corresponds to values calculated by solving the quantum mechanical equations that include the coupling between the surface vibration of the particle and surface phonons for barrier heights of a few k_BT [44]. For the intermediate frequency of $\nu_{diff} = 10^3 s^{-1}$ the diffusion is fast enough to move the adparticles away from each other but insufficient to establish quasi-equilibrium.

Generally, the higher the repulsive interaction the larger the shift of the two low temperature peaks to lower temperatures. Fig.5.8 shows the desorption rates for an immobile adsorbate with repulsive interaction $V_1/k_B = 1500K$ and random initial correlators. It is of interest that one does not see the desorption of three and four neighbors of a site as separate desorption peaks here, as implied by the first equation of the desorption hierarchy, Eqn.(3.24). The one- to five-site correlators in that expression suggest five separate contributions (stages) to the total desorption rate. Instead we see only the effect of two-site clusters in the intermediate temperature region. Moreover, for equilibrium initial conditions even this contribution disappears - see dotted lines in Fig.5.3. Even this latter result is surprising because, for the same conditions and parameters, desorption for a 1-D system exhibits a three-peaked spectrum corresponding to the existence of one-, two- and three-site clusters [20]. In this case the solution is exact, in terms of the two- and three-particle correlators. Thus, by extension, a 5-stage desorption spectrum of an immobile adsorbate could be expected for a 2-D system, as suggested by the correlators in Eqn.(3.24). However, our results show that the time evolution of the hierarchy of basis correlators is quite different to the evolution of this one equation, viewed in isolation.

In the case of attractions there is only one peak region for all initial coverages, but shifted to higher temperatures compared to the noninteracting case, because

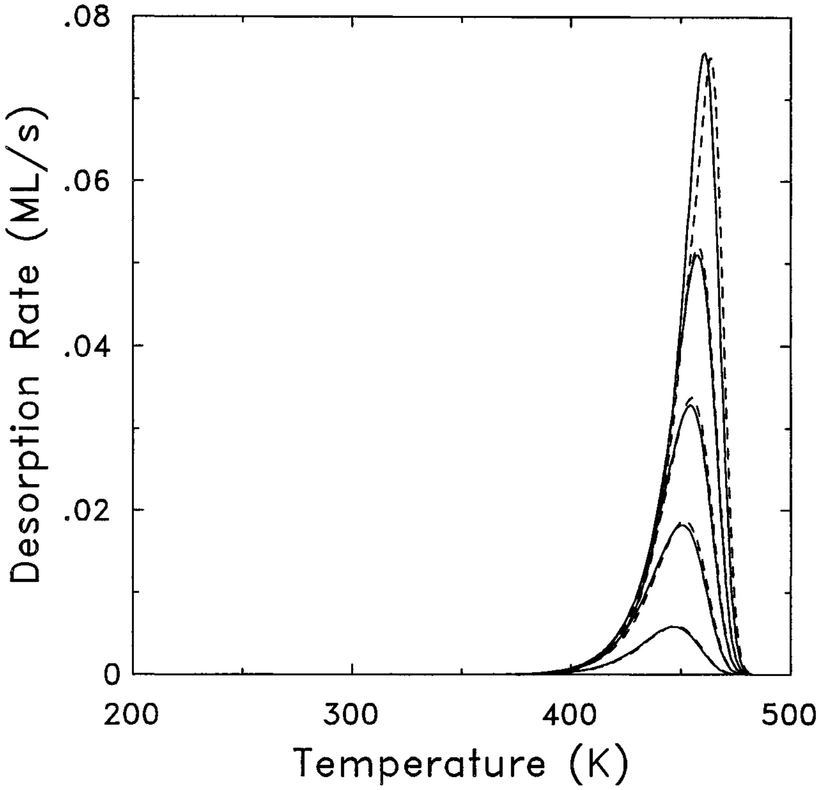


Figure 5.9: TPD rates for immobile (solid line) and mobile (dotted line) adsorbate and attractive interaction of $V_1/k_B = -200K$ for coverages θ =0.1, 0.3, 0.5, 0.7, 0.9, calculated in 5-basis set.

the adparticles present a higher activation energy for desorption from the surface. An example for $V_1/k_B = -200K$ is presented on Fig.5.9. The desorption trace for a mobile adsorbate is slightly shifted to higher temperatures, compared to the immobile trace generated for equilibrium initial correlators. The physical explanation of this small difference is that there is a greater likelihood of adparticles being surrounded by neighbors, upon rearrangement, in the mobile case; for immobile particles, the reduction of neighbors via desorption lowers, relatively, the binding energy of the remaining particle. The peak temperature is a measure of the binding energy of the particles at the edges of the clusters. Desorption from the interior, requiring the breaking of four bonds, is less likely. Because this clustering exists, initially, for the immobile case also, the spectra are practically indistinguishable for the two cases.

For a system desorbing under quasi-equilibrium conditions we can use the phenomenological rate equation, Eqn.(2.16), with the appropriate sticking function and chemical potential, to quantify the desorption rate. Thus, instead of determining the rate by solving the set of evolution equations for the correlators of our chosen basis set, we can use the chemical potential determined from our adsorption-desorption equilibrium solution for these correlators (specifically coverage) directly. If we do this with a Langmurian sticking of $(1-\theta)$ and the 5-basis set we recover the dotted lines of Fig.5.1. For the 15-basis set we found in section 4.1.2 that we get a chemical potential that agrees very well with that of the TM calculation, Fig.4.7. Thus for a system desorbing under quasi-equilibrium conditions we should almost recover the rates given by the solid lines in Fig.5.1. We do, but do not show on a separate plot here as the TM-generated and our 15-basis spectra are so close. Because we presently lack the diffusion equations for this 15-basis set we cannot present results of limited hopping. The direct solution of the 15-basis set evolution in the immobile and repulsive case confirms the results calculated with the 5-basis set. Namely, for random initial correlators there is only one smaller TPD peak between the two main peaks and, for equilibrium initially, only a two-peaked spectrum.

Chapter 6

Conclusions and Outlook

In this work the formulation and solution of the kinetic lattice gas model for adsorption, desorption and diffusion of particles on surfaces has been thoroughly examined. The model, which is based on the master equation for a Markovian process, results in a hierarchy of equations of motion for the coverage and many-particle correlators; the complete set is equivalent to the original master equation. However, there are as many correlators and thus evolution equations as adsorption sites. The challenge of this thesis has been to find a systematic procedure for truncating this hierarchy of equations at a manageable level. We have examined the effects of this truncation at the level of compact 5- and 15-site correlators, for a square lattice substrate and with repulsive and attractive nearest-neighbor interactions between the adparticles. This truncation is achieved by factorizing all correlators, that appear in the evolution equations and are not in the basis set, in terms of the 5- or 15-site basis. The truncations and the equations are developed with a series of codes. In fact, the choice of the basis and the factorization schemes is not trivial. To test these, we compared the equilibrium solutions of the resulting rate equations of the basis set, obtained from the zeroes of all rates, with exact results for these basis correlators obtained using the transfer matrix method, as a function of coverage, temperature and interaction strength. The 15-basis scheme, which involves up to 4-site overlaps in factorization, performs very well, giving almost exact results. The 5-site basis, with a maximum of 2-site overlap, performs well under diffusive equilibrium but not as well under adsorption-desorption equilibrium. The latter discrepancy is a known result for smaller basis sets. Nevertheless, this 5-basis set captures the effects of the ordering phenomenon much better than the simpler 1-site overlap schemes that have been used previously. Several factorization schemes, other than our best one, were examined. In addition, we have compared our equilibrium solutions with the best of the cluster-variation-method results. These also assume a basis, in effect, but require a detailed combinatoric analysis to arrive at a set of equilibrium conditions. Our method is clearly superior and systematic for generalizations of lattice coordination, basis size and range of interactions.

The main point of implementing solutions to the kinetic lattice gas model is that it gives the evolution of correlators away from equilibrium. The problem of choosing a successful factorization scheme persists. However, the obvious choice is that which is the best in the limit of adsorbate equilibrium. Having shown that the equilibrium solutions are correctly described, we are confident in applying the same factorization scheme to describe the nonequilibrium correlators. Thus we can describe diffusion of an adsorbate towards equilibrium prepared from a gas adsorbed at lower temperatures where diffusion may be impaired. We can also describe the time dependence of the coverage on a surface as the particles adsorb or desorb. As examples of the time evolution we have examined TPD spectra of an interacting adsorbate. For diffusion (hopping) rates fast compared to the desorption time scale the correlators maintain equilibrium and we recover the standard results of the quasi-equilibrium phenomenological model. In the case of limited diffusion or no diffusion we have obtained new results and have elucidated the mechanisms which distinguish the contributions to the observable desorption rate. We find no evidence for staged desorption for repulsive adsorbates prepared under initial equilibrium conditions. Only in one situation do we observe an intermediate peak in the TPD spectrum, namely for non-equilibrium initial correlators. For attractive interactions the TPD spectra are essentially identical to the quasi-equilibrium case.

One of the main reasons for modelling TPD spectra is to extract the adparticle binding and interaction energies. Our results have consequences for interpreting experimental spectra in non-equilibrium situations. These arise, for example, for systems where the heating rate is so fast as to effectively limit the diffusion rate on the time scale of desorption. Laser-induced thermal desorption produces such an effect, for example. The same technique also permits measurement of diffusion rates at constant coverage. Our model allows investigation of the effects of interactions in this case also.

The kinetic lattice gas model developed in this thesis describes surface phenomena in a most physical way making the connection between microscopic distributions and macroscopic observables without introducing too many ad hoc concepts and parameters. The approach automatically ensures that such fundamental principles as detailed balance are implemented properly. It is an analytic approach to the kinetics (and thermodynamics) of adsorbates and is not restricted to simple systems. For example, adding to the terms to the transition probabilities terms that describe association and dissociation processes will allow the description of reactions on a surface. One can also deal with rather complicated situations in a systematic approach such as multi-site and multi-component systems with or without precursor-mediated adsorption and surface reconstruction, including multilayers or subsurface species. The extension to two interacting species on a 2-D lattice has already been completed to the stage of deriving the equations but with combinatorial factorizations of the correlators. The resulting solution difficulties became the primary motivation for re-examining the factorization problem for the one-species system presented in this thesis.

For adsorbates out of local equilibrium, an analytic approach is a useful theoretical tool by which, in addition to numerical results, explicit formulae can be obtained to elucidate the underlying physics. One can extract simplified pictures of and approximations to complicated processes. This approach is increasingly overlooked with the availability of cheap computer power for numerical simulations. Sometimes computer simulations of the adsorbate kinetics are based on oversimplified or incorrect assumptions which often arise because the physical theory has been not been formulating rigorously, e.g. based on a master equation.

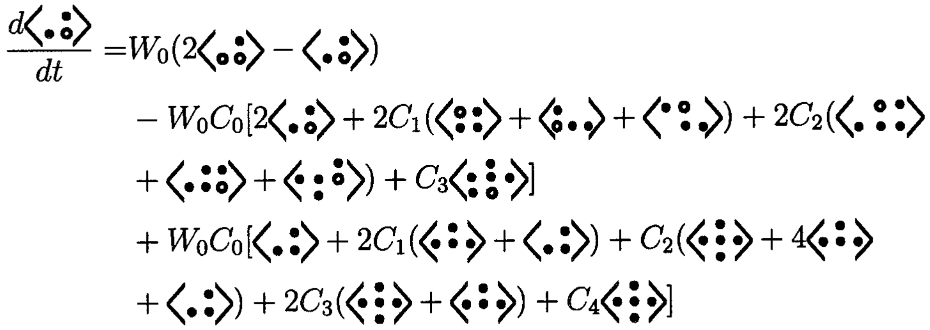
Appendix A

In this Appendix we list the time evolution equations of the correlators forming the 5-basis set ($\langle \bullet \rangle, \langle \bullet\bullet \rangle, \langle \begin{smallmatrix} & \bullet \\ \bullet & \bullet \end{smallmatrix} \rangle, \langle \begin{smallmatrix} & \bullet \\ \bullet & \circ \end{smallmatrix} \rangle, \langle \begin{smallmatrix} \bullet & \bullet \\ \bullet & \bullet \end{smallmatrix} \rangle$) First we specify the evolution for adsorption and desorption processes. Langmuir kinetics is assumed for adsorption. The coefficients W_0 and W_0C_0 are given by Eqn.(3.28) and (5.1) respectively.

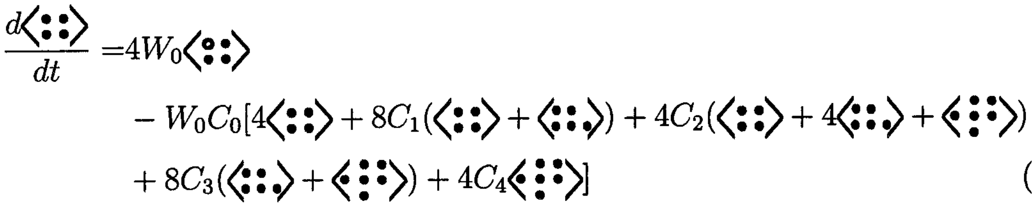
$$\begin{aligned}
\frac{d\langle \bullet \rangle}{dt} =& W_0\langle \circ \rangle \\
&- W_0C_0[\langle \bullet \rangle + 4C_1\langle \bullet\bullet \rangle + 4C_2\langle \begin{smallmatrix} & \bullet \\ \bullet & \bullet \end{smallmatrix} \rangle + 2C_2\langle \bullet\bullet\bullet \rangle + 4C_3\langle \begin{smallmatrix} & \bullet & \\ \bullet & \bullet & \bullet \end{smallmatrix} \rangle \\
&+ C_4\langle \begin{smallmatrix} & \bullet & \\ \bullet & \bullet & \bullet \\ & \bullet & \end{smallmatrix} \rangle]
\end{aligned} \tag{A.1}$$

$$\begin{aligned}
\frac{d\langle \bullet\bullet \rangle}{dt} =& 2W_0\langle \circ\bullet \rangle \\
&- W_0C_0[2\langle \bullet\bullet \rangle + 2C_1\langle \bullet\bullet \rangle + 2C_1\langle \bullet\bullet\bullet \rangle + 4C_1\langle \begin{smallmatrix} & \bullet \\ \bullet & \bullet \end{smallmatrix} \rangle + 2C_2\langle \bullet\bullet\bullet \rangle \\
&+ 4C_2\langle \begin{smallmatrix} & \bullet \\ \bullet & \bullet \end{smallmatrix} \rangle + 6C_2\langle \begin{smallmatrix} & \bullet & \\ \bullet & \bullet & \bullet \end{smallmatrix} \rangle + 2C_3\langle \begin{smallmatrix} & \bullet & \\ \bullet & \bullet & \bullet \\ & \bullet & \end{smallmatrix} \rangle + 6C_3\langle \begin{smallmatrix} & \bullet & \\ \bullet & \bullet & \bullet \end{smallmatrix} \rangle) + 2C_4\langle \begin{smallmatrix} & \bullet & \\ \bullet & \bullet & \bullet \\ & \bullet & \end{smallmatrix} \rangle]
\end{aligned} \tag{A.2}$$

$$\begin{aligned}
\frac{d\langle \begin{smallmatrix} & \bullet \\ \bullet & \bullet \end{smallmatrix} \rangle}{dt} =& W_0(2\langle \begin{smallmatrix} & \bullet \\ \circ & \bullet \end{smallmatrix} \rangle + \langle \begin{smallmatrix} & \bullet \\ \bullet & \circ \end{smallmatrix} \rangle) \\
&- W_0C_0[3\langle \begin{smallmatrix} & \bullet \\ \bullet & \bullet \end{smallmatrix} \rangle + 2C_1(2\langle \begin{smallmatrix} & \bullet \\ \bullet & \bullet \end{smallmatrix} \rangle + \langle \begin{smallmatrix} \bullet & \bullet \\ \bullet & \bullet \end{smallmatrix} \rangle + \langle \begin{smallmatrix} & \bullet & \\ \bullet & \bullet & \bullet \end{smallmatrix} \rangle + \langle \begin{smallmatrix} \bullet & & \\ \bullet & \bullet & \bullet \end{smallmatrix} \rangle + \langle \begin{smallmatrix} & \bullet \\ \bullet & \bullet \\ \bullet & \end{smallmatrix} \rangle) \\
&+ C_2(\langle \begin{smallmatrix} & \bullet \\ \bullet & \bullet \end{smallmatrix} \rangle + 2\langle \begin{smallmatrix} \bullet & \bullet \\ \bullet & \bullet \end{smallmatrix} \rangle + 4\langle \begin{smallmatrix} & \bullet & \\ \bullet & \bullet & \bullet \end{smallmatrix} \rangle + 2\langle \begin{smallmatrix} \bullet & & \\ \bullet & \bullet & \bullet \end{smallmatrix} \rangle + \langle \begin{smallmatrix} & \bullet & \\ \bullet & \bullet & \bullet \\ & \bullet & \end{smallmatrix} \rangle + 2\langle \begin{smallmatrix} & \bullet \\ \bullet & \bullet \\ \bullet & \end{smallmatrix} \rangle + 2\langle \begin{smallmatrix} & & \bullet \\ \bullet & \bullet & \bullet \\ & \bullet & \end{smallmatrix} \rangle \\
&+ 4\langle \begin{smallmatrix} \bullet & \bullet & \\ \bullet & \bullet & \bullet \end{smallmatrix} \rangle) + 2C_3(\langle \begin{smallmatrix} & \bullet & \\ \bullet & \bullet & \bullet \\ & \bullet & \end{smallmatrix} \rangle + \langle \begin{smallmatrix} & \bullet & \\ \bullet & \bullet & \bullet \end{smallmatrix} \rangle + \langle \begin{smallmatrix} & & \bullet \\ \bullet & \bullet & \bullet \\ & \bullet & \end{smallmatrix} \rangle + \langle \begin{smallmatrix} & \bullet & \bullet \\ \bullet & \bullet & \bullet \\ & \bullet & \end{smallmatrix} \rangle + 2\langle \begin{smallmatrix} \bullet & \bullet & \\ \bullet & \bullet & \bullet \end{smallmatrix} \rangle)
\end{aligned} \tag{A.3}$$

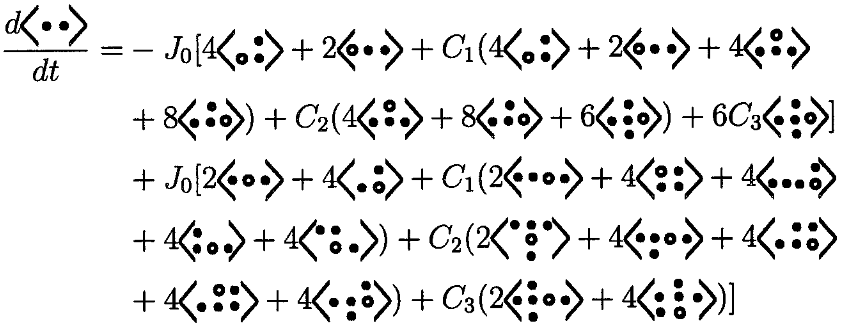


(A.4)

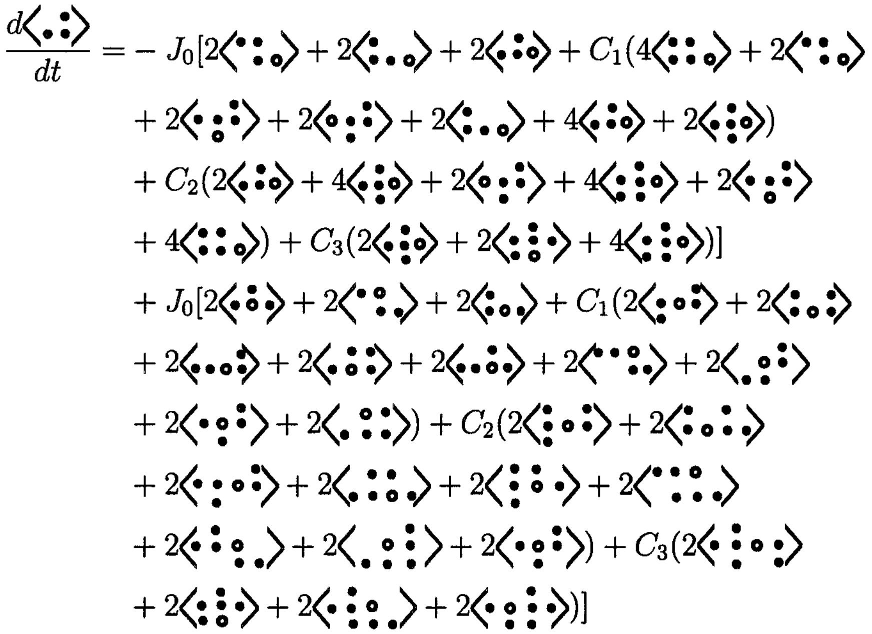


(A.5)

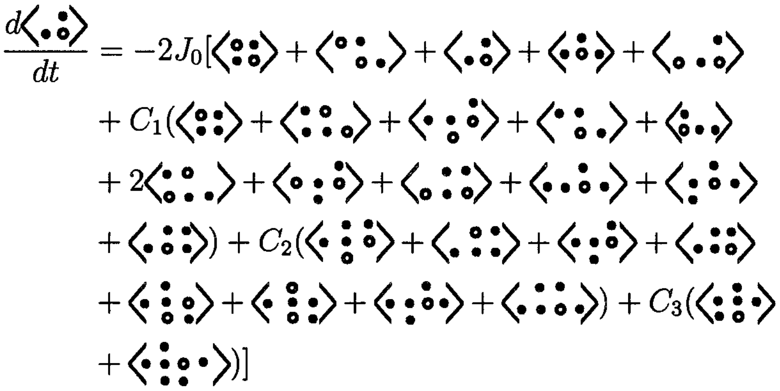
Time evolution equations for diffusion. J_0 is defined in Eqn.(3.10),

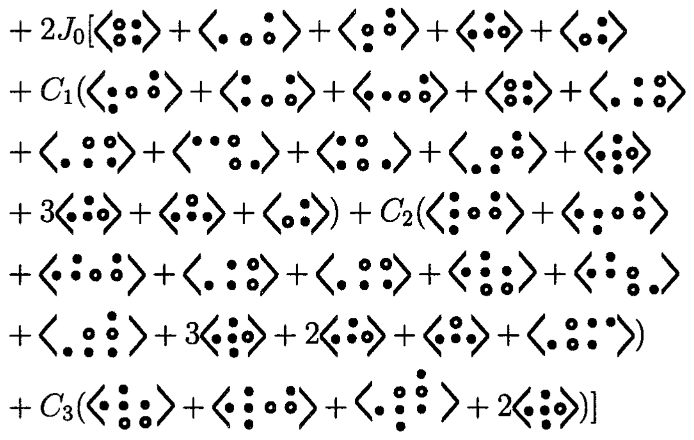


(A.6)

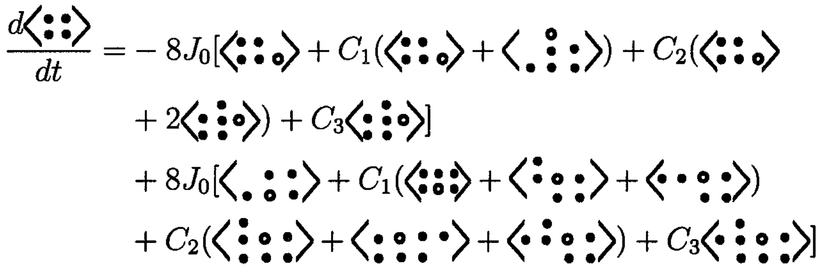


(A.7)





(A.8)



(A.9)

Appendix B

This Appendix tabulates the results of factorizing the higher-order correlators that appear in the evolution equations of the 5-basis set, given in Appendix A. The factorization is performed with 2-site overlap. The numbers in the columns are the powers of the respective correlator in the factorized expansion of the rate equations. The first five tables pertain to desorption, the rest to diffusion. The tables are the output of the Fortran codes given in Appendix C.

For example the first table represents the coefficient of W_0C_0 in the desorption term in Eqn.(A.1). Thus the correlator $\langle \bullet\overset{\bullet}{\bullet}\bullet \rangle$, which appears in Eqn.(A.1) with a multiplier $W_0C_0(-4C_3)$, is factorized as $\langle \bullet\overset{\bullet}{\bullet}\bullet \rangle = \langle \bullet\overset{\bullet}{\bullet} \rangle^2 / \langle \bullet\bullet \rangle$

Factorization terms for$\langle \bullet \rangle$

coeff	$\langle \overset{\bullet\,\bullet}{\bullet\,\bullet} \rangle$	$\langle \overset{\circ\,\bullet}{\bullet\,\bullet} \rangle$	$\langle \bullet\overset{\bullet}{\bullet} \rangle$	$\langle \bullet\overset{\bullet}{\circ} \rangle$	$\langle \circ\overset{\bullet}{\bullet} \rangle$	$\langle \circ\overset{\circ}{\bullet} \rangle$	$\langle \circ\overset{\bullet}{\circ} \rangle$	$\langle \bullet\bullet \rangle$	$\langle \bullet\circ \rangle$	$\langle \bullet \rangle$
-1	0	0	0	0	0	0	0	0	0	1
$-4C_1$	0	0	0	0	0	0	0	1	0	0
$-4C_2$	0	0	1	0	0	0	0	0	0	0
$-2C_2$	0	0	2	0	0	0	0	-1	0	0
$-2C_2$	0	0	0	0	2	0	0	0	-1	0
$-4C_3$	0	0	2	0	0	0	0	-1	0	0
$-C_4$	0	0	3	0	0	0	0	-2	0	0

Factorization terms for $\langle \bullet \bullet \rangle$

coeff										
-2	0	0	0	0	0	0	0	0	1	0
$-4C_1$	0	0	0	1	0	0	0	0	0	0
$-2C_1$	0	0	0	0	0	0	0	0	1	0
$-2C_1$	0	0	0	2	0	0	0	0	-1	0
$-2C_1$	0	0	0	0	0	2	0	0	0	-1
$-4C_2$	0	0	0	1	0	0	0	0	0	0
$-8C_2$	0	0	0	2	0	0	0	0	-1	0
$-2C_2$	0	0	0	0	0	2	0	0	0	-1
$-6C_3$	0	0	0	2	0	0	0	0	-1	0
$-2C_3$	0	0	0	3	0	0	0	0	-2	0
$-2C_4$	0	0	0	3	0	0	0	0	-2	0

Factorization terms for 

coeff										
-3	0	0	0	1	0	0	0	0	0	0
$-4C_1$	0	0	0	2	0	0	0	0	-1	0
$-4C_1$	0	0	0	1	0	0	0	0	0	0
$-C_1$	1	0	0	0	0	0	0	0	0	0
$-2C_1$	1	0	0	1	0	0	0	0	-1	0
$-2C_1$	0	1	0	0	0	1	0	0	0	-1
$-4C_2$	0	0	0	2	0	0	0	0	-1	0
$-6C_2$	1	0	0	1	0	0	0	0	-1	0
$-3C_2$	0	0	0	3	0	0	0	0	-2	0
$-C_2$	1	0	0	0	0	0	0	0	0	0
$-2C_2$	0	1	0	0	0	1	0	0	0	-1
$-2C_2$	0	0	0	1	0	0	0	0	0	0
$-4C_3$	1	0	0	1	0	0	0	0	-1	0
$-3C_3$	0	0	0	3	0	0	0	0	-2	0
$-2C_3$	1	0	0	2	0	0	0	0	-2	0
$-2C_3$	0	0	0	2	0	0	0	0	-1	0
$-2C_4$	1	0	0	2	0	0	0	0	-2	0
$-C_4$	0	0	0	3	0	0	0	0	-2	0

Factorization terms for $\langle \begin{smallmatrix} & \bullet \\ \bullet & \circ \end{smallmatrix} \rangle$

coeff	$\langle \begin{smallmatrix} \bullet & \bullet \\ \bullet & \bullet \end{smallmatrix} \rangle$	$\langle \begin{smallmatrix} \circ & \bullet \\ \bullet & \bullet \end{smallmatrix} \rangle$	$\langle \begin{smallmatrix} \circ & \bullet \\ \bullet & \circ \end{smallmatrix} \rangle$	$\langle \begin{smallmatrix} & \bullet \\ \bullet & \bullet \end{smallmatrix} \rangle$	$\langle \begin{smallmatrix} & \bullet \\ \bullet & \circ \end{smallmatrix} \rangle$	$\langle \begin{smallmatrix} & \bullet \\ \circ & \bullet \end{smallmatrix} \rangle$	$\langle \begin{smallmatrix} & \circ \\ \circ & \bullet \end{smallmatrix} \rangle$	$\langle \begin{smallmatrix} & \bullet \\ \circ & \circ \end{smallmatrix} \rangle$	$\langle \bullet\,\bullet \rangle$	$\langle \circ\,\bullet \rangle$
-2	0	0	0	0	1	0	0	0	0	0
$-2C_1$	0	0	0	0	1	1	0	0	0	-1
$-C_1$	0	1	0	0	0	0	0	0	0	0
$-2C_1$	0	1	0	1	0	0	0	0	-1	0
$-2C_1$	0	0	1	0	0	1	0	0	0	-1
$-2C_2$	0	1	0	0	0	1	0	0	0	-1
$-2C_2$	0	0	0	1	1	1	0	0	-1	-1
$-2C_2$	0	1	0	1	0	0	0	0	-1	0
$-2C_3$	0	1	0	2	0	0	0	0	-2	0
1	0	0	0	1	0	0	0	0	0	0
$2C_1$	0	0	0	2	0	0	0	0	-1	0
C_1	0	0	0	1	0	0	0	0	0	0
C_2	0	0	0	3	0	0	0	0	-2	0
$2C_2$	0	0	0	2	0	0	0	0	-1	0
C_2	0	0	0	1	0	0	0	0	0	0
C_3	0	0	0	3	0	0	0	0	-2	0
$2C_3$	0	0	0	2	0	0	0	0	-1	0
C_4	0	0	0	3	0	0	0	0	-2	0

Factorization terms for 

coeff										
-4	1	0	0	0	0	0	0	0	0	0
$-8C_1$	1	0	0	0	0	0	0	0	0	0
$-8C_1$	1	0	0	0	1	0	0	0	0	-1
$-8C_2$	1	0	0	0	0	0	0	0	0	0
$-8C_2$	1	0	0	0	1	0	0	0	0	-1
$-4C_2$	1	0	0	0	2	0	0	0	0	-2
$-8C_3$	1	0	0	0	1	0	0	0	0	-1
$-4C_3$	1	0	0	0	2	0	0	0	0	-2
$-4C_4$	1	0	0	0	2	0	0	0	0	-2

Factorization with two site overlap of diffusion terms in the time evolution equations of Appendix A.

Factorization terms for ⟨••⟩

coeff	⟨::⟩	⟨∷⟩	⟨8:⟩	⟨:8⟩	⟨88⟩	⟨.:⟩	⟨.8⟩	⟨•:⟩	⟨•°⟩	⟨•8⟩	⟨··⟩	⟨•·⟩	⟨••⟩
-4	0	0	0	0	0	0	0	1	0	0	0	0	0
-2	0	0	0	0	0	1	0	1	0	0	-1	0	0
-2	0	0	0	0	0	0	0	1	1	0	0	-1	0
$-4C_1$	0	0	0	0	0	0	0	1	0	0	0	0	0
$-10C_1$	0	0	0	0	0	1	0	1	0	0	-1	0	0
$-4C_1$	0	0	0	0	0	0	0	2	0	0	0	-1	0
$-2C_1$	0	0	0	0	0	0	0	1	1	0	0	-1	0
$-8C_2$	0	0	0	0	0	1	0	1	0	0	-1	0	0
$-4C_2$	0	0	0	0	0	0	0	2	0	0	0	-1	0
$-6C_2$	0	0	0	0	0	2	0	1	0	0	-2	0	0
$-6C_3$	0	0	0	0	0	2	0	1	0	0	-2	0	0
2	0	0	0	0	0	0	2	0	0	0	0	-1	0
2	0	0	0	0	0	0	0	0	0	2	0	0	-1
4	0	0	0	0	0	0	1	0	0	0	0	0	0
$4C_1$	0	1	0	0	0	0	1	0	0	0	0	-1	0
$4C_1$	0	0	1	0	0	0	0	0	0	1	0	0	-1

continued

coeff	⟨::⟩	⟨⸰:⟩	⟨8:⟩	⟨⸰8⟩	⟨88⟩	⟨.:⟩	⟨.8⟩	⟨∘:⟩	⟨∘●⟩	⟨∘8⟩	⟨··⟩	⟨•·⟩	⟨••⟩
$2C_1$	0	0	1	0	0	1	0	0	0	1	−1	0	−1
$2C_1$	0	0	0	1	0	0	1	1	0	0	0	−2	0
$2C_1$	0	0	0	0	1	0	0	1	0	1	0	−1	−1
$4C_1$	0	1	0	0	0	0	0	0	0	0	0	0	0
$4C_1$	0	1	0	0	0	1	0	0	0	0	−1	0	0
$4C_1$	0	0	0	1	0	0	0	1	0	0	0	−1	0
$4C_1$	0	0	0	0	0	0	1	1	0	0	0	−1	0
$2C_2$	0	1	0	0	0	0	1	1	0	0	0	−2	0
$2C_2$	0	0	1	0	0	0	0	1	0	1	0	−1	−1
$4C_2$	0	1	0	0	0	1	1	0	0	0	−1	−1	0
$4C_2$	0	0	1	0	0	1	0	0	0	1	−1	0	−1
$4C_2$	0	1	0	0	0	1	0	0	0	0	−1	0	0
$4C_2$	0	1	0	0	0	0	0	1	0	0	0	−1	0
$4C_2$	0	0	0	0	0	1	1	1	0	0	−1	−1	0
$2C_3$	0	1	0	0	0	2	1	0	0	0	−2	−1	0
$2C_3$	0	0	1	0	0	2	0	0	0	1	−2	0	−1
$4C_3$	0	1	0	0	0	2	0	0	0	0	−2	0	0

Factorization terms for $\langle\begin{smallmatrix}&\bullet\\\bullet&\bullet\end{smallmatrix}\rangle$

coeff	$\langle\begin{smallmatrix}\cdot&\cdot\\\cdot&\cdot\end{smallmatrix}\rangle$	$\langle\begin{smallmatrix}\circ&\cdot\\\cdot&\cdot\end{smallmatrix}\rangle$	$\langle\begin{smallmatrix}\circ&\cdot\\\circ&\cdot\end{smallmatrix}\rangle$	$\langle\begin{smallmatrix}\circ&\cdot\\\cdot&\circ\end{smallmatrix}\rangle$	$\langle\begin{smallmatrix}\circ&\cdot\\\circ&\circ\end{smallmatrix}\rangle$	$\langle\begin{smallmatrix}&\cdot\\\cdot&\cdot\end{smallmatrix}\rangle$	$\langle\begin{smallmatrix}&\cdot\\\cdot&\circ\end{smallmatrix}\rangle$	$\langle\begin{smallmatrix}&\cdot\\\circ&\cdot\end{smallmatrix}\rangle$	$\langle\begin{smallmatrix}&\circ\\\circ&\cdot\end{smallmatrix}\rangle$	$\langle\begin{smallmatrix}&\cdot\\\circ&\circ\end{smallmatrix}\rangle$	$\langle\cdot\,\cdot\rangle$	$\langle\circ\,\cdot\rangle$	$\langle\bullet\,\circ\rangle$
-4	0	0	0	0	0	1	0	1	0	0	-1	0	0
-2	1	0	0	0	0	0	0	1	0	0	-1	0	0
-2	0	1	0	0	0	0	0	0	1	0	0	-1	0
$-6C_1$	0	0	0	0	0	1	0	1	0	0	-1	0	0
$-6C_1$	1	0	0	0	0	0	0	1	0	0	-1	0	0
$-2C_1$	0	0	0	0	0	1	0	2	0	0	-1	-1	0
$-4C_1$	0	0	0	0	0	2	0	1	0	0	-2	0	0
$-2C_1$	0	1	0	0	0	0	0	0	1	0	0	-1	0
$-4C_2$	1	0	0	0	0	0	0	1	0	0	-1	0	0
$-2C_2$	0	0	0	0	0	1	0	2	0	0	-1	-1	0
$-4C_2$	1	0	0	0	0	1	0	1	0	0	-2	0	0
$-6C_2$	0	0	0	0	0	2	0	1	0	0	-2	0	0
$-2C_2$	0	0	0	0	0	1	0	1	0	0	-1	0	0
$-4C_3$	1	0	0	0	0	1	0	1	0	0	-2	0	0
$-2C_3$	0	0	0	0	0	2	0	1	0	0	-2	0	0
$-2C_3$	0	1	0	0	0	2	0	0	0	0	-2	0	0
2	0	1	0	0	0	0	1	0	0	0	0	-1	0
2	0	0	1	0	0	0	0	0	0	1	0	0	-1
2	0	0	0	0	0	0	1	1	0	0	0	-1	0
2	0	0	0	0	0	0	2	0	0	0	0	-1	0
$2C_1$	0	1	0	0	0	0	0	1	0	0	0	-1	0
$2C_1$	0	1	0	0	0	0	1	1	0	0	0	-2	0
$2C_1$	0	0	1	0	0	0	0	1	0	1	0	-1	-1
$2C_1$	0	2	0	0	0	0	0	0	0	0	0	-1	0
$2C_1$	0	0	2	0	0	0	0	0	0	0	0	0	-1

continued

coeff	⟨····⟩	⟨•···⟩	⟨••··⟩	⟨··••⟩	⟨••••⟩	⟨···⟩	⟨··•⟩	⟨•··⟩	⟨••·⟩	⟨•••⟩	⟨··⟩	⟨•·⟩	⟨••⟩
$2C_1$	0	2	0	0	0	1	0	0	0	0	−1	−1	0
$2C_1$	0	0	2	0	0	1	0	0	0	0	−1	0	−1
$2C_1$	0	1	0	1	0	0	0	1	0	0	0	−2	0
$2C_1$	0	0	1	0	1	0	0	1	0	0	0	−1	−1
$2C_1$	0	1	0	0	0	1	0	1	0	0	−1	−1	0
$2C_1$	0	0	0	1	0	0	0	2	0	0	0	−2	0
$2C_1$	0	0	0	0	0	0	1	2	0	0	0	−2	0
$2C_1$	0	1	0	0	0	1	1	0	0	0	−1	−1	0
$2C_1$	0	0	0	1	0	0	1	1	0	0	0	−2	0
$2C_1$	0	0	0	0	0	0	2	1	0	0	0	−2	0
$2C_1$	0	1	0	0	0	0	1	0	0	0	0	−1	0
$2C_2$	0	2	0	0	0	0	0	1	0	0	0	−2	0
$2C_2$	0	0	2	0	0	0	0	1	0	0	0	−1	−1
$2C_2$	0	1	0	0	0	1	1	1	0	0	−1	−2	0
$2C_2$	0	0	1	0	0	1	0	1	0	1	−1	−1	−1
$2C_2$	0	2	0	0	0	1	0	0	0	0	−1	−1	0
$2C_2$	0	0	2	0	0	1	0	0	0	0	−1	0	−1
$2C_2$	0	1	0	0	0	1	0	1	0	0	−1	−1	0
$2C_2$	0	0	0	0	0	1	2	1	0	0	−1	−2	0
$2C_2$	0	1	0	0	0	0	0	2	0	0	0	−2	0
$2C_2$	0	0	0	0	0	1	1	2	0	0	−1	−2	0
$2C_2$	0	1	0	0	0	1	1	0	0	0	−1	−1	0
$2C_2$	0	1	0	0	0	0	1	1	0	0	0	−2	0
$2C_3$	0	2	0	0	0	2	0	0	0	0	−2	−1	0
$2C_3$	0	0	2	0	0	2	0	0	0	0	−2	0	−1
$2C_3$	0	1	0	0	0	2	0	1	0	0	−2	−1	0
$2C_3$	0	1	0	0	0	2	1	0	0	0	−2	−1	0
$2C_3$	0	1	0	0	0	2	0	0	0	0	−2	0	0

Factorization terms for⟨.:°⟩

coeff	⟨::⟩	⟨°::⟩	⟨°°::⟩	⟨::°°⟩	⟨°°°°⟩	⟨.:⟩	⟨.:°⟩	⟨°.:⟩	⟨°.°:⟩	⟨°.:°⟩	⟨..⟩	⟨°.⟩	⟨°°⟩
-2	0	0	0	0	0	0	1	0	1	0	0	-1	0
-2	0	0	0	0	0	0	1	0	0	0	0	0	0
-2	0	0	0	1	0	0	0	0	0	0	0	0	0
-2	0	1	0	0	0	0	0	1	0	0	-1	0	0
-2	0	0	0	1	0	0	0	0	1	0	0	-1	0
-2	0	0	0	0	0	0	2	0	0	0	0	-1	0
$-2C_1$	0	1	0	0	0	0	0	0	1	0	0	-1	0
$-2C_1$	0	0	0	0	0	0	1	1	1	0	0	-2	0
$-2C_1$	0	0	0	0	0	0	1	1	0	0	0	-1	0
$-2C_1$	0	1	0	0	0	0	0	0	0	0	0	0	0
$-2C_1$	0	1	0	0	0	1	0	0	0	0	-1	0	0
$-6C_1$	0	0	0	1	0	0	0	1	0	0	0	-1	0
$-2C_1$	0	0	0	0	0	0	1	2	0	0	-1	-1	0
$-2C_1$	0	1	0	0	0	0	0	1	0	0	-1	0	0
$-2C_1$	0	1	0	0	0	1	1	0	0	0	-1	-1	0
$-2C_1$	0	0	0	1	0	0	1	1	0	0	0	-2	0
$-2C_1$	0	0	0	0	0	0	2	1	0	0	0	-2	0
$-2C_1$	0	1	0	0	0	0	1	0	0	0	0	-1	0
$-2C_2$	0	1	0	0	0	1	0	1	0	0	-2	0	0
$-2C_2$	0	1	0	0	0	0	0	1	0	0	0	-1	0
$-2C_2$	0	0	0	0	0	1	1	1	0	0	-1	-1	0
$-2C_2$	0	1	0	0	0	1	0	0	0	0	-1	0	0
$-2C_2$	0	0	0	1	0	0	0	2	0	0	0	-2	0
$-2C_2$	0	1	0	0	0	0	0	2	0	0	-1	-1	0
$-2C_2$	0	0	0	0	0	1	2	1	0	0	-1	-2	0

continued

coeff	⟨∷⟩	⟨⁘⟩	⟨⁑:⟩	⟨:⁑⟩	⟨⁑⁑⟩	⟨.:⟩	⟨.⁑⟩	⟨•:⟩	⟨•⁑⟩	⟨●⁑⟩	⟨··⟩	⟨•·⟩	⟨••⟩
$-2C_2$	0	1	0	0	0	1	1	0	0	0	−1	−1	0
$-2C_2$	0	1	0	0	0	0	1	1	0	0	0	−2	0
$-2C_3$	0	1	0	0	0	2	0	0	0	0	−2	0	0
$-2C_3$	0	1	0	0	0	2	1	0	0	0	−2	−1	0
2	0	0	1	0	0	0	1	0	0	0	0	−1	0
2	0	0	0	0	1	0	0	0	0	1	0	0	−1
2	0	0	1	0	0	0	0	0	0	0	0	0	0
2	0	0	0	0	0	0	0	0	0	2	0	0	−1
2	0	0	0	0	0	1	0	1	0	0	−1	0	0
2	0	0	0	0	0	0	0	1	0	0	0	0	0
$2C_1$	0	0	1	0	0	0	1	1	0	0	0	−2	0
$2C_1$	0	0	0	0	1	0	0	1	0	1	0	−1	−1
$2C_1$	0	1	1	0	0	0	0	0	0	0	0	−1	0
$2C_1$	0	0	1	0	1	0	0	0	0	0	0	0	−1
$2C_1$	0	1	1	0	0	1	0	0	0	0	−1	−1	0
$2C_1$	0	0	1	0	1	1	0	0	0	0	−1	0	−1
$2C_1$	0	0	1	1	0	0	0	1	0	0	0	−2	0
$2C_1$	0	0	0	0	2	0	0	1	0	0	0	−1	−1
$2C_1$	0	0	1	0	0	0	0	0	0	0	0	0	0
$2C_1$	0	0	1	0	0	1	0	0	0	0	−1	0	0
$2C_1$	0	0	1	0	0	0	0	1	0	0	0	−1	0
$2C_1$	0	0	1	0	0	1	0	0	0	1	−1	0	−1
$2C_1$	0	0	0	0	1	0	0	1	0	1	0	−1	−1
$2C_1$	0	0	1	0	0	0	0	0	0	1	0	0	−1
$2C_1$	0	0	0	0	0	0	0	1	0	2	0	−1	−1

continued

coeff	⟨::⟩	⟨●.:⟩	⟨●●:⟩	⟨:●●⟩	⟨●●●●⟩	⟨.:⟩	⟨.●.⟩	⟨●:⟩	⟨●●.⟩	⟨●.●⟩	⟨••⟩	⟨●•⟩	⟨●●⟩
$2C_1$	0	0	0	0	0	2	0	1	0	0	−2	0	0
$6C_1$	0	0	0	0	0	1	0	1	0	0	−1	0	0
$2C_1$	0	0	0	0	0	0	0	2	0	0	0	−1	0
$2C_1$	0	0	0	0	0	0	0	1	0	0	0	0	0
$2C_2$	0	1	1	0	0	0	0	1	0	0	0	−2	0
$2C_2$	0	0	1	0	1	0	0	1	0	0	0	−1	−1
$2C_2$	0	0	1	0	0	1	1	1	0	0	−1	−2	0
$2C_2$	0	0	0	0	1	1	0	1	0	1	−1	−1	−1
$2C_2$	0	1	1	0	0	1	0	0	0	0	−1	−1	0
$2C_2$	0	0	1	0	1	1	0	0	0	0	−1	0	−1
$2C_2$	0	0	1	0	0	1	0	0	0	0	−1	0	0
$2C_2$	0	0	1	0	0	0	0	1	0	0	0	−1	0
$2C_2$	0	0	1	0	0	2	0	0	0	0	−2	0	0
$2C_2$	0	0	1	0	0	1	0	0	0	1	−1	0	−1
$2C_2$	0	0	0	0	0	1	0	1	0	2	−1	−1	−1
$2C_2$	0	0	1	0	0	0	0	1	0	1	0	−1	−1
$6C_2$	0	0	0	0	0	2	0	1	0	0	−2	0	0
$4C_2$	0	0	0	0	0	1	0	1	0	0	−1	0	0
$2C_2$	0	0	0	0	0	0	0	2	0	0	0	−1	0
$2C_3$	0	1	1	0	0	2	0	0	0	0	−2	−1	0
$2C_3$	0	0	1	0	1	2	0	0	0	0	−2	0	−1
$2C_3$	0	0	1	0	0	2	0	0	0	0	−2	0	0
$2C_3$	0	0	1	0	0	2	0	0	0	1	−2	0	−1
$4C_3$	0	0	0	0	0	2	0	1	0	0	−2	0	0

Factorization terms for⟨::⟩

coeff	⟨::⟩	⟨8:⟩	⟨𝟖:⟩	⟨:8⟩	⟨88⟩	⟨.:⟩	⟨.8⟩	⟨∘:⟩	⟨∘:°⟩	⟨∘8⟩	⟨··⟩	⟨∘·⟩	⟨∘∘⟩
-8	1	0	0	0	0	0	0	1	0	0	-1	0	0
$-8C_1$	1	0	0	0	0	1	0	1	0	0	-2	0	0
$-16C_1$	1	0	0	0	0	0	0	1	0	0	-1	0	0
$-16C_2$	1	0	0	0	0	1	0	1	0	0	-2	0	0
$-8C_2$	1	0	0	0	0	0	0	1	0	0	-1	0	0
$-8C_3$	1	0	0	0	0	1	0	1	0	0	-2	0	0
8	0	1	0	0	0	0	1	0	0	0	0	-1	0
$8C_1$	0	1	0	0	0	0	1	1	0	0	0	-2	0
$8C_1$	0	2	0	0	0	1	0	0	0	0	-1	-1	0
$8C_1$	0	1	0	1	0	0	0	1	0	0	0	-2	0
$8C_1$	0	2	0	0	0	0	0	0	0	0	0	-1	0
$8C_2$	0	1	0	0	0	1	1	1	0	0	-1	-2	0
$8C_2$	0	2	0	0	0	0	0	1	0	0	0	-2	0
$8C_2$	0	2	0	0	0	1	0	0	0	0	-1	-1	0
$8C_3$	0	2	0	0	0	2	0	0	0	0	-2	-1	0

Appendix C

Two examples of computer codes are given in this Appendix. The first derives the evolution equations for surface diffusion for any specified correlator. A similar code is used for the desorption evolution. The output of such codes is then used in the second example code, which factorizes these equations in the chosen basis, to produce tables such as those given in Appendix B.

```
c234567
c      program diffusion_derive
c
c      This program derives the terms contained in the diffusion
c      equations of the time evolution equations.
c
c      Inputs -   term to be expanded
c
c      Outputs -  all terms in the diffusion equation for that term
c

       integer d
       parameter (d=9)
       parameter (g=3,h=7)
       integer subj(d,d),obj(d,d)
       integer o(4),p(4)
       integer med0(d,d),med1(d,d),med2(d,d),med3(d,d)
       integer i,j,a,b,m,q,r,s
       character *6 dump
```

```
      write(*,*) 'Enter name of new data file:'
      read *,dump

      open (7,file=dump,status='new')

      do 4 j=1,d
        do 3 i=1,d
           subj(i,j)=9
3       continue
4     continue

       write(*,*) ' Enter 3x3 matrix one row at a time'

       do 5 j=4,6
          read (*,*) (subj(i,j), i=4,6)
5     continue

      o(1)=0
      o(2)=1
      o(3)=0
      o(4)=-1
      p(1)=1
      p(2)=0
      p(3)=-1
      p(4)=0

      call fact(subj,'d/dt',d)
      call refresh(subj,obj,d)

c     negative part of master equation


      do 60 i=g,h
        do 50 j=g,h
          if (obj(i,j).eq.1) then
            do 40 k=1,4
              if ((obj(i+o(k),j+p(k)).eq.2).or.
     +        (obj(i+o(k),j+p(k)).eq.9)) then
                obj(i+o(k),j+p(k))=2
                call fact(obj,'-1  ',d)
```

```
              endif
              call refresh(subj,obj,d)
40          continue
          else if ((obj(i,j).eq.9).and.
     +    ((obj(i+o(1),j+p(1)).ne.9).or.
     +    ((obj(i+o(2),j+p(2)).ne.9).or.
     +    ((obj(i+o(3),j+p(3)).ne.9).or.
     +    (obj(i+o(4),j+p(4)).ne.9))))) then
            obj(i,j)=1
            do 45 k=1,4
              if (obj(i+o(k),j+p(k)).eq.2) then
                call fact(obj,'-1  ',d)
              endif
45          continue
            call refresh(subj,obj,d)
          endif
50      continue
60    continue


      do 90 i=g,h
        do 80 j=g,h
          if (obj(i,j).eq.1) then
            do 72 k=1,4
              if ((obj(i+o(k),j+p(k)).eq.2).or.
     +        (obj(i+o(k),j+p(k)).eq.9)) then
                obj(i+o(k),j+p(k))=2
                call refresh(obj,med0,d)
                do 70 m=1,4
                  if (m .ne. k) then
                    if (obj(i+o(m),j+p(m)).ne.2) then
                      obj(i+o(m),j+p(m))=1
                      call fact(obj,'-c1 ',d)
                    endif
                  endif
                  call refresh(med0,obj,d)
70              continue
              endif
              call refresh(subj,obj,d)
72          continue
```

```
        else if ((obj(i,j).eq.9).and.
     +  ((obj(i+o(1),j+p(1)).ne.9).or.
     +  ((obj(i+o(2),j+p(2)).ne.9).or.
     +  ((obj(i+o(3),j+p(3)).ne.9).or.
     +  (obj(i+o(4),j+p(4)).ne.9))))) then
          obj(i,j)=1
          call refresh(obj,med0,d)
          do 77 k=1,4
            if (obj(i+o(k),j+p(k)).eq.2) then
              do 75 m=1,4
                if (m .ne. k) then
                  if (obj(i+o(m),j+p(m)).ne.2) then
                    obj(i+o(m),j+p(m))=1
                    call fact(obj,'-c1 ',d)
                    call refresh(med0,obj,d)
                  endif
                endif
 75           continue
            endif
 77       continue
        endif
        call refresh(subj,obj,d)
 80   continue
 90 continue


    do 130 i=g,h
      do 120 j=g,h
        if (obj(i,j).eq.1) then
          do 105 k=1,4
            if ((obj(i+o(k),j+p(k)).eq.2).or.
     +      (obj(i+o(k),j+p(k)).eq.9)) then
              obj(i+o(k),j+p(k))=2
              call refresh(obj,med0,d)
              do 100 m=1,4
                if (m .ne. k) then
                  if (obj(i+o(m),j+p(m)).ne.2) then
                    obj(i+o(m),j+p(m))=1
                    call refresh(obj,med1,d)
                    do 95 q=1,4
```

```
                        if ((q .ne. m).and.(q .ne. k)) then
                          if (obj(i+o(q),j+p(q)).ne.2) then
                            obj(i+o(q),j+p(q))=1
                            call fact(obj,'-c2 ',d)
                          endif
                        endif
                        call refresh(med1,obj,d)
95                    continue
                    endif
                  endif
                  call refresh(med0,obj,d)
100              continue
               endif
               call refresh(subj,obj,d)
105         continue
          else if ((obj(i,j).eq.9).and.
     +    ((obj(i+o(1),j+p(1)).ne.9).or.
     +    ((obj(i+o(2),j+p(2)).ne.9).or.
     +    ((obj(i+o(3),j+p(3)).ne.9).or.
     +    (obj(i+o(4),j+p(4)).ne.9))))) then
            obj(i,j)=1
            call refresh(obj,med0,d)
            do 117 k=1,4
              if (obj(i+o(k),j+p(k)).eq.2) then
                do 115 m=1,4
                  if (m .ne. k) then
                    if (obj(i+o(m),j+p(m)).ne.2) then
                      obj(i+o(m),j+p(m))=1
                      call refresh(obj,med1,d)
                      do 110 q=1,4
                        if ((q .ne. m).and.(q .ne. k)) then
                          if (obj(i+o(q),j+p(q)).ne.2) then
                            obj(i+o(q),j+p(q))=1
                            call fact(obj,'-c2 ',d)
                          endif
                        endif
                        call refresh(med1,obj,d)
110                   continue
                    endif
                  endif
```

```
                 call refresh(med0,obj,d)
115              continue
              endif
              call refresh(med0,obj,d)
117          continue
          endif
          call refresh(subj,obj,d)
120     continue
130   continue



      do 180 i=g,h
       do 170 j=g,h
        if (obj(i,j).eq.1) then
         do 150 k=1,4
          if ((obj(i+o(k),j+p(k)).eq.2).or.
     +    (obj(i+o(k),j+p(k)).eq.9)) then
           obj(i+o(k),j+p(k))=2
           call refresh(obj,med0,d)
           do 145 m=1,4
            if (m .ne. k) then
             if (obj(i+o(m),j+p(m)).ne.2) then
              obj(i+o(m),j+p(m))=1
              call refresh(obj,med1,d)
              do 143 q=1,4
               if ((q .ne. m).and.(q .ne. k)) then
                if (obj(i+o(q),j+p(q)).ne.2) then
                 obj(i+o(q),j+p(q))=1
                 call refresh(obj,med2,d)
                  do 140 r=1,4
                   if (((r.ne.m).and.(r.ne.q)).and.(r.ne.k)) then
                    if (obj(i+o(r),j+p(r)).ne.2) then
c                 print *, 'k,m,q,r:',k,m,q,r
                     obj(i+o(r),j+p(r))=1
                     call fact(obj,'-c3 ',d)
                    endif
                   endif
                   call refresh(med2,obj,d)
140               continue
```

```
                 endif
                endif
                call refresh(med1,obj,d)
143            continue
              endif
             endif
             call refresh(med0,obj,d)
145         continue
            endif
            call refresh(subj,obj,d)
150         continue
          else if ((obj(i,j).eq.9).and.
     +    ((obj(i+o(1),j+p(1)).ne.9).or.
     +    ((obj(i+o(2),j+p(2)).ne.9).or.
     +    ((obj(i+o(3),j+p(3)).ne.9).or.
     +    (obj(i+o(4),j+p(4)).ne.9))))) then
           obj(i,j)=1
           call refresh(obj,med0,d)
           do 167 k=1,4
            if (obj(i+o(k),j+p(k)).eq.2) then
             do 165 m=1,4
              if (m .ne. k) then
               if (obj(i+o(m),j+p(m)).ne.2) then
                obj(i+o(m),j+p(m))=1
                call refresh(obj,med1,d)
                do 160 q=1,4
                 if ((q .ne. m).and.(q .ne. k)) then
                  if (obj(i+o(q),j+p(q)).ne.2) then
                   obj(i+o(q),j+p(q))=1
                   call refresh(obj,med2,d)
                   do 155 r=1,4
                    if (((r.ne.m).and.(r.ne.q)).and.(r.ne.k)) then
                     if (obj(i+o(r),j+p(r)).ne.2) then
                      obj(i+o(r),j+p(r))=1
                      call fact(obj,'-c3 ',d)
                     endif
                    endif
                    call refresh(med2,obj,d)
155                continue
                  endif
```

```
                  endif
                  call refresh(med1,obj,d)
160              continue
                endif
              endif
             call refresh(med0,obj,d)
165          continue
            endif
            call refresh(med0,obj,d)
167        continue
          endif
          call refresh(subj,obj,d)
170     continue
180    continue

c===================================================================
c     positive part of master equation
c

      do 260 i=g,h
        do 250 j=g,h
          if (obj(i,j).eq.2) then
            do 240 k=1,4
              if ((obj(i+o(k),j+p(k)).eq.1).or.
     +          (obj(i+o(k),j+p(k)).eq.9)) then
                obj(i+o(k),j+p(k))=1
                call prime(obj,d,i,j,k,o(k),p(k))
                call fact(obj,'+1  ',d)
              endif
              call refresh(subj,obj,d)
240         continue
          else if ((obj(i,j).eq.9).and.
     +    ((obj(i+o(1),j+p(1)).ne.9).or.
     +    ((obj(i+o(2),j+p(2)).ne.9).or.
     +    ((obj(i+o(3),j+p(3)).ne.9).or.
     +    (obj(i+o(4),j+p(4)).ne.9))))) then
            obj(i,j)=2
            do 245 k=1,4
              if (obj(i+o(k),j+p(k)).eq.1) then
                call prime(obj,d,i,j,k,o(k),p(k))
```

```
                call fact(obj,'+1  ',d)
              endif
245         continue
          endif
          call refresh(subj,obj,d)
250     continue
260   continue


      do 290 i=g,h
        do 280 j=g,h
          if (obj(i,j).eq.2) then
            do 272 k=1,4
              if ((obj(i+o(k),j+p(k)).eq.1).or.
     +        (obj(i+o(k),j+p(k)).eq.9)) then
                obj(i+o(k),j+p(k))=1
                call refresh(obj,med0,d)
                do 270 m=1,4
                  if (m .ne. k) then
                    if (obj(i+o(m),j+p(m)).ne.2) then
                      obj(i+o(m),j+p(m))=1
                      call prime(obj,d,i,j,k,o(k),p(k))
                      call fact(obj,'+c1 ',d)
                    endif
                  endif
                  call refresh(med0,obj,d)
270             continue
              endif
              call refresh(subj,obj,d)
272         continue
          else if ((obj(i,j).eq.9).and.
     +    ((obj(i+o(1),j+p(1)).ne.9).or.
     +    ((obj(i+o(2),j+p(2)).ne.9).or.
     +    ((obj(i+o(3),j+p(3)).ne.9).or.
     +    (obj(i+o(4),j+p(4)).ne.9))))) then
            obj(i,j)=2
            call refresh(obj,med0,d)
            do 277 k=1,4
              if (obj(i+o(k),j+p(k)).eq.1) then
                do 275 m=1,4
```

```
                  if (m .ne. k) then
                    if (obj(i+o(m),j+p(m)).ne.2) then
                      obj(i+o(m),j+p(m))=1
                      call prime(obj,d,i,j,k,o(k),p(k))
                      call fact(obj,'+c1 ',d)
                      call refresh(med0,obj,d)
                    endif
                  endif
275             continue
              endif
277         continue
          endif
          call refresh(subj,obj,d)
280     continue
290   continue


      do 330 i=g,h
        do 320 j=g,h
          if (obj(i,j).eq.2) then
            do 305 k=1,4
              if ((obj(i+o(k),j+p(k)).eq.1).or.
     +        (obj(i+o(k),j+p(k)).eq.9)) then
                obj(i+o(k),j+p(k))=1
                call refresh(obj,med0,d)
                do 300 m=1,4
                  if (m .ne. k) then
                    if (obj(i+o(m),j+p(m)).ne.2) then
                      obj(i+o(m),j+p(m))=1
                      call refresh(obj,med1,d)
                      do 295 q=1,4
                        if ((q .ne. m).and.(q .ne. k)) then
                          if (obj(i+o(q),j+p(q)).ne.2) then
                            obj(i+o(q),j+p(q))=1
                            call prime(obj,d,i,j,k,o(k),p(k))
                            call fact(obj,'+c2 ',d)
                          endif
                        endif
                        call refresh(med1,obj,d)
295                   continue
```

```
                    endif
                  endif
                  call refresh(med0,obj,d)
300              continue
               endif
               call refresh(subj,obj,d)
305         continue
          else if ((obj(i,j).eq.9).and.
     +    ((obj(i+o(1),j+p(1)).ne.9).or.
     +    ((obj(i+o(2),j+p(2)).ne.9).or.
     +    ((obj(i+o(3),j+p(3)).ne.9).or.
     +    (obj(i+o(4),j+p(4)).ne.9))))) then
               call refresh(subj,obj,d)
            obj(i,j)=2
            call refresh(obj,med0,d)
            do 317 k=1,4
              if (obj(i+o(k),j+p(k)).eq.1) then
                do 315 m=1,4
                  if (m .ne. k) then
                    if (obj(i+o(m),j+p(m)).ne.2) then
                      obj(i+o(m),j+p(m))=1
                      call refresh(obj,med1,d)
                      do 310 q=1,4
                        if ((q .ne. m).and.(q .ne. k)) then
                          if (obj(i+o(q),j+p(q)).ne.2) then
                            obj(i+o(q),j+p(q))=1
                            call prime(obj,d,i,j,k,o(k),p(k))
                            call fact(obj,'+c2 ',d)
                          endif
                        endif
                        call refresh(med1,obj,d)
310                   continue
                    endif
                  endif
                  call refresh(med0,obj,d)
315              continue
              endif
             call refresh(med0,obj,d)
317          continue
          endif
```

```
          call refresh(subj,obj,d)
320     continue
330   continue



      do 380 i=g,h
       do 370 j=g,h
        if (obj(i,j).eq.2) then
         do 350 k=1,4
          if ((obj(i+o(k),j+p(k)).eq.1).or.
     +    (obj(i+o(k),j+p(k)).eq.9)) then
           obj(i+o(k),j+p(k))=1
           call refresh(obj,med0,d)
           do 345 m=1,4
            if (m .ne. k) then
             if (obj(i+o(m),j+p(m)).ne.2) then
              obj(i+o(m),j+p(m))=1
              call refresh(obj,med1,d)
              do 343 q=1,4
               if ((q .ne. m).and.(q .ne. k)) then
                if (obj(i+o(q),j+p(q)).ne.2) then
                 obj(i+o(q),j+p(q))=1
                 call refresh(obj,med2,d)
                  do 340 r=1,4
                   if (((r.ne.m).and.(r.ne.q)).and.(r.ne.k)) then
                    if (obj(i+o(r),j+p(r)).ne.2) then
                     obj(i+o(r),j+p(r))=1
                     call prime(obj,d,i,j,k,o(k),p(k))
                     call fact(obj,'+c3 ',d)
                    endif
                   endif
                   call refresh(med2,obj,d)
340               continue
                 endif
                endif
                call refresh(med1,obj,d)
343            continue
              endif
             endif
```

```
           call refresh(med0,obj,d)
345       continue
          endif
          call refresh(subj,obj,d)
350       continue
        else if ((obj(i,j).eq.9).and.
     +  ((obj(i+o(1),j+p(1)).ne.9).or.
     +  ((obj(i+o(2),j+p(2)).ne.9).or.
     +  ((obj(i+o(3),j+p(3)).ne.9).or.
     +  (obj(i+o(4),j+p(4)).ne.9))))) then
         obj(i,j)=2
         call refresh(obj,med0,d)
         do 367 k=1,4
          if (obj(i+o(k),j+p(k)).eq.1) then
           do 365 m=1,4
            if (m .ne. k) then
             if (obj(i+o(m),j+p(m)).ne.2) then
              obj(i+o(m),j+p(m))=1
              call refresh(obj,med1,d)
              do 360 q=1,4
               if ((q .ne. m).and.(q .ne. k)) then
                if (obj(i+o(q),j+p(q)).ne.2) then
                 obj(i+o(q),j+p(q))=1
                 call refresh(obj,med2,d)
                 do 355 r=1,4
                  if (((r.ne.m).and.(r.ne.q)).and.(r.ne.k)) then
                   if (obj(i+o(r),j+p(r)).ne.2) then
                    obj(i+o(r),j+p(r))=1
                    call prime(obj,d,i,j,k,o(k),p(k))
                    call fact(obj,'+c3 ',d)
                   endif
                  endif
                  call refresh(med2,obj,d)
355              continue
                endif
               endif
               call refresh(med1,obj,d)
360           continue
             endif
            endif
```

```
             call refresh(med0,obj,d)
365          continue
            endif
            call refresh(med0,obj,d)
367        continue
          endif
          call refresh(subj,obj,d)
370     continue
380    continue

      write (7,550) 'fini',99

550   format (1x,a4,1x,i3)
600   format (5x,9(i1,1x))

      stop
      end

c==================================================================
c234567
      subroutine prime(x,d,i,j,k,o,p)
      integer d,i,j,k,o,p
      integer x(d,d)
      integer a,b


        if (x(i,j).eq.1) then
          x(i,j)=4
        else if (x(i,j).eq.2) then
          x(i,j)=3
        endif

        if (x(i+o,j+p).eq.1) then
          x(i+o,j+p)=4
          else if (x(i+o,j+p).eq.2) then
          x(i+o,j+p)=3
        endif

        do 1010 a=1,d
          do 1000 b=1,d
```

```
            if (x(a,b).eq.2) then
              x(a,b)=4
              else if (x(a,b).eq.1) then
               x(a,b)=3
            endif
1000      continue
1010    continue

        return
        end

c==================================================================
c234567
      subroutine refresh(x,y,n)
      integer n
      integer x(n,n),y(n,n)
      integer i,j

      do 3200 i=1,n
        do 2200 j=1,n
          y(i,j)=x(i,j)
2200    continue
3200  continue

      return
      end

c==================================================================
c234567
      subroutine fact(x,num,dim)
      integer dim,i,j
      integer x(dim,dim)
      character *4 num
      integer size
      parameter (size = 9)
      integer a(size)

      write (7,5500) num,1
```

```
        do 5000 j=1,dim
          do 4500 i=1,dim
            if (x(i,j).eq.9) then
              a(i)=0
            else if (x(i,j).eq.1) then
              a(i)=1
            else if (x(i,j).eq.2) then
              a(i)=2
            else if (x(i,j).eq.3) then
              a(i)=1
            else if (x(i,j).eq.4) then
              a(i)=2
            endif
4500       continue
           write(7,6000) (a(k), k=1,dim)

5000    continue
5500  format (1x,a4,1x,i3)
6000  format (5x,9(i1,1x))

      return
      end

c==================================================================
c
c                12345678901234567890123456789012345678901234567890
c
c==================================================================
```

```
c     program  factorize4
c
c     This program factorizes the correlators in terms of certain
c     4-site correlators with double site overlap.
c
c     Inputs -   file containing correlators for factorization
c
c     Outputs -  factorization tables
c
c     revision: input from file fact4_me.in

      integer i,j,k,d,dx,dy
      parameter (d=9)
      parameter (dx=16)
      parameter (dy=1000)
      integer field(d,d),table(dx,dy)
      integer sq(d,d,4),tr(d,d,4),db(d,d,4)
      integer a,b,c,number,count,dot,gap,num
      character *8 source,new
      character *6 word
      integer o(8),p(8),q(8),r(8)
      common o,p,q,r
      integer gamma
      common gamma

      o(1)=0
      o(2)=0
      o(3)=0
      o(4)=0
      o(5)=1
      o(6)=1
      o(7)=-1
      o(8)=-1

      p(1)=1
      p(2)=1
      p(3)=-1
```

```
      p(4)=-1
      p(5)=0
      p(6)=0
      p(7)=0
      p(8)=0

      q(1)=1
      q(2)=-1
      q(3)=1
      q(4)=-1
      q(5)=1
      q(6)=1
      q(7)=-1
      q(8)=-1

      r(1)=1
      r(2)=1
      r(3)=-1
      r(4)=-1
      r(5)=1
      r(6)=-1
      r(7)=1
      r(8)=-1

      open (8,file=’fact4_me.in’,status=’old’)
      open (9,file=’fact4_me.out’,status=’unknown’)
      write (9,300) ’n’,’C^’,’QS’,’QH’,’QE’,’QA’,’TS’,
     + ’TH’,’TO’,’TA’,’TE’,
     + ’DS’,’DH’,’DE’,’SS’,’SH’

      do 10 i=1,dy
        do 5 j=1,dx
           table(j,i)=0
5       continue
10    continue

      read (8,100) word,number
      do 20 i=1,d
        read (8,200) (field(i,j),j=1,d)
20    continue
```

```
count = 1

read (8,100) word,number

do 1000 while (word .ne. 'fini')

gamma=0

if (word .eq. '-1  ') then
  table(2,count)=-5
endif
if (word .eq. '+1  ') then
  table(2,count)=5
endif
if (word .eq. '-c1 ') then
  table(2,count)=-1
endif
if (word .eq. '+c1 ') then
  table(2,count)=1
endif
if (word .eq. '-c2 ') then
  table(2,count)=-2
endif
if (word .eq. '+c2 ') then
  table(2,count)=2
endif
if (word .eq. '-c3 ') then
  table(2,count)=-3
endif
if (word .eq. '+c3 ') then
  table(2,count)=3
endif
if (word .eq. '-c4 ') then
  table(2,count)=-4
endif
if (word .eq. '+c4 ') then
  table(2,count)=4
endif
```

```
      do 45 i=1,d
        do 44 j=1,d
          do 43 k=1,4
            sq(i,j,k)=0
            tr(i,j,k)=0
            db(i,j,k)=0
43        continue
44      continue
45    continue

      do 50 i=1,d
        read (8,200) (field(i,j),j=1,d)
50    continue

      dot=0
      gap=0

      do 70 i=1,d
        do 60 j=1,d
          if (field(i,j).eq.1) then
            dot=dot+1
          endif
          if (field(i,j).eq.2) then
            gap=gap+1
          endif
60      continue
70    continue

       table(1,count)=number
       print *, 'PROCESSING'

       call ssquar(field,table,sq,tr,db,d,dx,dy,count,num)
       call hsquar(field,table,sq,tr,db,d,dx,dy,count,num)
       call esquar(field,table,sq,tr,db,d,dx,dy,count,num)
       call asquar(field,table,sq,tr,db,d,dx,dy,count,num)
       do k1=1,4
       do i1=1,9
       write(*,101) (sq(i1,j1,k1),j1=1,9)
       enddo
       write(*,201)
```

```
       enddo
       write(*,301) '****'
101    format(5x,9(i1,1x))
201    format(/)
301    format(a)
       call stria(field,table,sq,tr,db,d,dx,dy,count,num)
       call htria(field,table,sq,tr,db,d,dx,dy,count,num)
       call otria(field,table,sq,tr,db,d,dx,dy,count,num)
       call atria(field,table,sq,tr,db,d,dx,dy,count,num)
       call etria(field,table,sq,tr,db,d,dx,dy,count,num)
       call stria(field,table,sq,tr,db,d,dx,dy,count,num)
       call htria(field,table,sq,tr,db,d,dx,dy,count,num)
       call otria(field,table,sq,tr,db,d,dx,dy,count,num)
       call atria(field,table,sq,tr,db,d,dx,dy,count,num)
       call etria(field,table,sq,tr,db,d,dx,dy,count,num)
       do k1=1,4
       do i1=1,9
       write(*,101) (tr(i1,j1,k1),j1=1,9)
       enddo
       write(*,201)
       enddo
       write(*,301) '****'
       call sdoub(field,table,sq,tr,db,d,dx,dy,count,num)
       call hdoub(field,table,sq,tr,db,d,dx,dy,count,num)
       call edoub(field,table,sq,tr,db,d,dx,dy,count,num)
       do k1=1,4
       do i1=1,9
       write(*,101) (db(i1,j1,k1),j1=1,9)
       enddo
       write(*,201)
       enddo
       write(*,301) '****'
       call ssing(field,table,sq,tr,db,d,dx,dy,count,num)
       call hsing(field,table,sq,tr,db,d,dx,dy,count,num)
       call nrmdbl(table,dx,dy,count,dot,gap)
c       call nrmsgl(table,dx,dy,count,dot,gap)
       count = count +1
       read (8,100) word,number
1000   enddo
       print *,'simplify'
```

```
       call simpl(table,dx,dy)
c       call cancl(table,dx,dy)
c       print *,'cancel'

       do 2000 i=1,count-1
       if (table(1,i).ne.0) then
         write(9,400) (table(j,i),j=1,dx)
       endif
2000   continue
         write(9,400) 0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0

100    format(1x,a4,1x,i4)
200    format(5x,9(i1,1x))
300    format(4x,a1,2x,15(a2,1x))
400    format(1x,i4,1x,15(i2,1x))

       stop
       end
c==================================================================

      subroutine ssquar(field,table,sq,tr,db,d,dx,dy,count,num)

      integer d,dx,dy,count
      integer field(d,d),table(dx,dy)
      integer sq(d,d,4),tr(d,d,4),db(d,d,4)
      integer i,j
      integer num,dumb

      num=1

      do 50 i=2,d-1
        do 40 j=2,d-1

         dumb=0
          if (field(i,j).eq.1) then
            if (field(i,j+1).eq.1) then
              if (field(i+1,j+1).eq.1) then
                if (field(i+1,j).eq.1) then
                  call criter1(sq,d,i,j,dumb,0)
                  if (dumb.eq.1) then
```

```
                  call updat1(sq,d,i,j,num)
                  table(3,count)=table(3,count)+1
                  num = num + 1
                endif
              endif
            endif
          endif
        endif
40      continue
50    continue

      return
      end
c==================================================================

      subroutine hsquar(field,table,sq,tr,db,d,dx,dy,count,num)

      integer d,dx,dy,count
      integer field(d,d),table(dx,dy)
      integer sq(d,d,4),tr(d,d,4),db(d,d,4)
      integer i,j
      integer num,dumb

      do 50 i=2,d-1
        do 40 j=2,d-1

         dumb=0

          if (field(i,j).eq.2) then
            if (field(i,j+1).eq.1) then
              if (field(i+1,j+1).eq.1) then
                if (field(i+1,j).eq.1) then
                  call criter1(sq,d,i,j,dumb,0)
                  if (dumb.eq.1) then
                    call updat1(sq,d,i,j,num)
                    table(4,count)=table(4,count)+1
                    num = num + 1
                  endif
                endif
              endif
```

```
  endif
endif

if (field(i,j).eq.1) then
  if (field(i,j+1).eq.2) then
    if (field(i+1,j+1).eq.1) then
      if (field(i+1,j).eq.1) then
        call criter1(sq,d,i,j,dumb,0)
        if (dumb.eq.1) then
          call updat1(sq,d,i,j,num)
          table(4,count)=table(4,count)+1
          num = num + 1
        endif
      endif
    endif
  endif
endif

if (field(i,j).eq.1) then
  if (field(i,j+1).eq.1) then
    if (field(i+1,j+1).eq.2) then
      if (field(i+1,j).eq.1) then
        call criter1(sq,d,i,j,dumb,0)
        if (dumb.eq.1) then
          call updat1(sq,d,i,j,num)
          table(4,count)=table(4,count)+1
          num = num + 1
        endif
      endif
    endif
  endif
endif

if (field(i,j).eq.1) then
  if (field(i,j+1).eq.1) then
    if (field(i+1,j+1).eq.1) then
      if (field(i+1,j).eq.2) then
        call criter1(sq,d,i,j,dumb,0)
        if (dumb.eq.1) then
          call updat1(sq,d,i,j,num)
```

```
                  table(4,count)=table(4,count)+1
                  num = num + 1
                endif
              endif
            endif
          endif
        endif

40      continue
50    continue

      return
      end

c==================================================================

      subroutine asquar(field,table,sq,tr,db,d,dx,dy,count,num)

      integer d,dx,dy,count
      integer field(d,d),table(dx,dy)
      integer sq(d,d,4),tr(d,d,4),db(d,d,4)
      integer i,j
      integer num,dumb

      do 50 i=2,d-1
        do 40 j=2,d-1

         dumb=0

          if (field(i,j).eq.2) then
            if (field(i,j+1).eq.1) then
              if (field(i+1,j+1).eq.2) then
                if (field(i+1,j).eq.1) then
                  call criter1(sq,d,i,j,dumb,0)
                  if (dumb.eq.1) then
                    call updat1(sq,d,i,j,num)
                    table(6,count)=table(6,count)+1
                    num = num + 1
                  endif
                endif
```

```
          endif
        endif
      endif

      if (field(i,j).eq.1) then
        if (field(i,j+1).eq.2) then
          if (field(i+1,j+1).eq.1) then
            if (field(i+1,j).eq.2) then
              call criter1(sq,d,i,j,dumb,0)
              if (dumb.eq.1) then
                call updat1(sq,d,i,j,num)
                table(6,count)=table(6,count)+1
                num = num + 1
              endif
            endif
          endif
        endif
      endif

40      continue
50    continue

      return
      end

c==================================================================

      subroutine esquar(field,table,sq,tr,db,d,dx,dy,count,num)

      integer d,dx,dy,count
      integer field(d,d),table(dx,dy)
      integer sq(d,d,4),tr(d,d,4),db(d,d,4)
      integer i,j
      integer num,dumb

      do 50 i=2,d-1
        do 40 j=2,d-1

         dumb=0
```

```
if (field(i,j).eq.2) then
  if (field(i,j+1).eq.2) then
    if (field(i+1,j+1).eq.1) then
      if (field(i+1,j).eq.1) then
        call criter1(sq,d,i,j,dumb,1)
        if (dumb.eq.1) then
          call updat1(sq,d,i,j,num)
          table(5,count)=table(5,count)+1
          num = num + 1
        endif
      endif
    endif
  endif
endif

if (field(i,j).eq.1) then
  if (field(i,j+1).eq.1) then
    if (field(i+1,j+1).eq.2) then
      if (field(i+1,j).eq.2) then
        call criter1(sq,d,i,j,dumb,2)
        if (dumb.eq.1) then
          call updat1(sq,d,i,j,num)
          table(5,count)=table(5,count)+1
          num = num + 1
        endif
      endif
    endif
  endif
endif

if (field(i,j).eq.1) then
  if (field(i,j+1).eq.2) then
    if (field(i+1,j+1).eq.2) then
      if (field(i+1,j).eq.1) then
        call criter1(sq,d,i,j,dumb,3)
        if (dumb.eq.1) then
          call updat1(sq,d,i,j,num)
          table(5,count)=table(5,count)+1
          num = num + 1
        endif
```

```
                endif
              endif
            endif
          endif

          if (field(i,j).eq.2) then
            if (field(i,j+1).eq.1) then
              if (field(i+1,j+1).eq.1) then
                if (field(i+1,j).eq.2) then
                  call criter1(sq,d,i,j,dumb,4)
                  if (dumb.eq.1) then
                    call updat1(sq,d,i,j,num)
                    table(5,count)=table(5,count)+1
                    num = num + 1
                  endif
                endif
              endif
            endif
          endif

40        continue
50      continue

      return
      end

c=================================================================

      subroutine stria(field,table,sq,tr,db,d,dx,dy,count,num)

      integer d,dx,dy,count
      integer field(d,d),table(dx,dy)
      integer sq(d,d,4),tr(d,d,4),db(d,d,4)
      integer i,j,k
      integer o(8),p(8),q(8),r(8)
      common o,p,q,r
      integer num,dumb

      num=1
```

```
      do 50 i=2,d-1
        do 40 j=2,d-1
          do 30 k=1,8

            dumb=0

            if (field(i,j).eq.1) then
              if (field(i+o(k),j+p(k)).eq.1) then
                if (field(i+q(k),j+r(k)).eq.1) then
                  call criter2(sq,tr,d,i,j,k,dumb,0)
                  if (dumb.eq.1) then
                    call updat2(tr,d,i,j,k,num)
                    table(7,count)=table(7,count)+1
                    num = num + 1
                  endif
                endif
              endif
            endif
30        continue
40      continue
50    continue

      return
      end

c===================================================================

      subroutine htria(field,table,sq,tr,db,d,dx,dy,count,num)

      integer d,dx,dy,count
      integer field(d,d),table(dx,dy)
      integer sq(d,d,4),tr(d,d,4),db(d,d,4)
      integer i,j,k
      integer o(8),p(8),q(8),r(8)
      common o,p,q,r
      integer num,dumb

      do 50 i=2,d-1
        do 40 j=2,d-1
          do 30 k=1,8
```

```
          dumb=0

          if (field(i,j).eq.1) then
            if (field(i+o(k),j+p(k)).eq.2) then
              if (field(i+q(k),j+r(k)).eq.1) then
                call criter2(sq,tr,d,i,j,k,dumb,0)
                if (dumb.eq.1) then
                  call updat2(tr,d,i,j,k,num)
                  table(8,count)=table(8,count)+1
                  num = num + 1
                endif
              endif
            endif
          endif
30      continue
40    continue
50  continue

    return
    end

c=================================================================

    subroutine etria(field,table,sq,tr,db,d,dx,dy,count,num)

    integer d,dx,dy,count
    integer field(d,d),table(dx,dy)
    integer sq(d,d,4),tr(d,d,4),db(d,d,4)
    integer i,j,k
    integer o(8),p(8),q(8),r(8)
    common o,p,q,r
    integer num,dumb

    do 50 i=2,d-1
      do 40 j=2,d-1
        do 30 k=1,8

          dumb=0
```

```
            if (field(i,j).eq.1) then
              if (field(i+o(k),j+p(k)).eq.2) then
                if (field(i+q(k),j+r(k)).eq.2) then
                  call criter2(sq,tr,d,i,j,k,dumb,1)
                  if (dumb.eq.1) then
                    call updat2(tr,d,i,j,k,num)
                    table(11,count)=table(11,count)+1
                    num = num + 1
                  endif
                endif
              endif
            endif
30        continue
40      continue
50    continue

      return
      end

c===================================================================

      subroutine otria(field,table,sq,tr,db,d,dx,dy,count,num)

      integer d,dx,dy,count
      integer field(d,d),table(dx,dy)
      integer sq(d,d,4),tr(d,d,4),db(d,d,4)
      integer i,j,k
      integer o(8),p(8),q(8),r(8)
      common o,p,q,r
      integer num,dumb

      do 50 i=2,d-1
        do 40 j=2,d-1
          do 30 k=1,8

            dumb=0

            if (field(i,j).eq.1) then
              if (field(i+o(k),j+p(k)).eq.1) then
                if (field(i+q(k),j+r(k)).eq.2) then
```

```
                call criter2(sq,tr,d,i,j,k,dumb,0)
                if (dumb.eq.1) then
                  call updat2(tr,d,i,j,k,num)
                  table(9,count)=table(9,count)+1
                  num = num + 1
                endif
              endif
            endif
          endif
30        continue
40      continue
50    continue

      return
      end

c===================================================================

      subroutine atria(field,table,sq,tr,db,d,dx,dy,count,num)

      integer d,dx,dy,count
      integer field(d,d),table(dx,dy)
      integer sq(d,d,4),tr(d,d,4),db(d,d,4)
      integer i,j,k
      integer o(8),p(8),q(8),r(8)
      common o,p,q,r
      integer num,dumb

      do 50 i=2,d-1
        do 40 j=2,d-1
          do 30 k=1,8

            dumb=0

            if (field(i,j).eq.2) then
              if (field(i+o(k),j+p(k)).eq.1) then
                if (field(i+q(k),j+r(k)).eq.2) then
                  call criter2(sq,tr,d,i,j,k,dumb,0)
                  if (dumb.eq.1) then
                    call updat2(tr,d,i,j,k,num)
```

```
                 table(10,count)=table(10,count)+1
                 num = num + 1
               endif
             endif
           endif
         endif
30         continue
40       continue
50     continue

       return
       end

c==============================================================

       subroutine sdoub(field,table,sq,tr,db,d,dx,dy,count,num)

       integer d,dx,dy,count
       integer field(d,d),table(dx,dy)
       integer sq(d,d,4),tr(d,d,4),db(d,d,4)
       integer i,j,k
       integer num,dumb
       integer o(8),p(8),q(8),r(8)
       common o,p,q,r

       num=1

       do 50 i=2,d-1
         do 40 j=2,d-1
           do 30 k=1,8

             dumb=0

             if (field(i,j).eq.1) then
               if (field(i+o(k),j+p(k)).eq.1) then
                 call criter3(sq,tr,db,d,i,j,k,dumb)
                 if (dumb.eq.1) then
                   call updat3(db,d,i,j,k,num)
                   table(12,count)=table(12,count)+1
                   num = num + 1
```

```
               endif
             endif
           endif
30       continue
40     continue
50   continue

     return
     end

c====================================================================

     subroutine hdoub(field,table,sq,tr,db,d,dx,dy,count,num)

     integer d,dx,dy,count
     integer field(d,d),table(dx,dy)
     integer sq(d,d,4),tr(d,d,4),db(d,d,4)
     integer i,j,k
     integer o(8),p(8),q(8),r(8)
     common o,p,q,r
     integer num,dumb

     do 50 i=2,d-1
       do 40 j=2,d-1
         do 30 k=1,8

           dumb=0

           if (field(i,j).eq.1) then
             if (field(i+o(k),j+p(k)).eq.2) then
               call criter3(sq,tr,db,d,i,j,k,dumb)
               if (dumb.eq.1) then
                 call updat3(db,d,i,j,k,num)
                 table(13,count)=table(13,count)+1
                 num = num + 1
               endif
             endif
           endif
30       continue
40     continue
```

```
50    continue

      return
      end

c==================================================================

      subroutine edoub(field,table,sq,tr,db,d,dx,dy,count,num)

      integer d,dx,dy,count
      integer field(d,d),table(dx,dy)
      integer sq(d,d,4),tr(d,d,4),db(d,d,4)
      integer i,j,k
      integer num,dumb
      integer o(8),p(8),q(8),r(8)
      common o,p,q,r

      do 50 i=2,d-1
        do 40 j=2,d-1
          do 30 k=1,8

            dumb=0

            if (field(i,j).eq.2) then
              if (field(i+o(k),j+p(k)).eq.2) then
                call criter3(sq,tr,db,d,i,j,k,dumb)
                if (dumb.eq.1) then
                  call updat3(db,d,i,j,k,num)
                  table(14,count)=table(14,count)+1
                  num = num + 1
                endif
              endif
            endif
30        continue
40      continue
50    continue

      return
      end
```

```
c==================================================================

      subroutine ssing(field,table,sq,tr,db,d,dx,dy,count,num)

      integer d,dx,dy,count
      integer field(d,d),table(dx,dy)
      integer sq(d,d,4),tr(d,d,4),db(d,d,4)
      integer i,j,k
      integer fail

      do 50 i=2,d-1
        do 40 j=2,d-1
          fail=0
          if (field(i,j).eq.1) then
            do 30 k=1,4
              if (sq(i,j,k).ne.0) then
                fail=1
              endif
              if (tr(i,j,k).ne.0) then
                fail=1
              endif
              if (db(i,j,k).ne.0) then
                fail=1
              endif
30          continue
            if (fail.eq.0) then
              table(15,count)=table(15,count)+1
            endif
          endif
40      continue
50    continue

      return
      end

c==================================================================

      subroutine hsing(field,table,sq,tr,db,d,dx,dy,count,num)

      integer d,dx,dy,count
```

```
      integer field(d,d),table(dx,dy)
      integer sq(d,d,4),tr(d,d,4),db(d,d,4)
      integer i,j,k
      integer fail

      do 50 i=2,d-1
        do 40 j=2,d-1
          fail=0
          if (field(i,j).eq.2) then
            do 30 k=1,4
              if (sq(i,j,k).ne.0) then
                fail=1
              endif
              if (tr(i,j,k).ne.0) then
                fail=1
              endif
              if (db(i,j,k).ne.0) then
                fail=1
              endif
30          continue
            if (fail.eq.0) then
              table(16,count)=table(16,count)+1
            endif
          endif
40      continue
50    continue

      return
      end

c==================================================================

      subroutine nrmsgl(tb,dx,dy,c,dot,gap)

      integer dx,dy,c,dot,gap
      integer i,j,k,hole,point
      integer tb(dx,dy)

        point = 4*(tb(3,c))+
     +          3*(tb(4,c)+tb(7,c))+
```

```
     +         2*(tb(5,c)+tb(6,c)+tb(8,c)+tb(9,c)+tb(12,c))+
     +         1*(tb(10,c)+tb(11,c)+tb(13,c)+tb(15,c))
        hole = 2*(tb(5,c)+tb(6,c)+tb(10,c)+tb(11,c)+tb(14,c))+
     +         1*(tb(4,c)+tb(8,c)+tb(9,c)+tb(13,c)+tb(16,c))


        tb(16,c)=tb(16,c)-(hole-gap)
        tb(15,c)=tb(15,c)-(point-dot)

      return
      end

c=================================================================

      subroutine nrmdbl(tb,dx,dy,c,dot,gap)

      integer dx,dy,c,dot,gap
      integer i,j,k,part,solid,empty
      integer tb(dx,dy),hole,point
      integer o(8),p(8),q(8),r(8)
      common o,p,q,r
      integer gamma
      common gamma

        point = 4*(tb(3,c))+
     +         3*(tb(4,c)+tb(7,c))+
     +         2*(tb(5,c)+tb(6,c)+tb(8,c)+tb(9,c)+tb(12,c))+
     +         1*(tb(10,c)+tb(11,c)+tb(13,c)+tb(15,c))
        hole = 2*(tb(5,c)+tb(6,c)+tb(10,c)+tb(11,c)+tb(14,c))+
     +         1*(tb(4,c)+tb(8,c)+tb(9,c)+tb(13,c)+tb(16,c))

      empty=gamma
      part=hole-gap-2*empty
      solid=(point-dot-part)/2

      tb(12,c)=tb(12,c)-solid
      tb(13,c)=tb(13,c)-part
      tb(14,c)=tb(14,c)-empty

      return
```

```
      end

c==================================================================

      subroutine criter1(x,d,i,j,yes,ext)

      integer d,i,j,yes
      integer x(d,d,4)
      integer k,l,over,fail,ext
      integer a1,a2,a3,a4
      integer o(8),p(8),q(8),r(8)
      common o,p,q,r
      integer gamma
      common gamma

      fail=1
      do 10 k=1,4
      a1=0
      a2=0
      a3=0
      a4=0
      over=0
        if (x(i,j,k).ne.0) then
          over=over+1
          a1=1
        endif
        if (x(i,j+1,k).ne.0) then
          over=over+1
          a2=1
        endif
        if (x(i+1,j+1,k).ne.0) then
          over=over+1
          a3=1
        endif
        if (x(i+1,j,k).ne.0) then
          over=over+1
          a4=1
        endif
        if ((over.eq.0).or.(over.eq.2)) then
          fail=0
```

```
          endif
          if (over.eq.2) then
            if (ext.eq.1) then
              if ((a1.eq.1).and.(a2.eq.1)) then
                gamma=gamma+1
              endif
            endif
            if (ext.eq.2) then
              if ((a3.eq.1).and.(a4.eq.1)) then
                gamma=gamma+1
              endif
            endif
            if (ext.eq.3) then
              if ((a2.eq.1).and.(a3.eq.1)) then
                gamma=gamma+1
              endif
            endif
            if (ext.eq.4) then
              if ((a1.eq.1).and.(a4.eq.1)) then
                gamma=gamma+1
              endif
            endif
          endif
10      continue

        if (fail.eq.0) then
          yes=1
        endif
        if (fail.eq.1) then
          yes=0
        endif

        return
        end

c==================================================================

        subroutine criter2(x,y,d,i,j,k,yes,ext)

        integer d,i,j,k,yes,ext
```

```
      integer x(d,d,4),y(d,d,4)
      integer l,m,over,fail,right,poss
      integer a1,a2,a3
      integer o(8),p(8),q(8),r(8)
      common o,p,q,r
      integer gamma
      common gamma

      fail=0
      poss=0
      do 100 l=1,4
        right=0
        a1=0
        a2=0
        a3=0
        over=0
        if (x(i,j,l).ne.0) then
          over=over+1
          a1=1
        endif
        if (x(i+o(k),j+p(k),l).ne.0) then
          over=over+1
          a2=1
        endif
        if (x(i+q(k),j+r(k),l).ne.0) then
          over=over+1
          a3=1
        endif
c          print *, 'overlap,poss:',over,poss
        if (over.gt.0) then
          if (over.eq.3) then
            fail=1
          endif
          if (over.eq.2) then
            if ((poss.eq.1).or.(poss.eq.0)) then
              poss=2
            else
              fail=1
            endif
            right=1
```

```
c            print *, x(i+o(k),j+p(k),1)
            if (x(i+o(k),j+p(k),1).eq.0) then
              fail=1
              right=0
            endif
          endif
          if (over.eq.1) then
            if ((poss.eq.0).or.(poss.eq.2)) then
              poss=poss+1
            else
              fail=1
            endif
          endif
        endif

c       print *,'Out Fail:',fail

        if ((right.eq.1).and.(ext.eq.1)) then
          if ((a2.eq.1).and.(a3.eq.1)) then
            gamma=gamma+1
          endif
        endif

100   continue

      do 200 l=1,4
        right=0
        a1=0
        a2=0
        a3=0
        over=0
        if (y(i,j,l).ne.0) then
          over=over+1
          a1=1
        endif
        if (y(i+o(k),j+p(k),l).ne.0) then
          over=over+1
          a2=1
        endif
        if (y(i+q(k),j+r(k),l).ne.0) then
```

```
            over=over+1
            a3=1
          endif

c          print *, 'over,poss:',over,poss

          if (over.gt.0) then
            if (over.eq.3) then
              fail=1
            endif
            if (over.eq.2) then
              if ((poss.eq.1).or.(poss.eq.0)) then
                poss=2
              else
                fail=1
              endif
              right=1
                if (y(i+o(k),j+p(k),1).eq.0) then
                  fail=1
                 right=0
              endif
            endif

            if (over.eq.1) then
              if ((poss.eq.0).or.(poss.eq.2)) then
                poss=poss+1
              else
                fail=1
              endif
            endif
          endif

c          print *, 'fail:',fail

          if ((right.eq.1).and.(ext.eq.1)) then
            if ((a2.eq.1).and.(a3.eq.1)) then
              gamma=gamma+1
            endif
          endif
```

```
200   continue

      if (poss.eq.1) then
        fail=1
      endif

c        print *, 'fail:',fail

      if (fail.eq.0) then
        yes=1
      endif
      if (fail.eq.1) then
        yes=0
      endif

c      print *, 'Fail:',fail

      return
      end

c==================================================================

      subroutine criter3(x,y,z,d,i,j,k,yes)

      integer d,i,j,yes
      integer x(d,d,4),y(d,d,4),z(d,d,4)
      integer t(8),s(8),u(8)
      integer k,l,m
      integer o(8),p(8),q(8),r(8)
      common o,p,q,r

      do 10 l=1,4
        t(l)=x(i,j,l)
        t(l+4)=x(i+o(k),j+p(k),l)
10    continue

      do 20 l=1,4
        s(l)=y(i,j,l)
        s(l+4)=y(i+o(k),j+p(k),l)
20    continue
```

```
      do 30 l=1,4
        u(l)=z(i,j,l)
        u(l+4)=z(i+o(k),j+p(k),l)
30    continue

      yes=1

      do 50 l=1,8
        if (t(l).ne.0) then
           yes=0
        endif
50    continue

      do 70 l=1,8
        if (s(l).ne.0) then
          yes=0
        endif
70    continue

      do 90 l=1,8
        if (u(l).ne.0) then
          yes=0
        endif
90    continue

      return
      end

c=================================================================

      subroutine updat1(x,d,i,j,num)

      integer d,i,j,num
      integer x(d,d,4)
      integer k,done

      done = 0
      do 10 k=1,4
        if ((x(i,j,k).eq.0).and.(done.eq.0)) then
```

```
            x(i,j,k)=num
            done = 1
          endif
   10   continue

        done = 0
        do 20 k=1,4
          if ((x(i,j+1,k).eq.0).and.(done.eq.0)) then
            x(i,j+1,k)=num
            done = 1
          endif
   20   continue

        done = 0
        do 30 k=1,4
          if ((x(i+1,j+1,k).eq.0).and.(done.eq.0)) then
            x(i+1,j+1,k)=num
            done = 1
          endif
   30   continue

        done = 0
        do 40 k=1,4
          if ((x(i+1,j,k).eq.0).and.(done.eq.0)) then
            x(i+1,j,k)=num
            done = 1
          endif
   40   continue

        return
        end

c==================================================================

        subroutine updat2(x,d,i,j,k,num)

        integer d,i,j,num
        integer x(d,d,4)
        integer k,l,done
        integer o(8),p(8),q(8),r(8)
```

```
      common o,p,q,r

      done = 0
      do 10 l=1,4
        if ((x(i,j,l).eq.0).and.(done.eq.0)) then
          x(i,j,l)=num
          done = 1
        endif
10    continue

      done = 0
      do 20 l=1,4
        if ((x(i+o(k),j+p(k),l).eq.0).and.(done.eq.0)) then
          x(i+o(k),j+p(k),l)=num
          done = 1
        endif
20    continue

      done = 0
      do 30 l=1,4
        if ((x(i+q(k),j+r(k),l).eq.0).and.(done.eq.0)) then
          x(i+q(k),j+r(k),l)=num
          done = 1
        endif
30    continue

      return
      end

c==================================================================

      subroutine updat3(x,d,i,j,k,num)

      integer d,i,j,num
      integer x(d,d,4)
      integer k,l,done
      integer o(8),p(8),q(8),r(8)
      common o,p,q,r

      done = 0
```

```
      do 10 l=1,4
        if ((x(i,j,l).eq.0).and.(done.eq.0)) then
          x(i,j,l)=num
          done = 1
        endif
10    continue

      done = 0
      do 20 l=1,4
        if ((x(i+o(k),j+p(k),l).eq.0).and.(done.eq.0)) then
          x(i+o(k),j+p(k),l)=num
          done = 1
        endif
20    continue

      return
      end

c==================================================================

      subroutine simpl(table,dx,dy)

      integer dx,dy
      integer table(dx,dy)

      integer i,j,k,match

      do 100 i=1,dy
        do 50 j=i+1,dy
          match = 1
          do 20 k=2,dx
            if (table(k,j).ne.table(k,i)) then
              match=0
            endif
20        continue
          if (match.eq.1) then
            table(1,i)=table(1,i)+table(1,j)
            do 30 k=1,dx
              table(k,j)=0
30          continue
```

```
          endif
50      continue
100   continue
      return
      end

c==================================================================

      subroutine cancl(table,dx,dy)

      integer dx,dy
      integer table(dx,dy)

      integer i,j,k,match

      do 100 i=1,dy
        do 50 j=i+1,dy
          match = 0
          if ((table(2,j)+table(2,i)).eq.0) then
            match = 1
            do 20 k=3,dx
              if (table(k,j).ne.table(k,i)) then
                match=0
              endif
20          continue
          endif
          if (match.eq.1) then
            if (table(1,i).gt.table(1,j)) then
              table(1,i)=table(1,i)-table(1,j)
            else if (table(1,i).lt.table(1,j)) then
              table(1,i)=table(1,j)-table(1,i)
            else if (table(1,i).eq.table(1,j)) then
              table(1,i)=0
            endif

            do 30 k=1,dx
              table(k,j)=0
30          continue
          endif
50      continue
```

```
100   continue
      return
      end

c==================================================================
c
c                 12345678901234567890123456789012345678901234567890
c
c==================================================================
```

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