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Simulation study of interfacial growth

Jiang, Zhihua, Ph.D.
The Ohio State University, 1990
Simulation Study of Interfacial Growth

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of the Ohio State University

by

Zhihua Jiang, B.S., M.S.

*****

The Ohio State University
1990

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Department of Physics
To My Parents, Of Course!
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CHAPTER I

Introduction

Interfaces and wetting phenomena have been studied since at least the beginning of the last century[1]. Mostly due to the development of statistical mechanics, especially the theories of phase transitions, a great deal of understanding has been achieved on these topics as evidenced by the large number of recent reviews[2, 3]. Interfaces and interfacial phenomena are of interest both because of their importance in many natural and technological processes and because they provide basic examples for developing theoretical methods for nonuniform many-particle system. For instance, the properties of interfaces are closely related to processes of crystal growth; and the statistical methods for studying interfaces have been extended to the study of the physics of membranes[4] which, besides their own importance, provide experimental realizations for problems arising in field-theory models of elementary particles[5]. Much research has been done in the general area of equilibrium properties; recently, dynamic properties, especially the question of the manner in which equilibrium is approached, have been receiving increased attention[3(a),3(d)].
The aim of this dissertation is to study, using simple models with computer simulations, crystal growth and wetting film growth which are basically processes of relaxation toward equilibrium. In this chapter, we first review the related equilibrium properties for interfaces and wetting and wetting phase transitions, then we give an outline of the remainder of this dissertation.

1.1 A free interface

The boundary between two coexisting phases (e.g., liquid and vapor) is called an interface. To create an interface of unit area or to extend an existing interface by the same amount require a necessary amount of work, this work is called the interfacial free energy or interfacial tension. Interfacial free energy is a characteristic thermodynamic quantity of the interface. On the other hand, the interface is in general not a sharp boundary where the density (or generally, the order parameter) suddenly changes from the value it has in one of the bulk phases to the value in the other; instead, the value varies continuously within the interface. The density profiles constitute what we call the structure of the interface.

Since the pioneering work of van de Waals[6] and Gibbs[7], there have been extensive and continuing theoretical works aimed at determining the thermodynamic and structural properties of interfaces, and relating the latter to the former[2]. Various methods used include exact solutions of lattice models[8], field-theory and renormalization group methods[9], and computer
simulations[10]. In this section, we shall briefly review the properties which are essentially relevant to the remaining parts of this dissertation. In particular, we are interested in the scaling behavior of the interface width in Ising-like systems (binary liquid, liquid-vapor, etc.).

Consider an interface which is on average a plane perpendicular to the $z$ axis. At finite temperatures, the interface will wander around its average position to increase its configurational entropy, see Figure 1.1. In the presence of quenched random impurities, the interface will also wander in order to adjust to the random potentials and to reduce its energy. The density (order parameter) profile across the interface will appear to be diffusive, and can generally be described by a scaling function of the form

$$
\rho(z) = f\left(\frac{z - z_0}{w}\right)
$$

(1.1)

where $z_0$ is the center of the interface, and $w$ is the width of the interface. $w$, usually defined via the second moment of the interface displacement, measures the 'diffuseness' of the interface. It generally depends upon thermodynamic quantities of the system such as the temperature, and even the system size. Due to long-wavelength (capillary-wave-like) fluctuations, the interface width could be divergent in the thermodynamic limit even at temperatures below the bulk critical temperature $T_c$. For a system of transverse size $L$, the width is thought to scale as

$$
w(L) \sim L^{\zeta}
$$

(1.2)

$\zeta$ is called roughness exponent which, as we shall see later, is a very im-
Figure 1.1:
An interface between two bulk phases ($\alpha$ and $\beta$) wanders around its average position to reduce its free energy. The interface width ($w$) depends upon the transverse size of the system ($L$) as $w \propto L^\zeta$, where $\zeta$ is the roughness exponent.
important quantity for understanding the effects of fluctuations in interfacial phenomena such as wetting and wetting transitions.

The roughness exponent $\zeta$ is generally a function of the dimensionality $d$ of the system. It also depends upon the mechanisms of the roughening such as thermal fluctuations (entropic mechanism) and quenched random impurities (energetic mechanism). If $\zeta = 0$, the interface is called flat or smooth. If $\zeta > 0$, it is called rough. For higher dimensionalities, the interface may be smooth below a temperature $T_R$ and become rough above $T_R$. In this case, we say there is a roughening transition\[11] at $T_R$, and $T_R$ is called the roughening transition temperature.

For thermal fluctuations, the order parameter has an error-function profile, e.g., for a liquid-vapor interface centered at $z_0$, the density profile is given by\[12]

$$\rho(z) = \frac{1}{2}(\rho_l + \rho_v) - \frac{1}{2}(\rho_l - \rho_v)\text{erf}\left(\frac{z - z_0}{\sqrt{2}w}\right)$$

(1.3)

where $\rho_l$ and $\rho_v$ are the densities of liquid and vapor respectively, $w$ is the interface width, and $\text{erf}(x)$ is an error function defined as

$$\text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x dte^{-t^2}.$$  

(1.4)

The roughness exponent is given by\[2(d)]

$$\zeta(d) = \begin{cases} 
\frac{1}{2}(3 - d) & 1 < d \leq 3 \\
0 & d > 3.
\end{cases}$$  

(1.5)

Equation (1.5) can be easily derived by noticing that, at equilibrium, the energy cost for the interface to deviate from its average position must be
of the same order of the thermal energy $k_B T$, where $k_B$ is the Boltzmann constant. For an interface of size $L^{d-1}$ and surface tension $\sigma$, this energy cost is about $\sigma(w/L)^2 L^{d-1} \sim \sigma w^2 L^{d-3}$.

In the marginal dimension $d = 3$, there is a roughening transition at finite temperature $T_R$ if the underlying lattice periodic structure, which imposes a periodic potential on the interface, is considered[13]. The roughening transition is of the Kosterlitz-Thouless type[14]. Below $T_R$, the interface is smooth; above $T_R$, the interface is marginally rough, that is,

$$w \sim \ln^{\frac{1}{2}}(L).$$

Moreover, when $T$ approaches $T_R$ from below, the excess interfacial free energy, i.e, the difference of interfacial free energy from its mean-field value, vanishes as

$$f \sim \exp(-c|T_R - T|^{-\frac{1}{2}}).$$

For roughening due to quenched impurities, the studies have been focused on two distinct cases, i.e, random fields which couple directly to the order parameter density, and random bonds which couple to the energy density. For random fields (RF)[15], the energy scale controlling the interface fluctuations is of order $\epsilon(wL^{d-1})^{\frac{1}{2}}$, $\epsilon$ being the average strength of the fields. Equating $\epsilon(wL^{d-1})^{\frac{1}{2}}$ to $\sigma w^2 L^{d-3}$, one obtains

$$\zeta_{RF}(d) = \begin{cases} \frac{1}{3}(5 - d) & 2 < d \leq 5 \\ 0 & d > 5. \end{cases}$$
This so called Imry-Ma-type scaling argument\cite{[16]} actually gives the correct roughness exponent\cite{[17]}. For random bonds (RB)\cite{[18]}, the energy scale controlling the interface fluctuations is of order $\delta (L^{d-1})^{\frac{1}{2}}$, where $\delta$ is the average strength of bonds, so the same sort of argument predicts the roughness exponent as

$$\zeta_{RB}(d) = \begin{cases} \frac{1}{4}(5-d) & 1 < d \leq 5 \\ 0 & d > 5. \end{cases}$$

(1.9)

However, this result fails to agree with the exact result\cite{[19]} $\zeta_{RB} = \frac{2}{3}$ in $d = 2$. Recently, a Flory-type\cite{[20]} argument with a nonlinear functional renormalization group predicts\cite{[21]}

$$\zeta_{RB}(d) = \begin{cases} \frac{2}{9}(5-d) & \frac{5}{3} < d \leq 5 \\ 0 & d > 5. \end{cases}$$

(1.10)

This is in agreement with the exact result in $d = 2$. It is also supported by Monte Carlo simulations\cite{[22]} in $d = 3$.

### 1.2 Wetting and wetting phase transitions

Wetting phenomena have been studied since the last century\cite{[1]}. However, the modern theories of wetting and wetting phase transitions have been developed only after the seminal works of Cahn\cite{[23]} and Ebner and Saam\cite{[24]} in 1977 when they predicted the first-order wetting phase transition.

To illustrate the basic concepts, consider a simple system of vapor ($\alpha$) on top of an inert substrate ($\gamma$) as in Figure 1.2(a). If the thermodynamic
Figure 1.2:

(a) A system of gas ($\alpha$) coexists with a substrate ($\gamma$). (b) When the thermodynamic quantities are adjusted close to the bulk coexistence curve of the gas and liquid ($\beta$), a liquid film intrudes and separates the gas from the substrate.
Figure 1.3:
Various wetting transitions are illustrated in a pressure-temperature phase diagram. Moving along the bulk liquid-gas coexistence curve (the solid curve), a wetting transition, which could be first order or continuous, happens at point W. Accompanying a first order wetting transition, a first order prewetting transition line (the broken curve) extends into the gas region and terminates at a critical point $C_{PW}$. $p$ shows a typical path producing complete wetting.
quantities such as temperature or chemical potential are adjusted close to the coexistence curve of the bulk vapor and liquid phases, a layer of liquid phase (β) may intrude between the vapor and the substrate as shown in Figure 1.2(b). If the equilibrium thickness \( l \) of this liquid phase is macroscopically large, i.e, \( l \to \infty \), we say the substrate is *wet* by the liquid; if \( l = 0 \), the substrate is *non-wet*; and if \( l \) is nonzero but finite, the substrate is *partially wet*. Changing the thermodynamic quantities along the bulk coexistence curve, there may be a sudden change of \( l \) from a finite value to \( \infty \) at a finite temperature \( T_W \), then we say there is a *first-order wetting transition* at \( T_W \); and \( T_W \) is called the *wetting transition temperature*. A wetting transition is a phase transition in the sense that the excess surface free energy has a singularity at \( T_W \). The value of \( l \) may also diverge continuously, then we have a *critical wetting transition*. If wetting is achieved by approaching the coexistence curve from the gas region, e.g, path \( p \) in Figure 1.3, we say there is a *complete wetting*. In the case of a first-order wetting transition, a first-order *prewetting transition* line extends into the gas (α) phase terminating at a critical point \( C_{pw} \) as shown in Figure 1.3. As this line is crossed, the film thickness has a finite jump.

Generally, the above concepts may apply to a system of any three coexisting phases \( \alpha, \beta, \) and \( \gamma \). The theories of wetting and wetting transitions try to understand the following problems:

(1) What is the equilibrium thickness of the wetting film for given thermodynamic parameters?
(2) Is there a wetting transition for a specific system of given microscopic interactions? If yes, what are the transition temperature and the order of the transition?

(3) What are the critical exponents if the transition is a critical wetting transition or at complete wetting?

(4) How is the wetting behavior affected by thermal fluctuations and impurities?

A great deal of theoretical effort has been made to understand these problems [25]. The answers generally depend upon the microscopic interactions among substrate and adsorbate molecules, and the nature of fluctuations. Even a simple model with short-ranged interactions turns out to have a quite complex phase diagram in a mean field theory [26]. Various mean field theories have also been developed for systems of long-ranged interactions [27]. The effects of fluctuations have been studied mostly in terms of the effective interface model (cf. Section 1.3) with the assistance of renormalization group methods. Computer simulations also play an important role especially in verifying analytical predictions [28, 29]. Experimentally, first order wetting transitions have been observed by several groups [30]; complete wetting has been observed on the systems of \(^4\text{He}\) and Ar films on graphite [31]; and two groups have seen signs of prewetting transitions [32] although more efforts still are needed to confirm these observations. However, no experimental observations of critical wetting transitions have been reported so far.
In the next section, in the language of the effective interface model, we shall discuss some theoretical understandings of wetting and wetting transitions. Since excellent reviews[3] already exist, we don’t intend to cover the details of these theoretical advances. We only choose those topics which are essentially important in the study of the dynamics of wetting film growth to be discussed in Chapter III and Chapter IV.

1.3 The effective interface model

The effective interface model can be derived[33, 34] from the more general Ginzburg-Landau type theories, assuming the interface is described by a sharp kink in the order parameter profile. It is a coarse-grained model valid at temperatures not too close to any bulk critical temperatures and above the roughening temperature. In this model, the free energy functional or effective Hamiltonian for the interfacial configurations is taken to be

$$H(l) = \int d^{d-1}x \left[ \frac{1}{2} \Sigma (\nabla l)^2 + V_W(l) - \delta \mu l \right].$$

(1.11)

where \(l(x)\) is the distance between the two interfaces (see Figure 1.4); \(\Sigma\) is the interfacial stiffness[35] which is related to the interfacial tension \(\sigma(\hat{n})\) by

$$\Sigma = \sigma(0) + (d^2 \sigma/d\theta^2)_0,$$

where \(\hat{n}\) is the unit vector normal to the \(\alpha\beta\) interface and \(\theta\) is the angle between \(\hat{n}\) and the \(z\) axis; \(V_W(l)\) describes the effective direct interactions of the interface with the wall; and \(\delta \mu\) is the chemical potential difference from its bulk coexistence value (\(\delta \mu > 0\) favors \(\beta\) phase).
Figure 1.4:
The effective interface model is schematically shown.
1.3.1 Direct interactions

The direct interaction \( V_w(l) \) depends upon the microscopic interactions\[36\] between the molecules in \( \alpha, \beta \) and \( \gamma \). If all molecular interactions decay at least exponentially for large separations between molecules, one has\[37\]

\[
V_w(l) \approx W \exp(-l/\xi_\infty) + U \exp(-nl/\xi_\infty)
\]  

(1.12)

for large \( l \). \( \xi_\infty \) is the correlation length within the \( \beta \) layer; \( n \) is a dimensionless constant with \( n > 1 \).

If the molecular interactions are of power law, \( V_w(l) \) has the general form\[38\]

\[
V_w(l) \approx W/l^p + U/l^s
\]  

(1.13)

with \( p < s \). \( p \) and \( s \) depend on the exponents of the microscopic interactions.

If both substrate-adsorbate and adsorbate-adsorbate molecular interactions vary as \( 1/r^\sigma \), then \( p = \sigma - d - 1 \). For the physically interesting non-retarded and retarded van der Waals potentials, \( \sigma = 6 \) and \( 7 \) respectively.

For a long-ranged substrate-adsorbate interaction and a short-ranged adsorbate-adsorbate interaction, one has\[33, 39, 40\]

\[
V_w(l) \approx W/l^p + U \exp(-l/\xi_\infty)
\]  

(1.14)

Note that in these potentials, \( W \) and \( U \) are generally functions of temperature, and they may change sign as temperature varies. For \( W > 0 \), there will be complete wetting at all temperatures; for \( U > 0 \) and \( W \) smoothly varying with temperature and becoming negative at low \( T \), there will be a critical wetting transition.
1.3.2 Fluctuation-induced interactions

The fluctuations can be effectively described by a repulsive potential of the form[41]

\[ V_{FL}(l) = W_{FL}/l^\tau, W_{FL} > 0 \]  

(1.15)

where the exponent \( \tau \) is generally given by \( \tau = 2(1 - \zeta)/\zeta \). \( \zeta \) is the roughness exponent of the interface. For thermal fluctuations, \( \tau = 2(d - 1)/(3 - d) \); in the marginal dimension \( d = 3 \), \( V_{FL}(l) \) has an exponential decay, i.e., \( V_{FL} \sim \exp(-C l), C \) being a constant.

It is easy to understand why the fluctuation-induced interaction is repulsive, since moving away from the wall will reduce constraints on the space for the interface to fluctuate, thus increasing the entropy. Heuristically, the interface will wander with a magnitude of order \( l \) in a transverse distance of order \( l^{\frac{\xi}{3}} \), so the free energy increase per unit area is of order \( \frac{1}{2} \Sigma (l/l^{\frac{\xi}{3}})^2 \sim l^{-\tau} \).

1.3.3 Mean field and fluctuation regimes

It has been found[43, 44] that for critical wetting there are four different regimes in which the scaling behaviors are nontrivially different. These regimes are determined by the relative strengths of the repulsive part of the direct interaction \( V_{WR}(l) \), the attractive part of the direct interaction \( V_{WA}(l) \), and the effective potential for fluctuations. They are

(1) the mean field (MF) regime[43] for which

\[ V_{WR}(l) >> V_{FL}(l) \text{ for large } l; \]  

(1.16)
(2) the weak-fluctuation (WFL) regime\[43\] characterized by

\[ V_{WR}(l) << V_{FL}(l) << V_{WA}(l) \text{ for large } l; \]  
(1.17)

(3) the intermediate-fluctuation (ITF) regime\[44\] characterized by

\[ V_{WR}(l) \sim V_{FL}(l) \sim V_{WA}(l) \text{ for large } l; \]  
(1.18)

and

(4) the strong-fluctuation (SFL) regime\[43\] with

\[ |V_{W}(l)| << V_{FL}(l) \text{ for large } l. \]  
(1.19)

Note that the effective interface energy per unit area can now be expressed as

\[ f(l) = V_{W}(l) + V_{FL}(l) - \delta \mu l = V_{WA}(l) + V_{WR}(l) + V_{FL}(l) - \delta \mu l, \]  
(1.20)

with \( \delta \mu \to 0^- \). Minimizing \( f(l) \) with \( V_{FL} \) given by Equation (1.15), one actually obtains the correct critical exponents in the MF and WFL regimes. However, this ansatz fails in the IFL and SFL regimes \[45\]. In these regimes, fluctuations in many length scales affect the critical behavior while \( V_{FL}(l) \) only takes care of the long wavelength fluctuations. The most interesting example of systems in the SFL regime is the three-dimensional system with short-ranged interactions. For this system, linear renormalization group methods based on the effective interface model predict nonuniversal critical behavior\[33, 37, 46\]. Although this prediction has been confirmed by
numerical work on the same model[47], simulations of an Ising model only find mean-field behavior[48]. This discrepancy is still not fully understood.

For complete wetting[49], the three fluctuation regimes are equivalent leaving only two regimes, i.e., the mean-field (MF) regime and the fluctuation (FL) regime. In the MF regime the direct interaction \( V_W(l) \) dominates for large \( l \), while in the FL regime \( V_{FL}(l) \) dominates for large \( l \). Assuming for large \( l \) the direct interaction has the form

\[
V_W(l) = W/l^p, \tag{1.21}
\]

one has the effective interface free energy per unit area as

\[
f(l) = V_W(l) + V_{FL}(l) - \delta \mu l = W/l^p + W_{FL}/l^\tau - \delta \mu l. \tag{1.22}
\]

Minimizing \( f(l) \) with respect to \( l \), one obtains

\[
l \sim (-\delta \mu)^{\beta_s}, \tag{1.23}
\]

where

\[
\beta_s = \begin{cases} 
-1/(p + 1), & \text{for } p < \tau, \text{ MF regime} \\
-/(1 + \tau), & \text{for } p \geq \tau, \text{ FL regime}
\end{cases} \tag{1.24}
\]

is the critical exponent for the divergence of the film thickness as complete wetting is approached, i.e, \( \delta \mu \to 0^- \). Since \( \tau = 2(d - 1)/(3 - d) \) for thermal fluctuations, one has the FL regime only for short-ranged direct interactions in \( d = 3 \); but in \( d = 2 \), all direct interactions with \( p \geq 2 \) belong to the FL regime.
1.4 Outline

Besides this chapter and Chapter V which contains some concluding remarks, the main body of this dissertation consists of three chapters. In Chapter II, we study dynamical roughening in the process of crystal growth using the standard Metropolis Monte Carlo method. A conjecture is made to construct the relation between the Monte Carlo ‘time’ and the real time, which enables us to systematically calculate the crystal growth rates in different growth regimes. The simulated growth rates are fit to various theoretical predictions. The step energy is extrapolated from the low temperature growth rates and found consistent with the Kosterlitz-Thouless prediction. We also find that the roughening transition is dynamically blurred as in an experiment\[50\] on the growth of $^4$He crystals.

In Chapter III, we investigate the growth of wetting films in the case of non-conserved order parameter. We first introduce the predictions of the effective interface model based on a simple Langevin equation. A Solid-on-Solid model is then designed to simulate the growth using the Monte Carlo method with Glauber dynamics. We study the film-growth laws for a variety of substrate potentials. We find the simulated growth laws are in full agreement with the predictions of the effective interface model. We also study the dynamical behaviors of the unbinding interface in the process of film growth.

In Chapter IV, we investigate the growth of wetting films in the case of
a conserved order parameter (diffusion-limited growth). As in Chapter III, the predictions of the effective interface model are introduced first. Then we apply an Ising lattice-gas model to simulate the growth using the Monte Carlo method with Kawasaki dynamics. The growth laws for various substrate potentials are studied and found in agreement with the predictions of the effective interface model.
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CHAPTER II

Dynamical roughening and crystal growth

2.1 Introduction

The properties of solid-fluid interfaces are very important in understanding the mechanisms and processes of crystal growth as well as the morphology of crystals\[1\]. The structure of the solid-fluid interface directly controls the growth mechanism, thus determining how the growth rate depends upon the driving force and temperature[2]; moreover, the interfacial tension plays an important role in determining the stability of the solid-fluid interface and the formation of various patterns such as dendrites[3].

It was first recognized by Burton et al [4] that a solid-fluid interface may undergo a roughening transition at a finite temperature $T_R$. Above the roughening transition temperature $T_R$, the interface is atomically rough; below $T_R$, the interface is flat. Due to this structural difference, the crystal growth mechanism is accordingly divided into three regimes: (1) the two-dimensional nucleation regime below $T_R$, (2) the continuous growth regime above $T_R$, and (3) a crossover regime for $T \approx T_R$. 

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Much of the theoretical understanding of the mechanism of crystal growth is based on the kinetic solid-on-solid (SOS) model. In this model, each lattice site is either vacant or occupied by a single atom; every occupied site must be directly above another occupied site, thus excluding overhangs and voids. The crystal growth is a result of interplay between evaporation and deposition. The deposition rate $k_+$ is assumed to be independent of the neighboring surface configuration.

$$k_+ = k_{eq} \exp(\frac{\delta \mu}{k_B T}) \quad (2.1)$$

where $k_{eq}$ is the equilibrium deposition rate; $\delta \mu$ is the difference of the chemical potential from the equilibrium value; $k_B$ is Boltzmann’s constant; and $T$ is the temperature. The evaporation rate of an atom at the surface with $m$ lateral neighbors is assumed to be

$$k_m = \nu \exp(-m \phi/k_B T) \quad (2.2)$$

where $\nu$ is the evaporation rate of an isolated atom at the surface, and $\phi$ is the strength of the atomic bond. With these assumptions, the growth dynamics is described by a set of kinetic equations[2]. However, so far no exact solutions of these equations have been achieved; results are only obtained[5, 6, 7] analytically under mean-field-type approximations which usually are only valid for high temperatures and large driving forces, or numerically by real-time kinetic Monte Carlo (MC) simulations using Equations (2.1) and (2.2). The best analytical result was achieved by Weeks et al[7] under the two-rate approximation in the continuum limit. This so called two-rate model predicts
the growth rate as

\[ \frac{R}{k} = \frac{2\sinh(\delta \mu / k_B T)}{\exp(\delta \mu / k_B T) + \cosh(\alpha \phi / k_B T)}. \]  

(2.3)

where \( \alpha, \) with values in the range of \( 0 \sim 2, \) is an empirical parameter which is generally a function of the temperature and driving force. As \( \phi / k_B T \to 0, \) in particular, if \( \phi = 0, \) Equation (2.3) correctly converts to the expected Wilson-Frenkel[8] rate

\[ \frac{R_{WF}}{k} = 1 - \exp(-\delta \mu / k_B T). \]  

(2.4)

Note that for small driving force \( \delta \mu \to 0, \) Equation (2.4) predicts linear growth, i.e., \( R_{WF}/k = \delta \mu / k_B T. \)

At low temperatures, the crystal surface is flat and growth can only occur via two-dimensional nucleation[9] of atomic clusters at the surface. Since the nucleation rate is proportional to \( \exp[-C(3\beta^2/(k_B T \delta \mu)] \), where \( \beta \) is the step energy, and \( C \) is a constant, the crystal growth rate for small driving force \( \delta \mu \) is modified to

\[ \frac{R}{k} \sim \frac{\delta \mu}{k_B T} \exp[-C \beta^2/(k_B T \delta \mu)]. \]  

(2.5)

More detailed studies[10] predict a growth rate given by

\[ \frac{R}{k} \sim \left(\frac{\delta \mu}{k_B T}\right)^{1/2} \exp[-\pi \beta^2/(3k_B T \delta \mu)]. \]  

(2.6)

Gilmer et al[11] have performed real-time kinetic Monte Carlo simulations at low temperatures and shown that Equation (2.6) fits the data nicely; however, they didn’t check the exponent \( \frac{5}{6} \) quantitatively.
In this chapter, using a Solid-on-Solid model with standard Metropolis Monte Carlo simulations, we shall systematically study the growth in various regimes emphasizing the crossover regime. The direct motivation is the experiments done by Gallet et al[12] and Wolf et al[13] in which they studied the growth of $^4$He crystals from the saturated fluid. They found that the roughening transition is blurred as a consequence of dynamical effects, and low temperature growth rates fit Equation (2.5) better than Equation (2.6). It is also one of our goals to explore the possibility of applying standard MC methods to investigate dynamical quantities.

The Metropolis Monte Carlo (MC) method has been widely used[15] to study equilibrium properties, especially phase diagrams, structures, and transitions, of thermodynamic systems. It is also very useful for the simulation of kinetic phenomena such as phase separation[16]. However, because of the unknown relation between the Monte Carlo "time" and the real time, the method is difficult to employ in a study of the temperature dependence of dynamical quantities.

By comparing the simulated growth rate at zero interparticle coupling (i.e, $\phi = 0$) with the Wilson-Frenkel[8] growth rate which is valid under this condition, we are able to determine how an interval of the real time $t$ and an interval of the Monte Carlo time $\tau$, measured in Monte Carlo steps per site (MCS), are related at each value of the temperature $T$ and the chemical potential $\delta \mu$. To the extent that the relation between $t$ and $\tau$ is not significantly altered when the interparticle coupling is introduced, and this
is the essential assumption in our work, we are then able to calculate from MC simulations such dynamical quantities as the $T$ and $\delta \mu$ dependence of the crystal growth rate. The simulations are simple to perform and we are able to study the growth in various regimes systematically.

We shall describe our model and the manner in which the MC time is related to the real time in Section (2.2); Section (2.3) contains results and comparison with theory and experiment; and Section (2.4) is a summary.

2.2 Model and Monte Carlo Methods

We employ[17] a solid-on-solid model with nearest-neighbor coupling $J (J > 0)$ on a two-dimensional square lattice of size $L \times L$, lying parallel to the crystal surface; $h_i$ measures the height of the crystal at site $i$, and $h_i$ can be any integer. The Hamiltonian is

$$H = J \sum_{<i,j>} |h_i - h_j| - \sum_i \delta \mu h_i$$

(2.7)

where $<i,j>$ denotes that the sum is over nearest-neighbor pairs of sites. The first term in the Hamiltonian is the energy contribution of atomic bonds broken by the interface; the second term is due to the chemical potential which provides the driving force that causes the $h_i$'s to increase for $\delta \mu > 0$; in equilibrium[18], $\delta \mu = 0$. This model is the extreme anisotropic limit of an Ising lattice gas model with lateral bond-strength $\phi = 2J$; overhangs of the interface are neglected[2]. The roughening temperature for this model[19] is $T_R \simeq 1.24J/k_B$. 
We use the standard Metropolis MC method with Glauber dynamics[20] to simulate the crystal growth. All simulations are done at fixed temperature and (positive) chemical potential. The initial condition is $h_i = 0$ for all $i$. To obtain smooth values for the rate of growth, we average over about 20 runs in each case. The lattice size $L$ is typically 20 to 40. Periodic boundary conditions are applied in the lateral directions.

After giving the initial condition, the simulation process goes as:

(a) A site $i$ is selected at random, and then a decision is made, based on the value of a random number on $[0,1]$ relative to $1/2$, whether to attempt an increase or a decrease in the height $h_i$ by one unit.

(b) The attempted change is accepted with a probability (choice 1)

$$\omega = \frac{1}{2}[1 - \tanh(\delta H/2k_B T)] \quad (2.8)$$

or (choice 2)

$$\omega = \begin{cases} 
\exp(-\delta H/k_B T) & \text{if } \delta H > 0 \\
1 & \text{otherwise}; 
\end{cases} \quad (2.9)$$

$\delta H$ is the change of $H$ produced by the attempted change in $h_i$.

(c) Repeat (a) and (b).

A cycle of (a) and (b) is called a Monte Carlo step. The Monte Carlo time $\tau$ is defined as the number of Monte Carlo steps per site (MCS).
The location of the interface is found from the height \( \Gamma \) of the crystal surface,
\[
\Gamma(\tau) = (1/N) \sum_i h_i(\tau)
\]  
(2.10)
where \( N = L^2 \) is the number of sites in the lattice. The crystal growth rate \( R_\tau \) in Monte Carlo time \( \tau \) is simply the derivative of \( \Gamma \) with respect to \( \tau \),
\[
R_\tau = d\Gamma/d\tau,
\]  
(2.11)
which is, after an initial transient regime, a constant for given \( T \) and \( \delta \mu \).

To convert \( R_\tau \) to the real growth rate in physical time \( R_t \), defined by
\[
R_t = d\Gamma/dt,
\]  
(2.12)
we have to understand the relation between \( \tau \) and \( t \). It is well-known\cite{21} that for an Ising-like system
\[
\tau = f(\delta \mu, T)t,
\]  
(2.13)
although knowledge about \( f(\delta \mu, T) \) is very limited. At \( J = 0 \) we compare the growth rate from simulations to the Wilson-Frenkel rate\cite{8}
\[
R_{wf} = k_+ (1 - e^{-\delta \mu/k_B T}).
\]  
(2.14)
The latter should be exactly \( R_t \) in this limit, and thus we may extract \( f(\delta \mu, T) \) from the comparison. In Equation (2.14), \( k_+ = k_{eq} \exp(\delta \mu/k_B T) \) is the deposition rate in the kinetic SOS model; \( k_{eq} = \nu \exp(-4J/k_B T) \) is the equilibrium (\( \delta \mu = 0 \)) deposition rate, with \( \nu \) constant. Thus we find \( f(\delta \mu, T) \) in the \( J = 0 \) limit from
\[
R_{wf} = f(\delta \mu, T)R_\tau
\]  
(2.15)
The MC procedure is not the real dynamical process as is clear from the fact that the choice of $\omega$ is not unique. To ensure that the procedure produces the true equilibrium thermodynamic state of the system, $\omega$ has to obey the detailed-balance condition[20]. Both recipes for $\omega$ given by Equations (2.8) and (2.9) have this property and both are frequently employed in simulations; the first is often used for kinetic properties and the second for equilibrium properties. In order to find the real temperature dependence of dynamical quantities one must know in each case how the MC time is related to the real time. For both choices of $\omega$, we obtain these relations in the limit $J = 0$. The crucial assumption in our work is that, for a given choice of $\omega$, when a non-zero interparticle coupling is introduced, the effect on the relation between $t$ and $\tau$ is not sufficient to be of any consequence for our results. The validity of this assumption is supported by the agreement of our simulations with earlier works[7]. The detail of the simulated results will depend upon the choice of $\omega$ which specifies the physical kinetics. To test this, we have done simulations using $\omega$ as given by Equations (2.8) and (2.9). The two sets of predictions do differ quantitatively, but in all qualitative aspects described in our results there is no difference. Specific examples are given in the next Section.
2.3 Results and discussion

As discussed before, the relation between \( t \) and \( \tau \) is determined by comparing the simulated growth rate at zero coupling to the Wilson-Frenkel rate. For \( J = 0 \), one can easily calculate \( R_\tau \) for any choice of \( \omega \). In particular, for choice 1, Equation (2.8) of \( \omega \) it is

\[
R_\tau = \frac{1}{2} \frac{e^{\delta \mu/k_BT} - 1}{e^{\delta \mu/k_BT} + 1},
\]

(2.16)

and for the second choice,

\[
R_\tau = \frac{1}{2}(1 - e^{-\delta \mu/k_BT}).
\]

(2.17)

Use of Equations (2.14) and (2.15) immediately gives, for choice 1,

\[
f(\delta \mu, T) = 2k_+(1 + e^{-\delta \mu/k_BT})
\]

(2.18)

The factor of two is a consequence of the fact that in the simulations we attempt an increase (as opposed to a decrease) of a column height in one-half of the attempted moves. For Choice 2 we find

\[
f(\delta \mu, T) = 2k_+.
\]

(2.19)

We shall now use these forms of \( f(\delta \mu, T) \), i.e., Equation (2.18) or (2.19) to determine the growth rates \( R_t \), with \( J \neq 0 \), from the corresponding simulated growth rate \( R_\tau \). Note that through \( k_+ \), \( f(\delta \mu, T) \) is actually dependent on \( J \), although not formally. We shall discuss our results in terms of the real growth rate \( R_t \), so we drop the subscript on \( R_t \) from hereafter; \( R_t \) always denotes \( R_t \).
We first investigate the dependence of $R$ on the choice of $\omega$. In Figure 2.1 we show $R/k_+ vs. k_B T/J$ for $\delta \mu/J = 2.0$ and 0.7 using $\omega$ given by both Equation (2.8) and Equation (2.9). The general behavior of $R$ for a given $\delta \mu$ is the same in both cases, although there are differences for the larger $\delta \mu$, in particular, when $T$ is somewhat above the roughening temperature. In fact, in all comparisons we have done, this is the regime of $\delta \mu$ and $T$ where the difference between the two predictions is the largest, about 25%.

The only qualitative difference we have found appears for $\delta \mu/J = 2$, but at temperatures well below $T_R$; here, there appears to be a cusp in the curve showing $R/R_{WF}$ as a function of $\delta \mu/J$ for the second choice of $\omega$, but not for the first. We suspect that this is a consequence of the nonanalytic behavior of this particular $\omega$ at $\delta H = 0$. Our belief is that of the two choices, the first is more physically appropriate at least in the sense that it gives non-zero probability to not accept a configuration change with $\delta H = 0$; nevertheless, our simulations show no significant qualitative difference between the results from the two choices of $\omega$, aside from the one just described. All of the results that follow were obtained using Equation (2.8) for $\omega$ and, of course, Equation (2.18) for $f$.

Figure 2.2 shows $R/k_+$ as a function of $\delta \mu/k_B T$ for several different fixed temperatures $k_B T/J = 2.0$, 1.3, 1.0, and 0.7. Also shown is the Wilson-Frenkel growth rate which should obtain in the high temperature limit. The other solid lines are fits of the two-rate model[7] to the simulations. This
Figure 2.1:

The simulated growth rate $R/k_+$ is plotted against $k_B T/J$ for $\delta \mu/J = 2.0$ (×), 0.7 (+) from choice 1 of $\omega$, and for $\delta \mu/J = 2.0$ (●), 0.7 (□) employing choice 2 for $\omega$. 
Figure 2.2:

The simulated growth rate $R/k_+$ is plotted against $\delta\mu/T$ for $k_B T/J = 2.0$ ($\times$), 1.3 ($+$), 1.0 ($*$), and 0.7 ($\square$). Also shown (solid lines) are fits of the two-rate model of Reference [7] to the simulations and the Wilson-Frenkel growth rate.
model predicts

\[ R/k_B = \frac{2\sinh(\delta\mu/k_BT)}{e^{\delta\mu/k_BT} + \cosh(2\alpha J/k_BT)}. \]  

Although \( \alpha \) should generally be a function of \( T \) and \( \delta\mu \), we have chosen \( \alpha = 1.57 \) so that the simulated value at \( \delta\mu/k_BT = 2.0 \) for \( k_BT/J = 1.3 \) agrees with Equation (2.20). Our results are in good agreement with simulations of the kinetic SOS model in Reference [7] where a similar fit to the two-rate model was also done. The quantitative discrepancy in the low temperature and low driving force region is not surprising since Equation (2.20) is derived under the continuum approximation. The consistency of our results with earlier work further supports the validity of the way \( f(\delta\mu, T) \) is established.

The reduced rate \( R/R_{Ref} \) is shown in Figure 2.3 for \( \delta\mu/J = 2.0, 0.7, \) and 0.05. For the smallest \( \delta\mu \), the reduced rate quickly increases around the roughening temperature \( T_R = 1.24J/k_B \) from nearly zero to a large value. As the driving force \( \delta\mu \) increases, this roughening effect is blurred and the regime with nearly zero reduced rate shrinks. At high temperature, the reduced rates for different \( \delta\mu \) fall on the same curve and finally go to 1, which implies that the crystal surface is essentially rough. These phenomena have been observed[12] in crystal growth experiments on \(^4\text{He}\) and studied using renormalization analysis[14] as clearly demonstrated in Figure 5 of Reference [12]. Regrettably, detailed comparison of experiment and simulations is not possible. The excess chemical potential in the experiments, expressed in our units, is around \( 10^{-5}J \). We are able to do simulations only for chemical potentials larger than about \( 0.05J \); for smaller ones, the growth rate is so
Figure 2.3:
The simulated reduced growth rate $R/R_{wf}$ is plotted against $k_B T/J$ for $\delta \mu/J = 2.0$ (□), 0.7 (+), and 0.05 (×).
small as to require unacceptably long runs.

Figure 2.4 displays the growth rate $R/k_+$ as a function of $\delta \mu /J$ for relatively small $\delta \mu$ at several temperatures ranging from above the roughening temperature to below $T_R$. As is well known, the growth rate behaves linearly above $T_R$ and nonlinearly at $T < T_R$ where the growth mechanism is described by 2D nucleation[2].

The low temperature growth rate is fit to the two-dimensional nucleation theory[10]. For small $\delta \mu$, this theory predicts

$$R/k_+ \sim g(\delta \mu) e^{-C \beta^2/(k_B T \delta \mu)}$$

(2.21)

where $\beta$ is the step energy, $C$ is a constant, and $g(\delta \mu) \sim \delta \mu^\theta$ with $\theta = 5/6$. Figure 2.5 displays plots of $\ln[(RJ^\theta)/(\delta \mu^\theta k_+)]$ vs. $J/\delta \mu$ at $T = 1.05J/k_B$ for $\theta$ equal to both $5/6$ and $1$, a value obtained by simply modifying the Wilson-Frenkel theory with the nucleation rate which is proportional to $\exp[-C \beta^2/(\delta \mu k_B T)]$. On the basis of this figure, and similar ones at other temperatures, it appears that the simulations better fit $\theta = 1$. Also, from the slopes of these lines and Equation (2.21), we can determine the step energy. We find that if we assume $\theta = 5/6$, the step energy does not approach zero as $T \rightarrow T_R$ but rather remains finite at considerably higher temperatures. For $\theta = 1$, on the other hand, the step energy does go to zero as $T$ approaches $T_R$. Thus our results are clearly more consistent with $\theta = 1$. The same is true of the experiments on the growth of $^4\text{He}$ crystals[12, 13]. In Figure 2.6, using $\theta = 1$, we plot $-\ln(\beta/J)$ vs. $(1-T/T_R)^{-1/2}$ assuming $T_R = 1.24J$. The points for $T$ close to $T_R$ can be reasonably fit to a straight line, in agreement
Figure 2.4:

The simulated growth rate $R/k_+$ is shown as a function of $\delta \mu/J$ for $k_B T/J = 2.0$ (×), 1.3 (+), and 1.0 (□) for relatively small driving force $\delta \mu$. 
Figure 2.5:
We plot simulated values of $\ln\left(\frac{R}{k}\right)\left(\frac{J}{\delta\mu}\right)^\theta$, for $\theta = 5/6$ (□) and 1 (×), against $J/\delta\mu$ at $k_B T = 1.05 J$. The straight line is a least squares fit to the simulations.
Figure 2.6:
The negative logarithm of the step energy in units of $J$, inferred from the simulations and Equation (2.21) with $\theta = 1$, is plotted against $(1 - T/T_R)^{-1/2}$; the straight line serves as a guide to the eye.
with the prediction of Kosterlitz-Thouless theory[22], which is appropriate for the two-dimensional SOS model[23],

\[ \beta \sim e^{-D(1-T/T_R)^{-1/2}}; \]  

(2.22)

where D is a constant independent of T.

2.4 Summary

In this Chapter we have presented results from Monte Carlo simulations of crystal growth, both above and below the roughening temperature, using a two-dimensional solid-on-solid model with Glauber dynamics. The simulations may be compared with real crystal growth provided one knows the relation between the Monte Carlo time (Monte Carlo steps per site) and the real time. This relation will naturally depend on the recipe one uses to determine whether an attempted Monte Carlo step is accepted. We have considered two standard choices, Equations (2.8) and (2.9), and have extracted relations between the times, given by Equations (2.18) and (2.19), by comparing the growth rate which would emerge from simulations of the SOS model with zero inter-column coupling with the Wilson-Frenkel growth rate. We then assumed that these relations remain valid also for \( J \neq 0 \). This idea was tested by comparing results for \( R \) (with \( J \neq 0 \)) using both choices of \( \omega \), cf. fig. 1. Although the results in the two instances are not the same, the differences are in general neither large nor qualitative. Results reported were achieved using primarily the first choice of \( \omega \), although the
second choice was also employed to make certain that the results are not significantly different.

We have compared our simulated growth rates with the two-rate theory of Weeks et al and the real-time kinetic MC simulations[7], and found that the results are in good agreement. Our simulations also show that the roughening transition is increasingly blurred by dynamical effects. This behavior was observed in experiments[12] on the growth of solid $^4$He and found in the related renormalization analysis of Nozières and Gallet[14]. However, quantitative comparison with these experiments is not possible because of computer time limitations. The simulated growth rates at low temperatures are fit to the two-dimensional nucleation theory[10]. We find (in agreement with the experiments[12]) that the dependence of $R$ on the chemical potential is slightly different from the prediction. Finally, from the comparison with nucleation theory, we have extracted the step energy of the model as a function of temperature and found that for $T \to T_R$ from below, it varies roughly as $(1 - T/T_R)^{-1/2}$, the prediction of Kosterlitz-Thouless theory[22] which is appropriate for the SOS model in two dimensions[23].
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CHAPTER III

Wetting film growth with non-conserved order parameter

As discussed in Chapter 1, the equilibrium properties of wetting and wetting transitions have been widely studied and quite well understood. Recently, increasing efforts have been made to study the dynamical aspects of these phenomena[1]. Two specific problems are investigated: (a) the spreading of liquid drops on liquid or solid surfaces[2, 3], and (b) the growth of wetting films. Both can be viewed as processes tending toward equilibrium, although they start with different initial configurations. These dynamical problems are interesting and important since, besides being relevant to many natural phenomena, the understanding of them serves as a guide for experimentalists to determine whether the systems under consideration have reached equilibrium states[4].

In this dissertation, we shall only discuss the problem of wetting film growth. We are interested in the manner in which the thickness of wetting films increases from its original small value. These growth laws will depend upon the substrate potentials as well as the conservation laws characterizing
the systems. Strictly speaking, the growth processes are controlled by many different modes, such as various hydrodynamic modes, acting on different time scales. Unfortunately, a treatment including all these modes is too difficult and some simplifications have to be made. We shall assume that the growth is dominated by the relaxation of the free energy of the system. We shall first discuss the growth of wetting films with non-conserved order parameter in this Chapter; the growth with a conserved order parameter will be discussed in Chapter 4. We address two questions: (1) How does the growth law depend upon the substrate potentials; (2) what is the effect of fluctuations?

In Section 3.1, we present the predictions of the growth laws from the effective interface model with Langevin dynamics. In Section 3.2, a solid-on-solid (SOS) model is designed to study the growth using Monte Carlo (MC) simulations with Glauber dynamics. The simulation results are presented and discussed in Section 3.3. Section 3.4 is a summary.

3.1 Predictions of the effective interface model

With a non-conserved order parameter, the Langevin[5] equation is appropriate to describe the approach toward equilibrium[6, 7, 8]; one has

\[
\frac{\partial l}{\partial t} = -\lambda \frac{\delta H\{l\}}{\delta l} + \xi, \tag{3.1}
\]
where $\lambda$ is an Onsager coefficient, $H[l]$ is given by Equation (1.10), and $\xi$ is a Gaussian random force with $\langle \xi \rangle = 0$ and

$$< \xi(x, t)\xi(x', t') > = 2\lambda \delta(x - x')\delta(t - t').$$  \hfill (3.2)

If fluctuations are effectively described by the fluctuation-induced potential $V_{FL}(l)$, then one has

$$\frac{\partial l}{\partial t} = -\lambda \frac{\partial f(l)}{\partial l},$$  \hfill (3.3)

where $f(l)$ is the effective interface free energy per unit area given by Equation (1.20). Solving Equation (3.3) one obtains for $\delta\mu = 0$,

$$l(t) \sim t^{\frac{3}{2\alpha + 2}}, \text{ with } \alpha = \min(\tau, p).$$  \hfill (3.4)

Thus, while reaching complete wetting, the film grows with a power law. For thermal fluctuations, $\tau = 2(d - 1)/(3 - d)$, and so one has

$$l(t) \sim t^\theta,$$  \hfill (3.5)

where $\theta$ is explicitly given by

$$\theta = \begin{cases} 1/(p + 2) & \text{for } d > d^*(p), \text{ MF regime}, \\ (3 - d)/4 & \text{for } d \leq d^*(p), \text{ FL regime}; \end{cases}$$  \hfill (3.6)

$d^*(p) = (3p + 2)/(p + 2)$ is the upper critical dimension[9]. In the mean field (MF) regime, the substrate potential $V(h)$ dominates thermal fluctuations and controls the film growth. For $d = 3$, we have this regime for any $p < \infty$. In $d = 2$, we have this regime for $p < 2$. In the fluctuation (FL) regime, fluctuations dominate the effects of the substrate potential and produce a
universal exponent which only depends upon the dimensionality of the system. Given short-ranged substrate potentials, we are in the FL regime for both $d = 2$ and 3. For $d = 2$, $\theta = 1/4$; for $d = 3$, $\theta \to 0$, the film grows with $l(t) \sim \ln t$.

For $\delta \mu < 0$, the substrate can only be partially wet. Solving Equation (3.3), one has

$$l(t) \sim l_{eq} - C \exp(-At),$$

so the film reaches its finite equilibrium thickness exponentially.

Note that the effective interface model is a coarse-grained model derived under the step-kink assumption in which the internal structure of the un-binding interface is ignored and the fluctuations are only effectively taken into account by $V_{FL}(l)$. It is worthwhile to study a more microscopic model which will naturally include the neglected ingredients; this is the task of the remainder of this Chapter.

### 3.2 Model and simulation method

#### 3.2.1 The solid-on-solid (SOS) model

We employ\(^{10, 11}\) a solid-on-solid model with nearest-neighbor coupling $J$ on a $(d - 1)$-dimensional square lattice lying parallel to the surface of the substrate; $J > 0$, and $d = 2$ or 3. At any site $i$ of the lattice there is a column of adsorbate atoms of height $h_i = 0, 1, 2...$ so that $h_i$ is the thickness of the
adsorbed film at that site. The Hamiltonian is

\[ H = J \sum_{\langle i,j \rangle} |h_i - h_j| + \sum_i [V(h_i) - \delta \mu h_i] \]  

where \( \langle i,j \rangle \) denotes that the sum is over nearest-neighbor pairs of sites; \( V(h) \) is the adsorbate-substrate interaction energy for a column of height \( h \); \( \delta \mu \) is the chemical potential difference from the bulk two-phase coexistence value. The first term on the right side of Equation (3.8) represents the energy cost for the interface to deviate from its average position; the sum over \( V(h_i) \) is the contribution of the substrate. Since we are interested in the dynamics of complete wetting which happen when the two-phase coexistence curve is approached, we shall take \( \delta \mu = 0 \). Obviously, excitations such as bubbles in the bulk phases and overhangs of the interface are neglected in this model.

We investigate two types of substrate potential. The first, which we call short-ranged, is simply zero everywhere,

\[ V(h) = 0, \]  

while the second is algebraic for \( h > 1 \),

\[ V(h) = \begin{cases} 7.85J & \text{if } h = 0 \\ 4.2J/h^p & \text{if } h > 0. \end{cases} \]  

The specific cases of \( p = 1, 2, \) or \( 3 \) are used extensively; In \( d = 3 \), \( p \) equal to 2 or 3 corresponds respectively to the nonretarded or retarded van der Waals interaction. Note that \( h_i \) is not allowed to be negative; this is equivalent to having a hard wall potential for \( h_i < 0 \). Temperatures used in the simulations
are, in the case of short-ranged $V(h)$, $T = 0.8J/k_B$ and $2.0J/k_B$ for $d = 2$ and $T = 1.6J/k_B$ and $4.0J/k_B$ for $d = 3$; $k_B$ is the Boltzmann constant. In the case of algebraic $V(h)$, we employ $T = 1.6J/k_B$ for $d = 3$ and $T = 1.0J/k_B$ for $d = 2$. Given the potentials used here, there is complete wetting at $T > 0$ in all cases. Also, for $d = 3$ there is a roughening transition at a temperature\[12\] $1.24J/k_B$ which is considerably less than the lowest temperature ($1.6J/k_B$) employed for simulations. Hence there are no complications arising from metastability associated with first-order layering or wetting transitions.

### 3.2.2 Monte Carlo method with Glauber dynamics

The standard Metropolis Monte Carlo method\[13\] with Glauber dynamics\[14\] is employed to simulate the growth of the wetting film, starting with initial conditions $h_i = 0$ for all $i$. The simulation process goes as

(a) Randomly choose a site $i$, then decide with equal probability whether to attempt an increase or a decrease in the height $h_i$ by one unit.

(b) The change of $h_i$ is accepted if a random number on $[0,1]$ is smaller than a probability

$$
\omega = \begin{cases} 
\exp(-\delta H/k_B T) & \text{if } \delta H > 0, \\
1 & \text{otherwise}; 
\end{cases} 
$$

where $\delta H$ is the change of $H$ due to changing $h_i$.

(c) Repeat (a) and (b) which compose a Monte Carlo step.
Individual runs are made with from $10^5$ to $3 \times 10^5$ Monte Carlo steps per site (MCS). For any given set of parameters, to reduce statistical fluctuations, the data are averaged over $N$ runs which are performed using different sets of random numbers. $N$ ranges from 30 to 300. The sizes of the lattice are $L^{d-1}$ with $L$ of 30, 100, 200, or 400 for $d = 2$ and 10, 14, 20, or 30 for $d = 3$. The quantity of primary interest is the coverage $\Gamma$, defined by

$$\Gamma(t) = L^{-d+1} \sum_i h_i(t).$$

(3.12)

Other quantities calculated are the intrinsic interface width $w(t)$ and the intrinsic interface profile $n(z, t)$. They are given by

$$w(t) = \sqrt{L^{-d+1} \sum_i [h_i(t) - \Gamma(t)]^2},$$

(3.13)

and

$$n(z, t) = L^{-d+1} \sum_i \theta(h_i(t) - \Gamma(t) - z)$$

(3.14)

where

$$\theta(x) = \begin{cases} 
1 & \text{for } x \geq 0 \\
0 & \text{for } x < 0.
\end{cases}$$

(3.15)

We shall compare our results to the predictions of the effective interface model. It must be kept in mind that in our simulations the size of the system is always finite while the predictions of the effective interface model are in the thermodynamic limit, i.e., for infinite systems. As we shall discuss in Section 3.3.3, for a finite system, the growth process will eventually revert to a one-dimensional random walker on a half-space ($h \geq 0$), leading to a
crossover to the diffusion-like behavior at longer times[15, 16]

\[ \Gamma(t) \sim t^{\frac{1}{2}} \quad (3.16) \]

### 3.3 Results and discussion

#### 3.3.1 Long-ranged substrate potentials

We first discuss our simulation results for long-ranged substrate potentials, \( V(h) \sim h^{-p} \) with \( p = 1, 2, \) and \( 3 \). In \( d = 3 \), we are always in the mean field (MF) regime where the growth exponent is expected to be \( \theta = 1/(p + 2) \).

Figure 3.1 is a plot of \( \ln(\Gamma) \) vs. \( \ln(t) \) for potentials with \( p=1, 2, \) and \( 3 \); also, \( T = 1.6J/k_B, \) \( L = 20, \) and \( \delta\mu = 0 \). From 30 to 90 runs of length \( 10^5 \) MCS are averaged to obtain each curve. With the exception of \( p = 3 \), all curves are fit well by straight lines of slope \( 1/(p + 2) \), consistent with the predictions; such lines are included in the figure to guide the eye. For \( p = 3 \), the expected \( t^{1/5} \) behavior is present for \( t \) not too large, but for the largest times the film grows at a rate consistent with some larger power of \( t \). As we shall discuss in Section 3.3.2, this is a finite-size effect signalling the crossover to \( t^{1/2} \) behavior at very long times.

The results in \( d = 2 \) are shown in Figure 3.2 where \( \ln(\Gamma) \) is plotted against \( \ln(t) \). The case of \( p = 1 \) is expected to be in the MF regime and to produce \( \Gamma \sim t^{1/3} \). The cases of \( p = 2 \) and \( 3 \) are expected to be in the FL regime and to produce \( \Gamma \sim t^{1/4} \). Comparison of the simulation results with lines of slope
Figure 3.1:
The logarithm of the coverage is shown as a function of the logarithm of the time for \( d = 3 \) and algebraic potentials with \( p = 1 \) \((N=30)\), \( 2 \) \((N=60)\), and \( 3 \) \((N=90)\), at \( T = 1.6J/k_B \) and with \( L = 20 \); \( t \) is in units of Monte Carlo steps per site (MCS). Lines of slope \( 1/3 \), \( 1/4 \), and \( 1/5 \) are also shown.
Figure 3.2:
The logarithm of the coverage is shown vs. the logarithm of the time for $d = 2$ and an algebraic potential with $p = 1$ ($N = 60$), $2$ ($N = 100$), and $3$ ($N = 120$), for $T = 1.0J/k_B$ and $L = 200$. Runs of $10^5$ MCS each are employed. Lines of slope $1/3$ and $1/4$ are also shown.
1/3 and 1/4 in Figure 3.2 shows that these expectations are justified.

### 3.3.2 Short-ranged substrate potentials

For short-ranged substrate potentials, we are in the fluctuation (FL) regime in both $d = 2$ and 3. Figure 3.3 presents $\ln(\Gamma)$ vs. $\ln(t)$ for $L = 200, d = 2$, $T = 2.0J/k_B$, and $2 \times 10^5$ MCS, averaged over 143 runs. There is a noticeable curvature in the data for $t < 2 \times 10^4$; at larger times the data approach a line of slope 1/4, which is the universal exponent in $d = 2$. Also, if $\Gamma$ is plotted against $t^{1/4}$, the result is a line without noticeable curvature for $t > 2 \times 10^4$ as opposed to plots of e.g. $\Gamma$ vs. $t^{1/3}$ or $t^{1/5}$.

In $d = 3$, the film is expected[6, 17] to grow as $\Gamma(t) \sim \ln(t)$. A typical set of data is shown in Figure 3.4 where we plot $\ln(\Gamma)$ vs. $\ln(t)$ for $L = 14$, $T = 4.0J/k_B$, and $3 \times 10^5$ MCS. 150 runs are averaged to obtain these results. If there is in fact a regime where $\Gamma \sim \ln(t)$, it is for $4 \leq \Gamma \leq 8$. This interval is shown in the inset to fig. 2 which presents $\Gamma$ vs. $\ln(t)$. The range of $\Gamma$ for which this behavior is present is sufficiently limited to prevent our claiming a definitive observation of it. For thicker films, $\Gamma > 20$, the behavior appears to be $\Gamma \sim t^{1/2}$, as one may see by fitting a straight line to the curve in Figure 3.4 at large $t$. A plot of $\Gamma$ vs. $t^{1/2}$ supports this conclusion. Similar phenomena have been observed by Mon et al[15] in their simulations of wetting film growth with a short-ranged substrate potential in $d = 3$ using an Ising model. The crossover to $t^{1/2}$ growth can be explained as a finite size effect.
Figure 3.3:

The logarithm of the coverage is shown vs. the logarithm of the time for \( d = 2 \) and a short-ranged \( V(h) \) at \( T = 2.0J/k_B \) with \( L = 200 \). Some 143 runs of duration \( 2 \times 10^5 \) MCS are averaged. A line of slope 1/4 is included.
Figure 3.4:

The logarithm of the coverage vs. the logarithm of time for $d = 3$ and short-ranged $V(h)$ at $T = 4.0J/k_B$ and with $L = 14$; 150 runs of duration $3 \times 10^5$ MCS are done to obtain these results. A line of slope $1/2$ is also given in the figure. The inset shows the coverage vs. $\ln t$ at short times for $L = 14$ and $N = 240$. 
3.3.3 Finite size effect

To demonstrate the crossover from the intrinsic growth rate to the size-limited growth rate, we show Figure 3.5 which is a plot of $\ln(\Gamma)$ vs. $\ln(t)$ for $d = 2$, $p = 3$, and $L$ of only 30. Lines of slope $1/4$ and $1/2$ are included to guide the eye. We clearly see the crossover from the expected $t^{1/4}$ behavior to the diffusion-like $t^{1/2}$ behavior.

This diffusion-like behavior at longer time is also observed in other cases when small sizes are used. It is a result of finite size effects[15, 16]. While the film is growing, the width of the unbinding interface also grows as we shall discuss in Section 3.3.4. At a long enough time, the interface width will saturate to the finite-size limited value $w \sim L^\zeta$. After the saturation, the interface can only fluctuate as a unit and so behaves like a one-dimensional random walker. Due to the broken symmetry induced by the substrate, the interface will move away from the substrate like a random walker with a displacement proportional to $(t/L^{d-1})^{1/2}$; where the size dependence enters because the effective mass of the interface is proportional to the area $L^{d-1}$. The crossover will happen when $t^\theta$ and $(t/L^{d-1})^{1/2}$ are of the same order, or when the film thickness is about $L^{2(d-1)/(1-2\theta)}$.

3.3.4 The unbinding interface

Now we turn to discuss the behavior of the unbinding interface, i.e., the interface between the growing wetting film and the existing bulk phase. Figure
Figure 3.5:
The logarithm of the coverage vs. the logarithm of the time for $d = 2$, $T = 1.0J/k_B$, and an algebraic potential with $p = 3$. The size of the system was $L = 30$, so that the crossover to the small $L$ regime may be seen; $N = 240$. Lines of slope $1/4$ and $1/2$ are also shown.
3.6 shows a log-log plot of the width $w(t)$ for three different cases of $V(h)$ given by Equation (3.9) with $p = 1$ and 2 and of $V(h) = 0$, along with a line of slope $\frac{1}{4}$. The three cases are separated in the figure by plotting $w, 2w$, and $4w$, respectively; in fact, the widths in all three cases are virtually indistinguishable. They all fit well a growth law $w \sim t^{\frac{1}{2}}$. The situation is distinctly analogous to that which arises in connection with the growth of $\Gamma$. Recall that in $d = 2$ one is in the fluctuation-dominated growth regime for $\Gamma$ when $V(h)$ falls off faster than $h^{-1}$, and that $\Gamma \sim t^{\frac{1}{4}}$ in this regime; for the width, we can see from the simulation results that the substrate potential plays no role in determining $w(t)$. Even the case in the mean-field growth regime for $\Gamma$, $p = 1$, shows the same behavior of $w$ as the case of $V(h) = 0$. Hence we are in all cases in the fluctuation-dominated growth regime for $w$. Finally, we note that the simulations are done using $L = 1000$, for which the size-limited width of the interface is about 12, cf. Figure 1 in Reference[11]; hence the results shown in Figure 3.6 are essentially in the $L \to \infty$ limit.

The profiles of the interface between the growing films and the bulk phase are shown for the case of $p = 1$, at times $t = 1, 10, 100, 500, \text{ and } 1000$, in units of 100MCS, in Figure 3.7. In each instance the profile is fit by an error function,

$$ n(z) = \frac{1 - erf(z/\sqrt{2}w)}{2}, \quad (3.17) $$

using the value of $w(t)$ inferred from the simulations. $erf(x)$ is the error function, c.f. Equation (1.4). One can see from the figure that the profile appears to be fit quite well by this function. The conclusion that may be
Figure 3.6:
In $d = 2$, the logarithms of $w$, $2w$, and $4w$, respectively, are plotted against the logarithm of $t$ for $V(h) \sim h^{-p}$ with $p=1$ and $2$ and for $V(h) = 0$; we have used $L = 1000$, and $T = 1.0J/k_B$. A line of slope $\frac{1}{4}$ is included for comparison.
Figure 3.7:

For $d = 2$, we plot the density $n(z,t)$ of growing wetting films against $z$. The substrate potential is of the form $V \sim h^{-1}$; $T = 0.5J/k$, $L = 400$, and $t = 1$ ($\Box$), 10 ($\triangle$), 100 ($+$), 500 ($\times$), and 1000 ($\ast$), in units of 100MCS. The solid lines show the error function profiles, Equation (3.17), using values of $w$ taken from the simulations.
drawn is that the profile attains its eventual equilibrium form, if not its
width, quite early during the film growth process. The profiles for the other
cases treated behave in the same manner.

To further understand these behaviors, let us review some of the dynamical
properties of a free interface. At temperatures above the roughening
temperature, the width of an initially flat interface \( w(t) \) will grow to its
equilibrium value which is infinite in the thermodynamic limit due to long
wavelength fluctuations. Desai and Grant[18] have used fluctuating hydrody-
namics to show that the width of a liquid-vapor interface in such a situation
should grow as \( \ln^{\frac{3}{2}}(t) \) in three dimensions; their argument applied to the case
of two dimensions gives \( w \sim t^{1/4} \). More recently, Abraham and Upton[19]
have solved the Langevin equation of a Gaussian model exactly and found
the same growth law before the interface width exponentially saturates to
its finite size limited value; moreover, the interface profile is described by an
error-function (cf. Equation (1.3)) with \( w \) given by the nonequilibrium value.
Therefore, it is clear that the observed behavior of the unbinding interface
is just like that of a freely fluctuating interface; as the film grows and the
interface moves far away from the substrate, the substrate potential has no
effect on the intrinsic structure of the unbinding interface. The reason is
probably that the energy cost induced by the substrate potential is of order
\( (w/\Gamma)^2 V(\Gamma) \) while that due to the surface tension is of order \( \Sigma (w/L)^2 \); the
later always dominates as \( w \) grows (driven by entropy increase) with increas-
ing \( t \), regardless of the form of \( V(l) \) as long as it is repulsive. Indeed, even for
a potential of the form $V(l) \sim l$ as in the case of crystal growth, simulations show the interface still has the same behavior.

In three dimensions, the width of the interface is very small, the size-limited width being of order unity, and our simulations of the interface are not very informative regarding the rate at which $w$ grows. For example, we show in Figure 3.8 $w$ as a function of $\sqrt{\ln t}$ for $L = 100$, $T = 1.6J/k$, and substrate potentials $V(h) \sim h^{-1}$ and $V(h) = 0$. Notice that at long times the width saturates to the size-determined value. On the basis of the simulations, we can say that $w(t)$ appears to grow no faster than some nominal power of the logarithm of $t$, given the potentials we have used. Hence our results are at least consistent with the theoretical prediction[18], although other interpretations are no doubt equally possible. We tentatively conclude that $w$ grows at the appropriate rate for the fluctuation regime in three dimensions. Results found using other potentials, e. g., $V(h) \sim h^{-2}$, are no different.

Figure 3.9 shows the profiles of the growing films for $d = 3$ at times 1, 10, 100, 500, and 1000 in units of 10MCS for $L = 50$. The solid lines are the error function profile with widths of 0.64, 0.88, 1.01, 1.08, and 1.08, respectively; the width has saturated to the size-limited value at the longer times.
Figure 3.8:

In $d = 3$, $w$ is plotted against $ln^{\frac{1}{2}}(t)$ for growing wetting films at $L = 100$ and $T = 1.6J/k$ for $V \sim h^{-1}$ and $V(h) = 0$. 
Figure 3.9:

For $d = 3$ we plot the profiles $n(z, t)$ of growing wetting films against $z$. The substrate potential is of the form $V \sim h^{-1}$; $T = 1.6J/k$, $L = 50$, and $t = 1$ (□), 10 (∆), 100 (+), 500 (×), and 1000 (*), in units of 10MCS. The solid lines show the error function profiles using values of $w$ taken from the simulations.
3.4 Summary

We have studied the growth of wetting film at complete wetting in both $d = 2$ and 3 for various substrate potentials. Our simulation results of a solid-on-solid model support the predictions of the Langevin dynamics of the effective interface model[6]. The substrate potentials used in the simulations are of the forms $V(h) \sim h^{-p}$ with $p = 1, 2, \text{ and } 3$, and $V(h) = 0$. The cases $p = 2$ and 3 in three dimensions especially are of physical interest as they correspond respectively to the van der Waals and retarded van der Waals potentials. The film thickness $\Gamma(t)$ is found to vary at long enough times as $t^\theta$ where $\theta = 1/(p + 2)$ in the MF regime, and $\theta = (3 - d)/4$ in the FL regime. For the FL regime in $d = 3$, we are unable to employ a large enough system to find unambiguously the claimed $ln(t)$ behavior for $L \rightarrow \infty$, but there is certainly some evidence that it is present, as in the simulations of Mon et al[15], for relatively short times. For a finite size system, there is a crossover at longer time to the diffusion-like growth regime where $\Gamma \sim t^{1/2}$; this happens when the width of the unbinding interface saturates to its size-limited value. For all substrate potentials simulated, in the process of film growth, the unbinding interface behaves just like a freely fluctuating interface. The width of the interface grows with a rate consistent with the fluctuation-dominated mechanism. The profile of the interface reaches its equilibrium shape (an error-function profile) while the width is still growing at an appreciable rate.
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[3] For recent theoretical works on spreading, see, e.g.,


CHAPTER IV

Wetting film growth with a conserved order parameter — diffusion limited growth

We have discussed the growth of wetting films with non-conserved order parameter in the previous chapter. Now we turn to discuss the diffusion-limited growth of wetting films in which the total number of adsorbate particles is conserved. We shall first present the predictions of the growth law based on the effective interface model. Then we present the simulation results for an Ising lattice-gas model.

4.1 Predictions of the effective interface model

Consider a system as shown in Figure 4.1(a) where a wetting film is growing with the constraint of the conservation of particles. Since the growth of the wetting film \( \beta \) consumes particles which can only come from the bulk phase \( \alpha \) by diffusion, there will be a particle-depletion zone right in front of the film. The width of the depletion zone \( \delta(t) \) is characterized by the diffusion length, i.e, \( \delta(t) \sim (Dt)^{1/2} \). Figure 4.1(b) schematically shows the
Figure 4.1:
(a) Wetting film \( \beta \) growth constrained by particle conservation. (b) The concentration profile is schematically shown. There is a depletion zone of width \( \delta(t) \sim (Dt)^{\frac{1}{2}} \) in front of the wetting film.
concentration profile. By conservation of particles

\[(\rho_\beta - \rho_\alpha)[l(t) - l(0)] \sim [\rho_\alpha - \rho(l)]\delta(t), \quad (4.1)\]

where \(\rho_\alpha\) and \(\rho_\beta\) are the concentrations in the bulk phases \(\alpha\) and \(\beta\) respectively. Assuming local equilibrium, i.e, \(\delta(t) \gg l(t)\), one has

\[\rho_\alpha - \rho(l) \sim [\mu(\rho_\alpha) - \mu(\rho(l))]\left(\frac{\partial \rho_\alpha}{\partial \mu}\right) \quad (4.2)\]

where \(\mu\) is the chemical potential. The difference of \(\mu\) can be related to the free energy per unit area \(f(l)\) by

\[(\rho_\beta - \rho_\alpha)[\mu(\rho_\alpha) - \mu(\rho(l))] = -\frac{\partial f(l)}{\partial l} \quad (4.3)\]

Thus

\[\frac{(l(t) - l(0))}{(Dt)^{\frac{1}{2}}} \sim -\frac{\partial f(l)}{\partial l} \quad (4.4)\]

Note that \(f(l)\) is given by Equation (1.22) if the substrate potential is of the form \(V_W(l) \sim l^{-p}\). Solving Equation (4.4) for \(\delta \mu = 0\), one obtains

\[l(t) \sim t^{\frac{1}{2(\alpha+2)}} \text{ with } \alpha = \min(\tau, p); \quad (4.5)\]

therefore, under conditions of two-phase coexistence, i.e, film formation beneath a coexisting bulk phase, the film thickness diverges with a power law

\[l(t) \sim t^\theta \quad (4.6)\]

where

\[\theta = \begin{cases} \frac{1}{2(p+2)} & \text{for } d > d^*(p), \text{ MF regime} \\ \frac{(3-d)}{8} & \text{for } d \leq d^*(p), \text{ FL regime} \end{cases} \quad (4.7)\]
For a sufficiently short-ranged potential in two dimensions, fluctuations dominate the growth process, leading to a $p$-independent value of $\theta$; otherwise, $\theta$ depends on the range of the potential.

For $\delta \mu < 0$, Equation 4.4 yields

$$l(t) \sim l_{eq} - Ct^{-\frac{1}{2}}.$$  \hfill (4.8)

In a regime where the bulk phase is stable but the system is sufficiently close to two-phase coexistence and the substrate favors the formation of a film of a phase different from the bulk phase, a film of finite thickness will grow until it reaches some equilibrium thickness. If this thickness is sufficiently large, then the film is expected to grow at intermediate times in the same manner as at two-phase coexistence, and at long times it should approach the equilibrium thickness $l_{eq}$ as $l_{eq} - l(t) \sim t^{-\frac{1}{2}}$.

Lipowsky and Huse[2] have derived Equation (4.7) more rigorously by solving a nonlinear diffusion equation using Green's Function techniques[3]. They also analyzed the stability of the planar interface and found that a Mullins-Sekerka-type instability[4] develops for $p \leq -1$. A special physical case of this instability is when the system is in a bulk metastable state, for which $\delta \mu > 0$, thereby having an equivalent potential of the form $V(l) \sim -\delta \mu l$, i.e, $p = -1$.

In the regime of unstable bulk phase, the above results will be invalid, but the domain growth theory of Lifshitz and Slyozov[5] is then appropriate. According to this theory, domains of the coexisting phases nucleate in the
bulk, and at long times these grow by coalescence of domains into larger ones. At the same time, the presence of a nearby substrate with a potential which preferentially attracts domains of one particular phase results in the growth of a film of this phase by essentially the same mechanism which produces the domain growth in the bulk. The result is that not only the bulk domains but also the film thickness are predicted to grow as $t^{\frac{1}{3}}$. This is the process of crust sintering [6].

4.2 Model and simulation method

4.2.1 The Ising lattice gas model

We employ [7] an Ising lattice-gas model on a simple cubic lattice of dimension $d$ equal to 2 or 3 with, respectively, a [10] or [100] direction perpendicular to the surface of the substrate. A site $i$ of the lattice is either occupied by an adsorbate atom or empty. Given a neighboring occupied site, there is an interaction energy $-J$ with $J > 0$; otherwise there is no interaction energy. In addition, there is an interaction energy $U_i$ between an adsorbate particle on site $i$ and the substrate. Thus, the Hamiltonian is

$$H = -J \sum_{<ij>} n_in_j + \sum_i U_in_i$$  \hspace{1cm} (4.9)

where $n_i = 0(1)$ if site $i$ is empty (occupied). The potential $U_i$ is taken to be a function only of the distance $z_i$, in units of the lattice constant, of site
from the substrate; it is given by

\[ U_i = \begin{cases} 
-5J & \text{if } z = 1 \\
-3J/z^{p+1} & \text{if } z > 1,
\end{cases} \tag{4.10} \]

where in the simulations we have used \( p = 1, p = 2, \) and \( p = \infty \) (short-ranged \( U_i \)). For \( d = 2 \), the lattice size used in obtaining results reported here is \( 100 \times 50 \); for \( d = 3 \), it is \( 20 \times 20 \times 50 \). Other sizes are employed to check the size dependence of various results. Run lengths are typically 50,000 MCS (Monte Carlo steps per site).

### 4.2.2 Monte Carlo method with Kawasaki dynamics

The Monte Carlo method[8] with Kawasaki dynamics[9] is used to simulate the growth process. Runs are started by distributing a given number of particles \( N \) randomly throughout the lattice; \( N \) is chosen so as to produce a particular overall concentration \( \rho_0 \) such as 20\% or 30\%. Thus the initial configuration can be thought of as a typical thermal distribution at infinite temperature. The configuration of the system then evolves at temperature \( T \) by repeating the following steps

(a) Randomly pick a particle and one of its neighboring sites.

(b) If the neighboring site is occupied, go to (a); otherwise, move the particle to this site with a probability

\[ \omega = 1/(1 + e^{\frac{\Delta H}{k_B T}}). \tag{4.11} \]
where $\Delta H$ is the change of $H$ due to the move.

(a) and (b) make up a Monte Carlo step. Time $t$ is measured as the number of Monte Carlo steps per site (MCS). For given thermodynamic and potential parameters, runs are repeated $N$ times with different initial configurations and random number seeds; we use values of $N$ from 10 to 100. A variety of time-dependent quantities such as the coverage $\Gamma(t)$ are accumulated and averaged over the $N$ runs. These quantities are given by, first,

$$\rho(z, t) = L^{1-d} \sum_i \rho_i(t)$$  \hspace{1cm} (4.12)

where the prime on the sum denotes that the sites $i$ which are summed must lie in the $z$th layer. Next, the film thickness $l(t)$ is defined by

$$\rho(l(t), t) = 0.5;$$  \hspace{1cm} (4.13)

note that it is necessary to interpolate $\rho(z, t)$ to nonintegral values of $z$ to make use of this definition. Finally, the coverage $\Gamma(t)$ is taken to be

$$\Gamma(t) = \sum_z [\rho(z, t) - \rho_0],$$  \hspace{1cm} (4.14)

where $\rho_0$ is the bulk density. Notice that the definition is such that the depletion layer which develops between the film and the bulk does not contribute negatively to the coverage because we do not include in the sum those $z$ for which $\rho(z, t) \leq \rho_0$.

It is perhaps worthwhile to point out at this juncture that our simulations cannot produce the predicted behavior at long time because we are using the
canonical ensemble, i.e., the total number of particles is fixed. Consequently, as the dense film grows, the bulk is depleted and at some point ceases to be saturated or supersaturated, and the film thickness must therefore approach a finite value at long times. For intermediate times, however, we can attempt to verify the predictions.

4.3 Results and discussion

4.3.1 Approach to equilibrium

We have studied the long-time behavior of the film growth following a quench into a regime where the bulk phase is initially stable or metastable. These are equivalent because, as the film grows, the material in the remainder of the system dilutes so that the bulk becomes stable even if initially metastable. Under these conditions we see the expected long-time behavior \( l(t) = l(\infty) - A t^{-\frac{1}{2}} \), where \( A \) is a constant and \( l(\infty) \) is the equilibrium film thickness. Figure 4.2 shows \( l(t) \) vs. \( t^{-\frac{1}{2}} \) for \( d = 3, p = 1, \rho_0 = 0.2, \) and \( T = 1.4J/k_B \); 36 runs are performed to achieve these results. The straight line shown is from a least-squares fit to the points. Extrapolated to \( t^{-\frac{1}{2}} = 0 \), it predicts \( l(\infty) = 3.02 \). This prediction is checked by doing separate grand-canonical ensemble simulations[10] at a number of distinct chemical potentials to infer the equilibrium film thickness as a function of the mean density of particles in the system. The result is shown in Figure 4.3. For the particular case presented in Figure 4.2, \( \rho_0 = 0.2 \) and the thickness from the grand-canonical
Figure 4.2:
The film thickness is plotted as a function of $t^{-\frac{1}{2}}$ for $d = 3, p = 1, \rho_0 = 0.2,$ and $T = 1.4J/k_B$; time is in units of 2500 MCS. The line is the result of a least-squares fit to the data.
The equilibrium film thickness $l(\infty)$ (□), found from grand-canonical ensemble simulations, is plotted against the mean density of particles in the system $\rho_0$ for $d = 3, p = 2, \text{ and } T = 1.4J/k_B$; the value of $l(\infty)$ inferred from canonical ensemble simulations (see Figure 4.2) is shown (×) for the particular case of $\rho_0 = 0.2$. The line is included to guide the eye.
ensemble simulations is about 2.82 which is in reasonable agreement with the canonical ensemble result of 3.02.

Similar results are obtained in two dimensions and also for \( p = 2 \) in both two and three dimensions. The fluctuations are relatively larger for \( d = 2 \) (using a 100 \( \times \) 50 lattice), necessitating about three times as many runs to obtain results as good as those shown in Figure 4.3. In general the equilibrium thickness obtained from the grand-canonical ensemble simulations is slightly smaller than inferred from the canonical ensemble, probably due to size effects.

### 4.3.2 The power-law growth

To check the power laws predicted by Equations (4.6) and (4.7), we have studied film growth under the same conditions but at the intermediate times. It turns out to be difficult to do simulations of sufficient length to see the expected power-law dependence of \( l(t) \) very clearly in most cases. The reasons for the difficulty are, first, that the exponent \( \theta \) is small and it is not easy to determine a small exponent accurately. Also, the film will not grow with this time dependence forever in the simulations because the number of particles is fixed and the total system size is quite limited (50 layers in the direction normal to the substrate). Consequently, as the film grows, the bulk phase is depleted and ceases at some point to be on the two-phase coexisting curve. Under these conditions the film thickness approaches a limiting value rather than continuing to grow (cf. Section 4.3.1). In order to maintain the ap-
appropriate conditions as long as possible, we have done runs using quite large initial uniform concentrations, $\rho_0 = 0.2$ to 0.3; it is therefore necessary to run at temperatures not far below the bulk critical temperature, giving rise to rather large fluctuation effects, thereby further increasing the difficulty of obtaining clear-cut results.

However, in at least some runs it is possible to interpret the observed growth rate before saturation begins to set in as $l(t) \sim t^\theta$ with $\theta$ given by Equation (4.7); however, $\theta$ is so small that a quantitative determination is not easy. As an example, consider Figure 4.4 which displays $l(t)$ versus $t^{1\theta}$ for $d = 3, \rho_0 = 0.22, p = 1,$ and $T = 1.12J/k_B$. Sixteen runs are done, producing distributions at various times with standard deviations of typically 4% of the mean value and an uncertainty in the mean of about 1%. A least-squares fit to a log-log plot of the same data produces a line of slope 0.18 ± 0.02. The predicted value of $\theta$ for this case is $1/6$. The simulation results are certainly not inconsistent with the predictions but neither is there quantitative agreement of a fully satisfactory sort. Figure 4.5 shows the thickness as a function of $t^{1\delta}$ for a case which differs from the preceding one in that $p = 2$ and eighteen runs are performed; the standard deviations of the distributions at various times are typically around 5% of the mean, leading to uncertainty in the mean of slightly more than 1%. For this case $\theta$ is predicted to be $1/5$. A least-squares fit to a log-log plot of the data yields $\theta = 0.14 \pm 0.03$. An alternative fitting procedure is to write $l(t) = l_0 + bt^\theta$ with $l_0, b,$ and $\theta$ as variable parameters. This method results in the data of Figure 4.4 being
Figure 4.4:

The thickness \( l(t) \) at intermediate times is plotted as a function of \( t^{1/a} \) for \( d = 3, p = 1, \rho_0 = 0.22, \) and \( T = 1.12J/k_B. \) The time is in units of 2500 MCS and a straight line is included to guide the eye.
Figure 4.5:
The same as Figure 4.4 except that $p = 2$ and $t^{\frac{1}{3}}$ is plotted along the abscissa.
best fit by \( \theta = 0.161 \) and those from Figure 4.5 by \( \theta = 0.131 \). On the basis of these results, we feel that we cannot claim unambiguous verification of the predictions for \( \theta \) predicted by Liopwsky and Huse[2], but the simulations are certainly quite consistent with them.

### 4.3.3 Sintering

Now we turn to present the results for the case that the starting configuration is in the bulk unstable regime. In our simulations, the initial configuration is a homogeneous (infinite temperature) phase with 20 – 30% of the sites occupied; we quench suddenly to a temperature below the critical temperature \( T_c \) so that the system is unstable; the substrate potential is such as to attract the dense phase to the substrate. Because we start from a fairly low concentration, the domains of the dense phase that form in the bulk do not percolate and so appear as isolated clusters. These diffuse toward the substrate and cause the film to grow. There also appears a "domain depletion layer" close to the film where the density of the (growing) domains of the dense phase is lower than the density far from the film-bulk interface. We have done simulations for \( d = 2 \) and \( d = 3 \) and have employed \( p = 1, p = 2 \), and a short-ranged substrate potential in both cases. A typical result well above the roughening temperature is shown in Figure 4.6 where \( \Gamma(t) \) and \( l(t) \) are plotted against \( t^{1/3} \) for \( d = 2, p = 1, T = 0.4J/k_B \), and \( \rho_0 = 0.2 \); the data are the results of ten separate runs giving, at various times, standard deviations in the coverage and the thickness ranging from 3% to 7%
Figure 4.6:
The coverage (□) and thickness (×) are shown as functions of the time (in units of 2500MCS) to the $\frac{1}{3}$ power for $d = 2$, $p = 1$, $\rho_0 = 0.2$, and $T = 0.4J/k_B$. The lattice measures $100 \times 50$; ten runs have been averaged to produce these results.
and uncertainties in the means (the plotted values) of $1 \pm 2\%$. Both sets of points fit a straight line quite well, demonstrating the predicted $t^{\frac{1}{3}}$ behavior even though the total coverage is not very large. One should bear in mind, however, that the growth rate of the film is determined by the influence of the potential on the material throughout the system and so is a reflection of the domain growth rate everywhere. If the same information is presented in a log-log format, the data for $\Gamma$ at times larger than about 10,000 MCS are fit by a straight line of slope $0.33 \pm 0.007$, while those for the film thickness are fit by a line of slope $0.28 \pm 0.016$. A nonlinear fit to the function $y = a + bt^\theta$ where $a$, $b$, and $\theta$ are parameters yields, for $y = \Gamma, \theta = 0.360$ and, for $y = l, \theta = 0.328$. The simplest interpretation of these fits is that $\theta$ is indeed $\frac{1}{3}$. Similar results are found in three dimensions and for the other substrate potentials, demonstrating consistency with the growth law, at least for the dimensions and substrate potentials employed here.

Figure 4.7 shows the domain structure in a typical run using the same parameters as above. The dots represent occupied sites while empty sites are blank; the substrate is at the bottom of each figure. Figure 4.7(a) presents the structure at a time of 2500MCS while Figure 4.7(b) is at 50,000MCS. The growth of both the film (at the bottom) and the bulk domains is apparent, as is the appearance of a depletion zone just above the film-bulk interface where the density of domains of the dense phase is much lower than in the bulk.
Figure 4.7:

The domain structure of the system is shown in one particular run for the same conditions as in Figure 4.6 at times (a) 2500MCS and (b) 50000MCS. Displacement parallel to the substrate is plotted along the abscissa; perpendicular to the substrate, along the ordinate. The substrate is located at the bottom of the figures, and a dot represents an occupied site.
4.4 Summary

In this chapter, we have studied diffusion-limited growth of wetting films in various bulk phase regimes. The growth behaviors are simulated using an Ising lattice gas model and compared to the predictions[2] based on the effective interface model. Due to finite size effects, the film thickness in our simulations will eventually reach a finite equilibrium value. Nevertheless, under conditions that the bulk is stable and the film thickness is sufficiently large, we are able to check the power laws given by Equations (4.6) and (4.7) in the intermediate times. At longer times, the film thickness approaches its saturated value as $t^{-\frac{1}{3}}$. In the case of an unstable bulk phase, the film thickness or coverage appears to grow at long times as $t^{\frac{1}{3}}$ in agreement with the theory of domain growth and sintering developed by Lifshitz and Slyozov[5]. The mechanism producing this behavior, the validity of the theory, and numerical simulations of domain growth in the bulk have been much discussed lately[11]. Our simulations of film growth provide an unequivocal verification of the exponent $\frac{1}{3}$. 
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In the grand-canonical ensemble simulations, a particle may be created at (removed from) a vacant (occupied) site with a probability given by $\exp(-\Delta \mathcal{H}/k_B T)$, where $\Delta \mathcal{H}$ is the change of the energy

$$\mathcal{H} = -J \sum_{<ij>} n_i n_j + \sum_i (U_i - \mu) n_i$$

due to creating (removing) this particle.

The recent literature on this topic is extensive and will not be listed in detail here. Some recent papers that summarize the field include

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CHAPTER V

Concluding remarks

Using simple models with Monte Carlo simulations, we have studied the dynamics of crystal growth and wetting film growth. Both growth processes involve a moving interface, while different mechanisms provide the driving forces. In the crystal growth process, the solid-fluid interface is driven by the chemical potential difference from the bulk coexistence value; in the wetting film growth process, the driving force is the substrate potential.

In the study of crystal growth, we were particularly interested in the effects of the roughening transition on the growth mechanism, and how the dynamical process affects the roughening transition. Since we used Glauber dynamics which physically corresponds to the evaporation-deposition mechanism, we have ignored the roles played by bulk and surface diffusions. When mass diffusion in the bulk phases is considered as in some recent simulations[1], the solid-fluid interface will display instability for relatively large driving forces and form complex growth shapes such as dendrites.

In the study of wetting film growth, we have only discussed the growth laws for temperatures above the roughening temperature. Below the roughening transition, we have done some simulations and seen signs of layer-
by-layer growth; although we were unable to achieve any quantitative understandings, our simulations showed that, for short-ranged substrate potentials, the ensemble-averaged film thickness grows not faster than logarithmically. This is consistent with a growth law of the form

$$l \sim [\ln(t)]^{\frac{1}{n}}, \quad n > 1$$

(5.1)
suggested by Grant et al[2]. Equation (5.1) is a typical slow relaxation behavior for systems with many metastable states such as Ising spin glasses[3]. In our recent simulations[4] of healing of crystal surfaces; we also found that the existing many metastable states at temperatures below $T_R$ play an important role in slowing down the kinetics. Nevertheless, further work is needed to fully understand the dynamics below the roughening transition temperature.
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