Film Growth and Surface Roughness with Fluctuating Covalent Bonds in Evaporating Aqueous Solution of Reactive Hydrophobic and Polar Groups: A Computer Simulation Model

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Abstract

A computer simulation model is proposed to study film growth and surface roughness in aqueous (A) solution of hydrophobic (H) and hydrophilic (P) groups on a simple three dimensional lattice of size $L_x \times L_y \times L_z$ with an adsorbing substrate. Each group is represented by a particle with appropriate characteristics occupying a unit cube (i.e., eight sites). The Metropolis algorithm is used to move each particle stochastically. The aqueous constituents are allowed to evaporate while the concentration of H and P is constant. Reactions proceed from the substrate and bonded particles can hop within a fluctuating bond length. The film thickness ($h$) and its interface width ($W$) are examined for hard-core and interacting particles for a range of temperature ($T$). Simulation data show a rapid increase in $h$ and $W$ is followed by its non-monotonic growth and decay before reaching steady-state equilibrium ($h_s, W_s$) in asymptotic time step limit. The growth can be described by power-laws, e.g., $h \propto t^\gamma$, $W \propto t^\beta$ with a typical value of $\gamma \approx 2$, $\beta \approx 1$ in initial time regime followed by $\gamma \approx 1.5$, $\beta \approx 0.8$ at $T = 0.5$. For hard-core system, the equilibrium film thickness ($h_s$) and surface roughness ($w_s$) seem to scale linearly with the temperature, i.e., $h_s = 6.206 + 0.302T$, $W_s = 1.255 + 0.425T$ at low $T$ and $h_s = 6.54 + 0.198T$, $W_s = 1.808 + 0.202T$ at higher $T$. For interacting functional groups in contrast, $h_s$ and $W_s$ decay rapidly followed by a slow increase on raising the temperature.
1 Introduction

Film formation of waterborne two component polyurethanes (WB 2K-PUR) consists of a hydrophobic polyisocyanate crosslinker and a hydrophilic polyester polyol in aqueous solution \[1-7\]. Simultaneous progression of physicochemical processes such as water evaporation, crosslinking reactions, droplet coalescence, etc. leads to complex heterogeneous structures. Numerous experimental studies are focused on studying the morphology of film surface and its roughness as a function of temperature, polymer chain architecture, solvent evaporation, and molecular weight etc. \[3, 6, 8-12\]. The hydrolysis reactions between isocyanate groups and water leads to formation of polyurea (PUA) while the reaction between isocyanate groups and hydroxyl groups of polyol results in polyurethane (PUR) \[7\]. Thus, the water solvent plays an important role in orchestrating the evolution of the film growth. Stochastic mobility of constituents drives the mixture towards its thermodynamic equilibrium while the kinetic reactions may arrest into heterogeneous domains of PUR and PUA. Water loss due to evaporation enhances the complexities as the thermal equilibration competes with the crosslinking. Recent laboratory data from ATR-FTIR spectra \[7, 13\] provides estimates for energy spectrum involved in stretching and bending vibrations of various bonds. From the spectral intensity, it is possible to extract the concentration of PUA and PUR and gain insight into its dependence on humidity (water concentration) \[14\]. AFM images provide information about their spatial distributions. In general, experiments show that increasing humidity leads to higher roughness \[1, 10\].

A systematic understanding of the global characteristics of the film growth from its basic constituents \((H, P, A)\) is highly desirable but not feasible with current experimental tools. Due to complexity, it is also not feasible to incorporate the thermodynamic equilibration involving stochastic mobility of constituents and kinetic reactions with covalent bonding in a selfconsistent analytical theory \[15\]. Therefore, computer simulations \[16-18\] remain the primary tool to complement and understand the laboratory observations \[1\]. Some attempts have been made recently to study the film growth in such a multicomponent \((H, P, A)\) system via computer simulations \[17, 18\]. The constituents \((H, P, A)\) are represented by particles with appropriate characteristics such as molecular weights, reaction functionality, and phenomenological interactions in such coarse grained model on a discrete lattice. The mixture equilibrates as the particles execute their stochastic motion via Metropolis algorithm and water component evaporates from the top of the sample. The kinetic reactions proceed from the adsorbing substrate and the film develops as the reacting particles tether together by covalent bonds. Evolution of the density profiles, film thickness, interface width (a measure of roughness) are studied as a function of temperature and concentrations of its constituents with a range of reaction rates \[18\]. The roughness of the film is found to increase on increasing the water concentration which is consistent with the experimental observations qualitatively. In these computer simulations \[18\], the stochastic movement of each particle is restricted to their six nearest neighbors on a cubic lattice. Each particle becomes immobile after forming a covalent bond with a constant bond length (lattice constant). Although, this approach is a good start, the degrees of freedom for particles hopping is minimal and the film morphology lacks dynamics.
In this paper we introduce a computer simulation model (see below) in which the number of degrees of freedom of constituents is increased considerably and the bond length is allowed to vary. The bond fluctuations are important to incorporate the elastic dynamics for equilibrating the film morphology. The model is described in the next section followed by results and discussion with a summary and conclusion at the end.

2 Model

We consider three types of particles, hydrophobic \( (H) \), hydrophilic \( (P) \), and water \( (A) \) on a simple three dimensional discrete lattice of size \( L_x \times L_y \times L_z \). A particle is described by a cube occupying its eight lattice sites. Initially, particles \( H \), \( P \), and \( A \) are randomly distributed on fraction \( p_H \), \( p_P \), and \( p_A \) of the lattice sites with excluded volume constraint which entails that a site cannot be occupied by more than one particle. An isolated particle can move to one of its 26 neighboring sites. In addition to excluded volume (hardcore) interaction, we consider short range interactions among the particles at the neighboring sites within a distance \( r = 3 \). The interaction energy \( E \),

\[
E = \sum_{ij} J(i, j),
\]

where, \( i \) runs over each particle and \( j \) runs over its neighboring sites within a range \( r \).

\[
J(H, H) = J(P, P) = J(H, A) = J(P, A) = \epsilon.
\]

In this study we use \( \epsilon = 0, 1 \). There is an attractive interaction between each particle and the adsorbing substrate (S) at the bottom \( z = 1 \),

\[
J(H, S) = J(P, S) = J(A, S) = 2.
\]

Additionally, each component ascribes a molecular weight \( (M_H, M_P, M_A) \) in arbitrary unit to incorporate the effect of gravitational precipitation. We choose, \( M_H = M_P = 1, M_A = 0.1 \) in this study. The gravitational potential energy at height \( z \) from the bottom,

\[
E_g = M_H/P/A \cdot z.
\]

The temperature \( T \), measured in arbitrary unit (i.e., in unit of the Boltzmann constant \( k_B \) and the interaction energy), is used as a parameter to control the stochastic motion of the particles. Each particle attempts to move to one of its randomly selected adjacent site (26) with the Metropolis algorithm. That is, a particle at a site say \( k \) and one of its neighboring adjacent sites \( l \) are selected randomly. If the proposed move does not violate the excluded volume constraint, then the total energies \( E_k \) and \( E_l \) in corresponding configurations with particle at the initial site \( (k) \) and its proposed move to randomly selected new site \( (l) \) are evaluated. The particle is moved from site \( k \) to \( l \) with probability \( \exp(\epsilon - E_l)/T \). Periodic boundary conditions are used along the transverse \( (x, y) \) directions while open boundary
conditions at the top and the bottom. Movements of particles are restricted at/near the impenetrable substrate at \( z = 1 \). The aqueous constituent (\( A \)) can evaporate, i.e., leave the sample from the top if it attempts to do so. However, constituents \( H \) and \( P \) cannot leave the sample, their concentrations are thus conserved. Attempts to move each particle once defines unit Monte Carlo step (MCS) time.

Each constituent attempts to react with one of its neighboring particles or substrate sites with a fixed reaction rate (probability) after each MCS time. In order to implement reaction kinetics, each reacting unit (\( H, P \)) is assigned a functionality of four (in this study), i.e., it can react up to four neighboring functional groups including the substrate. The rates (probabilities) of reactions with the substrate, \( R_{SH} = R_{SP} = 1 \) and among the functional groups \( R_{HH} = R_{HP} = R_{PP} = 1 \). Each hopping attempt is followed by covalent bonding among the reacting units. Further, each covalent bond resulting from such reaction kinetics is irreversible. However, its bond length can fluctuate between 2 and \( \sqrt{10} \) if the bonded unit attempts to move, as in bond fluctuation model of a polymer chain [19].

It is worth pointing out that we are able to incorporate more realistic features in this model than the previous studies for such a multicomponent film growth. Not only the degrees of freedom for each constituent to execute its stochastic movement has increased (from 6 in previous studies [17, 18] to 26 here), but also the range of interaction among the constituents. The second important feature of this model is the continued segmental mobility of the covalently bonded units with fluctuating bond length of the grown film which is in contrast to absence of mobility altogether in previous studies [17, 18] with fixed bond length. The elastic nature of the film is thus incorporated via vibrating covalent bonds an important feature (the vibration spectra) monitored in IRIR measurements [11]. This model is still far from a complete description of the laboratory system (i.e., arbitrary reaction rate) but it is a considerable improvement over the previous studies [17, 18].

Our simulation involves thermodynamic equilibration via stochastic motion of each constituent and segmental moves and kinetic reaction while the aqueous component continues to evaporate. Depending on the rate of reaction, the thermal equilibration can be arrested by covalent bonding. The rate of reaction and temperature along with the concentration of each component and their characteristics play important roles in designing the film and controlling its characteristics. In this study, we are restricted to a small set of these parameters (see below) to illustrate how it works.

### 3 Results and Discussion

Initially, all the component particles, polar (\( P \)), hydrophobic (\( H \)) and water (\( A \)) are distributed randomly with their number concentrations \( P_P = 0.01 \), \( P_H = 0.01 \) and \( P_A = 0.03 \), respectively. Note that the volume concentrations are eight times larger than the number concentrations as each particle occupies eight lattice sites of a cube. As time progresses, e.g., \( t = 5, 10 \), crosslinking grows and film begins to propagate in upward direction from the substrate until most of the reactive components are crosslinked (\( t = 40 \)). A remarkable feature of this model is the ability to move crosslinked particles by including the corresponding
bond fluctuations even though within a limited range (see preceding section). As a result, the crosslinked film may become more compact if subjected to downward pressure or gravity. In our computer simulation experiments the film thickness reaches a maximum value as water continually evaporates and reaches a steady state in asymptotic time limit as discussed in the following.

The film consists of all points that are covalently bonded from the substrate. The surface is the locus of all connected points with the maximum height. Thus, each substrate point \(i\) has a film height \(h_i\). The film thickness \(h\) is defined as,

\[
h = \frac{1}{N_s} \sum_i h_i, \tag{5}
\]

where, the number of substrate points \(N_s = L_x \times L_y\).

First we examine the simple case in which only hardcore interaction between the particles is considered during equilibration resulting from the stochastic motion in film formation, i.e., no interaction among polar, nonpolar and water particles was involved in calculating energy for their moves. Figure 1 shows the variation of the mean film thickness \(h\) with the time steps for a range of temperatures \((T = 0.5, 1, 1.5, ..., 5)\). Three stages of film growth are observed for all temperatures: an initial fast growth of the mean surface height followed by a relatively slow relaxation (kinetic reaction regime) before approaching a steady state. The first stage of the film growth may be expressed as

\[
h = At^\gamma + Bt^\delta + ..., \tag{6}
\]

with a leading power law index \(\gamma\) and correction term with exponent \(\delta\) for \(\gamma > \delta\); \(A\) and \(B\) are constants. For example, at temperature \(T = 0.5\) (indicated by dashed lines) there may be two growth rates described by \(\gamma \approx 2.0\) followed by \(\gamma \approx 1.6\) (see figure 1).

The initial growth of the film thickness (for \(t \leq 30\)) is followed by polymerization in the intermediate relaxation regime \((t \approx 30 \times 10^3)\) where most of the functional groups are already reacted. However, the bonded units continue to execute their stochastic movements allowed by corresponding bond fluctuations as the film thickness \(h\) equilibrates to a saturated value \(h_s\). Mobility of the constituents and corresponding bond lengths depends on the temperature, i.e., higher the temperature, larger is the bond length. Accordingly, the equilibrium film thickness \(h_s\) depend on temperature. Variation of \(h_s\) with temperature is presented in the inset (see figure 1) which shows that, on increasing the temperature, a fast linear expansion of the film thickness is followed by relatively slow expansion at high temperatures. Unlike the previous studies \[17, 18\], where the film thickness (surface height) remains constant after the reaction reaches its equilibrium saturating most of its functional groups, the mean film thickness further relaxes to its equilibrium value due to bond fluctuations in the asymptotic time limit. The mean surface height of the film is larger at higher temperature which may be due to more active vibration of bonded particles at high temperature. It is also clear from these data (figure 1) that the relaxation time required to reach equilibrium varies with temperature; films at higher temperatures require longer time to equilibrate.
The interface width $W$ of the film surface is defined as the root mean square (RMS) fluctuation of the film height $h$, i.e., the thickness,

$$W^2 = \langle h_i^2 \rangle = -h^2,$$

$$\langle h_i^2 \rangle = \frac{1}{N_s} \sum_i h_i^2.$$  

Figure 2 shows the variation of the interface width $W$ with the time step at different temperatures corresponding to height variation presented in figure 1. Initially, the interface width, $W$, grows with time $t$ with a power law,

$$W = At^\beta,$$

with exponent $\beta$ which changes from $\beta \approx 1.0$ to $\beta \approx 0.80$ in time at the temperature $T = 0.5$ (see figure 2). The interface width then decreases with an overshoot (maxima) before stabilizing somewhat with an increasing trend at higher temperatures in the intermediate time regime. It finally relaxes to steady state saturation in the long (asymptotic) time regime. The general non-monotonic approach before reaching saturation persists at all temperatures with obvious change in patterns with the temperature.

Response of the interface width growth can be explained by the three stage development of the film formation similar to evolution of the mean surface height, $h$. At early stage, films propagate upward unevenly from the substrate resulting in increasing fluctuations in the propagating front. Since the reaction propagates from the substrate, nearby functional groups have high probability to react. As a result, the interface width, i.e., the surface roughness increases with time. There after, it decreases as the film formation propagates to the top where most particles near the film air interface have reacted and become part of the film. The film starts shrinking toward the substrate as the interstitial water evaporates; the consolidation leads to decrease in the surface roughness. The film roughness grows up again due to the stochastic movement of the crosslinked particles and increasing pore space (empty sites) provided by water evaporation. As water content in the film reduces, the film stretches too far with an almost second maximum (overshoot) in the interface width (at high temperatures). The bond fluctuations respond and the film roughness eventually reaches a steady state where both the mean surface height and the root mean square interface width remain constant. A somewhat oscillatory response, more pronounce with the fluctuation in the film height, i.e., the interface width, is due to bond fluctuations of covalent bonded functional groups augmented by the interplay between the thermal energy and the free volume due to water evaporation. Such a pronounced non-monotonic and somewhat oscillatory response of the interface width (roughness) during the film formation and equilibration is unique characteristics cannot be captured by constant bond length in previous studies.

The saturated interface width $W_s$ is found to increase linearly with the temperature as shown in the inset figure 2. Similar to the film thickness (figure 1 inset), the saturated interface width, $W_s$, shows two linear scaling, a fast growth at low temperatures while a relatively slow growth at high temperatures. This is in contrast to previous studies where the interface continues to decay with the temperature.
Now let us examine what happens on including more interaction among mobile functional groups, i.e., the interaction eq. 1-4. As show in Figure 3, the variation of the mean surface height of the film, \( h \), with time remains nearly the same as the system with the hardcore interaction alone (see fig. 1) at higher temperature. The film thickness \( h \) at low temperature \((T = 0.5)\) exhibits much slower decrease after reaching its maximum. It would be interesting to have a closer look by examining the evaporating water concentration in the sample. Figure 4 shows the decay of water concentration as it evaporates during the film growth. Evidently, a considerable amount of water still persists in the film at low temperature \((T = 0.5)\). This provides an insight into the competition between the interaction energy and thermal energy causing water to evaporate. At low temperature, the mobility of the particles is relatively low. Attractive interaction between water constituents and the the polar groups makes it harder for water to escape the lattice which results in a swollen film. In this case (low temperature), the film has not reached a steady state equilibrium. At higher temperature, the overall mobility of particles increases, water evaporation is less hindered by its interaction with polar particles. Figure 3 (inset) shows this variation of mean surface height with temperature which shows a sharp decrease of film thickness at low temperatures followed by nearly constant with a slight increase of film thickness at high temperatures. Note the sharp contrast between the non-monotonic variation of the film thickness here with that of the hardcore constituents where the film thickness continues to increase with the temperature.

Corresponding growth of the interface width \( W \) for the interacting functional groups is presented in figure 5 for a range of temperatures. At a first glance, the interface growth pattern for interacting functional groups (fig. 5) appears similar to that with the hardcore interaction alone (fig. 2). However, a closer examination reveals important differences. The interface width \( W \) grows faster for interacting system with a higher growth exponent. For example, \( \beta_1 \approx 1.15 \pm 0.02 \) (initially) and \( \beta_2 \approx 0.83 \pm 0.02 \) (later stage) at \( T = 0.5 \) (fig. 5) in comparison to corresponding values \( \beta_1 \approx 1.10 \pm 0.02 \) and \( \beta_2 \approx 0.81 \pm 0.02 \) for hardcore constituents (fig. 2). The saturated interface width, i.e., the steady state roughness \( W_s \) decreases sharply with the temperature at low temperatures followed by a very slow linear growth on increasing the temperature (inset fig. 5). This must be contrasted from the linear increase of \( W_s \) with temperature for systems with hardcore interaction alone (inset fig. 2) and that of the monotonic decay in previous study [18]. The decay pattern of \( W_s \) with temperature for both film thickness \( (h) \) and the interface width \( (W_s) \) fits relatively well with exponential as well as power laws; the range of temperature is too small to differentiate between these empirical trends.

To make sure that there is no severe finite size effects, simulations are performed with different lattice sizes. Variations of film thickness and the interface width for these lattices are presented in figures 6 and 7 respectively. There is very little effect of the lattice size on the qualitative nature of the dependence of film thickness and its interface width.
4 Conclusions

A computer simulation model is proposed to study the film growth and surface roughness in a multi-component system consisting of hydrophobic and polar groups in evaporating aqueous solvent. The thermodynamic equilibration is implemented by moving these constituents stochastically with the Metropolis algorithm while incorporating the kinetic reactions from an adsorbing substrate resulting in flexible covalent bonding. The model is considerably improved over the recent studies on modeling the film formation in a waterborne polyurethane film while maintaining the efficiency of a discrete lattice. The degrees of freedom for each constituent to move and better relax effectively is much larger, 26 in this study in comparison to 6 in previous studies. In contrast to fixed bond length and immobile bonded units in previous studies, the flexibility of fluctuating covalent bonds between the reacted functional groups with ability to perform their stochastic movement not only make it a more realistic film growth but also adds elastic nature of the film.

The simulation is performed for a range of temperatures. Simulations show how the film thickness grows and its interface evolves and equilibrates. The growth of the film thickness and surface roughness are found to exhibit power-laws, i.e., \( h \propto t^\gamma \), \( W \propto t^\beta \) with \( \gamma \approx 1.5 - 2 \) and \( \beta \approx 0.8 - 1.0 \) in late and early stages of the growth. Both, the film growth and the interface width show a non-monotonic response while water evaporates and they equilibrate and approach their steady-state values \( (h_s, W_s) \). Scaling of these quantities with the temperature shows the effect of interactions among the constituents. For the components with the hard-core interaction alone, the film thickness and the roughness seems to increase linearly with the temperature in two steps. Including a short range interaction shows that a sharp decay of both the film thickness and the roughness is followed by a slow increase on increasing the temperature leading to a non-monotonic dependence. The non-monotonic dependence of the roughness with temperature is very different from the monotonic decay pattern of previous study [18]. It is somewhat similar to temperature dependence of roughness in a deposition of polymer chain model [22]. Many realistic features and variables are still to be incorporated such as rate of reactions, variations in concentration of each component, homo- and radical initiated polymerization, etc. some which will be considered in future in our on-going effort to understand the laboratory experiments.

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Figure 1: Growth of the average film thickness ($h$) for a range of temperatures for hardcore particles on a sample $40 \times 40 \times 30$ with 10 independent samples for $p_H = p_P = 0.01$ with initial water concentration $p_A = 0.03$. The inset figure shows variation of the saturated thickness $h_s$ with the temperature on a loglog scale.
Figure 2: Evolution of the interface width (W) of the film surface for a range of temperatures for hardcore particles on a sample 40 × 40 × 30 with 10 independent samples for $p_{H} = p_{P} = 0.01$ with initial water concentration $p_{A} = 0.03$. The inset figure shows variation of the saturated interface width, i.e., the roughness $W_{s}$ with the temperature.
Figure 3: Growth of the average film thickness ($h$) for a range of temperatures for interacting particles (eq. 14) on a sample $40 \times 40 \times 30$ with 10 independent samples for $p_H = p_P = 0.01$ with initial water concentration $p_A = 0.03$. The inset figure shows variation of the saturated thickness $h_s$ with the temperature.
Figure 4: Decay of the evaporating water concentration for a range of temperatures for interacting particles (eq. 14) on a sample $40 \times 40 \times 30$ with 10 independent samples for $p_H = p_P = 0.01$ with initial water concentration $p_A = 0.03$. 
Figure 5: Evolution of the interface width ($W$) for a range of temperatures for interacting particles (eq. 14) on a sample $40 \times 40 \times 30$ with 10 independent samples for $p_{H} = p_{P} = 0.01$ with initial water concentration $p_{A} = 0.03$. The inset figure shows variation of the saturated width, i.e., the roughness $W_s$ with the temperature.
Figure 6: Growth of the average film thickness \((h)\) at a temperature \(T = 5\) for interacting particles (eq. 14) on different sample sizes each with 10 independent runs for \(p_H = p_P = 0.01\) with initial water concentration \(p_A = 0.03\).
Figure 7: Evolution of the interface width ($W$) for a temperature $T = 5$ for interacting particles (eq. 14) on different sample sizes each with 10 independent samples for $p_H = p_P = 0.01$ with initial water concentration $p_A = 0.03$. 