Chapter 5
Stiffening while drying

Frits van Beckum [1] Jan Bouwe van den Berg [1] Sören Boettcher [2] Maarten de Gee [3]
Kundan Kumar [4] Joost van Opheusden [3] †

Abstract:
We present two models for the drying of waterborne paints, which consist of non-volatile latex particles suspended in water. One model considers the water and latex density in a layer as a function of time. Water evaporation at the surface represents the drying. This model results in a one-dimensional free boundary problem, which is solved numerically. Extensions to the model are given that describe the stiffening of the paint. A second model is a particle based dynamical simulation where latex particles form a network through which water particles move. A thin slab of the suspension in a three-dimensional box is studied. Water particles escaping the slab at the surface represent the drying, progressing network formation the stiffening of the paint. Both models allow for validation with material properties as determined experimentally on real coatings.

Keywords: *mathematical modelling, free boundary, liquid coating, evaporation*

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[1] VU University Amsterdam, The Netherlands
[2] Center for Industrial Mathematics, University of Bremen, Germany
[3] Wageningen University and Research Centre, The Netherlands
[4] Eindhoven University of Technology, The Netherlands
[†] corresponding author: `joost.vanOpheusden@wur.nl`

5.1 Introduction

Waterborne coatings (WBC's) are increasingly replacing traditional organic solvent-borne coatings (SBC's) due to stricter legislation originating from an ever-growing awareness in society about environmental issues and safety at work. One of the few disadvantages of WBC's is that they generally require longer drying times as compared to SBC's. For that reason the drying process of WBC's has received considerable attention from researchers in both industry and academia. From an industrial and applicational point of view, most interest lies in the understanding and control of the simultaneous drying and stiffening of the coating or film. If a coating needs to be handled or post-processed it should have adequate mechanical integrity, such as a sufficient shear stiffness (resistance to shearing), to prevent it from incurring damage. The formation of film at the surface, that is relatively solid, while the paint layer below is still relatively liquid is a common way to realize this in practice. On the other hand such a film can prevent further drying of the liquid paint layer below, which could compromise the required integrity again. Insight in how the detailed balance can be found is of prime importance. Modern waterborne paints can be considered as a stabilized suspension of (latex) polymer particles in water. It is usually applied as homogeneous thin layers on a hard substrates. The drying process can be seen to consist of four stages (see figure 5.1). When the paint layer is applied, it is still the original suspension (stage 1). Due to disappearance of the water as a result of evaporation a concentrated latex mass is formed, in which the polymer particles come into

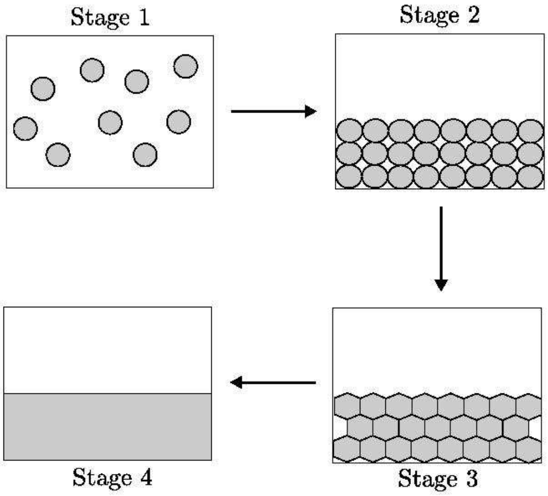

Figure 5.1: Four stages of latex film formation (cf. [4])

close contact (stage 2). Polymer particles are then subsequently deformed by the contact forces, while further water is removed by capillary forces, until most water has gone and particles start coalescing (stage 3). In the final stage particle boundaries disappear when they coalesce further to form a continuous polymer melt that further develops its mechanical integrity (stage 4). All four stages (in particular the second) have already been addressed in the literature (cf. [4]), but the development of the mechanical integrity of the layer (transition from liquid to solid) has hardly been touched upon.
The goal of this study is to develop mathematical models for the drying of waterborne coatings.

5.2 Derivation of the model

Waterborne paints consist of a stabilized suspension of particles in water. It is usually applied as a homogeneous film on a hard substrate. We will first develop a model in which we describe the drying and stiffening of this paint layer in terms of concentrations of water and latex.

5.2.1 One-dimensional model

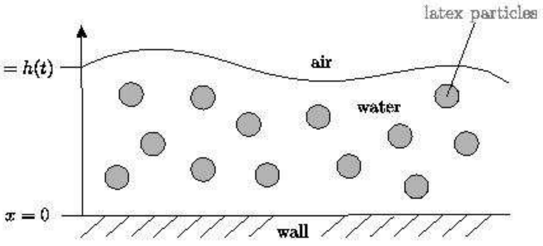

Figure 5.2: Sketch of the two-dimensional paint domain (cf. [6])

Our first model describes the shrinkage of the wet paint layer due to water evaporation as a one-dimensional process. All variation parallel to layer is ignored, we consider only variations in the perpendicular (x) direction. The impermeable substrate is at $x = 0$, the layer surface is at $x = h(t)$ (see figure 5.2). Evaporation causes the layer to shrink, hence we have a moving surface. The paint consists of latex particles and water, with volume fractions $p(x, t)$ and $w(x, t)$, respectively. We assume there are no air bubbles in the paint, so the relation

$$w(x, t) + p(x, t) = 1 \tag{5.1}$$

holds for all time and position. This will allow us to formulate the problem in terms of h and w only, eliminating p from the equations. The particles move by diffusion in the water, with diffusion constant $D > 0$:

$$p_t(x,t) = (D\, p_x(x,t))_x \quad \text{for} \quad 0 < x < h(t),\ t > 0. \tag{5.2}$$

In this model the diffusion coefficient D can be state-dependent, i.e. , D can be a function of the particle fraction p (or equivalently, through (5.1), of w). We come back to this later. By taking into account equation (5.1) within our model the water phase satisfies a similar diffusion equation :

$$w_t(x,t) = (D\, w_x(x,t))_x \quad \text{for} \quad 0 < x < h(t),\ t > 0. \tag{5.3}$$

Note that this does not imply we assume the water itself moves diffusively, which would be physically incorrect. As long as the motion of the latex particles is mainly diffusional, our model applies. At the substrate there is no flux of water or latex:

$$w_x(0,t) = 0, p_x(0,t) = 0. \tag{5.4}$$

The free and moving upper surface takes into account the water evaporating from the layer, while the total amount of liquid remains the same. Analogous to Newtons law of cooling, we assume the evaporation rate is proportional to $w(h(t),t) - Hw_{amb}$, where w_{amb} is some ambient water concentration and H is a Henry coefficient. As the total volume of water is given by $\int_0^{h(t)} w(x,t)\, dx$, we use that the change in this volume is given by the evaporation

$$\begin{aligned} -\alpha(w(h(t),t) - Hw_{amb}) &= \frac{d}{dt}\int_0^{h(t)} w(x,t)\, dx && (5.5)\\ &= h'(t)w(h(t),t) + \int_0^{h(t)} w_t(x,t)\, dx && (5.6)\\ &= h'(t)w(h(t),t) + \int_0^{h(t)} (Dw_x(x,t))_x\, dx && (5.7)\\ &= h'(t)w(h(t),t) + [Dw_x(x,t)]_{x=0}^{x=h(t)} && (5.8)\\ &= h'(t)w(h(t),t) + Dw_x(h(t),t), && (5.9)\end{aligned}$$

where α is a positive constant. From the assumption that the volume of the latex fraction in the drying layer is conserved, similarly, one finds for the polymer particles:

$$\begin{aligned} 0 &= \frac{d}{dt}\int_0^{h(t)} p(x,t)\, dx && (5.10)\\ &= h'(t)(1 - w(h(t),t)) - \int_0^{h(t)} w_t(x,t)\, dx && (5.11)\\ &= h'(t)(1 - w(h(t),t)) - Dw_x(h(t),t). && (5.12)\end{aligned}$$

Combining these equations, one finds

$$h'(t) = -\alpha(w(h(t),t) - Hw_{amb}), \tag{5.13}$$

which establishes a constituting equation for the thickness h of the paint layer, and

$$-\alpha(w(h(t),t) - Hw_{amb})(1 - w(h(t),t)) = Dw_x(h(t),t), \tag{5.14}$$

which establishes a boundary condition for w at the moving surface. Finally we choose for our one-dimensional model an initial thickness of the paint layer, and an initial water (and latex particle) distribution, which will typically be uniform. Thus, the system of equations for the volume fraction w with layer thickness h is given by:

$$\begin{align}
w_t(x,t) &= (Dw_x(x,t))_x, \tag{5.15}\\
w_x(0,t) &= 0, \tag{5.16}\\
w_x(h(t),t) &= -\frac{\alpha}{D}(w(h(t),t) - Hw_{amb})(1 - w(h(t),t)), \tag{5.17}\\
w(x,0) &= w_0(x), \tag{5.18}\\
h'(t) &= -\alpha(w(h(t),t) - Hw_{amb}), \tag{5.19}\\
h(0) &= h_0 \tag{5.20}
\end{align}$$

for $0 < x < h(t)$ and $t > 0$.

Note that equation (5.1) allows us to find the associated volume fraction profile of the latex, which is in practice the more relevant physical property. So far we have not specified the diffusion coefficient D of the latex particles. In the dilute, and possibly also the semi-dilute regime it could well be taken constant, but at higher densities that would not be a very realistic approximation. One possible choice is a Heaviside function to account for the transition from a liquid to a solid phase. In the computations later the approximation $D = D_s + d_w w$ with $D_s, d_w > 0$ was used, to avoid problems with the discontinuity. Typically this choice describes a low diffusivity at low water content, and a high one for more dilute situations. Note that w is a volume fraction, so its value can not be larger than unity. Note that we have left the equations in a dimensional form, which hopefully makes them easier to interpret for non-mathematically oriented readers. A simple dimension analysis shows that there two important time scales involved in the process; α/h_0 is the rate at which the thickness of the layer is decreasing (initially) due to the evaporation of the water. A second time scale is given by the D/h_0^2, the rate at which the diffusion is able to transport the water over the full layer. Important is their ratio $\epsilon = D/\alpha h_0$. If ϵ is small, the diffusive rate is not able to compensate the water loss at the surface quickly enough to keep the layer homogeneous. Close to the surface the water content w will drop, and we have a dry surface layer. The drying is then predominantly governed by the rate at which the water from the lower part of the layer permeates this dry film. If on the other hand ϵ is large, the diffusion will keep the water concentration throughout the layer the same, and the evaporation is the limiting process.

We note that this derivation of the mathematical model for drying of a paint layer is similar to [2, 3, 4, 6, 9]. Furthermore, in [8] stress-driven diffusion was incorporated in such a model. We also refer the interested reader to the existence and uniqueness results obtained in [7].

5.2.2 Clustering and stiffening

The above model can describe the drying of the paint layer, but neglects all detail of the latex phase. Already at moderate volume fractions one may expect particles to cluster and possibly even coalesce, thus adding to the mechanical stability of the material. In this section we discuss an extension to the basic model, in which cluster formation is taken into account by not considering a single particle volume fraction, but a series of volume fractions, one for each cluster size. The silent assumption here is that there is something like a primary latex particle, a monomer, that can be identified as such. In reality the particles in the original suspension, already before application of the paint and the initiation of the drying process, have a range of sizes (polydispersity), and there will be clusters, maybe small and reversible.

In the next stage of model development, we incorporate the effect that latex particles may form clusters. Let n be the cluster size, i.e. the number of particles in the cluster. Then $P(n,x,t)$ is defined as the number of clusters of size n, multiplied by the volume of one particle, divided by unit volume. Thus $nP(n,x,t)$ is the joint volume fraction of the clusters of size n, and since the total volume fraction of all components, including the water, is unity, we have

$$1 - w(x,t) = \sum_{n=1}^{N} nP(n,x,t),\ 0 < x < h(t),\ t > 0, \tag{5.21}$$

where N denotes the upper bound to the cluster size. In principle this N can be infinite, in practice we must choose some finite value of course; the model does not include gel formation. The diffusion rate $D = D_n$ now depends also on the cluster size. The larger clusters tend to have a smaller diffusion coefficient than the smaller ones. Coagulation takes place with a certain probability when two smaller clusters meet, resulting in a reaction-diffusion equation for each separate cluster size

$$P_t(n,x,t) = (D_n P_x(n,x,t))_x - A(n,x,t) + B(n,x,t). \tag{5.22}$$

Here

$$A(n,x,t) = \sum_{m=1}^{N-n} C_{n,m} P(n,x,t) P(m,x,t) \tag{5.23}$$

denotes the loss of clusters of size n (dissipation rate) due to further aggregation, while

$$B(n,x,t) = \frac{1}{2} \sum_{m=1}^{n-1} C_{n,n-m} P(m,x,t) P(n-m,x,t) \tag{5.24}$$

stands for the gain in clusters of that size by aggregation of smaller ones. The factor $\frac{1}{2}$ is present to take care of "double counting". It is reasonable to assume that the coefficients $C_{n,m}$ increase as function of m and n since the chance of hitting a large particle is larger than the chance of hitting a small particle. When the form of a cluster is a chain, its surface is about proportional to n. The same applies to planar clusters. However, for a spherical cluster, the surface is proportional to $n^{\frac{2}{3}}$. Thus, a sensible model for probability would be an exponential law $C_{n,m} \cong (nm)^b$ where b is between $\frac{2}{3}$ and 1.
Similar choices have to be made in modelling the diffusion rate. Among others, the diffusion rate is affected by the size of a cluster and its affinity to water. It seems natural to assume that the diffusion rate decreases with the cluster size. In the numerical computations the model $D_n = n^c D$ with $c = -1$ is used. The full set of equations now reads

$$\begin{aligned} P_t(n,x,t) &= (D_n P_x(n,x,t))_x - A(n,x,t) + B(n,x,t) && (5.25)\\ P_x(n,0,t) &= 0 && (5.26)\\ D_n P_x(n,h(t),t) &= -h'(t) P(n,h(t),t) && (5.27)\\ w(x,t) &= 1 - \sum_{n=1}^{N} n P(n,x,t) && (5.28)\\ h'(t) &= -\alpha(w(h(t),t) - H w_{amb}) && (5.29) \end{aligned}$$

for $0 \leq x \leq h(t)$ and $t > 0$.

Stiffness is modelled using the assumption that it increases with cluster size. More precisely, the full sample stiffness is determined as a harmonic mean of local stiffnesses, that in turn are determined by the local cluster size distributions:

$$\frac{1}{S(t)} = \frac{1}{h(t)} \int_0^{h(t)} \frac{1}{S_{local}(x,t)}\,dx,\ t > 0 \tag{5.30}$$

$$S_{local}(x,t) = \sum_{n=1}^{N} a(n)P(n,x,t),\ 0 < x < h(t),\ t > 0 \tag{5.31}$$

where a should be a convex function of n satisfying $a(n+m) > a(n) + a(m)$, otherwise clustering would not enhance stiffness. Without detailed physio-chemical information on the composition of the paint and the nature of the aggregation process, this function cannot be specified further. In the numerical computations $a(n) = n^2$ is chosen.

5.3 Numerical implementation

A transformation to a fixed domain makes the problem numerically treatable. Using the method of lines (spatial semi-discretization), the system of partial differential equations (PDE's) is approximated by a system of ordinary differential equations. A numerical solution can be obtained with standard procedures in MATLAB$^{\mathrm{TM}}$(cf. [1, 5]). The moving boundary is transformed into a fixed one by introducing the new variables $\xi = \frac{x}{h(t)}$ and (somewhat formally) $\tau = t$. Hence

$$\frac{\partial}{\partial x} = \frac{1}{h(t)}\frac{\partial}{\partial \xi}, \tag{5.32}$$

$$\frac{\partial}{\partial t} = -\frac{\xi h'(t)}{h(t)}\frac{\partial}{\partial \xi} + \frac{\partial}{\partial \tau}. \tag{5.33}$$

Let us make all this explicit for the non-clustering model. A similar,more elaborate system of equations was used to study the development of the cluster distribution in the layer. Writing $t = \tau$, equation (5.15) reads:

$$w_t(\xi,t) - \frac{\xi h'(t)}{h(t)} w_\xi(\xi,t) = \frac{1}{h(t)}\left(\frac{D}{h(t)} w_\xi(\xi,t)\right)_\xi. \tag{5.34}$$

This is a diffusion equation with a pseudo convection term:

$$w_t(\xi,t) = \frac{\xi h'(t)}{h(t)} w_\xi(\xi,t) + \left(\frac{D}{h^2(t)} w_\xi(\xi,t)\right)_\xi,\ 0 < \xi < 1,\ t > 0 \tag{5.35}$$

Thus we have as physical transport model

$$w_t(\xi,t) = \frac{\xi h'(t)}{h(t)} w_\xi(\xi,t) + \left(\frac{D}{h^2(t)} w_\xi(\xi,t)\right)_\xi, \; 0 < \xi < 1,\, t > 0 \tag{5.36}$$

$$w_\xi(0,t) = 0 \tag{5.37}$$

$$w_\xi(1,t) = -\frac{\alpha h(t)}{D}(w(1,t) - H w_{amb})(1 - w(1,t)) \tag{5.38}$$

$$w(\xi,0) = w_0(\xi) \tag{5.39}$$

$$h'(t) = -\alpha(w(1,t) - H w_{amb}) \tag{5.40}$$

$$h(0) = h_0 \tag{5.41}$$

for $0 < \xi < 1$ and $t > 0$.

Figures 5.3 and 5.5 show the joint volume fraction $P(n,x,t)$ of the clusters of size n, divided by the number of latex particles in the cluster. In the upper left plot, the volume fraction of the latex particles is presented as a function of the space variable for different time steps. Initially ($t = 0$), the volume fractions of the latex particles and the water are taken the same $p_0 = w_0 = 0.5$, no clusters are present (above size one). The volume fraction of single latex particles decreases with time because of cluster formation. This process is faster at the upper boundary ($x = 1$) because the evaporation takes place at the surface of the paint layer, hence the drying process there is more rapid than at the lower boundary ($x = 0$). The water near the substrate must first be transported through the layer before it can escape to the air. According to our choice of parameter values, the rate of the diffusional transport of water is rather small compared to that of the evaporation rate, so we should expect the formation of a film. The other plots show similar results for the clusters of size 2, 3 and 4.

Figures 5.4 and 5.6 show the volume fraction of water $w(x,t)$ (left) as a function of x for certain values of t and the thickness of the paint layer $h(t)$ (mid) as well as the stiffness $S(t)$ as a function of time. As the initial thickness is $h_0 = 1$ and the initial water fraction is chosen $w_0 = 0.5$, the paint layer shrinks to a thickness $h = 0.5$ with the evaporation of the water. The stiffness increases with time because of progressing cluster growth.

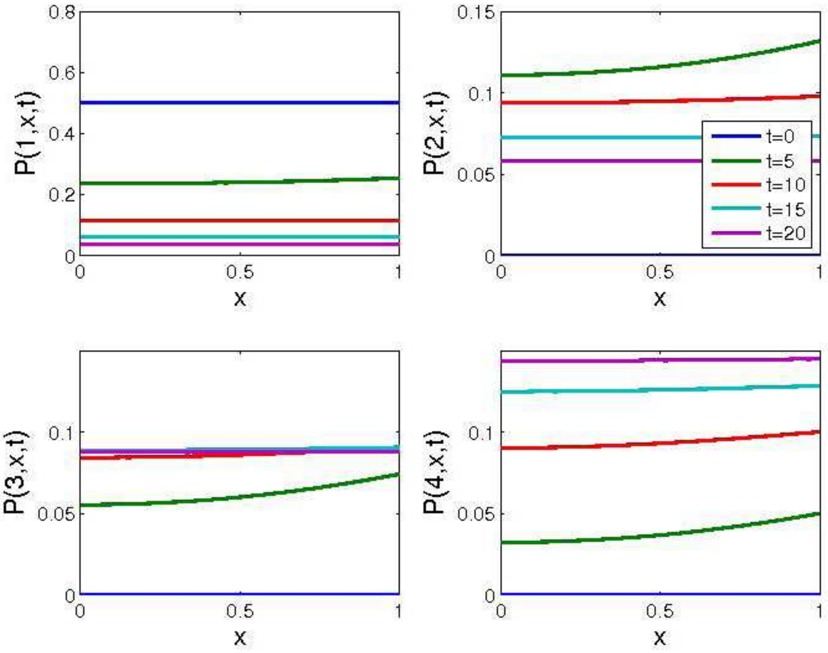

Figure 5.3: The joint volume fraction $P(n,x,t)$ of the clusters of size n, divided by the number of particles with initial data $\alpha = 0.5$, $Hw_{amb} = 0$, $w_0 = 0.5$, $h_0 = 1$, $C_1 = 0.5$, $D_s = d_w = 0.1$.

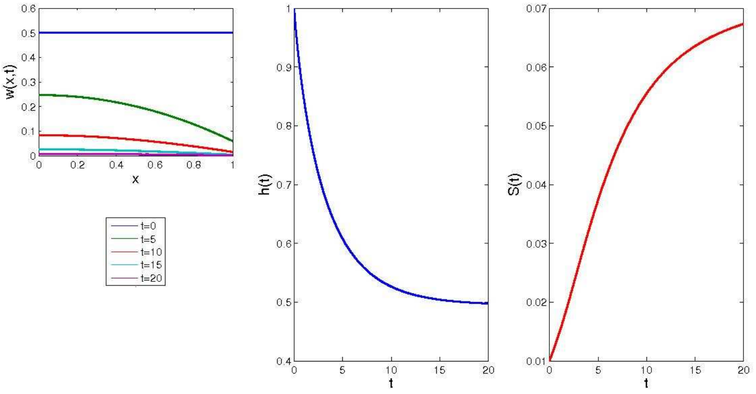

Figure 5.4: The volume fraction of water $w(x,t)$ (left), the thickness of the paint layer $h(t)$ (mid) and the stiffness $S(t)$ (right) as a function of time with parameter values $\alpha = 0.5$, $Hw_{amb} = 0$, $w_0 = 0.5$, $h_0 = 1$, $C_1 = 0.5$, $D_s = d_w = 0.1$.

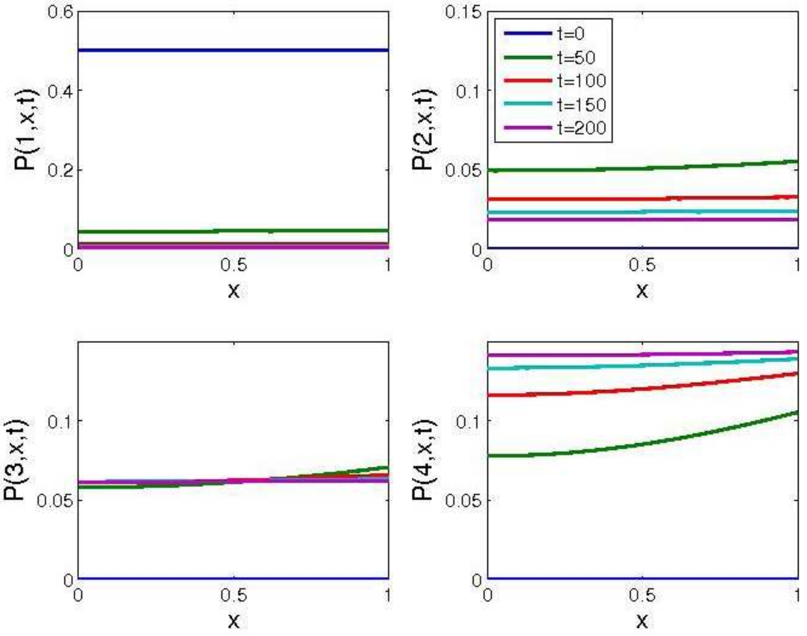

Figure 5.5: The joint volume fraction $P(n, x, t)$ of the clusters of size n, divided by the number of particles with parameter values $\alpha = 0.2$, $Hw_{amb} = 0.2$, $w_0 = 0.5$, $h_0 = 1$, $C_1 = 0.2$, $D_s = d_w = 0.01$.

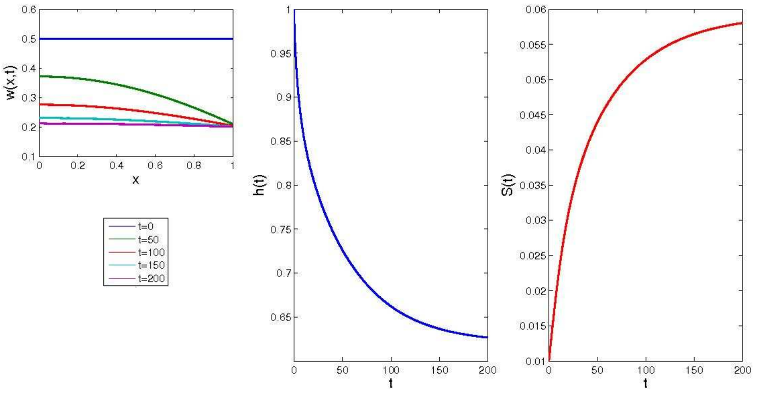

Figure 5.6: The volume fraction of water $w(x, t)$ (left), the thickness of the paint layer $h(t)$ (mid) and the stiffness $S(t)$ (right) as a function of time with parameter values $\alpha = 0.2$, $Hw_{amb} = 0.2$, $w_0 = 0.5$, $h_0 = 1$, $C_1 = 0.2$, $D_s = d_w = 0.01$.

5.4 Particle simulation

A completely different approach is chosen in the model we call the particle simulation. Here both the water and the latex phase are described as soft particles, moving diffusively due to the effect of thermal fluctuations. The interaction between the particles belonging to the two different phases is described by a potential force. Moreover the latex particles can form bonds when they come into close contact and form clusters. When the bonds are stretched, for instance by cluster reorganization due to stresses in other parts of the cluster, external forcing, or collisions with other clusters or water particles, these bonds may break. The forces as generated by the potentials can be directly calculated, averaged over the sample and related to material properties of the sample as a whole. The thermal fluctuations are represented by a random force. Mathematically the motion of the individual particles is described by a Langevin equation of motion, that is integrated numerically. The generic term for these type of simulation is Brownian Dynamics (BD), with the random force generating the Brownian (diffusive) motion of the particles. The latex particles in the model are indeed supposed to be like those in the actual system, and the water particles stand for relatively large volumes of water, about the same size as the latex particles (the order of micrometers), many length scales above the size of water molecules (less than a nanometer). Hence the appropriate term of the particle model scale would be mesoscopic. By calculating densities of particles, a relation could be made with the previously describe continuous model. Note that the particle simulation is fully three-dimensional. Most of the techniques we use are quite common, and are described in detail in many standard textbooks on molecular and mesoscopic simulation techniques.

5.4.1 Model description

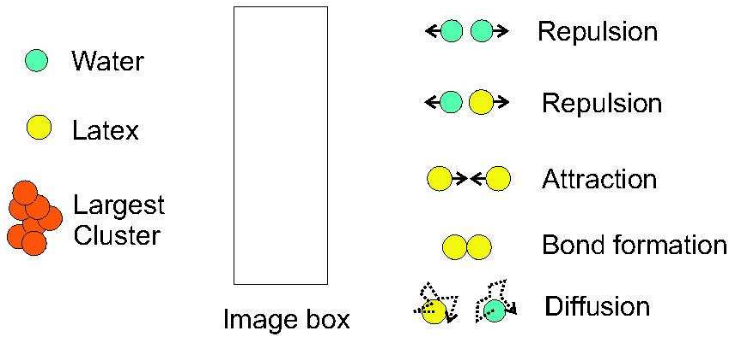

Figure 5.7: The elements of the particle simulation model.

In the BD model we have latex particles (yellow) and water particles (cyan) (cf. figure 5.7). The latex particles form clusters, and the largest cluster in the system is shown in orange. The interactions between the particles are a constant force with a finite range, attractive for the latex particles and repulsive for the water particles. Also the interaction between latex and water particles is repulsive. When latex particles come close, a bond may be formed. When that occurs the length of the bond is subject to a simple Hookean potential, a linear spring, that breaks again above a certain extension. Overlap between particles is removed by a repulsive force with the same Hookean potential. The whole system is contained in an image box, and we use periodical boundary conditions in all directions. The equations of motion for the particles are integrated numerically in time using an Euler Forward method. The time step is physically restricted by the oscillation period of the linear springs, higher order methods would not allow for substantially larger time steps.

5.4.2 Results

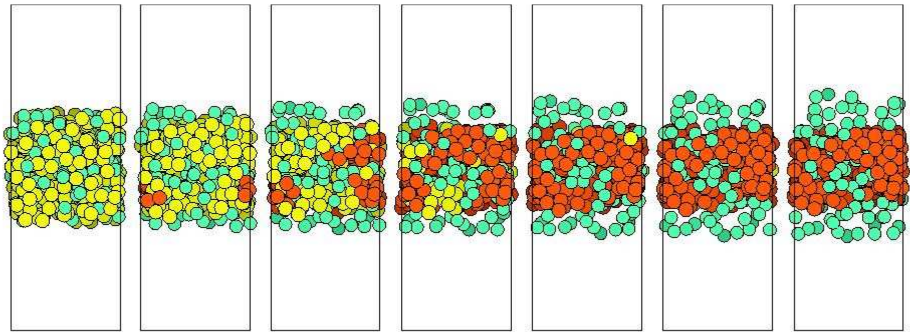

Figure 5.8: Series of snapshots from the BD simulation, as time increases water evaporates from the layer and the latex particles form a single cluster.

As the implementation of such a model is quite elaborate, we used existing private code that we modified for our purpose of the drying of a paint layer. The initial configuration consists of 200 latex and 100 water particles randomly positioned in a thin slab in the xz-plane of the image box. As the box is elongated in the vertical y-direction, and periodic in the other two directions, the system actually describes an infinite paint layer freely floating in space. The water particles may escape from the layer, describing the drying, the latex particles will form bonds and stay within the layer, describing the stiffening. There is no actual substrate present, though the model as such would allow it, unfortunately the available code does not.

Figure 5.8 depicts what happens as a function of time by providing a series of snapshots of the model system. One observes indeed the blue particles escaping the layer, be it slowly. In the current realization they still stay close to the layer, indicating that diffusion even outside the layer is slow. A relatively large number of water particles is still inside the layer, even when all the latex particles have joined into a single cluster, forming a solid slab. Some water will be trapped inside holes in that solid, other may still escape later through channels as the slab continues contracting. Apart from evaporation and coagulation, the particle simulation also describes the compactification of the partially dried paint layer.

Since the detailed motions of all individual particles and all the forces in the system that influence that motion, are readily available, a host of numerical data is available in this model system, even for relatively small system size and short simulation times. In practice one would calculate from these data observables that can be compared with actual experimental data on real samples. For the current feasibility study we present as an example the largest cluster size in the system. In fact such a parameter is not at all readily accessible in real systems, but the pronounced S-shape of the curve depicted in figure 5.9 agrees very well with results from particle gelation models. At early times there are many small clusters, which move relatively fast. When larger clusters form, which diffuse more slowly, the cluster-cluster aggregation leads to a rapid growth of large clusters when they come into contact not because of their diffusion, but rather of their growth. Once a fraction of the particles has formed the gel, that gel grows by the addition of smaller clusters joining it. Slowing down of the diffusion of larger clusters is incorporated in the model directly through the random force acting on the individual particles. The larger the cluster, the more these random forces will average out.

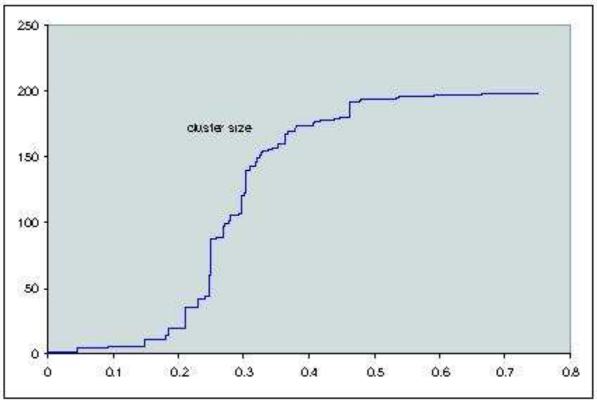

Figure 5.9: Growth of the largest cluster of latex particles in the system.

To calculate material properties of the sample, like surface tension of the drying layer, it suffices to sample the data from the simulation as described above. Such parameters are

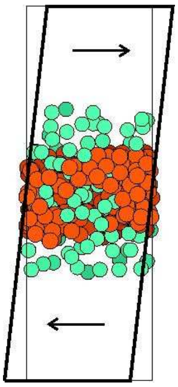

Figure 5.10: Affine deformation of the sample with the image box under shear.

said to be calculated in equilibrium, using the fluctuations generated by the random force, and relations from equilibrium statistical physics, like the virial theorem, to relate those to macroscopic observables. Because the random forces are small, and consequently so are the fluctuations, only material properties for small deformations can be determined. To investigate how such a sample would behave under larger deformations, non-equilibrium techniques are used. One example that is depicted in figure 5.10 is shear deformation, in this case shearing of the whole layer in the parallel direction. All particles are moved affinely under this deformation, while the image box is changed accordingly using the so called Lees-Edwards boundary conditions. This induced shearing motion leads to increasing stresses in the material that can only partially be relaxed by internal reorganization.

In figure 5.11 we give the sample stress as a function of shear strain parallel to the layer. The simulation was performed on a sample that had fully gelated, all latex particles form a single cluster. Since the deformation is rather small the system response is quite linear, apart from a small effect at very low deformation. Bonds are not stretched to the point where they start breaking, and the sample reacts as an elastic solid. A soft solid for that matter, since a strain of 0.25 for a stiff solid would be far in the non-linear regime. Stiffness is readily calculated within this model simulation, directly from the forces in the cluster network.

5.5 Conclusions and discussion

We have presented two different modelling approaches for the understanding of the drying and stiffening process of a paint layer. The first approach was a PDE model where we combined a moving boundary value problem, with a model for the stiffening of the

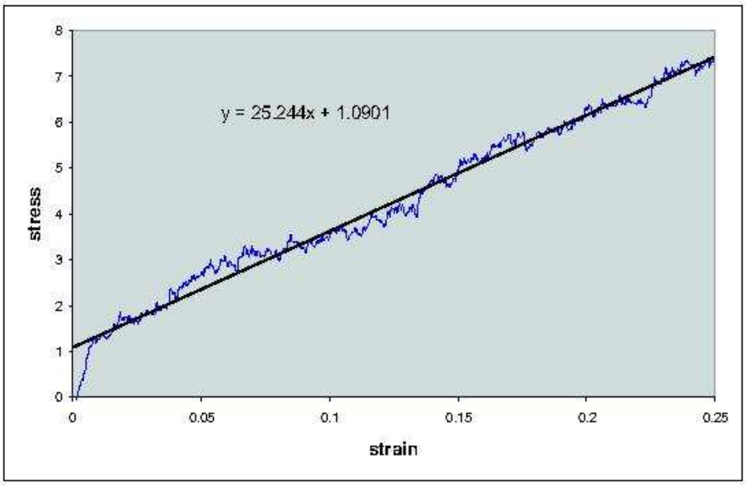

Figure 5.11: Stress in the sample as a function of imposed shear strain. Bonds do not break here and the response is quite linear.

paint. For the latter a coagulation process of the latex particles has been incorporated. The numerical studies of this PDE model show that it leads to reasonable results, which at this stage can not be be compared with those of actual samples. One reason is that we did not have access to actual data, more important is that the model contains a large number of parameters, such as diffusion constants and aggregation probabilities. Moreover we can only expect the model to be applicable in the range where the motion of the latex particles is largely diffusional (stage 1 of the process as described in the introduction). The aggregation model finally does not take into account a sol and a gel phase. In fact that relates directly to the proviso we mention about the diffusion, a gel is actually not much more than a very large cluster that has ceased diffusing, but within an open gel still diffusion of the sol phase might take place. If, as again suggested by the intuitive model from the introduction, large rearrangements in the clusters and the gel, and actual coagulation and deformation of the latex particles plays a large role in the development of the system, a gelation model would not provide much additional insight. In principle it would be possible within the model we present to include ageing effects of the clusters by making the parameters depend on the time passed since the formation of the cluster, like in structured population models developed in biology. Whether the addition of yet another set of model parameters will add to the predictability of the model for actual paint samples is obviously quite questionable. Possible extensions of this work could be the investigation of stress-driven water flow, the cracking of the paint film, two- and three-dimensional flow and the physics of the film formation process. One main shortcoming of the model as presented is that it does not allow for external disturbances.

Forced drying could be taken into account by changing the parameter α, but mechanical properties are restricted to the rather phenomenological description of the stiffness. The numerical calculations did show the feasibility of the application of the model, with modest requirements as to calculational equipment, and using quite straightforward simple implementation techniques.

Direct particle simulations provide an alternative approach for modelling. The advantage is that most real system observables can be directly compared to model results, no additional modelling is needed once the potential force parameters are specified. The disadvantage is that such potentials often present a too much simplified physical picture of reality. The model we used does not allow for deformation of the latex particles, though the effect is taken into account somewhat by the flexible bonds between the particles. The diffusional motion of the water particles in the early stage may adequately describe the dynamics of such samples, once the water has evaporated it certainly is an awkward caricature at best. Maybe it would better if such particles, when they have actually escaped from the layer, are removed in full. The rate at which that happens could then for instance stand for a form of forced drying by ventilation. Still the large size of the water particles limits the applicability of this model. Smaller sizes can be included straightforwardly, but at the price of an considerable increase in computational effort. Much more promising seems a hybrid approach, where the latex particles are described by a Brownian Dynamics type of model, while for the water phase for instance a coupled Lattice Boltzmann type of model is used. Similar hybrid models are used extensively in CFD techniques to describe the hydrodynamics of particle laden flows. Without significant material flow, as is the case for the drying paint layer, simplified versions of such models may well apply.

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