Viscoelastic behavior of dental restorative composites during setting

Dauvillier, B.S.

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Abstract

The viscoelastic behavior of resin composites during the setting process is an important factor in the relation between the cause - shrinkage strain - of adhesive restorative material and the effect – shrinkage stress - development in the restored tooth. The search for a mechanical model for describing the viscoelastic behavior of a two-paste resin composite during setting is described in this chapter. Uni-axial stress-strain data on Clearfil F2 during setting were obtained by a pulse sinusoidal test method and by mercury dilatometry. The stress-strain relation was analyzed using three mechanical models (Maxwell, Kelvin, and the Standard Linear Solid model). With an identification procedure, the model's stress response was compared with experimental stress data, and the material parameters were calculated. On the basis of the modeling and evaluation results, a model for describing the viscoelastic behavior of the shrinking resin composite was selected. The viscoelastic behavior of Clearfil F2 during setting, as excited by the conditions of the dynamic test, cannot be described by a single mechanical model. Up to 30 minutes in the setting process, the best prediction was achieved by the Maxwell model, while during the remainder of the setting process the Kelvin model can be used to describe the viscoelastic behavior of the two-paste resin composite.
Introduction

In the early nineties, a co-operative study with the department of Engineering of the University of Wales was started for the purpose to gain information on the viscoelastic behavior of shrinking dental restorative materials by mathematical modeling [1]. In this numerical study many mechanical models were investigated on the basis of the experimental stress-strain data provided by our laboratory. Adequate modeling results were achieved with the Maxwell model, if only the build-up of stress through polymerization shrinkage was taken into account.

At the start of this research project, we employed the Maxwell model to describe the stress relaxation behavior of a conventional glass ionomer and a chemically activated resin composite during setting [2]. The Maxwell parameter values were calculated by performing a least square method to a system of normal equations derived from the model differential equation (4.4). In this approach, however, we were not able to evaluate the Maxwell model under shrinkage strain condition, because the model differential equation was used, not solved. An additional disadvantage of this approach is that it does not calculate the error in the parameter values.

It is unlikely that the Maxwell model, which is a viscoelastic liquid model, can account for the viscoelastic behavior of the resin composite during the whole setting process. This is due to the fact that during setting, the restorative material is transformed from a viscoelastic liquid, in which the viscous flow is permanent, into a viscoelastic solid, where the viscous flow is reversible [3]. Therefore, a model that describes both the viscoelastic liquid behavior and the viscoelastic solid behavior, such as the Standard Linear Solid model, would be more suitable for describing the mechanical behavior of resin composite during setting.

As the research on modeling the viscoelastic behavior of dental restorative materials continues, certain aspects of the test system, which are important for obtaining reliable experimental data, have been further improved [4]. A big improvement gained for modeling stress-strain data was that the application software is capable of applying a strain as a sine function. In this way, the differential equation of the model can be solved analytically, which enhances the accuracy of the prediction of the mechanical behavior. In addition, two modeling procedures were developed [5]; (i) a parameter identification procedure, which does not provide only the material parameters, but also the error estimates on the parameters, and (ii) an evaluation procedure, which make it possible to
evaluate the appropriateness of the various mechanical models, by comparing the model response with the axial shrinkage stress of resin composites, as measured with the test system.

The improvements to the dynamic test method made it necessary to repeat the investigation of Hübsch on modeling the viscoelastic behavior of dental restorative materials during setting. The aim of this study was to find the best-fitting, simple, mechanical model to describe the viscoelastic behavior of a resin composite during setting. Stress-strain data were obtained by applying sinusoidal strain pulses to a two-paste resin composite, which was kept at a constant height during setting. On the basis of the experimental stress-strain data, a suitable mechanical model was selected, taken into account (i) the results of the parameter identification procedure, in which the parameters associated with the model were determined, and (ii) the evaluation of the model response under shrinkage strain conditions.

The range of validity of the model was limited to the shrinkage strain rate, because our main interest was the mechanical behavior of the composite under shrinkage condition. The small strain pulses were applied to gain informative stress-strain data in the later setting stage of the material, where the shrinkage strain rate is very low. The magnitude of the strain pulse was sufficiently low (<0.5 %) to ensure that the behavior of the composites could be studied by the theory of linear viscoelasticity [6]. Linear viscoelasticity can be described using mechanical models consisting of springs and dashpots [5].

Materials and methods

Chemically activated resin composite

The dental restorative material used in this study was Clearfil F2 (Table 5.1). This chemically activated resin composite was handled and mixed according to the manufacturer’s instructions.

Dynamic test: pulse sinusoidal cycles

The stress-strain data on the resin composite during setting were obtained from a pulse sinusoidal strain measurement on an automated universal testing machine (H10KM, Hounsfield). Details of this test system are described extensively in chapter 3 of this thesis. The freshly mixed resin composite (1:1 w/w) was bonded between the opposing
Table 5.1 Basic composition of Clearfil F2 Newbond (Kuraray). All percentages are in weight.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Description</th>
<th>Universal paste (batch: 1641)</th>
<th>Catalyst paste (batch: 1542)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resin</td>
<td>bisGMA/TEGDMA/unknown remainder monomer species</td>
<td>Appr. 23%</td>
<td>Appr. 23%</td>
</tr>
<tr>
<td>Filler</td>
<td>Quartz (dp = 5.0 μm)</td>
<td>Appr. 77%</td>
<td>Appr. 77%</td>
</tr>
<tr>
<td></td>
<td>Fumed silica (dp = 0.04 μm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Activator</td>
<td>Amine-type</td>
<td>&lt;0.5%</td>
<td></td>
</tr>
<tr>
<td>Initiator</td>
<td>Benzoyl peroxide</td>
<td></td>
<td>&lt;0.5%</td>
</tr>
<tr>
<td>Others</td>
<td>Pigments</td>
<td>&lt;0.5%</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\text{dp} = \text{mean particle size}\)

steel disks with diameter (d) of 5.4 mm and separated by a distance (h) of 5.0 ± 0.05 mm, creating a C-factor of 0.5 (=d / 2h). During the measurement, the cross head (i) continuously counteracted the specimen axial shrinkage, in order to maintain the specimen height constant at h = 0.01 μm, and (ii) periodically applied a sinusoidal displacement pulse to the specimen with an amplitude of 1 μm (=0.02 % strain) and frequency of 0.1 Hz (Fig. 5.1). The measurements were repeated three times at room temperature (23 ± 1 °C). During the measurement, the data (time, load, and displacement signal) were collected simultaneously at a sample rate of 18 points per second. One hour after the start of the

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**Figure 5.1** Experimental setup with (1) cylindrical specimen and (2) displacement transducers. (A2) Sinusoidal pulses are applied to the specimen, which is kept within −0.01 m at a (A1) constant height. The load response to the (R2) pulses is superimposed on the (R1) polymerization shrinkage load. The gray area represents the time interval for which the parameter identification was applied.
experiment, the resin composite was subjected to tensile loading until fracture.

**Volumetric shrinkage measurement**

During the pulse strain measurement, the axial shrinkage strain of the specimen was not measured, because the height of the specimen during setting was kept constant. However, the displacement caused by axial shrinkage must be taken into account when modeling the stress data. For that reason, volumetric shrinkage measurements \( n = 3 \) were performed with a mercury dilatometer at \( 23 \pm 0.1 \, ^\circ C \), using the procedure described by De Gee et al. [7].

**Stress-strain analysis**

The data obtained from a pulse sinusoidal strain measurement consisted of an array of load and displacement values for a large number of points in time. The normal stress \( (\sigma) \) and strain \( (\varepsilon) \) were calculated from the load and displacement values by Equation (5.1) and (5.2) respectively.

\[
\sigma = \frac{F}{A} \quad (5.1)
\]

\[
\varepsilon_{\text{axial}} = \frac{\Delta L}{L_0} \quad (5.2)
\]

in which \( A \) is the cross-sectional area of the cylindrical specimen \( (m^2) \), \( F \) the recorded load response of the specimen \( (N) \), \( \Delta L \) is the displacement recorded by the LVDT transducers \( (m) \), \( L_0 \) the height of the specimen before setting \( (m) \).

In addition to the applied sinusoidal strain, the strain caused by axial shrinkage must be taken into account when modeling the stress data. The axial shrinkage strain of the specimen bonded between the disks \( (C=0.5) \) was obtained from volumetric shrinkage strain data by the conversion factor provided by Feilzer et al. (Table 3.1).

The functional expression of the axial shrinkage strain in time was calculated by a cubic spline fit on the mean strain data [4]. Finally, for the modeling of the stress data, the strain recorded in the pulse sinusoidal
experiment was added to the axial shrinkage strain for all the points in
time of the experiment. Data analysis was performed with Origin
(version 5.0, Microcal) on a desktop computer (Windows© 98 platform).

Parameter identification procedure

The mechanical models investigated in this study were in one dimension
only, because the experimental stress-strain data were monitored in
only one direction. The models are described in detail in chapter 4 of this
thesis. The identification of the parameters associated with the model
was applied to small time intervals \([t_0, t_0+\Delta t]\) in the measured stress data
of the resin composite (Fig. 5.1). The first part of the time interval
corresponds to the stress response to the axial shrinkage of the specimen,
and the second part represents the stress response to the axial shrinkage
strain and the sinusoidal strain pulse applied to the specimen. The time
span \([\Delta t]\) of the isolated intervals was kept small (appr. 16 seconds), and
thus the material parameters \(E_1^*, E_2, \) and \(\eta\) may be assumed to be
constant when modeling the stress of the isolated interval. As the strain
due to the axial shrinkage strain of the specimen in the isolated interval
behaves linearly in time, the total strain in the first (Eq. 5.3) and the
second part (Eq. 5.4) of the interval can be described analytically:

\[
\varepsilon(t) = \varepsilon(t_0) + At
\]

\[
\varepsilon(t) = \varepsilon(t_0) + At + B \sin(\omega t)
\]

in which \(\varepsilon(t_0)\) is the strain at begin interval, \(A\) is the slope of the
shrinkage strain \((1/s)\), \(B\) the amplitude, and \(\omega\) the angular frequency
\((\text{rad/s})\) of the applied sinusoidal strain pulse.

Since the functional form of the strain was known, the differential
equation for the Maxwell and Standard Linear Solid model was solved
analytically (appendix A), which in every case yielded the stress as a
function of strain and the unknown material parameters. When modeling
small intervals from the stress curve, it is important to take into account
the stress at the beginning of the interval (initial stress \(\sigma(t_0)\)). The initial
stress can be obtained from experimental stress data or calculated with
the aid of the initial strain \(\varepsilon(t_0)\). In this study, the initial stress was
obtained from experimental stress data, because the evaluation of the
initial stress by integrating the initial strain and the variable material
parameters over the time period \([0,t_0]\) prior to the isolated interval
requires extensive computation.
To assess how well the model stress ($\sigma_{\text{model}}$) approximates the stress measured in the experiment ($\sigma_{\text{exp}}$), using a certain set of material parameters, a least square method was performed at equidistantly spaced $k$ points in the time domain of the isolated interval:

$$\delta = \sum_{i=1}^{k} \alpha_i (\sigma_{\text{model}}(t_i) - \sigma_{\exp}(t_i))^2$$  \hspace{1cm} (5.5)

The material parameters were calculated by minimizing the residual ($\delta$) using an optimization routine based on a quasi-Newton algorithm, the Gauss-Newton method [8]. A scheme of the parameter identification procedure is shown in Figure 4.3. The procedure provides (i) the parameters, (ii) the error estimates on the parameters, and (iii) the residual ($\delta$) that is a quantitative measure of the difference between experimental and model stress.

Evaluation of the viscoelastic model

To evaluate the appropriateness of the various mechanical models under shrinkage strain conditions, the experimental axial shrinkage stress development of Clearfil F2 was compared with the model response. In chapter 4 of this thesis, an evaluation procedure to calculate the model response on basis of the input of the axial shrinkage strain and the calculated material parameters, is described. The parameter identification procedure and evaluation of the models were performed with the software Matlab (version 5.3, Mathworks) under Windows® 98 on a desktop computer.

Results and discussion

Stress-strain data

A complete survey of the stress-strain data recorded during a complete pulse strain experiment is given in Figure 5.2b-d for the resin composite. The positive strain of the sinusoidal cycles represents the cross head displacement away from the specimen (tension), while the negative strain represents the cross head displacement towards the specimen (compression). As the specimen height was kept constant between the sinusoidal strain pulses, the stress response on the applied strain pulses is superimposed on the continuous shrinkage stress development of the specimen. There was no premature debonding from
either of the steel disks, because after tensile loading the fracture, evaluated visually, was in all cases totally cohesive.

Figure 5.2a shows the mean axial shrinkage strain of Clearfil F2 at room temperature, as calculated from the volumetric measurements. The strain data used for the modeling procedure (Fig. 5.2c) consist of the applied strain curve, added to the axial shrinkage strain curve. An interesting feature of the stress-strain data is that after 330 s (5.5 min) of mixing, 50% of the total axial shrinkage strain results in a stress response of 0.35 MPa, which is less than 10% of the total polymerization stress of Clearfil F2. The fact that at room temperature a large proportion of polymerization stress is developed in the later phase of the setting reaction is in agreement with the results of a previous study on Clearfil F2 [2].

The graphic results of the parameter identification procedure on two stress intervals isolated from one pulse strain measurement are shown in Figure 5.3. The continuous line represents the measured stress, while...
Figure 5.3 Parameter identification results for two stress cycles of Clearfil F2 during setting at (left) time=404 s and (right) time=1473 s for the (top) Kelvin model, (middle) Maxwell model, and (bottom) Standard Linear Solid model.

The dots are the values computed by the model, using the material parameters calculated by the procedure. Table 5.2 shows the calculated parameter values for the three models for several stress intervals of one experiment. Figure 5.4 shows the mean parameter values development graphically. The viscosity (η) values of all models were all positive and developed according to the spring-dashpot arrangement in the model with setting time. The Young’s modulus (E) values were also positive and increased monotonically with the setting time. The evaluation results for all models are illustrated in Figure 5.5.

On the basis of these modeling results, the models investigated can be divided into three categories: the good, the bad and the ugly. The Kelvin model fails to predict the experimental stress in the early stage of setting
Table 5.2 Material parameters for several cycles during one measurement of Clearfil F2 during setting with standard deviation in parenthesis. Parameters: $E(\varepsilon)$=Young's modulus, $\eta$=viscosity, and $\delta$=quantitative measure of the difference between experimental and model stress.

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>Kelvin model</th>
<th>Maxwell model</th>
<th>Standard Linear Solid model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E$ (GPa)</td>
<td>$\eta$ (GPa.s)</td>
<td>$\delta$</td>
</tr>
<tr>
<td>265</td>
<td>0.07 (&lt;0.01)</td>
<td>0.05 (0.01)</td>
<td>0.0045</td>
</tr>
<tr>
<td>404</td>
<td>1.10 (0.08)</td>
<td>0.87 (0.20)</td>
<td>1.16</td>
</tr>
<tr>
<td>630</td>
<td>4.00 (0.14)</td>
<td>1.47 (0.26)</td>
<td>2.00</td>
</tr>
<tr>
<td>907</td>
<td>6.16 (0.12)</td>
<td>1.48 (0.21)</td>
<td>1.27</td>
</tr>
<tr>
<td>1473</td>
<td>8.09 (0.16)</td>
<td>1.29 (0.27)</td>
<td>1.94</td>
</tr>
<tr>
<td>2356</td>
<td>9.60 (0.17)</td>
<td>1.11 (0.28)</td>
<td>2.05</td>
</tr>
<tr>
<td>3572</td>
<td>10.5 (0.17)</td>
<td>0.90 (0.30)</td>
<td>2.25</td>
</tr>
</tbody>
</table>

(404 s). The model responds too stiffly to the shrinkage part of the interval, i.e., the slope of the model curve is substantially higher than that of the resin composite in the experiment. In comparison with the other models, the $\delta$ parameter (Table 5.2) shows the highest value. As expected, in this stage of setting the material undergoes permanent viscous flow.

Later on in the setting process (1473 s), the stress curves show a significant disparity between experiment and model on only a very small portion of the curve. In this stage of setting, the resin composite undergoes reversible viscous flow. Since the Kelvin model predicts only reversible viscous flow, the model responds significantly higher to the overall shrinkage strain history of the resin composite than the composite in the experiment (Fig. 5.4).

A general problem with the Kelvin model is that it predicts discontinuous stresses, if the strain rate is not continuous (Eq. 4.5). When a sinusoidal strain pulse is applied, the strain rate is cosine shaped, i.e., it is zero before the pulse starts and jumps as the strain pulse is applied.
Therefore, on the basis of the absence of the discontinuous stress change in the experimental stress curve, Hübsch concluded that the behavior of shrinking resin composite is by nature viscoelastic liquid [1]. However, the absence of a stress jump in the experimental stress curve may indicate an important restriction of pulse sinusoidal strain analysis, namely the absence of strain history. A mathematical sinusoid has no beginning or end (Fig. 3.14). Thus, due to the damping of the specimen, we would expect a stress jump in the experimental stress response at the beginning of the sinusoidal stress, resulting in a phase shift between the stress and strain sinusoidal curve. The absence of the stress jump could be due to the fact that the “sinusoid” was applied experimentally, and thus did have a starting point. In future studies, therefore, the sinusoidal strain should be applied not as a pulse but continuously. This slight modification of the measuring procedure not only enhances the accuracy of the modeling procedure, but also makes it possible to analyze the stress-strain data directly by means of phase shift calculation [9]. The analysis of the stress-strain data makes a direct contribution to the study, providing a better understanding of the viscoelastic behavior of shrinking dental restorative materials.

The Maxwell model produced the most accurate results. The model predicts good composite behavior on the shrinkage part of the interval, but not in the area of rapid stress change. This is in agreement with the modeling results of Hübsch [1]. The stress curves in Figure 5.3 show that in the area of the sinusoid curve, the model responds with the same stiffness, but with a less viscous flow than the resin composite in the experiment. A closer look in the last section of the sinusoid curve at 404 seconds reveals that the model responds slightly softer than the material in the measurement. This can be explained by the fact that the material parameters were held constant in time, whereas in reality polymerization continues, leading to an increase in the stiffness.

The Young’s modulus values of Clearfil F2 are in agreement with the values calculated by Hübsch [1] and in previous work [2]. The value of 10.6 GPa obtained at a 60-minute setting (Table 5.2) likewise seems realistic when compared with the value of 12.4 GPa provided by the manufacturer. Any difference between these values can be explained by differences in batches, mixing ratios, age of the composites, and test methods. Therefore, a valid comparison with Young’s modulus of restoratives requires that the conditions of specimen handling and the method must be specified.

The viscosity values of this study are in agreement with the findings of Hübsch, but differ significantly from those calculated in previous work.
Figure 5.4 Mean parameter values of the (top) Kelvin model, (middle) Maxwell model, and (bottom) Standard Linear Solid model versus the setting time of Clearfil F2. The results obtained by Hübsch [1] and previous study [2] for Clearfil F2 are also incorporated in the Maxwell graph ((▲, △) and (■, □) respectively). Error bars indicate the relative standard error in the calculated mean (n=3).
The parameter identification procedure used by Hübsch differs in only one aspect from that employed in the present study [5]. In this study, the differential equation of the Maxwell model was solved analytically, whereas in Hübsch's study it was solved numerically (Runge-Kutta algorithm [8]). In previous research, however, the material parameters where calculated by a different modeling procedure, namely directly, using a least squares method to a system of normal equations derived from the differential equation. Thus, the differential equation was not solved and no iteration process (indirect method) was used. Obviously, not only the noise accompanying the experimental stress data [5], but also the architecture of the modeling procedure has a decisive influence on the viscosity values. For the present, it is not possible to check whether the viscosity values are realistic for dental resin composites, because there is no information in the literature on this material parameter of setting dental resin composites.

The results of the evaluation of the Maxwell model reveal several interesting features. First, the Maxwell prediction agrees very well with the experimental stress up to 11 minutes into the setting process, during which 78% of the axial shrinkage of the composite at one hour takes place. This means that a large proportion of the shrinkage is accompanied by permanent viscous flow of the material.

![Figure 5.5. Axial shrinkage stress development (— measured, □ Kelvin model, ▲ Maxwell model, and ◆ Standard Linear Solid model) of Clearfil F2 during setting at configuration factor C=0.5. Error bars indicate the relative standard error in the calculated mean (n=3).]( hypothetical image link )
A second feature is that the composite undergoes permanent viscous flow in the post-gel phase of the resin composite for a considerable time (8 min). Thus, even when the elastic behavior dominates over the viscous flow behavior, the material is capable of flowing permanently. This justifies the use of the Maxwell model to reveal significant differences in the development of the material parameters of dental restorative materials from different classes during the early stage of setting [2].

Finally, for the setting time period of 11-30 minutes, the Maxwell model predicts higher stresses. The reason could be that the material parameters were calculated from a stress response, generated with an exclusively dynamical strain input (Fig. 5.3), while in reality the composite undergo slow shrinkage strain (Fig. 5.2a). The viscosity values might therefore be predicted too high - the Maxwell response is dominated by the instantaneous spring - while in reality the composite can show a more stress relief behavior. Although the prediction is not as good as for the first 11 minutes of setting, it is quite satisfactory for modeling purposes. In the remainder of the setting phase, the Maxwell model predicts too much stress relief, which is clearly not the case in the experimental situation.

As expected, the Standard Linear Solid model is able to describe both viscoelastic liquid and viscoelastic solid behavior of the resin composite during setting. This is reflected in a gradual decrease in the $E_1$ modulus and a simultaneous increase in the $E_2$ modulus (Fig. 5.4). For the first two stress intervals analyzed, the $E_2$ modulus is very close to zero (Table 5.2), so that the Standard Linear Solid model degenerates into the Maxwell model. However, the presence of the $E_2$ modulus parallel to the Maxwell unit in the Standard Linear Solid model gives rise to the more viscous flow behavior of the model. This is shown by the low viscosity values for the Standard Linear Solid model in comparison with the Maxwell model, while the $E_1$ modulus value in the Standard Linear Solid model is approximately the same as for the $E$ modulus in the Maxwell model.

Unfortunately, the evaluation results clearly show that the Standard Linear Solid model fails to predict the viscoelastic behavior of the two-paste resin composite as excited by the conditions of the test method (Fig. 5.5). The reason for predictive failure in the remainder of the setting process is that the experimental conditions of the test method are not good enough for predictive modeling with a 3-parametric model. As the shrinkage strain rate declines, and the contribution of shrinkage strain to the applied strain deteriorates as the setting process continues, the stress response becomes more exclusively dynamical, i.e., more
dependent on the sinusoidal strain of one frequency alone Validation results revealed that the three parameters cannot be determined properly when the shrinkage strain rate drop under the value of 0.0003 %/s [5], which was reached by Clearfil F2 at approximately 7 minutes after mixing (Fig. 4.5). Although the modeling results of the Standard Linear Solid model at 1473 s are better than for the Kelvin model (Table 5.2), the values of $E_1$ and $E_2$ must therefore be considered questionable.

**Conclusions and recommendations**

Three viscoelastic models were proposed for the description of the linear viscoelastic behavior of a commercially available two-paste resin composite during setting. The Standard Linear Solid model could only predict the viscoelastic behavior of the two-paste composite for 6 minutes in setting time. This is not due to model incapability, but due to the fact that the experimental conditions of the test method are not good enough for predictive modeling with a 3-parametric model. Modifications in the application software of the test system would make it far better suited for the identification of the three parameters of the Standard Linear Solid model. It is advisable to perform sinusoidal deformations with different frequencies simultaneously; *i.e.*, as a multi-sine. With in mind not to exceed the strain limitation for linear viscoelasticity (0.5 %), this would result in better predictive modeling with the Standard Linear Solid model.

Until then, good predictive modeling can be carried out by using the Maxwell model up to 30 minutes into the setting process and the Kelvin model during the remainder of the setting process. In future studies, the sinusoidal strain should be applied not as a pulse, but continuously. This slight modification of the test method not only enhances the accuracy of the modeling procedure, but also makes it possible to analyze the stress-strain data directly by phase shift calculation, leading to the material parameters $E'$ (storage modulus) and $E''$ (loss modulus).

**References**

3. See chapter 2 of this thesis.
4. See chapter 3 of this thesis.
5. See chapter 4 of this thesis.