Influence of Microstructure on the Drying Kinetics of
a Foamed Amorphous Model Food Concentrate

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presented by
Friedrich Witschi
Dipl. Lm.-Ing. ETH
born March 23, 1968
citizen of Kirchlindach (BE)

accepted on the recommendation of
Prof. Dr.-Ing. E. Windhab, examiner
Dr. W. M. MacInnes, co-examiner
Dr. H. Watzke, co-examiner

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“Prima di essere ingegneri voi siete uomini”

Francesco de Sanctis (1817-1883)
Professor for Italian literature at the ETHZ (1856-60)

In memory of my grandmother Lisa Witschi
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<th>Description</th>
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<td>n</td>
<td>rotor speed</td>
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<td>OR</td>
<td>overrun</td>
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<td>mm</td>
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<td>-------------</td>
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<td>$T_o$</td>
<td>temperature of viscosity divergence, VTF equation</td>
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<td>$V_f$</td>
<td>free volume</td>
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<td>$V_y$</td>
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<tr>
<td>$v$</td>
<td>velocity</td>
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<td>$\bar{v}^2$</td>
<td>mean square fluctuation velocity (Kolmogorov)</td>
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<td>$w$</td>
<td>fractional concentration</td>
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<td>$X$</td>
<td>moisture content (wet basis)</td>
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<tr>
<td>$X_{ds}$</td>
<td>moisture content (dry basis)</td>
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<td>$x$</td>
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<td>shear strain</td>
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<td>$\dot{\gamma}$</td>
<td>shear rate</td>
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<td>$\Delta$</td>
<td>difference</td>
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<td>$\delta$</td>
<td>phase shift angle</td>
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<td>$\varepsilon$</td>
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<td>$\varepsilon_1$</td>
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<td>$\zeta$</td>
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<tr>
<td>$\eta^*$</td>
<td>dynamic complex viscosity</td>
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<tr>
<td>$\eta_0$</td>
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<tr>
<td>$\eta_m$</td>
<td>high temperature limiting value of the viscosity</td>
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<td>$\theta$</td>
<td>contact angle</td>
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<td>$\rho$</td>
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<td>$\tau_d$</td>
<td>drying time</td>
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<td>$\tau_{rel}$</td>
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<tr>
<td>$\omega$</td>
<td>angular velocity</td>
<td>s$^{-1}$</td>
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Indices

0   section 0
1   component/section 1
2   component/section 2
av  average
bed bed
blend blend of components
cl  closed
crit critical
cond condensation
cont continuous phase
conv convection
disp disperse
evap evaporation
fo  foam
g  glass transition
gas gas
H  helium
in  inlet
liq liquid
M  matrix
max maximal
op  open
out outlet
p  powder
R  reference
Re  Reynolds
r  ratio
s  solids
sol solution
vap/v vapor
w  water

Abbreviations

ARES Advanced Rheometric Expansion System
CPA Computerized Particle Analyzer
DMTA Dynamic Mechanical Thermal Analysis
DSC Differential Scanning Calorimeter
GAB Guggenheim-Anderson-de Boer equation
IQR Interquartile range
KFT Karl Fischer Titration
PVP Polyvinylpyrrolidone
RRSB Rosin, Rammler, Sperling and Bennett
SDS Sodium dodecyl sulfate
SEM Scanning Electron Microscope
SR Stress Rheometer
VTF Vogel, Tamman, and Fulcher equation
WLF William, Landel, and Ferry equation
Seite Leer / Blank leaf
Summary

Freeze-drying is a widely used drying technique in the pharmaceutical and food industry. The process uses low product temperatures (up to 40°C) and low partial pressures (lower than 50 mbar). Vacuum freeze-drying is an expensive and complex process but it offers advantages in terms of product stability and quality. The result is a porous, non-shrunken structure in the dried product that facilitates rapid and almost complete re-hydration when water is added to the substance at a later time.

In this work the solutions to be dried had a high initial concentration (> 70% total solids) to avoid ice formation in the fast cooling solidifying step and to reduce the amount of water to be removed during the drying process. The mass transport of water in desorption drying strongly depends on the structure of the matrix to be dried. Increased volume specific surface improves the drying rates significantly.

A new dispersing technique was evaluated to increase the volume specific surface of the powders to be dried by adding gas in a controlled and continuous way. The foaming equipment used was a dynamic mixer (rotor-stator mixer) developed at the ETH Zürich. The geometry is made of individual rotor and stator elements which offers a great flexibility in the configuration of the mixer. This allows a better control on the dispersing stresses and therefore of the resulting foam structure. Other process parameters like rotor speed, pressure in the mixer, product temperature and type and amount of gas to be incorporated have been studied in the frame of this work. They show that the gas dispersion in highly viscous concentrated solutions is possible in the laminar flow regime of the dynamic mixer. Pressure and type of gas are the most important foaming parameters to control the amount of gas incorporation and the bubble size distribution in the foam.

Polyvinylpyrrolidone (PVP), a water-soluble polymer, was used as concentrated food model solution. To improve the foam generation and stability, a surface-active agent (Sodium dodecyl Sulfate) was added. The foam was solidified by rapid cooling in liquid nitrogen and cut into pellets before drying.

The pellets were dried under controlled conditions in a vacuum dryer. The dryer was instrumented to follow the temperature and water loss in the powder bed during the drying process. The freeze-drying temperatures are limited by the collapse phenomena. Collapse or loss of structure in amorphous materials is related to the glass transition. The glass transitions temperatures are dependent on the moisture content of the sample. In the present study, the temperatures of collapse of PVP powders in relation to the glass transition temperature were investigated. The glass transition temperatures $T_g$ as a function of concentration were determined with Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Thermal Analysis (DMTA). An extrapolation of the DMTA $E''$ peak temperature data to 0.0001 Hz was found to correspond with the glass transition temperature measured with DSC (10°C/min). The powder collapse was measured optically on a heating stage and with a sticky point method in vials. The Vogel-Tamman-Fulcher (VTF) and the equivalent William-Lande-Ferry (WLF) equations proved to be adequate to describe temperature dependence of the viscosity of PVP. The observed “iso-viscosity” values at the collapse/stickiness transitions are in the range of $10^6$-$10^8$ Pa s. The resulting collapse temperatures and corresponding viscosity values were plotted in a State Diagram.
Summary

The description of the collapse phenomena in the State Diagram is a useful tool to study the structure stability as a function of drying process parameters time and temperature. Since stickiness and collapse are time-dependent phenomenon, the dimensionless Deborah-number that relates molecular relaxation time to observation time was introduced. The Deborah number values for the collapse observation are as expected around 1.

The drying kinetics of the foamed powder samples showed no difference in the drying rate for the microstructure parameter bubble size distribution. This could be an indication that the rate is limited by the heat transfer in the powder bed. In this case small differences in bubble size have little influence on the overall heat transfer between the powder particles in the bed. As expected the density of the powder, controlled by the amount of gas in the foam, had a strong influence on the drying rate. The denser particles dry almost 50% slower compared to the less dense ones. From the drying experiments a model using finite volume elements was developed to describe the heat and mass transfer coefficients as a function of the foam structure and the processing conditions.
Zusammenfassung


In der vorliegenden Arbeit hatten die zu trocknenden Lösungen eine hohe Anfangskonzentration (> 70% Trockenmasse), um Eisbildung beim raschen Abkühlen der Lösungen vor dem Trocknen zu verhindern. Gleichzeitig verkleinert sich der Wasseranteil der im Trocknungsschritt verdampft werden muss. Der Stofftransport des Wassers aus der Pulverschüttung hängt von der inneren und äußeren Struktur der Pulverpartikel ab. Eine Vergrösserung der inneren Oberfläche durch Aufschäumen der Lösungen erhöht die Trocknungsrate.


Zusammenfassung


Die Trocknungsraten der Pulver mit verschiedenen Gasblasenverteilungen zeigten keine Unterschiede, was ein Hinweis sein könnte, dass die Trocknungsrate in der Pulverschüttung durch den Wärmetransport limitiert ist. Kleine Veränderungen in den inneren Porosität der Pulverpartikeln hätten in diesem Fall keinen grossen Einfluss auf die Trocknungsraten in der Schüttung. Veränderungen der Dichte der Partikeln, welche über den Gasanteil im Schaum eingestellt werden, hatten grossen Einfluss auf die Trocknungsraten. Die dichteren Pulvern trockneten 50% langsamer im Vergleich zu den weniger dichten. Die Trocknungskinetik für die Pulverschüttung wurde mit einem einfachen Schichtenmodell beschrieben.
1 Introduction

An important goal of food research is to develop desirable food structure and texture. Structure and texture in food are the result of interactions among the food’s components and the phase/state transitions induced in them during processing and storage. Knowing the composition of foods and the chemical, rheological, as well as structural changes that occur during these transitions, it is possible to design processes which allow for obtaining desired structure and texture properties of food products.

Drying is one of the oldest preservation methods to extend the shelf life of foods avoiding spoilage caused by the growth of bacteria, molds, and insects. The risk of unfavorable oxidative and enzymatic reactions is also reduced. As a rule, freeze-drying produces the highest quality food product obtainable by any drying method. The result is a porous, non-shrunken structure in the dried product that facilitates rapid and almost complete re-hydration when water is added to the product at a later time. Freeze drying of food has also the advantage of little loss of flavor and aroma.

An important factor of the process is the structural rigidity of the product during the sublimation and desorption of the water. To a large extent this rigidity prevents collapse of the porous structure during the drying process and preserves the quality and structure of the product.

Freeze-drying is an expensive form of dehydration for foods because of the slow drying rates, expense involved in the freezing and the use of vacuum. One of the limiting process parameters is the drying temperature due to the collapse phenomena.

The aim of this work is to understand and develop a new approach to freeze-drying of foamed amorphous food solutions starting at high concentrations (X >70 % total solids), where no ice is formed during the freezing process. This approach uses the state diagram to better understand and improve the freeze-drying process in terms of drying rates and stability of the product regarding the collapse phenomena. The state diagram describes the phase and state transitions as a function of temperature and concentration.

The drying rate strongly depends on the microstructure of the matrix to be dried, such as bubble size distribution and cracks. The freeze drying of highly concentrated systems is problematic due to high density and viscosity which leads to a strong reduction of the diffusion velocity. A possible solution investigated in this work is to increase the surface area to improve mass transfer (evaporation) by foaming the material before freezing. To increase the volume specific surface area of the solutions to be dried, a dispersing technique to incorporate gas into highly concentrated and viscous solutions was tested. The result is a foamed structure that offers advantages in terms of fast drying, good solubility and controlled density of the end product. The foam is frozen as powder pellets with the final particle shape, structure and size distribution. These are important quality aspects, determining powder handling and reconstitution properties.

The powders are then dried in a batch vacuum dryer. From the drying data the drying rates are measured and a model is derived to determine the heat and mass transfer as a function of the microstructure of the foamed amorphous powders. The analytical tools that are used to describe the microstructure and the state diagram are rheometry, calorimetry and microscopy with quantitative image analysis.
The processes are described with classical engineering approaches like dimension analysis and modeling.

This work is divided in three parts:
In the first part we describe and determine the rheological properties and the state diagram of a concentrated food model solution. The rheological properties are then coupled with the state diagram as a function of water content and temperature. The collapse phenomena are described based on optical collapse and stickiness observations of powders at different water contents and at different heating rates. The resultant "collapse temperatures" are represented in the state diagram as a function of concentration. The viscosity at collapse temperature is calculated from the VTF-equation fitted viscosity.

The second part deals with the gas-liquid dispersion technique in a continuous dynamic mixer. This foaming technique offers the possibility to generate a controlled microstructure in the powders to be dried. The foaming process is described in terms of recipe and process parameters. The viscosity and the surface tension are the key recipe parameters. Surface tension is measured with a pendant drop and a Wilhelmy plate method.

The process parameters include the energy dissipation and the flow regime in the mixer. They are described with the Newton-Reynolds characteristic. The foam bubble size distributions are determined optically. The dispersion is characterized with the dimensionless Weber number.

The third part describes the vacuum drying kinetics of the foamed amorphous powders in a batch process and the modeling work to define the heat and mass transfer coefficients for the powders under study.

Drying experiments for the different powders are recorded with an instrumented laboratory-scale freeze dryer and the data is analyzed to compare the drying rates.

A finite volume model is used for the simultaneous solution of the partial differential equations of energy and water transport through the semi-dry, porous structure.

Two transport parameters of the numerical solution are evaluated for the powders under study. The two parameters are the Mixed Coefficient (MC) which describes an average heat and mass transfer and Length of Vapor (LV) characterizing the diffusion rate. The Mixed Coefficient gives the fraction of water molecules that condenses in the next volume slice of the model in the powder bed. The Length of Vapor describes the tortuosity of the vapor diffusion in the pores of the packed bed of porous particles.

The resulting model parameters are compared for different powder structures and a simulation of the drying allows to estimate the critical temperature condition to avoid powder collapse during the process.
2 Background

2.1 Phase and State Transition Phenomena in Foods

Phase transitions are changes that occur in the physical phase i.e. solid↔solid, solid↔liquid, solid↔gas and liquid↔gas transition of a substance. State transitions refer essentially to non-equilibrium changes between two configurations, typically in the solid state i.e. the amorphous-crystalline and the glass-rubber transitions.

Food materials are complex systems that undergo various changes in phase and state during processing and storage (Roos, 1995). Food materials are often composed of compounds that have different phase behavior, or they may contain compounds that are or become phase separated; e.g., carbohydrates, lipids, proteins, and water may all exist in different states or phases or in phases separated from each other.

A main component of most foods is water. Water in foods exhibits phase transitions of its own, such as freezing and evaporation, and water has several effects on phase and state transitions of other food components as well as on related food stability and quality. The effect of water on stability is often due to depression of phase and state transition temperatures or the need for water in phase/state transformations. In this relationship water is often referred to as a plasticizer because it increases the molecular mobility of the system (Roos et al., 1996).

Common phase transitions in the food area are melting (dissolution of crystalline materials) and crystallization, protein denaturation (loss of native protein structure), starch gelatinization (disruption of starch granules and melting of crystalline regions in starch components polymers) retrogradation (re-crystallization of these regions) (Slade and Levine, 1991; Roos, 1995). The state transition of interest within this work is the glass transition between the solid “glassy” state and the super-cooled liquid “rubbery” state of amorphous materials.

Phase and state transitions of water and other food components are used in food processes to achieve desired material properties during processing as well as for the final product to meet storage stability requirements and consumer expectations (Roos and Karel, 1991; Slade and Levine, 1991; Roos, 1995, Roos, 1998).

Particular attention has been given to the phase and state transitions occurring in low-moisture and frozen foods, which often contain food solids in the amorphous state (Shalaev and Franks, 1995; Slade and Levine, 1995; Roos, 1995; Roos et al., 1996). The physico-chemical properties of these amorphous materials are strongly influenced by the glass transition and plasticization effect of water (Slade and Levine, 1991). The investigation of the relationships between glass transition, water content, and food properties has increased the understanding of the mechanical properties of food materials (Kalichevsky et al., 1992; Peleg, 1996), the stability of frozen foods (Ried, 1995), and the stability of low-moisture foods and food powders (Roos and Karel, 1991). The effects of glass transition on diffusion-controlled reactions as well as encapsulation and release of encapsulated compounds (Shimada et al., 1991; Karmas et al., 1992; Nelson and Labuza, 1994; Bell, 1996) has also been studied. The glass transition is the main state transition occurring in amorphous, non-equilibrium food systems (Roos, 1998).

In the following sections the phase/state transitions affecting food properties will be defined in terms of thermodynamics.


2.1 Phase and State Transition Phenomena in Foods

2.1.1 First Order Transitions
The thermodynamic definition of phase transitions is based on observations of changes occurring in Gibbs energy at the transition temperature. The Gibbs equation for the free enthalpy $G_G$ is defined from the enthalpy $H$, temperature $T$ and entropy $S$ as follows:

$$G_G = H - T \cdot S \quad \text{Eq. 2.1.1}$$

First-order transitions are defined as those in which the first derivatives of the Gibbs free enthalpy for temperature (Eq. 2.1.2) and pressure $P$ (Eq. 2.1.3 and Eq. 2.1.4) exhibit discontinuity at the transition temperature (Roos, 1998).

$$y = \left( \frac{\partial G_G}{\partial P} \right)_T \quad \text{Eq. 2.1.2}$$

$$H = G_G - T \left( \frac{\partial G_G}{\partial T} \right)_P \quad \text{Eq. 2.1.3}$$

$$S = -\left( \frac{\partial G_G}{\partial T} \right)_P \quad \text{Eq. 2.1.4}$$

The second derivatives of the free enthalpy for temperature and/or pressure define the thermal expansion coefficient $\zeta$ and the heat capacity $c_P$ as follows:

$$\zeta = \frac{1}{V} \left( \frac{\partial^2 G_G}{\partial T \partial P} \right) \quad \text{Eq. 2.1.5}$$

$$c_P = -T \left( \frac{\partial^2 G_G}{\partial T^2} \right)_P \quad \text{Eq. 2.1.6}$$

Figure 2.1.1 shows the step change in enthalpy, entropy, and volume at the first order transition temperature, and the second derivatives (e.g., heat capacity) show discontinuity at the transition temperature.
2.1 Phase and State Transition Phenomena in Foods

2.1.1 First Order Transitions

It may also be observed that first order transitions occur at material-specific, well-defined temperatures, and there is a change in enthalpy that corresponds to the latent heat of the transition. Generally first-order phase transitions are those occurring between the equilibrium solid and liquid, solid and gaseous, and liquid and gaseous phases, i.e., crystallization and melting, condensation and sublimation, as well as condensation and evaporation, respectively. In food materials the main first-order transitions are those of water and lipids, but also protein denaturation and starch gelatinization can also be considered as transitions having first-order transition characteristics. Other common first-order transitions in food include crystallization and melting of carbohydrates.

Time dependent crystallization phenomena are often observed in amorphous non-equilibrium materials as they transform into the equilibrium, crystalline, solid state. However, most first-order transitions in foods are affected by components of the food material, and the transitions do not always occur at a single temperature, but rather over a temperature range. Typical examples are the melting of ice in solutions and fats. The transition temperature, for example of the crystallization and melting of sugars, protein denaturation, and starch gelatinization, depend greatly on water content.

2.1.2 Second Order Transitions

Second-order phase transitions are thermodynamically defined as those in which the second derivatives of the Gibbs free enthalpy (Eq. 2.1.5 and Eq. 2.1.6) exhibit discontinuity at the transition temperature (Figure 2.1.2).

Figure 2.1.1: Changes in Gibbs free enthalpy $G$, enthalpy $H$, entropy $S$, volume $V$, and heat capacities $C_p$ and $C_v$, at a first-order phase transition temperature. (Adapted from Roos, 1998)
2.1 Phase and State Transition Phenomena in Foods

The Gibbs energy is the same for both phases at the transition temperature. H, S, or V

Second-order transition temperature

Figure 2.1.2: Changes in Gibbs free enthalpy G, enthalpy H, entropy S, volume V, and heat capacity Cp, at the second-order phase transition temperature. (Adapted from Roos, 1998)

The glass transition of amorphous materials, including foods, has the properties of a second-order phase transition. Whereas a true second order transition occurs between equilibrium phases, the glass transition is a non-equilibrium change in the amorphous state. It always occurs over a heating and cooling rate-dependent temperature range, as shown in Figure 2.1.3 for the change in heat capacity.

Figure 2.1.3: Determination of glass transition temperature Tg of PVP K15 (X= 96%) from thermograms obtained using differential scanning calorimetry. Effect of scanning rate on the location of the transition temperature.
Most glass transition temperatures reported for foods and other materials have been determined using differential scanning calorimetry (DSC). The transition temperature is taken as the onset or mid-point temperature of the step change in heat capacity occurring over the glass transition range, as shown in Figure 2.1.3.

While the change in heat capacity is very small, the complex viscoelastic mechanical modulus $E^*$ measured under imposed oscillatory compression/tension or bending forces can change by several orders of magnitude through the glass transition. This is shown in Figure 2.1.4 for the storage modulus $E'$ ( = real part of $E^*$) for a polyvinylpyrrolidone solution measured with Dynamic Mechanical Thermal Analysis (DMTA) as a function of temperature for various scanning frequencies while heating at 0.3°C/min. In this work the glass transition temperature is also evaluated in terms of mechanical relaxation properties described by the temperature dependent changes in the bending viscoelastic (storage bending modulus, $E'$ and loss modulus, $E''$) (see Chapter 4.1.2) and oscillatory shear (elastic (storage) shear modulus $G'$ and viscous (loss) shear modulus $G''$) (see Chapter 4.1.3) modulii. Again, the mechanical property changes during the glass transition are heating rate and measurement frequency dependent and occur over a much wider temperature range than the corresponding heat capacity change (compare Figure 2.1.3 and Figure 2.1.4). Maximum energy dissipation during this transition occurs when the imposed frequency dependent bending or shear deformation couples most strongly with the vibration of the molecules. This is manifested by a frequency dependent peak in the loss bending modulus $E''$ or in the loss shear modulus $G''$, shown in Figure 2.1.5 and Figure 4.1.9 at a given temperature.

At the $E''$ peak temperature for each frequency, the average molecular relaxation time $\tau_{mol}$ can be estimated by the following equation:

$$\tau_{mol} = \frac{1}{2 \cdot \pi \cdot f}$$

Eq. 2.1.7

where $f$ is the frequency.

Figure 2.1.4: Drop in the storage modulus, $E'$ for a PVP-K15 (X= 70%) sample
As the glass transition is a kinetic phenomenon, its temperature value shifts with scan speed in enthalpy relaxation (Figure 2.1.3) and with frequency in the mechanical relaxation measured with the DMTA (Figure 2.1.5). The shift in $T_g$ as a function of scanning rate or frequency can be used to compare the average molecular relaxation times at $T_g$.

Analysis of the dependence of the glass transition measured with DSC at different heating rates shows that $T_g$ defined by the onset of the heat capacity change for the common scan rate of 10°C/min corresponds to the temperature at which the average molecular relaxation time of super-cooled liquid is $\approx 200$ s (Angel 1983).

In order to compare the DMTA measured $T_g$ temperatures, taken as the $E''$ peak temperature in an oscillatory bending test, to the calorimetrically measured ones, it is necessary to extrapolate the $E''$ peak temperatures to the relaxation time scale of the DSC transition. At the DMTA measurement frequencies of 0.1, 1, and 10 Hz the molecular relaxation times at the corresponding $E''$ peak $T$ (Eq. 2.1.7) are 1.59, 0.159, and 0.0159 seconds. This is far below the 200 seconds value. As it is not realistic to perform DMTA measurements at the frequency of 0.0008 Hz corresponding to 200 Hz is found.

2.1.3 Application of the state diagram in food processing

The physical state of water in solutions can be illustrated by a state diagram (Figure 2.1.6) which represents the various states in which a system can exist as a function of temperature and concentration. Consequently state diagrams are as well used to characterize food systems as a function of temperature and concentration (Slade and Levine, 1991; Roos et al., 1996).

Figure 2.1.6 shows a typical state diagram for solutions where the solute does not crystallize during cooling.
2.1 Phase and State Transition Phenomena in Foods

The solid bold ice-melting point line is a crystallization phase transition limit indicating the concentration dependent temperature $T_m$ attainable for crystalline water while heating under equilibrium conditions.

The composition dependent glass transition temperature line $T_g$ defines the transition of a solution from a rubbery into a glassy state. $T_g$ is essentially an iso-viscosity line where the DSC onset temperature of the change in heat capacity is used to define the glass transition as a function of concentration. The viscosity of the glass at this transition line is generally expected to be of the order of $10^{12}$ Pa s. The viscosity of a solution above $T_g$ decreases rapidly as a function of temperature. The viscosity as a function of temperature for solutions close to the glass transition will be discussed in Chapter 2.1.6. In Figure 2.1.6, a line of lower iso-viscosity is indicated and is approximately parallel to the glass transition line $T_g$.

As shown in Figure 2.1.6, when cooling solutions under non equilibrium conditions (fast or quench cooling), the concentration dependent $T_g$ transition and, after "de-vitrification", the concentration independent transition $T_g'$ on heating, can be observed. This is true for solutions, whose concentrations are lower than the maximal cryo-concentration $C_g'$ and for a limited concentration range.

As cooling is the first step in the freeze-drying process, these transitions and the solution behavior upon cooling will be discussed in more detail.

The solution to be dried is first cooled down to a temperature where it is essentially a rigid solid. In practice, food materials display one of two different types of freezing or solidification behaviors:
1. The solvent suddenly crystallizes at a temperature that depends on the nature of solids in the sample;
2. The solvent does not crystallize but the solution just becomes more and more viscous until it finally takes the form of a very stiff, highly viscous liquid (glass formation).

These two freezing behaviors are best illustrated using the state diagram for a typical aqueous solution (Figure 2.1.7).

![State diagram showing different cooling behavior for aqueous solutions](image)

Figure 2.1.7: State diagram showing different cooling behavior for aqueous solutions

If a solution \( \Theta \), whose concentration is less than \( C_g' \), is slowly cooled then ice can crystallize. The equilibrium melting point line \( T_m \) gives the maximum temperature at which this can occur. As the temperature of the solution is lowered towards \( T_m \), more and more ice is formed. Since the ice contains no solute, the remaining solution around the ice is cryo-concentrated to \( C_g' \) at \( T_1 \). When the temperature reaches the \( T_m \) curve, the solution is maximally cryo-concentrated to \( C_g' \). Below \( T_m \), the rubbery solution is rigid enough to be self-supporting, without flow, for a finite time of observation. This temperature is also called by Karel et al. (1994) "the onset of ice melting" upon heating of a cryo-concentrated solution. It is readily identified in DSC scans on frozen solutions as the large endo-exothermic (ante-incipient melting) transition. It was labeled originally as \( T_{g'} \) by Levine and Slade (1988).

Upon further reduction in temperature of this cryo-concentrated solution, one observes the true glass transition \( T_g' \) of the cryo-concentrated solute matrix surrounding the ice crystals in a maximally frozen solution. The rubbery matrix transforms into a rigid glass. Thus in theory, for any starting concentration \( C_1 < C_g' \), these primed melting and glass transition temperatures \( T_m \) and \( T_g' \) are always the...
same. In practice they are found to decrease slightly with concentration due to viscosity effects on cryo-concentration in the rubbery-glassy region. Note that these transitions are completely reversible on slow cooling/heating. On heating the \( T_m \) temperature corresponds to the onset of de-cryo-concentration and is the maximum temperature giving the needed rigidity to the material for successful freeze-drying without collapse.

During cooling of a highly concentrated solution \( 2 \), no crystallization of the solvent occurs and the solution becomes more and more viscous and finally transforms into a glass below \( T_g \). This glass transition temperature is concentration dependent.

State diagrams are being used as important tools for establishing proper processing and storage conditions for dehydrated and frozen foods. They help to describe food structure and stability modifying events e.g. collapse and stickiness in powders, crystallization behavior of water or other solutes like sugars, as shown in Figure 2.1.8 (Karel et al., 1994; Shalaev and Franks, 1995; Roos, 1998).

The knowledge of such transition regions combined with reaction kinetics can be used to indicate the path of food processes such as concentration, spray-drying, agglomeration, and freezing.

In this work, the state diagram will be applied to the freeze drying process in order to describe optimal drying conditions avoiding collapse of the powder matrix to be dried.
2.1.4 The classical freeze-drying process in the state diagram

Freeze-drying is the most prominent example of separation by sublimation. In freeze-drying, water is removed as vapor from a frozen substance. The water passes from the solid phase directly into the vapor phase without becoming liquid. Consequently it is necessary that the pressure of the sublimation zone in a material being freeze-dried is held below the triple point pressure of the water or aqueous solution in the material being dried (Figure 2.1.9).

![Phase diagram of water](image)

Figure 2.1.9: Phase diagram of water

The classical freeze-drying separation process involves three stages: the freezing stage, the primary drying and the secondary drying stage (Figure 2.1.10).

![Freeze-drying process](image)

Figure 2.1.10: Freeze-drying process
2.1 Phase and State Transition Phenomena in Foods

Figure 2.1.11 shows the classical freeze-drying temperature concentration pathway starting from a concentrated solution (X = 40 to 50%) in the state diagram.

2.1.4.1 Freezing stage
The freezing stage represents the first step in the freeze drying process. The material is first cooled down to a temperature where it is essentially a rigid solid. The freezing behavior of the solution to be dried was discussed in the previous section. The shape and size distribution of the pores and connectivity of the porous network in the dried layer after sublimation of the frozen water during the primary drying stage depends on the ice crystals that are formed during the freezing stage. This dependence is of extreme importance because the mass and heat transfer rates are influenced significantly by the porous structure of the dried layer. If the ice crystals are small and discontinuous, then the mass transfer rate of the water vapor will be limited by the material surrounding the pores. On the other hand, if large homogeneously distributed dendritic ice crystals are formed in the frozen solution, the mass transfer rate of the vapor is high due to the open or sponge-like porous structure. Consequently the product dries faster in the following drying stages.

2.1.4.2 Primary drying stage
After the freezing stage, the drying chamber is evacuated and the water in the product is removed by sublimation in the primary drying stage (C < C_{g'}) in order to sublimate the water the pressure must be less than or near to the equilibrium vapor pressure of
2.1 Phase and State Transition Phenomena in Foods

the frozen solvent to remain solid. The equilibrium vapor pressure for ice at 0°C is 6.1 mbar.
When the water molecules sublimate and enter the vapor phase, they also keep with them the latent heat of sublimation (2840 kJ/kg ice) and thus the temperature of the frozen product is again reduced. If there is no heat supplied to the product by a heat source, then the vapor pressure of the water at the product temperature reaches the same value as that of the partial pressure of the water vapor in the drying chamber. The system reaches equilibrium and no additional water would sublimate. Thus, in order to have continuous sublimation of water from the product, the latent heat of sublimation must be provided to the material from a heat source. The heat is supplied usually by conduction, convection, and/or radiation. Conduction is realized by contact between heated plates and product-supporting containers.
The vapor produced by the ice sublimation in the frozen layer and by desorption of sorbed (non-frozen) water in the cryo-concentrated matrix during the primary and secondary drying stage moves by diffusion and convective flow through the porous structure of the matrix and enters the drying chamber of the freeze-dryer. The vapor must be continuously removed from the drying chamber in order to maintain non-equilibrium conditions in the system. This is usually accomplished by fitting a refrigerated condenser between the drying chamber and the vacuum pump. The water vapor de-sublimates to ice on the cooled surface of the condenser.
The amount of supplied heat to remove the water can not be increased freely because there are certain limiting temperature conditions during the primary drying stage. As will be discussed below, the maximum allowable drying temperature in the frozen layer is determined by the structural stability of the matrix, which is limited by collapse phenomena above T_m'. This temperature will also determine the maximum pressure to maintain the ice solid at and below T_m', and is considerably less than 6.1 mbar. For example, if T_m' = -20°C the maximum pressure will be 1 mbar.

2.1.4.3 Secondary drying stage
The secondary drying stage involves the removal of water that did not freeze. This water is rather uniformly distributed in the cryo-concentrated matrix and is often referred to as "bound" or "un-freezable" water. While the amount of bound water (1-C_g) only ranges from X= 10-40% its effect on the drying rate and overall drying time is very significant. The time to remove the absorbed water can be as long or longer than the time required for the removal of the "free" frozen water by ice sublimation (see Figure 2.1.10).
In the secondary drying step, after all ice has been sublimated, the temperature is increased to improve the drying rate. As in the case of primary drying, the amount of heat that can be supplied to the product cannot be increased freely, due to the collapse phenomena.
The drying is finished when the product reaches its final moisture content often at a constant drying temperature followed by cooling of the product to room temperature.

2.1.5 The collapse phenomena during freeze-drying
During freeze drying, collapse phenomena occur when the material temperature, locally or in bulk, exceeds a collapse temperature T_c. This temperature is higher than the concentration dependent glass transition temperature T_g or T_g'.

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Bellows and King (1973) introduced the idea of a limiting amorphous viscosity of collapse in freeze-drying. The theory was based on the fact that freezing of solutions separates water as pure ice and the non-crystalline solutes form a concentrated amorphous solution. From dimensional analysis they obtained Eq. 2.1.8 to relate the viscosity $\eta$, and surface tension $\sigma$, to the time $\tau_c$ for a collapse of pores with radius, $r$, that were left by the ice crystals:

$$\tau_c = \frac{\eta \cdot r}{2\sigma}$$  \hspace{1cm} Eq. 2.1.8

Reducing the viscosity shortens the collapse time $\tau_c$ which therefore must be longer than the drying time $\tau_d$ at that viscosity. Surface tension $\sigma$ was taken as the driving force for collapse. For drying times in the range of 1 to 1000 sec. and assuming the surface tension of water of 70 mN/m and a pore diameter of 20 $\mu$m they predicted a viscosity of the matrix of $10^4 - 10^7$ Pa s to allow collapse.

In fact, it is the reduction in viscosity or rigidity of the material, which is determined by its local temperature and water content, that results in material flow, porous structure collapse and enhanced surface diffusion. These phenomena lead to "bridging" between particles and bridge/neck growth. The collapse phenomena occur during freeze-drying, and they can severely reduce the drying rate and eliminate the "freeze-dried" porous texture. The same collapse phenomena are associated with "caking" and agglomeration of dry powders.

Collapse during freeze-drying was observed under the microscope by MacKenzie (1975). The process was always accompanied by the segregation of quantities of freeze concentrated solute, the disappearance of the freezing pattern and flow of the residual material. Collapse behavior was found to be remarkably dependent on the freeze-drying temperature. The temperatures at which material during freeze-drying collapses were designated as "collapse temperatures". To maintain the porous structure without collapse, freeze-drying must be carried out below these collapse temperatures $T_c$.

To and Flink (1978a,b,c) determined the collapse temperatures of freeze-dried materials with two methods: optical collapse of powder particles and stickiness behavior of powders in vials.

The collapse temperature depends on the nature of the solute as do $T_g$ and $T_g'$. It is determined in large part by the molecular weight and the solute molecules structure. The loci of the $T_c$ values for different solution concentrations are usually "iso-viscosity" lines in the state diagram (Figure 2.1.6 and Figure 2.1.8) approximately parallel to the $T_g$ and $T_g'$ transition lines (Shalaev and Franks, 1995; Roos, 1998).

Below $T_c$, the matrix is sufficiently viscous and acts like a rigid solid. At the $T_c$ line for a given iso-viscosity collapse occurs in a given time. In fact, the exact values must be determined for the material under consideration, and the temperature-concentration dependence of the viscosity must be known to be able to make these correlations.

### 2.1.6 Viscosity as a function of temperature and concentration in amorphous polymers.

Viscosity plays a major role in the collapse phenomena. During the study of polymer viscoelasticity, Vogel (1921), Doolittle (1951), and Williams et al. (1955) have laid
the foundation to describe the temperature dependence of viscous properties in the temperature range above the glass-liquid transition.

Various methods have been developed to characterize the viscosity changes of foods in the glass transition range: Dynamic mechanical thermal analysis (Wetton et al., 1985; MacInnes, 1993 and Wagner, 1997), stress controlled rheometers (Ollett et al., 1990) and strain controlled rheometers (Arvanitoyannis and Blanshard, 1993). The authors stress the importance of sample preparation, as some liquids or food materials absorb water rapidly or show aging effects.

The above mentioned methods have been used to study different types of food and food models such as food polymers (Roos, 1995), super-cooled sugar solutions (Ollett et al., 1990; Arvanitoyannis and Blanshard, 1993; Kerr and Reid, 1994), frozen systems (Maltini et al., 1995), proteins (Angell, 1995) and polyvinylpyrrolidone of different molecular weight (MacKenzie 1972; Challa and Tan, 1976; Oksanen and Zografi, 1990; Buera et al., 1992; Bell and Hageman, 1995).

Bellows and King (1973) pointed out that the viscosity of concentrated amorphous solutions were strongly concentration dependent and increased due to an Arrhenius-type temperature effect. As Nelson and Labuza (1994) summarize, the Arrhenius relationship (Eq. 2.1.9) is the major mathematical model used to describe the temperature dependence of most chemical reactions and physical properties such as diffusion and viscosity.

\[ k = k_0 \cdot \exp \left( \frac{E_a}{RT} \right) \]  

Eq. 2.1.9

where \( k \) is the rate constant at temperature \( T \), \( k_0 \) is a rate constant at \( T_0 \), \( R \) is the ideal gas constant and \( E_a \) is the activation energy.

A plot of \( \ln(k) \) versus \( 1/T \), if a straight line, indicates the applicability of the Arrhenius model and that the activation energy over the specific temperature range is constant. If the plot deviates from a straight line, the test results and/or methods are either poor, or other effects influence the reaction rate being studied.

Levine and Slade (1988) stated that the Arrhenius model is applicable for describing the temperature dependence of reactions within the glassy state of a food matrix and also above about 100°C above the glass transition temperature, but is not applicable within the rubbery state.

Perez (1994) in his review paper describes several theories of the liquid-glass transition phenomena to characterize atomic (molecular) movement through the glass transition. He states that the structure of a glassy solid may be considered as a random distribution of local regions of spatially fluctuating density and high energy (and entropy) in an atomically disordered continuum. These local regions have often been described in terms of free volume or alternatively as quasi-point defects (qpd) by Perez. Above \( T_g \), the concentration, \( C_d \), of qpd is temperature dependent as the system remains in a metastable thermodynamic equilibrium, but when the temperature is decreased below \( T_g \), \( C_d \) becomes constant. The temperature dependence of molecular mobility obeys the Arrhenius law at \( T < T_g \) (iso-configurational state) but this dependence is much more complex at \( T > T_g \) (metastable supercooled liquid state). In the latter case Perez (1994) suggests it is governed by the Vogel-Tamman-Fulcher (VTF) or the equivalent William-Landel-Ferry (WLF) expressions.
The molecular mobility at the liquid-glass transition can be characterized at the macroscopic level by the viscosity $\eta$. The molecular mobility can be expressed as the shear relaxation time for viscous flow $\tau_{vf}$ related to shear viscosity $\eta$ and the limiting low T modulus $G_{\infty}$ by the following equation (Angel et al., 1994):

$$\tau_{vf} = \frac{\eta}{G_{\infty}}$$

Eq. 2.1.10

For $\eta$ at $T_g$ of $10^{12}$ Pa s and usual $G_{\infty}$ values of $10^9 - 10^{10}$ Pa a relaxation time $\tau_{vf}$ at the glass transition between $10^2$ and $10^3$s is obtained (Perez, 1994).

Historically the concept of “free volume” has been used to explain the significant changes in mobility, viscosity, and other properties of polymers at and above the glass transition temperature (Ferry, 1980). Free volume $V_f$ can be defined as the excluded volume present in a polymer system due to the arrangement of the polymer chains. The volume of a polymer sample, $V$, is considered to be the sum of the volume occupied by the polymer, $V_0$, and the free volume $V_f$. In Figure 2.1.12 the effect of temperature on both the total volume, $V_0 + V_f$, and the occupied volume $V_0$, is illustrated.

Figure 2.1.12: Effect of temperature on the total volume of a polymer material, $V_0 + V_f$, and the occupied volume, $V_0$.

The free volume $V_f$ decreases to a minimum fractional value of about 0.03 for polymers at the glass transition temperature, $T_g$ (Soesanto and Williams, 1981). The glass transition temperature can be defined as the temperature at which the free volume reaches this minimum size upon cooling. Below $T_g$ the free volume is constant. The free volume is viewed as the volume created by rotational and translational motions of polymer molecules. In the context of this free volume theory, $T_g$ is the temperature below which the rotational and translational contributions to molecular motion are considerably reduced, but there is still some vibrational motion present as in a true solid.

The effect of temperature on the volume in which molecules are free to move has been treated in the theoretical framework of the Vogel-Tamman-Fulcher equation, which gives the viscosity as:

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2.1 Phase and State Transition Phenomena in Foods

\[ \eta = A \cdot \exp \left( \frac{B}{T - T_0} \right) \]  
Eq. 2.1.11

where \( A \) is the high temperature limiting value of the viscosity and \( B \) is equivalent to an activation energy. The factor \( A \) in the VTF equation seems to have a universal value of \( 10^{15} \) Pa s (Angell et al., 1994). \( T_0 \) represents the temperature where the viscosity would theoretically diverge (become infinite).

Angell et al. (1994) proposed a “strong/fragile” classification scheme for viscosity behavior as the temperature is lowered towards the glass transition temperature. This classification is based on a description of the viscosity in terms of relaxation behavior and involves that the glass transition temperature provides an appropriate scaling temperature for corresponding structural states. \( T_g \) scaling of viscosity data in the Arrhenius form (Eq. 2.1.9) yields the pattern shown in Figure 2.1.13, in which one extreme is represented by the Arrhenius equation for viscosity \((T_0 = 0)\).

The other extreme behavior shows a significant deviation from the Arrhenius behavior. This pattern of increasing deviation from the Arrhenius form may be accounted for by the VTF form (Eq. 2.1.11) using only the “strength” parameter \( D \), as variable as proposed by Angell:

\[ \eta = \eta_m \exp \left( \frac{D T_0}{T - T_0} \right) \]  
Eq. 2.1.12

\( T_0 \), the temperature of viscosity divergence, lies below \( T_g \) by an amount that depends on the parameter \( D \).

“Strong” materials are those for which the temperature coefficients for the dynamic properties under study (i.e. the slope of the curves) do not vary very much when the temperature is raised above the \( T_g \). They have large \( D \) parameters and are the closest to an Arrhenius behavior. “Fragile” materials, on the contrary, show a rapid degradation of their mechanical properties, and consequently of their microstructure.

To simplify the application of the concept of fragility to systems near their glass transition temperature Angell et al. (1994) uses the parameter \( m \), simply called “the fragility”. \( m \) is the slope of the \( T_g \)-scaled Arrhenius plot of any relaxation time (or a quantity, such as viscosity, which is proportional to a relaxation time) measured at \( T_g \). It is related to the conventional Arrhenius activation energy for a property \( P \) by:

\[ m = \frac{d \log P}{d(1/T_g/T)} = \frac{E_a}{2.303 \cdot R \cdot T_g} \]  
Eq. 2.1.13

and is related to the parameter \( D \) of Eq. 2.1.12 by:

\[ m = 16 + 590/D \]  
Eq. 2.1.14

Figure 2.1.13 shows the “fragility” of the viscosity behavior plotted for different \( D \) and \( m \) values assuming that \( T_0 \) is below \( T_g \) by the factor of the universal constant \( C_2 \) from the WLF Eq. 2.1.15.
In food science reporting, it has been common to discuss the temperature dependence of relaxation times at the glass transition in terms of the Williams-Landel-Ferry (WLF) equation (Angell et al., 1994). Williams et al. (1955) applied a shift coefficient deduced from drawing master curves for molecular relaxation times of polymers to the VTF equation. The following transformation of the VTF equation gives the WLF equation:

\[
\frac{\eta}{\eta_g} = A \cdot \exp\left(\frac{B}{T - T_0}\right) = A \cdot \exp\left(\frac{B}{T_g - T_0}\right)
\]

Eq. 2.1.15

\[
\frac{\eta}{\eta_g} = \exp\left(\frac{B}{T - T_0} - \frac{B}{T_g - T_0}\right)
\]

Eq. 2.1.16

where \(\eta\) and \(\eta_g\) are the viscosities at \(T\) and \(T_g\) respectively. Defining the WLF C₁ and C₂ constants as follows:

\[
C_1 = \left(\frac{B}{T_g - T_0}\right) \frac{1}{\ln(10)}
\]

\[
C_2 = T_g - T_0
\]

the equation can be re-written in the classical form found in the literature:

Figure 2.1.13: Scaled Arrhenius plot of viscosity for different D values
Average values for the WLF constants $C_1$ and $C_2$ were calculated by Williams et al. (1955) using the available values for many synthetic polymers. It is quite common in literature to use these average constants, which have the values of $C_1 = 17.44$ and $C_2 = 51.6$, for establishing the applicability of the WLF model (Soesanto and Williams, 1981, Roos and Karel, 1991). Peleg (1992) discussed several problems associated with the use of average constants in the WLF equation. He found disagreement for prediction purposes 20-30°C above the glass transition temperature.

According to Angell et al. (1994) the average value for $C_1$ is probably true and constant if the expression is used for the variation of viscosity ($C_1 \sim 17$) or if applied to relaxation time ($C_1 \sim 16$). This is not true, however, for parameter $C_2$. The variation of $C_2$ corresponds to the classification of strong/fragile liquids, and can vary with solution concentration.

To determine the viscosity behavior at the collapse temperature of the amorphous powders the viscosity as a function of temperature of the solutions will be measured and the viscosity will be extrapolated to the glass transition temperature by fitting the VTF equation to the experimental data.

**2.1.7 Time-dependence of the collapse phenomena**

The vast majority of materials show a rheological behavior that classifies them to a domain somewhere between liquids and solids. Ideal liquids and gases deform irreversibly, they flow because the energy required for the deformation is dissipated within the fluid in the form of heat and cannot be recovered simply by removing the stresses. Ideal solids deform elastically, the energy required for the deformation is fully recovered when the stresses are removed. Materials are in varying extents both elastic and viscous and are therefore referred to as “visco-elastic”.

This classification of the rheological behavior of materials related to their response to applied stresses can be further extended by the introduction of a dimensionless time scale of the deformation process. Such time scale is defined by the non-dimensional Deborah Number:

$$\text{De} = \frac{\tau_{\text{mol}}}{t}$$  \hspace{1cm} \text{Eq. 2.1.18}$$

where $\tau_{\text{mol}}$ is the mean relaxation time and $t$ the observation or characteristic process time. This difference between solids and fluids is then defined by magnitude of $\text{De}$. If the time of observation is very large, or, conversely, if the time of relaxation of the material under observation is very small, the material appears to flow ($\text{De} \ll 1$). On the other hand, if the time of relaxation of the material is larger than the time of observation, the material, for all practical purposes, appears as a solid ($\text{De} \gg 1$).
2.2 Foaming of concentrated solutions

Most products after freeze-drying show a porous microstructure. Looked at under the light microscope they show an open porous structure that are the voids left after the sublimation of the dendrite ice crystals. Some products to be freeze-dried are foamed by adding gas in a dispersing apparatus to reduce the final product density and to improve the drying rate. The gas bubbles add to the porous structure but can be clearly distinguished from the ice crystal generated voids.

Figure 2.2.1 and Figure 2.2.2 show SEM images of two different freeze-dried powders. Figure 2.2.1 shows a typical freeze-dried powder with ice crystals and gas bubbles. The starting concentration before drying is below the maximally cryo-concentrated solution concentration $C_g$ and ice forms upon cooling.

Figure 2.2.1: Freeze-dried coffee powder

Figure 2.2.2 shows powder dried from a foamed concentrated PVP solution without ice crystals. In this case the starting concentration ($X = 70\%$) was close to the $C_g$ concentration and no ice formation occurs upon (rapid) cooling of the solution.

Figure 2.2.2: Freeze-dried powder from concentrated PVP solution
2.2 Foaming of concentrated solutions

The freeze-drying rate increases with an increase in product specific surface area. Foaming increases the porosity of the product to be dried and consequently allows for generating additional inner surface area which improves the drying rate. Bellows and King (1973) showed that ice does not nucleate readily for very high initial solute concentrations, e.g. ice formation ceases above $X = 70\%$ for sucrose solutions. If no pre-seeding of ice is effected using a scraped surface heat exchanger then in practice for the cooling rates used in the freeze-drying process ice is not formed already for concentrations between 66 and 70 % dissolved solids. They also state, that if an extensive ice network is not formed during freezing, freeze-drying becomes “prohibitively” slow.

The aim of this work is to study the drying kinetics of concentrated solutions near and above $C_g^*$. When no ice is formed during freezing the drying rates are indeed expected to be very slow. To compensate the reduced molecular mobility the characteristic diffusion length is reduced by increasing the porosity. Therefore the concentrated solutions are foamed with a dynamic mixer. After whipping the foam has to be stabilized by rapid cooling into the glassy state before drying. The next section will give an overview of the foaming process.

2.2.1 Foams: Physics and Structure

Foams are dispersions of a gas in a liquid or solid. Foams are thermodynamically unstable. Surface and gravitation forces tend to phase-separate the gas dispersed in the liquid. The phase separation can be reduced and even stopped by reducing the surface tension at the gas liquid interface and/or by increasing the viscosity of the continuous liquid phase.

Food foams are generally stabilized by combining the surface tension reducing effect of added surface-active agents and viscosity increase of the liquid phase.

There are several types of instabilities described in the colloid and surface science literature (Walstra, 1987, Prins, 1987):

**Ostwald ripening**, involving the growth of larger bubbles at the expense of smaller ones by diffusion of gas from one bubble to another through the continuous liquid phase. The driving force for Ostwald ripening is the higher solubility of a gas under higher gas pressure. This leads to disproportionation of the bubbles (small bubbles decrease and large ones grow) which can be explained by the reciprocal dependency from the bubble radius $r$ of the Laplace pressure difference $\Delta P$, given by

$$\Delta P = 2\sigma/r$$  \hspace{1cm} \text{Eq. 2.2.1}$$

Where $\sigma$ is the surface tension, and $r$ is the bubble radius. From Eq. 2.2.1 it is obvious that $\Delta P$ is larger for small bubbles between two bubbles of different size. The resulting pressure difference leads to a concentration gradient of gas in the liquid causing the mass (gas) transfer from the small to the large bubble. The small bubbles shrink as the gas diffuses through the liquid to the larger bubbles. Shrinkage is rapid, since the surface tension and the solubility of most gases in water is high.

Cooney (1974) obtained highest foam stability and overrun (gas to liquid volume ratio) with nitrogen followed by oxygen, hydrogen and carbon dioxide. The higher foam stability with nitrogen can be explained by the fifty times less solubility of nitrogen compared to carbon dioxide.
2.2 Foaming of concentrated solutions

Prins (1987) discusses in more detail the solubility of gas N₂ and CO₂, the diffusion coefficient and the relation to foam stability.

Creaming, which causes the bubbles to mount to the product surface, leading to the formation of a layer in which the bubbles are closer packed. For dilute dispersions of spherical bubbles, creaming velocity can be estimated by the Stoke’s equation:

\[ v = \frac{2g\Delta \rho r^2}{9\eta} \]  

Eq. 2.2.2

Where \( v \) is the creaming velocity, \( g \) is the acceleration due to gravity, \( \Delta \rho \) is the density difference between bubble gas and the continuous phase, and \( \eta \) is the viscosity of the latter.

Flocculation, in which groups of bubbles assemble for a far longer time than would occur simply on the basis of their Brownian motion, due to the presence of a net attractive inter-particle free energy. Flocculation is of little interest in low-density foams since the bubbles are normally close together in any case.

Coalescence is the fusion of two bubbles into one. This process is initiated by the formation of a small hole in the thin film between a pair of bubbles in close proximity. Coalescence plays a major role for the dispersion of bubbles in the whipping process.

Foaming surfactants

As a general rule, foam is not generated in a pure liquid phase. A surfactant that adsorbs at the gas/liquid interface is necessary in order to produce foam in aqueous solutions. The formation of foam from a bulk liquid involves the expansion of the interface area due to the work acting upon the system. The new interface area formed per unit energy input will be higher, the lower the surface tension. Thus the reduction of surface tension by the surfactant is a primary requirement for foam formation. During foam formation, rapid adsorption of surfactant at the newly created surface is desirable. The rate of adsorption of surfactant during foam formation is critical for foam stability or re-coalescence respectively and will greatly depend on such conditions as surfactant concentration and adsorption kinetics as well as from the dispersing speed.

2.2.2 Foaming process

In most cases in the food industry, foam is produced in two different ways (Walstra 1989):

By supersaturating a liquid with gas, either by dissolving gas under pressure and releasing the pressure (as in beer) or by generating gas in situ (e.g. by fermentation).

By mechanical means, either injection of gas through narrow openings, or beating (formation of bubbles in the wake of a fast moving rod). This method is used widely in industry because the amount of gas in the foam and the mechanical power/energy input can be controlled.

There are two main mixing or whipping apparatus principles: static and dynamic mixers.
2.2 Foaming of concentrated solutions

Static mixers
A static mixer consists of a tube with mixing elements. The gas and the liquid phases are dispersed by the flow regime at the mixing elements. From process parameter point of view the shape of the mixing elements, the overall length of the tube and the volume flow rate influence the mixing and dispersing characteristics. Static mixers are simple to operate and cheap. The disadvantages are that the energy input and consequently the dispersing intensity can only be varied by changing the volume flow rate or the geometry of the mixer.

Dynamic mixers
A dynamic mixer consists of a rotor-stator system with whipping blades, which disperses the gas bubbles in a controlled flow field generated by the rotor (Hanselmann, 1996).

Continuous rotor-stator mixers are the most common whipping equipment used for industrial applications. They consist of a rotor and a stator each having several blades. Each blade has a certain number of pins. These stator pins are often welded directly onto the mixing head housing. The rotor pins are welded onto a shaft. By rotating the rotor, a complex dispersing flow field between rotor and stator pins is generated. A rotor-stator mixer produces foam continuously depending on the feeding rates of gas and liquid. A large variety of empirically designed continuous mixers can be found, differing in size, pin geometry, gap size, number of pins, number of blades etc.

In this work, a dynamic rotor-stator mixer, built by Kinematica AG Luzern, Switzerland was used to generate highly viscous foams. The rotor-stator geometries were developed at the Federal Institute of Technology Zürich, Laboratory for Food Engineering (Windhab, 1997).

This new type of rotor-stator geometry (Figure in Appendix 7.1) offers several advantages compared to traditional foaming geometries. As every single mixing element (stator and rotor blades) can be assembled independently, the configuration and the number of mixing elements can be easily changed. This allows to change the mixing geometry as a function of the desired shear stresses or energy input to disperse the gas fraction into the liquid. Thus the mixer can be adapted to the requirements of different products and the energy input into the system can be optimized (Leplat, 1998). Another advantage of this mixing head is the small adjustable gaps between rotor and stator and the small mixing volume. This offers advantages for dispersing gas into highly viscous solutions and for operation under pressure.

2.2.3 Engineering relationships in the whipping process
In a dynamic mixer the dispersion of the gas in a continuous fluid phase occurs in the flow field generated in the gap between rotor and stator. To describe the foaming process in engineering terms the dimensionless Newton (Ne) and Reynolds (Re) numbers denote the so called power characteristics \( \text{Ne} = f(\text{Re}) \) and the dimensionless Weber number (We) characterizes the bubble dispersion.

2.2.3.1 The Newton-Reynolds-characteristics (Power characteristics)
The energy dissipation in the whipping head is an important parameter to determine the shear stresses that control bubble formation. The dimensionless Reynolds (Re) and the Newton (Ne) number define the power characteristics \( \text{Ne} = f(\text{Re}) \) which
determines the whipping flow field in whipping head with a given geometry. The Newton number denotes the dimensionless power input (Althaus, E., 1993):

\[ Ne = \frac{F \cdot L}{m \cdot v^2} \]

Eq. 2.2.3

where \( Ne \) is the Newton number, \( F \) the force, \( L \) a characteristic dimension, \( m \) the mass and \( v \) the velocity. Windhab (1991a,b) defined the Newton number for a dispersing process with an axial mixing head as follows:

\[ Ne = \frac{P}{\rho_f \cdot d^3 \cdot n^3 \cdot s^2} \]

Eq. 2.2.4

where \( P \) is the net power input, \( \rho_f \) the foam density, \( d \) the rotor diameter, \( n \) the rotational speed and \( s \) the axial gap between rotor and stator teeth.

The flow characteristic is described by the dimensionless Reynolds number:

\[ Re = \frac{v \cdot L \cdot \rho}{\eta} \]

Eq. 2.2.5

where \( Re \) is the Reynolds number, \( v \) the circumferential rotor velocity, \( L \) a characteristic dimension, \( \rho \) the density and \( \eta \) the dynamic viscosity.

Windhab (1991a,b) defined the gap-Re number for a dispersing process with an axial mixing head taking for \( v \) the rotor tip speed at the rotor diameter \( d \), and as characteristic length \( L \) the gap distance \( s \):

\[ Re = \frac{\pi \cdot n \cdot d \cdot s \cdot \rho_f}{\eta} \]

Eq. 2.2.6

Figure 2.2.3 shows a typical power characteristics (\( Ne = f(Re) \)) for the dynamic mixer equipment used in this work. In Figure 2.2.3 the influence of different rotor-stator configurations (2, 4, 6, and 8 rotor stator dispersing elements) of the foaming head on the power characteristics is additionally demonstrated (Alex, 1998).
2.2 Foaming of concentrated solutions

2.2.3.2 The Weber number for the dispersion of gas bubbles

The relationship between the shearing forces leading to deformation/disruption of the gas bubbles and the surface tension related capillary forces can be described with the dimensionless Weber number (We) (Windhab, 1991a,b). The dimensionless Weber number for drop or bubble disruption is defined as:

\[
We = \frac{\tau \cdot x}{\sigma \cdot 4}
\]

Eq. 2.2.7

where \(\tau\) is the acting shear stress, \(\sigma\) the surface tension and \(x\) the bubble diameter. The capillary pressure \(\sigma \cdot 4 / x\) stabilizes the bubbles while normal and shear stresses deform/disrupt the bubbles. The bubbles are disrupted when the shear stress exceeds a critical shear stress \(\tau_{\text{crit}}\). Thus a critical Weber number \(\text{We}_{\text{crit}}\) gives the maximum bubble size \(x_{\text{max}}\) that can exist for a given shear stress \(\tau\):

\[
\text{We}_{\text{crit}} = \frac{\tau \cdot x_{\text{max}}}{\sigma \cdot 4}
\]

Eq. 2.2.8

One difficulty for the determination of the critical Weber number is to know the shear stress acting in the complex flow field of the dispersing equipment.

In the laminar flow regime the shear stresses are dominated by viscous forces and in the turbulent flow regime by inertial forces.

For the calculation of the shear stresses \(\tau\) in the laminar flow regime, Windhab (1991a,b) suggested the following procedure:
2.2 Foaming of concentrated solutions

Newton’s law describes the flow function for $\tau$ for the continuous phase as a function of the shear rate $\dot{\gamma}$:

$$\tau(\dot{\gamma}) = \eta_{\text{cont}}(\dot{\gamma}) \dot{\gamma} \quad \text{Eq. 2.2.9}$$

where $\eta_{\text{cont}}(\dot{\gamma})$ is the shear rate dependent viscosity function of the continuous phase.

The shear rate for a rotor stator mixer in the axial gap between rotor and stator elements is defined as:

$$\dot{\gamma} = \frac{\pi dn}{s} \quad \text{Eq. 2.2.10}$$

where $d$ is the characteristic rotor diameter, $s$ the gap and $n$ the rotor speed.

For laminar flow conditions, the maximum bubble size will then be given by:

$$x_{\text{max}} = \frac{4\sigma \cdot We_{\text{crit}} \cdot \eta_{\text{disp}}}{\eta_{\text{cont}}^2(\dot{\gamma}) \cdot \dot{\gamma}} \quad \text{Eq. 2.2.11}$$

and is seen to depend to the square of the shear rate dependent viscosity of the continuous phase.

For turbulent flow conditions the theory of turbulence of Kolmogorow (1958) may be used to describe the acting shear stresses in further detail. The theory describes the turbulence in terms of eddies of similar magnitude to the geometry dimensions of the flow in the mixer. The energy of the largest eddies is transferred to smaller eddies and finally dissipated by viscous friction (Nagata et al., 1975).

The mean square turbulent fluctuation velocity $\bar{v}^2$ over a distance $L$ in a turbulent flow field can be estimated by the following equation (Windhab 1991a,b):

$$\bar{v}^2 = C1 \cdot \left(\frac{P}{V}\right)^{2/3} \cdot \left(\frac{L}{\rho}\right)^{2/3} \quad \text{Eq. 2.2.12}$$

where $P/V$ is the power dissipation per unit volume and $C1$ is a constant. Batchelor (1951) found a value of 2 for $C1$. The shear stress $\tau$ for the disruption of the bubbles under turbulence is given by the Reynolds shear stress $\tau_{Re}$:

$$\tau_{Re} = \bar{v}^2 \cdot \rho \quad \text{Eq. 2.2.13}$$

For the conditions in the mixer it can be assumed that the maximal bubble size is in the order of magnitude of the smallest eddies of a distance $L$. From Eq. 2.2.8, Eq. 2.2.12, and Eq. 2.2.13 the maximal bubble diameter $x_{\text{max}}$ is derived as:

$$x_{\text{max}} = \left(\frac{We_{\text{crit}}}{C1}\right)^{0.6} \cdot \sigma^{0.6} \left(\frac{P}{V}\right)^{-0.4} \cdot \rho^{-0.2} \quad \text{Eq. 2.2.14}$$

When foaming under pressure the effect of pressure on the compression of the gas bubbles and the related change in density in the mixer has to be taken into account.
2.2 Foaming of concentrated solutions

As a result from Eq. 2.2.14, the foam dispersability depends on the power input per unit volume ratio for a defined solution.

The other dimensionless number characterizing the dispersion process is the viscosity ratio $\lambda_V$ between the disperse phase $\eta_{\text{disp}}$ and the continuous phase $\eta_{\text{cont}}$.

$$\lambda_V = \frac{\eta_{\text{disp}}}{\eta_{\text{cont}}} \quad \text{Eq. 2.2.15}$$

Grace (1982) showed the $W_{\text{crit}}$ values for dispersion in a laminar shear flow field as a function of the viscosity ratio $\lambda_V$ (Figure 2.2.4).

![Figure 2.2.4: Critical Weber number for dispersion of droplets/bubbles in laminar uniaxial shear flow as a function of the viscosity ratio between dispersed and continuous phase (Grace, 1982)](image)

For foam dispersion the gas phase viscosity is relatively independent of the nature of the gas and temperature. The viscosity value of air at 20°C is approximately $18 \times 10^{-6}$ Pa s.
2.3 Freeze drying kinetics of foamed amorphous powders

An important feature of the freeze-drying process is its high cost, for both capital (vacuum and freezing technology) and running costs. On an industrial scale, Flink (1977) considered that the running cost of freeze-drying processes is from four to five times higher than that of the spray-drying technique, and eight to ten times higher than that of a single-stage evaporator. The use of large-scale freeze-drying in food industries is consequently restricted to high added value products such as coffee, tea and infusions, ingredients for ready-to eat foods (vegetables, pasta, meat, fish, etc.) and several aromatic herbs (Hammami and Rene, 1997).

A major problem with vacuum freeze-drying experiments is the duration of the process (1-3 days). This is due to poor heat transfer inside the product as heat transfer by convection is very low due to the low gas pressures in the dryer. The principal heat transfer phenomena under vacuum are radiation and conduction between contacting surfaces. This explains why the prime interest in freeze-drying research has dealt with the understanding and improvement of heat transfer and the influence of processing conditions (working pressure and heating temperature) on freeze-drying time (King, 1971; Goldblith, Rey and Rothmayr, 1975; Pikal et al., 1990; Rene et al, 1993; Liapis and Bruttini, 1995). Alternative heating systems have been tested, e.g. the use of microwaves or infrared radiation (Le Loch et al., 1992). Other workers (Wolff and Gibert, 1988; Mumenthaler and Leuenberger, 1991) have studied the advantages of atmospheric pressure freeze-drying for food and pharmaceuticals. Capital investment and operating costs were lower than those of vacuum freeze-drying, but processing time was much longer and the quality of the freeze-dried products was inferior.

In general freeze-drying of solutions starts below the maximally cryo-concentration \( C_g' \) more often even below \( X= 50\% \) where there is ice formation upon cooling. As mentioned above, concentration of solutions in evaporators is eight to ten times cheaper in running costs compared to freeze-drying. Therefore is of interest to remove most of the water through evaporation before freeze-drying. An additional advantage of concentrating the solution to be dried above the \( C_g' \) concentration is the absence of ice upon cooling. This reduces as well the freezing costs considerably. To compensate the lack of porosity and related mass exchanging surface of the matrix to be dried, the highly concentrated (\( C>C_g' \)) solution is foamed here before freezing and freeze dried as described in Chapter 2.2.

As mentioned in Chapter 2.1.4 the freeze drying of solutions with concentrations above the maximal cryo-concentration \( C_g' \) is defined as the secondary drying stage. In this stage the physical state of the water in hydrophilic amorphous systems is generally regarded as being molecularly dispersed or dissolved in the amorphous phase, essentially forming a solid solution of water in the glassy amorphous phase (Levine and Slade, 1988).

Potential rate determining steps in the removal of water from an amorphous solid are:
- molecular diffusion of water in the glassy solid from the interior of a particle to the surface of a pore;
- evaporation at the solid/vapor interface;
- vapor phase transport through the porous partially dried cake;
- vapor phase transport from headspace over the powder bed to the condenser.
2.3 Freeze drying kinetics of foamed amorphous powders

2.3.1 Moisture-solid relationships

The drying kinetics of amorphous solutions above \( C_g' \) will depend on the desorption behavior of the solutions. Sorption and desorption isotherms describe the water activity as a function of water content.

**Moisture Sorption**

The water activity is one of the most important parameters characterizing the status of a product. It is a measure of the availability of water in an equilibrium system. The sorption of water to solids will change the activity of the water and the vapor pressure \( p_v \). The ratio of this reduced pressure to the vapor pressure for pure water \( p_0 \) at the same temperature is expressed in the water activity \( a_w \) (Herrinton et al., 1995).

\[
a_w = \frac{p_v}{p_0} \tag{Eq. 2.3.1}
\]

The water activity can be considered as a direct measure of whether moisture will be absorbed or desorbed. The hygroscopic behavior of foodstuffs is very different. It depends on the food structure, internal surface area and the molecular composition. The water activity is depressed by solids, which are dissolved in water. This colligative effect has its greatest importance at high water activity values and can be evaluated by Raoult’s law. A second effect, which reduces the water activity, is the capillary effect. The vapor pressure of water above a curved liquid meniscus is less than over a flat water surface due to the reduced water vapor pressure of a liquid in a capillary, which is inversely proportional to the capillary diameter \( d \).

\[
p = \frac{4 \cdot \sigma}{d} \tag{Eq. 2.3.2}
\]

Water also interacts directly with other chemical groups or molecules through dipole-dipole forces, ionic bonds, van-der-Waals forces and hydrogen bonds. These “bound” water molecules require extra energy to be transferred from the liquid into the vapor state and thus are less free to the vapor, resulting in reduced \( a_w \) (Labuza, 1984).

The sum of all these effects is shown in the sorption isotherm. These temperature dependant curves give the relationship between moisture content and water activity. A typical sigmoid sorption isotherm is shown in the following plot.
2.3 Freeze drying kinetics of foamed amorphous powders

Sorption Isotherm

Figure 2.3.1: Sigmoidal sorption isotherm with different sections

Domain A shows the effect of monomolecular adsorption, whereas polymolecular adsorption, including double and multiple bonding, increases within section B. The higher the water activity values, the more important is capillary condensation and swelling. The increasing slope in section C results from this capillary condensation and further swelling. Often the maximal hygroscopic moisture content \( (a_w = 1) \) is never achieved in food products.

By applying the Guggenheim-Anderson-de Boer (GAB) sorption equation, the relation of water content and water activity can be well described (Weisser, 1986):

\[
\frac{X}{X_a} = \frac{C \cdot K \cdot a_w}{(1 - K \cdot a_w) \cdot (1 - K \cdot a_w + C \cdot K \cdot a_w)}
\]

Eq. 2.3.3

\( X_a \) is the water content (dry basis) at active sorption sites fully occupied by one molecule of water, \( C \) is the GAB constant related to monolayer properties and \( K \) the GAB constant related to multilayer properties.

The pressure influence on the sorption isotherm is neglectible in most cases (Labuza, 1984).

**Hysteresis**

The moisture sorption curve can be generated from the absorption and desorption process often results in different curves. The typical behavior (Figure 2.3.2) is explained with a higher water binding for the desorption curves compared to the sorption curves at the same \( a_w \).
2.3 Freeze drying kinetics of foamed amorphous powders

Reasons for the difference in moisture contents are first that during drying some solutes may supersaturate below their crystallization aw and this would hold more water in the desorption case. The hysteresis can be found during water adsorption and desorption of food concentrates. Furthermore capillaries can empty differently upon desorption i.e. narrow end of surface pores will trap and hold water internally down to a lower aw than the one at which it should have been normally released, while during absorption the narrow ends prevent the larger body from rapid filling (Labuza, 1984).

**Temperature influence on sorption isotherms**

Sorption isotherms are influenced by temperature, so that each sorption isotherm is only valid for a specific temperature value. Higher temperatures depress the binding forces, so that less water can be sorbed at the same water activity. The Clausius-Clapeyron equation is widely used to express the temperature variation of the water activity:

\[
\ln \frac{aw_1}{aw_2} = \frac{Q_s}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)
\]

Eq. 2.3.4

The heat of sorption Qs, which is a function of the water content X, is obtained from the slope of a logarithmic plot of the water activity versus the reciprocal value of the absolute temperature T.

Weisser (1986) described the temperature dependence of the GAB equation (Eq. 2.3.3) by using an exponential function for the three GAB constants C, K and Xm. While K and Xm are virtually independent of the temperature, the constant C is the main parameter governing the temperature influence on the water activity.

\[
C = C' \cdot \exp \left( \frac{Q_{s1} - Q_{s0}}{R \cdot T} \right)
\]

Eq. 2.3.5

Qs1 and Qsm are the total heat of sorption, respectively of the first layer on primary sites and of the multilayer.
2.3 Freeze drying kinetics of foamed amorphous powders

2.3.2 Heat and mass transfer

The physical basis for the drying process is heat and mass transfer. Limitations on either of them determine the rate of drying.

2.3.2.1 Heat transfer

The heat transfer is via three different avenues: convection, conduction and radiation. Convection may occur in gas or liquid media. It can be described by macromolecule movement of the fluid and is therefore a fast heat transfer. Heat transfer by convection is expressed by the following equation:

\[
\frac{dQ}{dt} = \alpha \cdot S_A \cdot (T_e - T_i)
\]

Eq. 2.3.6

where \( S_A \) is the area of the surface at temperature \( T_s \) and \( \alpha \) is the heat transfer coefficient. The kind of fluid, the surface and the type of flow determine the rate of heat transfer.

The most important kind of heat transfer during the vacuum drying process is the heat transfer by conduction. Under a stationary temperature profile, the heat flux is described by the first law of Fourier:

\[
\frac{dQ}{dt} = -\lambda \cdot S_A \cdot \frac{dT}{dt}
\]

Eq. 2.3.7

where \( \lambda \) is the thermal conductivity of the medium. The overall heat transfer coefficient \( \alpha \) can be calculated from \( \lambda \) and the “outside” heat transfer coefficients \( \alpha_l \) and \( \alpha_H \).

\[
\frac{1}{\alpha} = \frac{1}{\alpha_l} + \frac{x}{\lambda} + \frac{1}{\alpha_H}
\]

Eq. 2.3.8

For non-stationary conditions, the second law of Fourier can be applied using the following scheme of heat transfer:

\[
c_p \cdot \rho \cdot \frac{\partial T}{\partial t} = \frac{\lambda_s}{\lambda_s + dx} \cdot \frac{dT}{dx} \bigg|_{x+dx} - \frac{\lambda_s}{\lambda_s - dx} \cdot \frac{dT}{dx} \bigg|_x
\]

Eq. 2.3.9

Figure 2.3.3: Heat transfer by conduction
2.3 Freeze drying kinetics of foamed amorphous powders

With constant thermal conductivity $\lambda$, the second law can be simplified (Besson et al., 1994) as:

$$\frac{\partial T}{\partial t} = \frac{\lambda}{c_p \rho} \frac{\partial^2 T}{\partial x^2}$$

Eq. 2.3.10

where $\rho$ and $c_p$ are the material density and heat capacity respectively. The thermophysical data $\lambda$, $\rho$, and $c_p$ are basic data needed for designing and simulating heat treatment processes.

In order to determine the heat capacity and the density of a food material, the mass fraction of each component $i$ has to be taken into consideration:

$$c_p = \sum_{i=1}^{n} x_i \cdot c_{p_i}$$

Eq. 2.3.11

$$\frac{1}{\rho} = \sum_{i=1}^{n} \frac{x_i}{\rho_i}$$

Eq. 2.3.12

The total thermal conductivity depends on whether the conduction through the food components is regarded as serial, parallel or follows a mixed model:

$$\lambda_{\text{parallel}} = \sum_{i=1}^{n} \varepsilon_i \cdot \lambda_i$$

Eq. 2.3.13

$$\lambda_{\text{serial}} = \sum_{i=1}^{n} \frac{\varepsilon_i}{\lambda_i}$$

Eq. 2.3.14

where $\varepsilon_i$ is the volumetric fraction of the considered component.

In this work the Maxwell "mixed model" is used for the determination of an effective total conductivity:

$$k_m = k_c \left( \frac{k_p + 2k_c - 2\varepsilon_D (k_c - k_D)}{k_p + 2k_c + \varepsilon_D (k_c - k_D)} \right)$$

Eq. 2.3.15

Figure 2.3.4: Scheme of models for determination of thermophysical material properties related to heat transfer coefficients
2.3 Freeze drying kinetics of foamed amorphous powders

$km$ is the effective conductivity, $kc$ denotes the conductivity of the continuous medium, $kD$ the conductivity of the discontinuous medium and $εD$ the volume fraction of the discontinuous medium.

Heat transfer by radiation appears in-between two surfaces with different temperatures. It is based on emission and absorption of electromagnetic fluxes, and is inversely proportional to the wavelength of the radiation. In radiation, no physical contact between the media and the material is required and radiation is therefore even present in vacuum. It is described by the law of Stefan-Boltzmann:

$$\frac{dQ}{dt} = ε \cdot S_A \cdot σ \cdot T^4$$  \hspace{1cm} \text{Eq. 2.3.16}

$S_A$ denotes the product surface area. The constant $ε = 0.8 - 0.9$\text{[}] (Besson et al., 1994) can be assumed for foods; the Stefan Boltzmann constant $σ$ is $5.669 \cdot 10^{-8}$ [Wm$^{-2}$K$^{-4}$]. Considering the outside temperature, the law of Kirchhoff derived from Eq. 2.3.17 can be applied.

$$\frac{dQ}{dt} = ε \cdot S_A \cdot σ \cdot (T^4 - T_{outside}^4)$$  \hspace{1cm} \text{Eq. 2.3.17}

### Specific enthalpy

For the calculation of the product enthalpy, the water content $X$ plays a major role due to its high evaporation/condensation energy $Q_{\text{evap}}$ [J kg$^{-1}$] = $Q_0$ [J kg$^{-1}$] - $2250$ T[°C] with $Q_0$=$2.5 \cdot 10^6$ J kg$^{-1}$. The specific enthalpy $h$ can be determined with the following equation (Kessler, 1988):

$$h = \frac{H}{m_{\text{dls}}} = c_p \cdot T + X \cdot (Q_{\text{evap}} + c_{pw} \cdot T)$$  \hspace{1cm} \text{Eq. 2.3.18}

where $X$ is the fractional water content, $c_p$ the heat capacity of waterfree product, $c_{pw}$ the heat capacity of water and $Q_{\text{evap}}$ the energy for liquid-vapor phase change.

#### 2.3.2.2 Mass transfer

The whole drying process is accomplished by the mass transfer of water in liquid or gaseous form from the internal part of the product to the environment. The transfer of the water is based on several phenomena. The diffusion of a liquid or gas through a solid material is due to differences in concentration $c$, or pressure $P$ between two points within the material. In analogy to the law of Fourier for the heat transfer, diffusion can be expressed by the first Fick’s law:

$$\frac{dm}{dt} = -D \cdot S_A \cdot \frac{∂c}{∂x}$$  \hspace{1cm} \text{Eq. 2.3.19}
2.3 Freeze drying kinetics of foamed amorphous powders

where \( m \) is the mass, \( D \) is the diffusion coefficient and \( S_A \) the area. The equation for the changes of concentration under non-stationary conditions is described by the second Fick’s law:

\[
\frac{\partial c}{\partial t} = -D \frac{\partial^2 c}{\partial x^2}
\]

Eq. 2.3.20

There are many different paths for diffusion for liquids through solids (Thorvaldsson et al., 1995). However, the diffusion process can be described as a combination of several main mechanisms:

- capillary flow,
- liquid diffusion in pores,
- surface diffusion along the walls of pores,
- hydraulic flow in pores,
- diffusion of liquid in the solid phase, which is very low compared to other diffusion mechanisms.

The diffusion coefficient, \( D \), is a measure of the diffusion rate of the substance through the material. \( D \) is a function of the properties of the system, like the structure of the material, the molecular size and charge of the diffusing substance and its physical state: solid, liquid or vapor.

The values for the water diffusion coefficient of Polyvinylpyrrolidone are estimated from pulsed field gradient NMR technique and sorption-desorption measurements (Oksanen, 1992) (see model script in Appendix 7.2).

Vapor diffusion

In general, the vapor diffusion is based on the following equation, which can be derived from the first Fick’s law:

\[
\frac{dm}{dt} = -S_A \left( \frac{b}{\mu} \right) \frac{\partial p}{\partial x}
\]

Eq. 2.3.21

with \( \mu \) as the “length resistance factor” and \( b \) as the “movement constant”. The diffusion of gases through solids with pores, which are smaller than the average pathway of a molecule, is described by the Knudsen molecular movement (Kneule, 1975):

\[
b = \frac{4}{3} \cdot d \cdot \sqrt{\frac{1}{2\pi R T} \cdot \frac{M}{T}}
\]

Eq. 2.3.22

where \( d \) is the pore diameter and \( M \) the molecular mass of water. For bigger pore sizes, ordinary diffusion is established to explain the mass transfer. The movement factor then becomes:

\[
b = \frac{D_p}{R T} \cdot \frac{p}{p - p_m}
\]

Eq. 2.3.23
where $p_m$ equals the partial vapor pressure in a vapor-air-mix, $D_v$ is the vapor diffusivity and $R$ is the molar gas constant. However, if the water vapor does not come from evaporation of liquid water, and pure vapor diffusion is taken into account, the water vapor transfer can be simplified (Thorvaldsson et al., 1995):

$$\frac{dm}{dt} = \frac{D_v}{k_i} \frac{1}{R \cdot T} \frac{\partial p}{\partial x}$$

Eq. 2.3.24

The constant $k_i$ defines the diffusion resistance.

The rate of vapor evaporation on a surface is often described as (King et al., 1989; Besson et al., 1994):

$$\frac{dm}{dt} = -k_m \cdot S_A \cdot (p_0(T) - p_{air}) \cdot M$$

Eq. 2.3.25

where $p$ is the partial vapor pressure in the surrounding atmosphere.

2.3.3 Vacuum drying modeling

2.3.3.1 Basis and comparison of existing models

Although the vacuum drying has been used in different forms for decades, there is still a lack of understanding of some of the basic phenomena. This leads to the possibility of improving the process. Several attempts have been made to model the vacuum drying process based on different assumptions.

Some authors (Saiki et al., 1980; Nastaj, 1989; Farges et al., 1995) used the approach with a moving evaporation front, whereas others (Lombrana et al., 1993) suppose that the dry and wet zone often can not be clearly separated. The drying process is sometimes split into two or three different drying periods (Strek et al., 1980; Kharin et al., 1996) in order to get a more accurate estimation of the drying rate. The drying rate is initially limited by heat transfer and at the later period by the mass transfer (King et al., 1989; Kharin et al., 1996). In combined models, both the heat and mass transfer are considered continuously. The heat transfer is based on conduction through the product, whereas many authors (Farges et al., 1995) include also the energy of the transmitted vapor. The mass transfer is considered in some cases as water diffusion with negligible vapor diffusion or, most of the times, as vapor diffusion (Migunov et al., 1990; Imakoma et al., 1992; Lombrana et al., 1993). At high water contents, the liquid phase drives the mass transfer, whereas at low moisture contents the vapor is the influencing force. The transfer phenomena are described through the thermal properties, which have therefore a central importance in the modeling. The importance of the heat transfer coefficient $\lambda$ and especially the mass transfer coefficient $D$, given as a function of temperature and particularly of the water content, should be mentioned here.

2.3.3.2 Considerations for the drying simulation

A mathematical model of simultaneous heat and mass transfer build by Raederer (1997) for the prediction of moisture and temperature distribution during vacuum
Freeze drying kinetics of foamed amorphous powders

drying of a malted drink is used in this work. The model takes into account the effect of moisture-solid interaction by means of the desorption isotherms of the product. A finite volume method is used to solve the simultaneous heat and mass transfer equations. B. Watzke and D. Pretre of the Modelisation group at the Nestle Research Center Lausanne adapted the existing model for the drying of foamed PVP powders. The experimental trials were carried out in a small scale batch vacuum dryer. The model is described in Chapter 4.4 and the model script can be found in the Appendix.

In order to be used for simulating the process, the model is adapted with adequate parameter values for the equations, corresponding to the present drying conditions. However, one has to be aware that the model is established for continuous heat and mass flow, whereas the simulation is carried out considering finite time and volume steps. Therefore e.g. temperature changes are linearized between the time steps by applying the method of Crank-Nicolson. This is especially important for large time steps. In order to define the thermal properties between two volume steps, the arithmetic average is normally used. However, the accurate thermal conductivity between two volumes has to be computed by considering the uniform heat flow (Patankar, 1980):

$$\lambda = \left(\frac{1-V_r}{\lambda_1} + \frac{V_r}{\lambda_2}\right)^{-1}$$  \hspace{1cm} \text{Eq. 2.3.26}

where $V_r$ is the volumetric ratio of the chosen sections.
Material and Methods

3.1 State diagram

3.1.1 Polyvinylpyrrolidone (PVP) as a food model system

PVP is a polar water-soluble polymer. It has been used as a model food system in process applications and reaction kinetics studies on food (Mackenzie, 1972; Buera et al., 1992). The structure formula and the molecular weight of a monomer are shown in Figure 3.1.1.

\[ M_0 (C_6H_9NO) = 111.14 \text{ g/mol} \]

![Figure 3.1.1: Polyvinylpyrrolidone (PVP) monomer](image)

From the scientific viewpoint, polyvinylpyrrolidone is interesting in several respects. Considering the structure of the monomer unit, it is seen to have an amphiphilic character since it contains a highly polar amide group conferring hydrophilic and polar-attracting properties, and also apolar methylene and methine (CH) groups in the backbone and the ring conferring hydrophobic properties. Furthermore, the dipolar amide group has a different environment at each end, since an examination of molecular models readily shows, the oxygen end is exposed while the nitrogen end is largely buried in the surrounding methylene and methine groups.

PVP is also interesting from the biological viewpoint, since it has structural features similar to those of proteins, which have led to its being proposed as a simple protein model (Molyneux 1984). Indeed, its behavior shows similarities to proteins, i.e., water solubility, complexing ability towards many types of small molecule substances, and precipitation by many protein precipitants such as ammonium sulfate, trichloracetic acid, tannic acid and other phenols.

Commercial samples of PVP are commonly designated in terms of the \( K \) value, which was originally proposed as a concentration-independent parameter, and which is derived from the relative viscosity \( \eta/c_2 \) of the solution by the relation:

\[
\log (\eta / c_2) = \left[ 75 k^2 c_2 / (1 + 1.5 k c_2) \right] + k c_2 \quad \text{Eq. 3.1.1}
\]

where \( c_2 \) is the polymer concentration in g/dl (%w/v) and \( k \) is \( K/1000 \).
The four most common commercial grades of PVP with their K values, the average molecular weights generally quoted for them, and the intrinsic viscosity’s derived from the K value are

\[
\begin{align*}
K-15: M &= 10'000 \quad : \eta = 7.3 \text{ cm}^3/\text{g} \\
K-30: M &= 40'000 \quad : \eta = 22.5 \text{ cm}^3/\text{g} \\
K-60: M &= 160'000 \quad : \eta = 76 \text{ cm}^3/\text{g} \\
K-90: M &= 360'000 \quad : \eta = 160 \text{ cm}^3/\text{g}
\end{align*}
\]

The molecular weights quoted for the various grades should be considered as average values because normal commercials grades of PVP have fairly broad molecular weight distributions.
Polyvinylpyrrolidone is quite stable in the solid state under normal conditions of storage. Ball milling leads to degradation of the polymer.
In this work PVP K15 (MW= 10000g/mol) was used for the foaming and drying trials.

3.1.2 Preparation of the PVP samples

3.1.2.1 Preparation of powders

The freeze dried powder was made out of a concentrated PVP solution containing about 30% water. PVP powder was dissolved in an agitator vessel with de-mineralized water at 60°C to a concentration of X= 70%. Then 0.25% SDS (% total weight) was dissolved in the solution. The solution was left to de-aerate for 1 week at room temperature.
The PVP solution was then foamed as described in Chapter 3.2 in a dynamic mixer FM12 (Kinematica AG, Littau, Switzerland). The mixing conditions were the following:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Residence time in mixer</td>
<td>11.5 s</td>
</tr>
<tr>
<td>Volume flow rate</td>
<td>10 l/h</td>
</tr>
<tr>
<td>Product temperature in</td>
<td>50°C</td>
</tr>
<tr>
<td>Product temperature out</td>
<td>70°C</td>
</tr>
<tr>
<td>Cooling temperature</td>
<td>25°C</td>
</tr>
<tr>
<td>Mixer Pressure</td>
<td>4-6 bar</td>
</tr>
<tr>
<td>Rotor speed</td>
<td>1200 rpm</td>
</tr>
</tbody>
</table>

Both CO₂ and N₂ were used for foaming. The overrun of the foams was controlled with the amount of gas dosed to the mixer. The overrun is the liquid to gas volume ratio expressed in %. The overrun was determined by weighing 110ml beakers of foam (see Chapter 3.2.5).
After leaving the dynamic mixer the foam flowed through a nozzle and the spaghetti (Ø 3mm) so formed were then directly immersed in liquid nitrogen. During the freezing process in liquid nitrogen the spaghetti were fragmented to a powder by mixing continuously by hand with a beater.
The PVP powder was mechanically sieved using a five level vibrating sifter (Retsch, Germany) in a cold-room at - 45°C. The powder was separated using five different sieves (Retsch, Norm DIN 4188) with openings of 400, 800, 1000, 2000 and 3150 μm. Only the fractions 1000 - 2000 and 2000 - 3150 μm were used for drying trials.
Table 3.1.1 shows the foaming parameters chosen for the drying trials:
### Table 3.1.1: Foamed PVP powders for drying trials

<table>
<thead>
<tr>
<th>PVP solid concentration</th>
<th>70%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Foaming gas</td>
<td>N₂</td>
</tr>
<tr>
<td>Overrun</td>
<td>low</td>
</tr>
<tr>
<td>100-130%</td>
<td>200%</td>
</tr>
<tr>
<td>Powder size fraction</td>
<td>1-2 mm</td>
</tr>
</tbody>
</table>

The PVP powders were dried using an experimental freeze dryer Lyolab G, manufactured by LSL Secfroid S.A., Lausanne as described in Chapter 3.3.

#### 3.1.2.2 Humidifying of samples

PVP powder and CO₂ and N₂ foamed PVP powders were placed into dessicators containing different saturated salt solutions with known relative humidities (Table 3.1.2 and Table 3.1.3) at 25°C and 2°C. The moisture equilibration was achieved within a storage time of 6 weeks respectively of 3 months at 2°C. After equilibration Karl Fischer titration (Chapter 3.1.2.3) was used to determine the water content of the samples.

#### 3.1.2.3 Water content of PVP solutions and powders

Karl Fischer Titration was used to determine the water content of the PVP solutions before foaming and for the powders in the collapse measurements and drying trials (Karl Fischer Titrator, KF Titristo 701; Metrohm AG, Herisau, Switzerland). The method is based on the ability of iodine to react with water in the presence of sulfur dioxide (sulfurous anhydride):

\[
2 \text{H}_2\text{O} + \text{SO}_2 + \text{I}_2 \rightarrow \text{H}_2\text{SO}_4 + 2 \text{HI}
\]

The sample is dissolved in methanol and the reacting water is titrated with Karl Fischer reagent (Hydranal Composite 5, Riedel-de-Häen No. 34805) up to the equivalence point, which is determined by voltametry (platinum electrode). The measurements were carried out at room temperature.

The moisture content is defined on dry-basis \(X_d\) or wet-basis \(X\) as follow:
where m\(_w\) is the water mass and m\(_s\) the dry solid mass.

### 3.1.3 Determination of the viscosity of PVP solutions

**Controlled Stress Rheometer (SR5)**

A SR5 (Stress Rheometer, Rheometrics Scientific, USA) was used for oscillatory shear viscosity measurements. A parallel-plate geometry (diameter: 40 mm) was used. The plate-plate gap was set between 1-2 mm. The set stresses (oscillatory stress) for each measurement were between 20 and 50 Pa.

Before each test scan the gap was “zeroed”. The PVP K15 solution (X= 70%) was loaded at 60°C (still in the liquid state) in order to minimize air bubble formation. Once the measurement gap was adjusted, a layer of paraffin oil was put around the sample edge to avoid the drying out of the borders during the measurement. The viscosity \(\eta^*\) was measured at three frequencies (0.1, 1, 10 Hz) following a temperature program (55, 30, 10, 0.5, 20, 40, 55, 70, 85, 55 °C). The SR5 software collected the PVP K15 results and the VTF equation was fitted for the 0.1 Hz data.

**Controlled Strain Rheometer (ARES)**

The ARES (Advanced Rheometric Expansion System, Rheometrics Scientific, USA) was also used for the measurement of the oscillatory shear tests. The measurement setup was similar to that of the SR5 (parallel plate diameter 50 mm, gap 0.5-1.5 mm). The ARES was equipped with a 10'000 g cm force transducer. This transducer allowed the measurement of the complex viscosity into the glassy state as will be shown in the results (Chapter 4.1.3).

Strain sweep tests before the actual dynamic measurements were also conducted to determine the linear viscoelastic range. As a result a strain of 7% was chosen for the oscillatory measurements.

The sample loading procedure was the same as for the SR5. The viscosity \(\eta^*\) was measured at three frequencies (0.1, 1, 10 Hz) while scanning the temperature of the sample first to -40°C and then up again to 60°C at 0.3°C/min.

### 3.1.4 Determination of the glass transition temperature

**3.1.4.1 Differential Scanning Calorimetry (DSC)**

Differential Scanning Calorimetry is based on the measurement of heat flow to or from a material while maintaining its temperature equal to that of a reference material during a temperature scan. DSC was used to determine the glass transition temperature \(T_g\). For amorphous materials, \(T_g\) is manifested as a discontinuous change in heat capacity, which is observed as an endothermic step change (i.e. baseline shift) in a DSC heat flow curve. The temperature \(T_g\) is usually taken as the onset temperature of the endothermic reduction in the heat capacity using a specific scanning rate. This is illustrated in the idealized thermogram shown in Figure 3.1.2.
The glass transition of amorphous materials shows the characteristics of a second-order phase transition. However, the glass transition is a non-equilibrium change in state and always occurs over a heating rate-dependent temperature range as shown in Figure 2.1.3 in Chapter 2.1. The observed T_g at different heating rates for two different powders were plotted on an Arrhenius-Plot (Figure 3.1.3). The linear fit shows that heating rates higher than 10°C/min deviate from linear Arrhenius-behavior. Therefore a temperature scanning rate of 10°C/min was chosen for the determination of T_g. As shown in Figure 2.1.3, the change in heat capacity for a rate of 10°C/min gave a clear signal for the determination of the glass transition.

![Image of Arrhenius Plot](image_url)

**Figure 3.1.3: Arrhenius Plot for PVP K15 with a water content of 4%**

The calorimeter used was a Mettler TA 8000 thermal analysis system, with a DSC820 DSC cell (Mettler Toledo, Switzerland). Samples of moisture equilibrated PVP powders were transferred into DCS pans (ME-29990, Ø7 mm) and then sealed. An empty aluminum pan was used as a reference in all measurements. Samples were scanned twice to eliminate thermal relaxation effects, typical of the glass transition (Roos and Karel, 1991). DSC scans were done in triplicate.

The Gordon & Taylor-Equation (Gordon and Taylor, 1952) was used to plot the T_g curves shown in state diagrams. Eq. 3.1.4 relates T_g of miscible polymer blends to the...
fractional concentration of their constituents and their $T_g$ as pure compounds, for binary mixtures:

$$T_{\text{blend}} = \frac{w_1T_{g1} + kw_2T_{g2}}{w_1 + kw_2}$$

Eq. 3.1.4

where $T_{\text{blend}}$ is the observed $T_g$ of the binary mixture, $w_1$ and $w_2$ are the fractional concentration of the first and second component, $T_{g1}$ and $T_{g2}$ are the $T_g$’s of the first respectively of the second component and $k$ a constant. Buera et al., 1992 reported a $k$ value for PVP K15 of 2.66 and $-135^\circ C$ was taken as the $T_g$ of pure water.

3.1.4.2 Dynamic Mechanical Thermal Analysis (DMTA)

Dynamic Mechanical Thermal Analysis was also used to determine glass transition temperature. The DMTA is based on the measurement of materials mechanical properties (viscoelastic modulii) in cyclic bending tension or shear as a function of frequency of deformation and temperature, while scanning the temperature. The viscoelastic modulii $E'$ and $E''$ were measured as a function of temperature and frequency of the oscillatory bending strain. The “storage modulus” $E'$ corresponds to the elastic energy and $E''$ (“loss modulus”) to the energy dissipated. Their ratio is the damping factor $\tan \delta (=E''/E')$, with $\delta = 0^\circ$ for ideal elastic solids and $90^\circ$ for ideal Newtonian viscous liquids. The viscoelastic properties of solutions and powders of PVP K15 were measured using a Rheometrics DMTA (Rheometrics Scientific, Inc., Piscataway, USA) using a specially developed disc-bending sample holder. MacInnes (1993) developed a “disc-bending” method able to measure liquid and powder samples in bending mode. In this technique the sample (liquid or solid) is placed between two thin plastic discs (KEPTON or PET) to prevent the sample flow and loss (Figure 3.1.4). The center of the disc has a screw that is subjected to an oscillatory deflection by the DMTA drive shaft at defined frequencies, while the temperature is scanned at a given rate.

In the case of liquid samples they are injected into the center ring between the two plastic discs. The upper and lower rings clamp the central ring with the sample and the whole block is rigidly attached to the DMTA. The center of the sample is subjected to an oscillatory small amplitude (64 µm) by the DMTA drive shaft. The frequencies used were 0.1, 1, 10 Hz. The sample temperature was measured with a thermocouple located inside of the sample and it was linearly scanned at 0.3 °C/min.

Figure 3.1.4: Disc bending sample holder for liquid or solid and compressed powder
A typical DMTA Thermo-Mechanical Profile is shown in Figure 3.1.5. The measurement frequency dependency of the moduli as a function of temperature is clearly shown.

Figure 3.1.5: Typical DMTA Thermo-Dynamical Profile (PVP K15 60% solids)
3.1.5 Determination of collapse and stickiness behavior of PVP powders

3.1.5.1 Sticky Point Test

Once the PVP sample had been equilibrated to a certain moisture content, a particle mono-layer of it was transferred to the bottom of a 10 ml glass tube and closed with a Silicon-Septa and an aluminum cap (Infochroma AG, Zug, Switzerland). The glass tubes containing humidified samples were stored at the beginning in a bath for 30 min with a temperature 5°C lower than the glass transition temperature. After that, the samples were judged by their physical appearance (flowability and caking) by turning over the glass tubes. The same procedures were repeated after increasing the temperature in 5°C intervals.

To study the dependence of sticky point temperature on holding time the samples were also stored in a bath for 1 minute, 30 minutes and 24 hours between the 5°C intervals.

3.1.5.2 Optical determination of collapse

For the optical determination of the collapse of powder particles a special heating stage with an observation microscope was build. The method was first developed by To and Flink (1978a,b,c) for the observation of collapse of freeze dried flakes of maltose, sucrose and maltodextrin.

The method was modified to observe the structural transitions by following the change in size of powder particles of PVP with different water contents and glass transition temperatures in the range between 40 and 100°C.

The collapse as a function of temperature and heating rate was evaluated from the images of the change in projection area of the particle.

A schematic view of the temperature controlled sample holder with the optical equipment is shown in Figure 3.1.6.

![Figure 3.1.6: Heating stage and video equipment for “optical collapse” measurements](image)

The optical equipment consisted of a video camera (AVT-BC1 from AVT-Horn, Aalen, Germany) mounted to a magnifying glass (Wild MZ8 from Leika, Germany) coupled to a Macintosh computer with a frame-grabbing card (Scion Corporation,
USA), and an image analysis software (Object Image 7+) for image analysis and numeric calculations.
The images were analyzed using NIH-Image with a macro developed by Guy Mayor (1998) from Nestlé Research Center, Lausanne.

The heating system consisted of three parts: a brass sample holder with a heating pad and a water cooled brass block (heat sink), a Pt-resistance thermometer RTD embedded with epoxy cement in the brass holder to trace the temperature of the sample, and a programmable heating control unit (Yokogawa UP25, from Yokogawa, Tokyo, Japan).

The heating control unit allowed the temperature of the heating stage to be scanned at different heating rates (1-20°C/min). It could also be operated in isothermal mode to hold a temperature for a given time period. The sample temperature was sent continuously via a RS232 communication port directly to the image acquisition computer.

In a typical determination, a foamed particle of PVP at given moisture content, was placed on the sample holder. A cover slip was carefully placed on the particle to hold the sample in place and apply a controlled pressure on the particle. Silicon oil (HTF 190, Perel AG, Switzerland) was filled into the sample holder to prevent the sample from drying out during the collapse determination. The silicon oil gave also a good thermal contact between the sample and the heating stage. The sample was brought into focus and the image analysis and the heating program started.

An image was taken every 20 to 60 seconds depending on the duration of the heating program. After the end of the program and the frame grabbing (100-400 frames), the surface of the projection area was computed by the software and the first and second derivative of the relative increase in surface were calculated. Figure 3.1.7 shows an example of a collapse temperature measurement.

![Figure 3.1.7: Collapse temperature determination](image)
A major problem in the optical determination of the collapse temperatures was gas bubbles leaving the particles during the heating process. They are responsible for the noisy signal of the area change during the collapse of the particle (Figure 3.1.8). In this work particles were measured at three different heating rates (2, 5, and 10°C/min) for a given holding time period (10 and 30 min) increasing the temperature after the holding time by 5°C until collapse was observed.

The image analysis program followed the silhouette of a “solid” foam particle by time lapse video image acquisition along temperature ramps. Temperature ramps where associated with a time stamp and a temperature value read directly from a sensor via an RS-232 communication port. After the end of frame grabbing (100-400 frames where used), the surface of the silhouette was computed by image analysis, then first and second derivative of relative increase of this surface were computed. Speed and acceleration peaks where correlated with corresponding critical temperatures. A description of the program and the practical procedure can be found in Bonato (1999).
3.2 Foaming

3.2.1 Foaming solutions and surfactant
Solutions of Polyvinylpyrrolidone PVP K15 with a mean molecular weight of 10'000 g/mol (Fluka Chemie AG, Buchs, Switzerland) at different concentrations were used for the foaming and drying trials.

A surfactant that strongly adsorbs at the air interface is necessary in order to produce foam from aqueous solutions. The formation of a foam from a bulk liquid involves the expansion of the surface area due to the work acting upon the system against the surface tension. The amount of new area formed (i.e. the foam) will be larger for lower surface tension. Thus the reduction of surface tension by the surfactant is a primary requirement of foam formation.

Sodium Dodecyl Sulfate (SDS) (Fluka AG, BioChemika 71729, Buchs, Switzerland) was used as surfactant due to its known foaming properties (Porter, 1994).

3.2.2 Measurement of the surface tension of PVP
As a first approximation to determine the surface tension for the foaming trials and for optimization of the PVP/SDS solutions, two static surface tension measurements methods: pendent drop and Wilhelmy plate were used.

Pendent drop method
The pendent drop method is applicable to the measurements of both surface and interfacial tension for polymer liquids and melts (Wu, 1982). The rate of equilibration is fast, because the solid-liquid contact area is quite small. The equilibrium process involves mainly the movement of liquid-liquid interface at the drop surface, which is much faster than the movement of solid-liquid interface (Wilhelmy Plate method). The method has been used extensively to measure the surface and interfacial tensions of many polymer liquids and melts (Wu, 1982).

The profile of a pendent drop (or bubble) at hydrostatic and interfacial equilibrium (Figure 3.2.1) was derived from the Laplace equation (Eq. 2.2.1) by Bashforth and Adams (1892).

\[ \sigma = \frac{\Delta \rho g (d_e)^2}{H} \]

Eq. 3.2.1

Figure 3.2.1: Profile of a pendent drop

The interfacial (or surface) tension is given by:
where \( \sigma \) is the interfacial (or surface) tension, \( \Delta \rho \) the density difference of the two phases (the drop and the surrounding medium), \( g \) the gravitational acceleration, \( d_e \) the equatorial diameter of the drop, and \( H \) is the correction factor determined by the shape parameter \( \lambda_s \), defined by

\[
\lambda_s = \frac{d_s}{d_e}
\]

Eq. 3.2.2

where \( d_s \) is the horizontal diameter at a selected plane measured at a specific distance from \( d_e \). Values of \( 1/H \) as a function of \( \lambda_s \) have been obtained by numerical solution of the equation of Bashforth and Adams (1892), and tabulated (Wu, 1982).

It is important to assure that the drop attains its equilibrium configuration. This is usually attained instantaneously in low viscous fluids, but may take minutes to hours in highly viscous polymers.

The interfacial tension is determined by measuring the shape of a drop using an optical microscope in conjunction with an image analysis program, and mathematical equations which describe the equilibrium shape (Couper, 1993).

A drop shape analysis system (Drop Shape Analyzer DSA10, Krüss, Hamburg, Germany) was used to determine the static surface tension of PVP/SDS solutions.

The density data required was obtained using an oscillating U-Tube densimeter (Densimeter DMA 35, Paar, Austria).

**Wilhelmy Plate**

The Wilhelmy plate method was used as a comparative measurement of the static surface tension. The apparatus consists of a vessel that contains the liquid being analyzed and a plate, which is attached to a sensitive force measurement device (Figure 3.2.2).

![Wilhelmy plate method of determining the surface tension of liquids](image)

The vessel is capable of being moved upwards and downward, while the plate remains stationary. The vessel is positioned so that the liquid just comes into contact with the plate. Some of the liquid "climbs" up the edges of the plate because this reduces the unfavorable contact area between the plate and the air. The amount of liquid that moves up depends on its surface tension and density. If the force-measuring device is zeroed prior to bringing the plate into contact with the liquid, then the force recorded by the device is equal to the weight of the liquid climbing up the plate. The weight is balanced by the vertical component of the surface tension multiplied by the length of the plate perimeter:
3.2 Foaming

\[ F = 2 (l + L) \sigma \cos \theta \]  
Eq. 3.2.3

where \( l \) and \( L \) are the length and thickness of the plate and \( \theta \) is the contact angle. Thus the surface tension of a liquid can be determined by measuring the force exerted on the plate. Plates are often constructed of materials, which give a contact angle that is close to zero, such as platinum or platinum/iridium, as this facilitates the analysis.

Surface tensions of PVP/SDS solutions were measured with a Kriiss Processor Tensiometer K12 Hamburg, Germany. All the measurements were performed at 25°C with a platinum plate flame cleaned between each measurement.

3.2.3 Preparation of the bulk solution

The model system with a dry matter content within the range of \( X = 62-70 \% \) was prepared using a double jacketed mixer (A.Stephan u. Söhne GmbH & Co; Hameln, Germany). Distilled water was heated up to 55°C and Sodium dodecyl sulfate (0.25 % of total solution weight) was dissolved. The polyvinylpyrrolidone was dissolved while mixing gently to avoid pre-foaming and to get a homogenous bulk solution.

3.2.4 Whipping equipment

A rotor-stator dynamic mixer head that was developed at the Swiss Federal Institute of Technology Zürich was implemented into a foaming process line as shown in the flow diagram in Figure 3.2.3.

![Figure 3.2.3: Flow diagram for foaming trials](image)

The equipment consists of a mixing vessel 1 with double jacket where the liquid can be pre-heated, an eccentric screw pump 2 (Hilge EDS 2.2 Luzern, Switzerland) for feeding the mixing-head 7. Before entering the mixing head, gas (nitrogen or carbon dioxide) was added directly into the pipe through a dosing valve 6. The solution-gas
3.2 Foaming

mixture enters the mixing head where the flow profile generated between stator and rotor disrupts the gas bubbles dispersing them into the liquid. The mixing head is jacketed to control the temperature inside the head. The back-pressure valve 8 after the mixing head regulates the pressure in the mixing head. This pressure and the flow rates of the solution and the gas, determine the residence time in the head. The foam flows through a pipe equipped with a pressure transducer to determine the pressure between the mixing head and the nozzle.

The whipping machine with the mixing-head (ETH Zürich, Switzerland) has the following technical specifications (see also drawing in Appendix 7.1):

- volumetric flow (l/h) 4-15
- back-pressure (bar) ≤5
- rotations per minute (rpm) 0-2950
- stator core diameter (mm) 52
- rotor core diameter (mm) 16
- length of mixing head (mm) 127
- total number of rods (per rotor-stator element) 13
- rows of rods rotor/stator 10/11
- number of rods per row (axial direction) 21
- rod size (mm) 2.5 x 4.5 x 5.0
- gap size between stator and rotor (mm) 1
- total free volume (ml) 92

3.2.5 Foaming process: Offline measurements

Water content
Karl Fischer Titration (Chapter 3.1.2.3) was used to determine the water content of the PVP solutions before foaming.

Foam density (Overrun)
The overrun OR is the liquid to gas volume ratio expressed in %. The overrun was determined by weighing 110 ml beakers of foam taken at the exit of the whipping equipment.

\[ \text{Overrun} = \frac{\rho_{\text{sol}} - \rho_{fo}}{\rho_{fo}} \cdot 100 \]  
Eq. 3.2.4

where \( \rho_{fo} \) denotes the density of the foam and \( \rho_{\text{sol}} \) is the density of the solution. A PVP K15 solution with X=70% has a density of 1.11 g/ml at 25°C.

Viscosity of solution and foam
A stress controlled rheometer (SR5, Rheometric Scientific, USA) was used to determine bulk and foam viscosity of PVP. The PVP solutions were measured in shear and oscillatory modes.

All measurements were performed with the plate-plate geometry of 50 mm diameter and a gap between 1 - 2 mm.

The foam was only measured in the oscillatory mode to avoid degradation of the foam structure. For both, bulk and foam, temperature scans were included to check temperature/time dependent degradation.
Image analysis

The bubble size distribution is the most relevant information on foam structure. The bubble size distribution is very important for understanding the influence of process parameters on foam structure.

A small volume of foam was taken right after production from the pipe outlet and put into a Neubaur-Blau Brand Glass plate (Germany), usually used for counting blood cells, with a known surface (0.0025 mm²) and clearance (0.1 mm depth). Ten pictures were taken in steps of 0.01 mm from the top to the bottom of the defined depth of the foam sample. The pictures taken with an inverse light microscope Fluovert (Leitz, Switzerland) were transferred by a color video camera (SONY CCD-Iris, Model DXC-93 OP) to a computer (Power Macintosh G3). The pictures were analyzed using NIH-Image with a macro developed by Mayor (1998) from Nestlé Research Center Lausanne. To describe the bubble size distribution the mean diameter, standard deviation and the median diameter were calculated based on the diameter distribution of the projected bubble surfaces.

3.2.6 In-line measurements of processing parameters

In order to describe the foaming process the following process parameters were measured and recorded with a data acquisition system (ETHZ/Hunter and Caprez, Zumikon, Switzerland):

- T_in: temperature of the liquid before the mixing head
- T_out: temperature of the foam after the mixing head
- T_cooling_in: temperature of the coolant before the mixing-head jacket
- T_cooling_out: temperature of the coolant after the mixing head jacket
- P_before: pressure before the mixing head
- P_after: pressure after the mixing head = pressure in mixing head
- Power: power consumption (measured with a power meter)
- Rpm: rotational speed
- M_gas: mass flow rate of the gas
- M_liq: volume flow rate of the solution

Temperature probes (type K, Jumo AG, Switzerland); power meter (type 2535-30, Yokogawa, Japan); pressure transducers (ED 510, Haenni AG, Switzerland); gas flow controllers (Mod. 5875, Brooks Instrument B.V, Holland); volume flow meter (Endress & Hauser, Switzerland).

The power consumption of a mixer depends on the following parameters: geometrical dimensions like rotor-stator, pin or gap size, product properties like density and viscosity functions, and process parameters like rotor speed, mass/volume flow rate and pressure. Power input is a key process parameter and determines the bubble size distribution and thus the structure and related properties of foams.

An electrical power measurement represents the sum of electrical power consumption of the motor, the sealing and bearing friction and finally the mechanical power input into the product. To obtain the net power input into the product, it is thus necessary to measure the “zero power consumption” without any product. The net power input is then calculated from the difference between the “zero power” and the total (product loaded) power, measured under the same process condition i.e. rotor speed, temperature and pressure.
3.3 Freeze drying kinetics

3.3.1 Experimental equipment

The experimental freeze dryer used is a Lyolab G (LSL Secfroid S.A., Lausanne, Switzerland). The equipment (Figure 3.3.1) consists of a freeze drying chamber, a refrigeration system and a vacuum pump connected to the chamber. In the chamber there are two plates (for heating or cooling with heat transfer oil) and below a condenser with 0.8m² surface working at T= -55°C. The operating pressure is electronically regulated by an air-injection micro leak valve (Balzers AG, Balzers, FL).

A set of 14 temperature probes are fitted inside the chamber. One is fixed to the heating plate and two are fixed to the bottom of the tray containing the powder. The tray is suspended from a balance (Mettler PR 5002, Mettler, Switzerland) for measurement of the product's mass during drying.

The sample holder is a stack of 10 mm thick polystyrene rings. The rings have an inner diameter of 200 mm and an outer diameter of 270 mm. Each ring has a
3.3 Freeze drying kinetics

thermocouple centered in the ring to record the temperature in the bed center. 10 rings are stacked to load a powder bed several centimeters deep for the drying trials. Figure 3.3.2 and Figure 3.3.3 show the sample holder with the rings removed and loaded with PVP powder. The sample holder is positioned in the center of an aluminum tray (2 mm thick) and is suspended from the balance as shown in Figure 3.3.4.

Figure 3.3.2: Ring sample holder with thermocouples on aluminum tray

Figure 3.3.3: Ring sample holder loaded with PVP powder
3.3 Freeze drying kinetics

3.3.2 Data acquisition

The weight loss in the sample and the temperature at different bed heights are recorded with a data acquisition and instrument control system on a PC. Process parameters like heating plate temperature and operating pressure were measured and controlled via a PID-controller in the data acquisition and instrument control software. The NiCr type K thermocouples (accuracy ± 0.5 °C) are vertically positioned at the center of each sample holder ring. The temperature probes are wired up through a vacuum tight connector to the data acquisition system. The data from the Mettler balance is transmitted through a RS-232 serial connection. The pressure in the drying chamber is measured with a Pirani pressure gauge. The pressure reading is converted to 0-10 V signal for the data acquisition system. Data acquisition and control is made via an A/D card CIO-DAS16 (Computer Boards Inc, Mansfield, MA, USA).

A program was written with Test Point (Capital Equipment Corporation, Billerica, MA, USA) for data acquisition and control. The program records the measured values every 30 or 60 sec. depending on the duration of the drying trial. The pressure in the drying chamber was set in the program and a PID controls the Balzers ED16 leak valve through one of the analog out channel of the A/D card. The temperature of the heating plate was also set from the Test Point software to act on the oil heater of the Lyolab freeze-dryer.

Figure 3.3.4: Front view of the freeze-drier with sample holder and tray suspended on the balance.
Practical procedure
The experiments were carried out using the following procedure:
The ring sample holder and the support tray are cooled down to -45°C during 2 hours in a cold-room.
The powder to be dried is loaded in the -45°C cold-room into the sample holder to a height of about 80 mm for most of the trials.
The plate temperature in the freeze-dryer is set to the drying temperature (40°C).
The cold tray with the sample holder is loaded into the drying chamber of the dryer.
The tray is suspended on the balance and the temperature probes are connected to the data acquisition system.
The drying chamber is closed and the vacuum pump lowers the pressure to the operating value (0.5 mbar for most drying experiments).
The data acquisition and control system is started and the drying temperature and pressure values are set.
After the drying time (10-48 hours) the data acquisition system is stopped and the vacuum in the chamber is broken.
The tray is unloaded and the weight lost by the sample is determined on a second balance previously tarred.
For partially dried samples the powder bed is cooled down by pouring liquid N₂ on the bed to stop further drying. The sample holder is then carried to the -45°C cold-room where the powder samples in the rings are sliced and collected ring by ring to determine the water content in the different bed levels corresponding to the height of the rings. For totally dried samples two powder samples of the bed are taken and the water content is determined with KF-Titration.
From the water content and the powder weight at the end of the drying and the mass loss recorded by the balance during the drying the initial water content of the powder is back calculated.

3.3.3 Experimental design
To establish the kinetics for the drying process as a function of microstructure, different powder samples were produced (Chapter 3.1.2.1)
The following table shows foaming and drying parameters chosen for samples investigated here:

| Table 3.3.1: Experimental design parameters for the drying samples |
|-----------------------|------------------|
| Heating plate temperature | 40°C |
| Pressure in the drying chamber | 0.5 mbar |
| PVP starting solid concentration | 70% |
| Foaming gas | N₂, CO₂ |
| Mean bubbles size of the foam | 12.3 μm, 67.2 μm |
| Overrun | 100-130%, 200% |
| Powder size fraction | small, large |
| | 1 - 2 mm, 2 - 3.15 mm |
3.3 Freeze drying kinetics

3.3.4 Determination of physical-chemical properties of the powders

3.3.4.1 Water content
The water content is the most important physical characteristic for the description of the drying process. The water content of the powders after the drying trials was determined by Karl Fischer titration (Chapter 3.1.2.3).

3.3.4.2 Water activity
The water activity is an important parameter to establish an accurate desorption isotherm and to calculate the water content via sorption isotherm. The values for the desorption isotherms for PVP were taken from literature (MacKenzie, 1975) and fitted the GAB equation.

From the humidification of PVP powder samples for the determination of the collapse phenomena some experimental values were added to the values from MacKenzie (1975).

3.3.4.3 Thermal conductivity and heat transfer coefficient
The thermal conductivity is of fundamental importance for the drying rate. For its determination, the thermal diffusion method (Woodams et al., 1968) is used. The temperature is recorded at different heights of the already dried powder bed during a second heating under vacuum. Assuming no further mass transfer (absolutely dry powder bed), homogeneous structure and linear temperature gradient between the sections, the heat flow can be described using the following schematic:

Discretising the 2nd law of Fourier and implementing the Crank-Nicolson temperature change (Patankar, 1980) gives the result:

$$\rho \cdot c_p \cdot \frac{\Delta x \cdot (T_1^1 - T_0^0)}{\Delta t} = \frac{\lambda}{2} \left[ \frac{T_0^0 - T_1^1}{\Delta x_{01}} + \frac{T_1^1 - T_2^1}{\Delta x_{12}} \right]$$

Eq. 3.3.1

3.3.4.4 Powder Density and Porosity
The porosity of the powder bed $\varepsilon_{bed}$ is composed of the porosity of the voids due to the packing of the particles, $\varepsilon_1$ (inter-particle porosity) and the porosity of the open and closed pores in the particles, $\varepsilon_2$ (intra-particle porosity)(see Figure 3.3.6).
3.3 Freeze drying kinetics

The porosity of the bed $\varepsilon_{\text{bed}}$ can be defined with Eq. 3.3.2:

$$\varepsilon_{\text{bed}} = \frac{V_v}{V} = \frac{1}{V} \left( \varepsilon_1 \cdot V + \varepsilon_2 \cdot (1 - \varepsilon_1) \cdot V \right)$$  \hspace{1cm} \text{Eq. 3.3.2}

where $V$ is the volume of the bed, $V_v$ the volume of the voids. Eq. 3.3.2 can be rewritten to give Eq. 3.3.3:

$$\varepsilon_{\text{bed}} = \varepsilon_1 + \varepsilon_2 - \varepsilon_1 \times \varepsilon_2$$  \hspace{1cm} \text{Eq. 3.3.3}

The bulk density $\rho_{\text{bed}}$ of a powder bed can be determined from the volume $V$ and the mass of the powder bed $m_{\text{bed}}$ as follows:

$$\rho_{\text{bed}} = \frac{m_{\text{bed}}}{V} = (1 - \varepsilon_{\text{bed}}) \cdot \rho_M + \varepsilon_{\text{bed}} \cdot \rho_{\text{gas}}$$  \hspace{1cm} \text{Eq. 3.3.4}

where $\rho_M$ is the density of the matrix and $\rho_{\text{gas}}$ the density of the gas in the voids. The porosity $\varepsilon_{\text{bed}}$ can then be calculated as follows:

$$\varepsilon_{\text{bed}} = \frac{\rho_M - \rho_{\text{bed}}}{\rho_M - \rho_{\text{gas}}}$$  \hspace{1cm} \text{Eq. 3.3.5}

assuming that the density of the gas is very small compared to the other two densities Eq. 3.3.5 can be simplified:
3.3 Freeze drying kinetics

\[ \varepsilon_{\text{bed}} \equiv 1 - \frac{\rho_{\text{bed}}}{\rho_M} \]  

Eq. 3.3.6

For a given foam overrun OR (gas to liquid volume ratio in the foam, Eq. 3.2.4) the porosity of the particles \( \varepsilon_2 \) (intra-particle porosity) can be written as:

\[ \varepsilon_2 = \frac{OR}{OR + 100} \]  

Eq. 3.3.7

Eq. 3.3.7 is only valid under the assumption, that the volume of gas in the foam is the same as in the solid particles. The inter-particle porosity \( \varepsilon_1 \) can be calculated from Eq. 3.3.3:

\[ \varepsilon_1 = \frac{\varepsilon_{\text{bed}} - \varepsilon_2}{1 - \varepsilon_2} \]  

Eq. 3.3.8

As mentioned above \( \varepsilon_2 \) includes the "open" and "closed" porosity of the particles. The powder "open" porosity is measured using helium pycnometry. Helium was used because of its inertness and the small size of the helium atom, which enables them to penetrate even into the smallest open pores. The difference between the density measured with helium pycnometry and the matrix density provides the "closed" pores related porosity of the powder (pores with no connection to the exterior). The apparatus used to measure solid volumes is a pycnometer (AccuPyc 1330 Pycnometer, Micromeritics Instrument Corporation, Germany). A schematic diagram of this pycnometer is shown in Figure 3.3.7.

The Volume \( V_c \) is considered for the powder sample cell. After purging the system with helium and bringing all volumes to ambient pressure, the sample chamber is pressurized to \( P_2 \). Valve \( v_1 \) is opened to connect the reference volume \( V_R \) to that of the cell. Consequently, the pressure drops to a lower value \( P_1 \) in the sample chamber while increasing from ambient to \( P_1 \) in the reference volume. The pressure value is
3.3 Freeze drying kinetics

taken once a given pressure equilibration rate is reached. Using $P_1$ and $P_2$, the non-
helium penetrated powder volume $V_p$ is calculated according to:

$$V_p = V_c + \frac{V_k}{1 - P_1/P_2}$$  \hspace{1cm} \text{Eq. 3.3.9}

The non-helium penetrated density $\rho_H$ is then calculated from the powder mass $M_p$
and its volume $V_p$:

$$\rho_H = \frac{M_p}{V_p}$$  \hspace{1cm} \text{Eq. 3.3.10}

The closed porosity within a particle $\varepsilon_{cl}$ can consequently be calculated from $\rho_H$, $\rho_M$, and the density of the particle $\rho_p$:

$$\varepsilon_{cl} = \left( \frac{1}{\rho_H} - \frac{1}{\rho_M} \right) \cdot \rho_p$$  \hspace{1cm} \text{Eq. 3.3.11}

The density of the particle can be determined from the overrun OR:

$$\rho_p = \frac{100 \cdot \rho_M}{OR + 100}$$  \hspace{1cm} \text{Eq. 3.3.12}

Eq. 3.3.11 can be rewritten with Eq. 3.3.7 and Eq. 3.3.12 as follows:

$$\varepsilon_{op} = (1 - \varepsilon_p) \cdot \left( \frac{\rho_M}{\rho_H} - 1 \right)$$  \hspace{1cm} \text{Eq. 3.3.13}

The open porosity within a particle $\varepsilon_{op}$ is given by:

$$\varepsilon_{op} = \varepsilon_{cl} - \varepsilon_{op}$$  \hspace{1cm} \text{Eq. 3.3.14}

3.3.4.5 Particle size distribution

Particle size analysis allows to determine the particle size distribution. The sample of
dried PVP foamed powder particles were measured with a Computerized Particle
Analyzer CPA (Haver CPA, manufactured by Haver & Boecker, Oelde Westfalen, Germany). The CPA operates on the basis of a photo-optical measurement principle.
Free-falling objects are detected and registered by a CCD camera. The CPA
reconstructs the particle images from the camera signals and the particle size is
subsequently analyzed. The measured powder size distributions were characterized
using a RRSB-distribution function (Schubert et al., 1990). The RRSB-Distribution
function ("stretched" exponential distribution used by Rosin, Rammler, Sperling and
Bennett) is often used to describe mass distribution functions $H_3(x)$ with a pronounced
coarse particle fraction in sieve analysis as:
3.3 Freeze drying kinetics

\[ H_3(x) = 1 - \exp \left[ -\left( \frac{x}{x_{63,3}} \right)^n \right] \]  
Eq. 3.3.15

Where \( x_{63,3} \) characterizes the diameter of the particles and \( n \) the uniformity of the particle size distribution. The index of particle size \( x_{63,3} \) corresponds to the size of sieve meshes, which would retain 37% of the product, which also means that 63% of the particle mass of the sample is contributed from the particles smaller than \( x_{63,3} \):

\[ H_3(x_{63,3}) = 1 - \frac{1}{e} = 0.632 \]  
Eq. 3.3.16

3.3.5 Microstructure images

The Scanning Electron Microscope (SEM) gives clear visual information about the microstructure, such as bubble size distribution and cracks. For SEM analysis the powders were glued to a specimen support. The powders were then coated with a 20 nm gold layer in a Balzers Union MED 010 sputter (Baltec, Lichtenstein) to avoid charging. The particle structures were then imaged with a Philips SEM 550 (Philips, Eindhoven, Holland).

3.3.6 Modeling software

The model was build using Aspen Custom Modeler (Aspen Technology, Cambridge MA, USA) software. Aspen Custom Modeler is an object oriented modeling language that runs under Windows 95/NT (Microsoft, Seattle, USA). It uses a simultaneous algebraic differential equation solver. More details to the construction of the model can be found in Chapter 4.4.
4 Results and Discussion

4.1 State diagram

4.1.1 Water sorption behavior of PVP powders

The predominant factor governing for determining a sorption isotherm is the period necessary to establish equilibrium between the sample and its headspace gas volume. The moisture uptake of sample powders are illustrated in Figure 4.1.1. The sorption curves show that under static air conditions, most of the adsorbed water was already taken up by the samples during the first days. The equilibrium was established after 48 days for samples stored at 25°C. At 2°C, after 78 days equilibration time, the samples were still taking up water. The water needs more time to adsorb at 2°C because of the exponential decrease in the diffusion coefficient with temperature. Samples were stored at 2°C to obtain products with higher water content without collapse and consequently a larger range of humidities for the collapse characterization as a function of water content.

![Figure 4.1.1: Kinetics of Water Adsorption of PVP at 25°C and 2°C](image)

The powder humidified with saturated Mg(NO₃)₂ at 2°C didn’t reach the expected water content of about 21% even after 4 months equilibration time and consequently the data was not taken into consideration for the sorption isotherm calculation. In order to evaluate the sorption data, the G.A.B. model was used to construct sorption isotherms and is shown Figure 4.3.1 in Chapter 4.3.
4.1 State diagram

4.1.2 The glass transition temperature

4.1.2.1 Glass Transition of PVP-Powders measured with DSC

Water plays a central role as a plasticizer of amorphous products. Figure 4.1.2 shows the experimental $T_g$ DSC values for the powder with different moisture contents. The effect of water content on lowering the $T_g$ is well illustrated. This effect is described using the Gordon and Taylor equation (Eq. 3.1.4). The $T_g$ of water ($T_{g2}$) is reported to be $-135^\circ$C. The value of $k$ in the Gordon and Taylor equation was determined by Buera et al. (1992) and corresponds for PVP K15 to 2.66. The Gordon & Taylor equation was fitted by minimizing the difference between the experimental values, keeping $k$ constant = 2.66. The $T_{g1}$ value of PVP at 0% moisture was kept free and a value of 93.83°C was found. This value agrees well with the $T_{g1}$ value of 95°C reported by Buera et al (1992) for PVP K15.

![Figure 4.1.2: Effect of solids content on $T_g$ measured with DSC](image)

4.1.2.2 Glass Transition of PVP-Powders measured with DMTA

Figure 4.1.3 shows the DMTA bending test results for three different frequencies, namely 0.1, 1 and 10 Hz. Measurements with frequencies below 0.1 Hz were not done as they require very long measuring times.

As mentioned in Chapter 2.1.2, maximum energy dissipation during the glass transition in the DMTA measurement occurs when the imposed frequency dependent bending deformation couples most strongly with the vibration of the molecules. The viscous (loss) modulus $E''$ starts to increase from the glassy state value when the viscous behavior appears as the sample “softens” when approaching the glass transition temperature. This behavior can be seen in Figure 2.1.5 in Chapter 2.1.2. At the glass-rubber transition the transition from elastic to viscous behavior is manifested by a peak in the $E''$ modulus. After the glass transition the $E''$ modulus decreases fast with increasing temperature. Higher imposed measurement frequencies reduce the “time of viscous relaxation” (energy dissipation), weighing more the elastic material properties. This effect shifts the $E''$ peak temperatures to higher values with increasing...
measurement frequency. Therefore an extrapolation of the $E''$ peak temperatures towards lower frequencies is needed in order to compare the DMTA mechanical bending modulii and DSC results for the $T_g$ onset. The frequency dependence of the $E''$ peak temperatures to lower frequencies was extrapolated, assuming Arrhenius temperature dependence of $E''$ peaks (Chapter 2.1.2). Previously MacInnes (1993) found such an extrapolation to $f = 0.001$ Hz leads to correspondence of the extrapolated $E''$ peak temperature and the DSC onset temperature for glucose, maltose and other low molecular weight carbohydrates. With PVP, it is necessary to extrapolate to about $0.0001$ Hz to obtain agreement, perhaps due to the much higher molecular weight and the fragile character of the PVP solutions.

As shown in Figure 4.1.4 the $E''$ peak temperatures ($0.0001$ Hz) fitted with the Gordon & Taylor equation, lies only slightly above the Gordon & Taylor $T_g$ (DSC onset). The average molecular relaxation time at the glass transition for this frequency (Equation 2.1.7) is calculated as $1591$ s. Thus higher compared to the molecular relaxation time of $200$s determined from shear and conductivity relaxation times for concentrated salt solutions at the corresponding DSC onset temperature (Angell, 1983). Perez (1994) reports values for average relaxation times for viscous flow between $10^2$ and $10^3$s.

This analysis shows that the frequency dependency of the DMTA scans can provide a comparison between DMTA and DSC glass transition temperature measurements.

![Figure 4.1.3: $E''$ peak temperatures from DMTA measurements at 0.1, 1 and 10 Hz of PVP samples on slow heating (0.3 °C/min) after rapid cooling](image)
4.1 State diagram

Figure 4.1.4: Extrapolation of $E''$ peaks temperatures with Arrhenius temperature dependence to a frequency of 0.0001 Hz and the corresponding Gordon and Taylor equation fitted curve.

4.1.3 Viscosity of PVP-solutions

The results for the complex viscosity $\eta^*$ measurement with the SR5 rheometer are shown in Figure 4.1.5.

Figure 4.1.5: Complex Viscosity $\eta^*(f)$ of PVP K15 (X= 70%) using SR5
The solid line shows the fit of the VTF equation (Eq. 2.1.11) to the 0.1 Hz data. Only the first two VTF constants shown in Table 4.1.1, were adjusted. As the fit was little sensitive to \( T_0 \), it was set to \( T_g - C_2 \), where \( C_2 \) is the “universal” WLF constant.

### Table 4.1.1: VTF-Constants

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>( T_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>-3.675</td>
<td>1489.9</td>
<td>193.5</td>
</tr>
</tbody>
</table>

Extrapolating the VTF equation to the \( T_g \) (DSC) value of -28°C (PVP K15 X= 70%) the viscosity at the glass transition temperature was found to be \( 10^{3.85} \) Pa s. From the VTF constants a value of 12.52 for the WLF constant \( C_1 \) was calculated (Chapter 2.1.6).

The viscosity temperature dependence can also be shown as a function of \( T-T_g \) (Figure 4.1.6) or on a \( T_g \) scaled Arrhenius Plot (Figure 4.1.7). This representation of the viscosity as a function of \( T_g/T \), suggested by Angell (1985), is also used to show “strong/fragile” classification scheme (Chapter 2.1.6). The \( D \) parameter of Eq. 2.1.12 and the fragility parameter \( m \) from Eq. 2.1.13 can be calculated for PVP from the VTF parameters \( B \) and \( T_0 \) in Table 4.1.1.

\[
D = \frac{B}{T_0} \quad \text{Eq. 4.1.1}
\]

\[
m = 16 + \frac{590}{D} \quad \text{Eq. 4.1.2}
\]

and have a \( D \) value of 7.7 and a \( m \) value of 92, indicating the “fragile” character of PVP.

---

Figure 4.1.6: Temperature-dependence of complex viscosity \( \eta^* \) plotted on \( T-T_g \) scale
The oscillatory shear viscosity values measured with the ARES rheometer are shown in Figure 4.1.8. The temperature dependence of the viscosity was again fitted with the VTF equation. To compare this fit with the fitted values of the SR5 measurements only data points in the temperature range from 10 - 55°C were taken. The two lines show good agreement between the SR5 and the ARES values.

Figure 4.1.8 also shows the cut-off of the complex viscosity at a given frequency as the temperature approaches the rubber-glass transition. The viscous component of the complex viscosity, \( G'' \) peaks at this cut-off temperature as shown in Figure 4.1.9. This cut-off can be interpreted as the transition from viscous rubbery to elastic glassy for the measured system at the given frequency in analogy to the DMTA measurements. The \( G'' \) peaks values are shown in Table 4.1.2. As with the DMTA data an extrapolation of the temperatures to lower frequency is necessary to obtain correspondence with \( T_g(DSC) \) of -28°C for this PVP solution.

MacInnes (1993) found previously that as the \( G'' \) peak temperature measured with in oscillatory shear mode occur at higher temperatures than the DMTA \( E'' \) peaks, it is necessary to extrapolate about one order of magnitude further in frequency to obtain correspondence with the \( T_g(DSC) \), as seen in Table 4.1.2.
4.1 State diagram

Figure 4.1.8: Oscillatory Viscosity results for PVP K15 (70% solids) using ARES

![Graph showing oscillatory viscosity results](image1)

Figure 4.1.9: $G''$-peaks for PVP K15 at a solid content $X=70\%$ using ARES

![Graph showing $G''$-peaks](image2)

Table 4.1.2: $G''$-peaks temperatures and extrapolation to 0.00001 Hz

<table>
<thead>
<tr>
<th>$G''$-peak (Heating) [°C]</th>
<th>10Hz</th>
<th>1Hz</th>
<th>0.1Hz</th>
<th>Extrapolation to 0.00001Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>G''-peak (Heating) [°C]</td>
<td>4.05</td>
<td>-2.41</td>
<td>-7.46</td>
<td>-27.98</td>
</tr>
<tr>
<td>G''-peak (Cooling) [°C]</td>
<td>4.73</td>
<td>-2.15</td>
<td>-6.95</td>
<td>-27.84</td>
</tr>
</tbody>
</table>

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4.1.4 Stickiness and collapse behavior of PVP powders

4.1.4.1 Stickiness behavior
Downton et al. (1982) proposed that particles of amorphous powders would stick together if sufficient liquid can flow to build strong enough bridges between the particles. According to Roos (1995) the main cause of stickiness is plasticizing of the particle surface by water, which allows inter-particle binding and formation of clusters.

In Figure 4.1.10 the viscosities at the sticky point temperatures were calculated with the VTF-equation (parameters see Table 4.1.1) and the iso-viscosity lines were fitted using the Gordon & Taylor equation by keeping $T_g$ and $(T-T_g)$ free. The viscosity values can also be read from Figure 4.1.6, where they are plotted as a function of $(T-T_g)$. As shown in Figure 4.1.10, stickiness can be considered to be a time-dependent property of amorphous materials. When the viscosity is high, near $T_g$, the contact time between particles must be very long to result in bridging. The dramatic decrease in viscosity below glass transition temperature obviously reduces the contact time and causes inter-particle fusion resulting in stickiness. The Gordon & Taylor fit of the sticky point after 30 min lies only slightly above the $T_g$ (DSC) fit (Figure 4.1.10). This confirms that the PVP is a fragile liquid (see Figure 4.1.7) as the viscosity drops very fast at temperatures above $T_g$, and at $T_g$ it is already far below an “expected” value at $T_g$ ($10^{12}$ Pa s) for strong liquids in the glassy state.

The two points well above the fits were measured with a non-equilibrated powder humidified at 2°C. They were not taken into consideration in fitting the data.

![Figure 4.1.10: Effect of water content and contact time on sticky temperatures](image)

4.1.4.2 Optical collapse temperatures
The influence of heating rate on the optically detected collapse behavior was studied using the sample projected area as a measure of degree of collapse (see Chapter 3.1.5). Heating rates of 2, 5, 10 °C/min were used to heat the sample.
In Figure 4.1.11, the iso-viscosity lines were fitted using the Gordon & Taylor-equation to the collapse temperatures as a function of concentration $T_c(X)$. The adjustment parameters were $T_g$ and $(T-T_g)$:

$$T_c(X) = \frac{w_1(T-T_g) + k w_1 T_g}{w_1 + k w_2} \quad \text{Eq. 4.1.3}$$

The viscosities corresponding to the observed collapse temperatures $(T-T_g)$ in Figure 4.1.11 were calculated from the VTF-equation (parameters see Table 4.1.1). The viscosity values can also be read from Figure 4.1.6, where they were plotted as a function of $(T-T_g)$. The three points above the fits were measured with a non-equilibrated powder humidified at 2°C and were not taken into consideration for fitting the data.

![Figure 4.1.11: Effect of heating rate on collapse temperature at various solids contents](image)

### 4.1.5 Deborah numbers for collapse and stickiness phenomena

Since stickiness and collapse are time-dependent phenomena, a Deborah-Number (Chapter 2.1.7) for PVP K15 was calculated. The “observation time” was calculated as the holding times for each 5°C step (Table 4.1.3). The average (mechanical) molecular relaxation time $\tau$ at $T_g$ was calculated from the extrapolated frequency of the DMTA $E''$ peak temperature at the glass transition (0.0001 Hz) as $\tau_g = 1/(2\pi f) = 1591$ seconds (Chapter 4.1.2.2). The relaxation time $\tau$ at collapse $T_c$ for a given value $T_c-T_g$ can be calculated from the WLF equation as follows:

$$\log \tau(T_c - T_g) = \log(\tau_g) + \frac{C_1(T_c - T_g)}{C_2 + (T_c - T_g)} \quad \text{Eq. 4.1.4}$$
4.1 State diagram

The uncertainty (± STD) in the \((T_c - T_g)\) values gives a range of \(\tau\) values and Deborah Numbers as shown in Table 4.1.1.

Table 4.1.3: Deborah-Number for powder collapse \(T_c\) and stickiness (SP) temperatures for PVP powders

<table>
<thead>
<tr>
<th></th>
<th>SP (30min)</th>
<th>SP (1min)</th>
<th>(T_c) (2°C/min)</th>
<th>(T_c) (5°C/min)</th>
<th>(T_c) (10°C/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time step / 5°C [min]</td>
<td>30</td>
<td>1</td>
<td>2.5</td>
<td>1</td>
<td>0.5</td>
</tr>
<tr>
<td>Observation time t [s]</td>
<td>1800</td>
<td>60</td>
<td>150</td>
<td>60</td>
<td>30</td>
</tr>
<tr>
<td>((T_c + STD) - T_g)</td>
<td>-0.6</td>
<td>3</td>
<td>3.5</td>
<td>6</td>
<td>11</td>
</tr>
<tr>
<td>(T_c - T_g)</td>
<td>0.6</td>
<td>5</td>
<td>5</td>
<td>7</td>
<td>13</td>
</tr>
<tr>
<td>((T_c - STD) - T_g)</td>
<td>1.6</td>
<td>7</td>
<td>6.5</td>
<td>8</td>
<td>15</td>
</tr>
<tr>
<td>(\tau + STD)</td>
<td>2236</td>
<td>327</td>
<td>256</td>
<td>79</td>
<td>10</td>
</tr>
<tr>
<td>(\tau - STD)</td>
<td>1144</td>
<td>125</td>
<td>125</td>
<td>51</td>
<td>5</td>
</tr>
<tr>
<td>(De) start (“solid”)</td>
<td>1.2</td>
<td>5.5</td>
<td>1.7</td>
<td>1.3</td>
<td>0.3</td>
</tr>
<tr>
<td>(De) mid (at (T_c))</td>
<td>0.6</td>
<td>2.1</td>
<td>0.8</td>
<td>0.9</td>
<td>0.2</td>
</tr>
<tr>
<td>(De) end (“liquid”)</td>
<td>0.4</td>
<td>0.9</td>
<td>0.4</td>
<td>0.7</td>
<td>0.08</td>
</tr>
</tbody>
</table>

At the collapse \(T_c\), Deborah numbers \(De\) around 1 are expected and decrease through the collapse transition, as the collapse proceeds from a “solid” state (\(De >> 1\)) to a “liquid” state (\(De << 1\)). This can be illustrated e.g. for the optical collapse observation measured at a heating rate of 5°C/min. The collapse temperature \(T_c\) is 7°C higher than the glass transition temperature \(T_g\) for an observation time of 60 seconds resulting in a relaxation time of 51 seconds. This gives a \(De\)-number of 0.9. If the observation time at that the collapse temperature is reduced by factor 10 to 6 seconds collapse will not be observed (\(De\)-number = 9, solid behavior). If the observation time at the collapse temperature is increased by factor 10 to 600 seconds the sample would loose its structure in a liquid-like behavior (\(De\)-number = 0.09). This illustration of the collapse phenomena can also be done for a constant observation time and varying the temperatures and the corresponding relaxation times. Higher temperatures and corresponding higher relaxation temperatures result in \(De\)-numbers << 1 (liquid behavior) and lower temperatures in \(De\)-numbers >> 1 (solid behavior).

The calculated \(De\)-numbers are strongly dependent from the collapse observation method and thus from the experimental set up. In this first experiments a rather large temperature step (5°C) for the collapse observation was chosen, therefore the measured collapse temperatures are not very precise. Also the observation time of 1 minute in the sticky point measurement (SP 1min) is to short in relation to the thermal inertia of the sample in the vial. This results in higher measured values for sticky point temperatures and consequently the calculated relaxation times are to high.

All these factors have to be taken into account when determining the temperature of the dynamic collapse phenomena. In special when measuring collapse of a fragile material as PVP. The high fragility of PVP accounts for the relative low viscosity at the glass transition temperature \((10^{8.8} \text{ Pa s})\) compared to \(10^{12}\) for strong materials) and for the sharp drop in viscosity below the glass transition temperature. The literature values for collapse viscosity are in the range \(10^4\) to \(10^7\) (Bellows and King, 1973). In the case of a fragile material, this values are reached a few degrees below the glass transition temperature (see Figure 4.1.6).
The importance of a precise determination of the water content and control of the humidity of the samples has also to be mentioned. An error of 1% in water content at X= 90% \( (T_g(DSC)= 42°C) \) changes the glass transition temperature by 5°C.

### 4.1.6 Heating rate dependence of the collapse temperatures

The results of the stickiness and optical collapse experiments showed the dependence of the collapse phenomena for different powders as a function of water content. Both measurement techniques show the viscous structure collapse deformation to a different degree of intensity. The optical collapse temperature is measured for an extensive viscous flow of the particle observed as the projected surface area of the particle increases while heating the particle at a constant heating rate. On the other hand the stickiness is observed as the surface of the particles gets “sticky” enough to build “bridges” between particles and also to the vial glass wall.

In order to compare the heating rate dependence of the different levels of collapse intensity (sticky point and optical collapse observations), the sticky point data was transformed to heating rates (5°C/min, 0.166°C/min and 0.00347 °C/min) for “sticky point” temperature determination for a 5°C change after a holding time of 1, 30 minutes and 24 hours respectively. The results were then compared to the heating rates of the collapse experiments (i.e. 2, 5, 10 °C/min). The results for two powders with different solids content were plotted in an Arrhenius type plot (Figure 4.1.12).

The log of the inverse of the heating rate was plotted versus \( \frac{1}{T} \) where \( T \) is the sticky point or the optical collapse temperatures. The analysis of the effect of heating rate on the collapse temperature was then done using the Arrhenius equation. The lines in Figure 4.1.12 show the linear fit through the data points. From this linear fit, the activation energies for sticky point and optical collapse were calculated for PVP powders with 89% (508 kJ/mol) and 92% (617 kJ/mol) solids content.

![Arrhenius dependence of collapse and sticky point temperatures for PVP](image)

Levi and Karel (1995) obtained similar collapse activation energies of 322-489 kJ/mol measuring the volumetric shrinkage for sucrose-raffinose freeze-dried particles with low moisture contents (0-5%). This could be an indication that the observed collapse from the sticky point and optical collapse values describe the same collapse phenomena as for amorphous carbohydrates above their glass transition temperature.
Higher values were obtained here for PVPk15 which is probably due to the collapse temperatures which were much closer to \( T_g \) (0 to 12°C above \( T_g \) (DSC)) compared to the range of 10 to 35°C in the work of Levi and Karel (1995).

### 4.1.7 State diagram for freeze-drying of PVP

Figure 4.1.13 shows the state diagram of PVP K15. The state diagram was plotted from measured data in this work and from additional literature values for PVP.

The glass transition line \( T_g \) is derived from the experimentally determined DSC onset temperatures using the Gordon & Taylor equation for the concentration dependence. The value of the viscosity at \( T_g \) (=10^8.9 Pa s) was obtained by extrapolating the viscosity data using the VT equation.

The equilibrium ice melting line \( T_m \) for PVP K15 was extrapolated from the \( T_m \) values measured for PVPk30 (Mackenzie, 1972), using the following equation:

\[
T_m = -A \cdot \ln \left( \frac{C_g - C}{C_g'} \right)^{\frac{1}{B}}
\]

Eq. 4.1.5

where \( A \) and \( B \) are constants and \( C_g' \) is the maximally freeze concentrated solution. \( C_g' \) for PVP K15 corresponds to 61%. The calculated \( A \) and \( B \) parameters were 1.66 and 0.58. The maximum ice formation line \( T_m' \) corresponds to the DMTA tan \( \delta \) peak value at 0.001 Hz for solutions below \( C_g' \). The glass transition temperature \( T_g' \) of the maximally cryo-concentrated solution was determined to be -52°C from the DMTA measurements and its value is assumed to be concentration independent.

Figure 4.1.13: State Diagram of PVP K15
As shown in Figure 4.1.14, by plotting $T-T_g$ as a function of concentration, the difference between stickiness, collapse and glass transition temperatures can be magnified, by subtracting the $T_g$ concentration dependence.

Freeze drying practice shows that the temperature of the onset of de-cryo-concentration $T_m'$ is the maximum temperature giving the needed rigidity to the material for successful freeze drying without collapse, for $C < C_{g'}$.

Above $C_{g'}$, the temperatures of collapse during freeze-drying are iso-viscosity lines parallel to $T_g$. To maintain the porous structure without collapse, freeze-drying must be carried out under conditions where the Deborah Number is $>>1$ (solid like state) as defined in Chapter 2.1.7. Since both viscosity and molecular relaxation time decrease sharply above $T_g$, the drying time (= “observation” or processing time) must also be similarly reduced to maintain $De >>1$. Conservative drying conditions would follow $T_g'$ and $T_g$ as shown in Figure 4.1.14. However if heat and mass transfer rates can be increased, the freeze-drying can follow a path above $T_g'$ and $T_g$ as shown.

Figure 4.1.14: $T-T_g(C)$ Normalized State Diagram of PVP K15
4.2 Foaming

The aim of foaming high concentrated PVP solution was to produce foamed powders with different controlled inner structure (bubble size distribution), density (overrun) and outer structure (size fractions of the powder) for the subsequent drying studies.

4.2.1 Surface tension of PVP solutions

Wilhelmy plate method

Figure 4.2.1 and Figure 4.2.2 show the measured surface tension of PVP solutions for concentrations with and without surfactant as a function of measurement time.

Figure 4.2.1: Surface tension of PVP solutions with different concentration and water without surfactant as a function of time at 20°C

Figure 4.2.2: Surface tension as a function of time for PVP solutions at different concentration with 0.25% SDS surfactant at 20°C
Figure 4.2.1 shows the surface activity of PVP solutions without surfactant which decreased the surface tension compared to water. The solution with X= 45% shows an increase in surface tension compared to the solutions at lower concentrations. This can be an effect of the increased viscosity and interaction of the polymer chains with the platinum plate.

The addition of SDS to the solutions increases significantly the surface activity of the solution, thereby decreasing the surface tension (Figure 4.2.2). The surface tension decreases with increasing concentration of the PVP polymer after 10 minutes measurement time. As can be observed there is a time effect to reach the asymptotic value of surface tension with increasing concentration. This has to do with the diffusion rate of the surfactant to the surface. The higher the concentration, the slower is the diffusion rate and more the surface tension drops with time.

The diffusion based kinetics of this effect can be shown by plotting the surface tension as a function of the inverse square root of the time (Miller et al, 1994). The diffusion controlled surface activity should show a linear behavior in this plot as demonstrated in Figure 4.2.3.

![Figure 4.2.3: Surface tension as a function of 1/ square root of time for PVP solutions with surfactant measured with the Wilhelmy plate method](image)

**Pendent drop method**

The pendent drop method enabled the measurement of the surface tension of concentrated PVP solution above X= 45 % and higher temperatures. The measurement could be performed under controlled water vapor saturated atmosphere, to avoid the skin building at the surface of the PVP solution.

Figure 4.2.4 shows the results of the pendant drop surface tension measurements of PVP solutions with different solid content at 20, 50 and 70 °C. The solid symbols denote the solutions with 0.25 % SDS.
4.2 Foaming

Figure 4.2.4: Surface tension measurements of PVP solutions as a function of solid content. The error bars indicate the standard deviation of 3 measurements.

With the pendent drop method similar tendency for the surface activity of the PVP solution with surfactant was observed as for the Wilhelmy plate measurements. The surface tensions with the pendant drop method show much higher values for the solutions without surfactant at concentrations (X= 15 and 30%). The concentration variation of the surface tension is more consistent with the pendent drop method compared to the Wilhelmy plate values.

The pendent drop measurements with SDS are comparable to those measured with the Wilhelmy plate method. SDS significantly lowers the surface tension of the solution. At higher solid concentrations, the surface tension increases again (see Figure 4.2.4). This could be explained by interactions of the PVP polymer and the surface activity of the surfactant; the ratio of PVP polymers to surfactant molecules is increasing with concentration in these solutions. The surface tension of PVP plotted as a function of the inverse square root of time (Figure 4.2.5) deviates of the linear behavior for higher concentrations and long measurement times. This shows that there is another effect beside the diffusion kinetics effect of the surfactant influencing the measurements. This long time effect could be drying out or water adsorption at the surface of the droplet in the pending drop method.
4.2 Foaming

For PVP solutions with and without surfactant, the surface tension generally decreases with increasing temperature (see Figure 4.2.4). But there are no significant differences between the surface tension values measured at 50 and 70°C.

As a first approximation to calculate the critical Weber number, the surface tension value of 48 mN/m for the PVP solution with X = 70% at 50°C was taken (see Figure 4.2.4). The PVP solutions were foamed at that concentration and temperature.

4.2.2 Viscosity of PVP as a function of temperature

Viscosity is an important parameter for the calculation of the Newton and Reynolds characteristic and for the calculation of the critical Weber number. The viscosity of PVP solutions and related foams was measured as a function of temperature in oscillatory mode with a controlled stress rheometer. Viscosity of PVP shows non-linear behavior on the Arrhenius plot as demonstrated in Figure 4.2.6 showing the measurements carried out in the oscillatory mode at a frequency of 0.1 Hz with a plate-plate geometry. The gap was 1.25 mm and a paraffin layer prevented the sample from drying out. The dotted line is a linear trendline, which highlights the non-Arrhenius behavior and the temperatures are indicating the approximate temperature in °C. The temperature dependency of viscosity was fitted to the VTF Equation 2.1.11 (solid line in Figure 4.2.6).
4.2 Foaming

Figure 4.2.6: Temperature dependency of viscosity of PVP X= 70%; oscillatory scan

In Figure 4.2.7 foam with 74% overrun was measured in oscillatory mode at three different frequencies, 0.1 Hz, 1 Hz, 10 Hz. The sample is loaded at 55°C and the first point was measured at that temperature, then at the following temperatures 30, 10, 0, 20, 40, 55, 70, and back again at 55 °C. Again the temperature dependency of the foam viscosity only for the frequency of 0.1 Hz was fitted with the VTF Equation 2.1.11 (solid line in Figure 4.2.7). The dotted line in Figure 4.2.7 shows the VTF fit for the PVP solution (bulk). A shift of the foam curve of about one order of magnitude higher compared to the non-foamed solution in viscosity could be found.

Figure 4.2.7: Temperature dependency of viscosity of PVP X= 70% and foam with 74% overrun
4.2.3 Power consumption as a function of the rotor speed

In order to determine the Newton Reynolds characteristic of the dynamic mixer (Kinematica FM12) the net power input into the product in the mixer was measured. The power input was determined from the electrical power consumption. The net power input was determined by subtracting from the total electrical power the zero power input at corresponding rotation speed. Figure 4.2.8 shows the electrical power consumption of the empty Kinematica FM12 foaming head and for a PVP solution with X= 63% solid content while cooling the mixing head down to 21°C. Increasing rotor speed leads to increasing product temperature after the mixing head due to viscous energy dissipation.

![Figure 4.2.8: Power consumption vs. rotor speed of the Kinematica foaming head](image)

4.2.4 Determination of the Newton-Reynolds characteristics

Figure 4.2.9 shows the Newton/Reynolds characteristics measured with water, PEG, glucose syrup solutions (Leplat, 1998), and PVP solutions. The viscosity of the solutions varied between 42 mPas and 74 Pas. A distinction of the different flow domains can be seen in Figure 4.2.9. A laminar and turbulent region can be clearly distinguished from the Newton/Reynolds characteristics. According to Nagata (1975), there is a linear dependency between Newton and Reynolds number in the laminar flow region:

\[
Ne = \frac{Cl}{Re} \quad \text{Eq. 4.2.1}
\]

where \(Cl\) is a mixer geometry specific constant. For the laminar flow field, \(Cl \approx 17000\) was estimated.
4.2 Foaming

In the turbulent flow domain, the Newton number is no longer a function of the Reynolds number.

\[ Ne = C2 = \text{constant} \]

A \( C2 = 14000 \) was measured for the turbulent flow domain. It can be assumed that all the foaming trials performed with PVP were performed in the laminar flow domain.

![Graph showing Newton/Reynolds characteristic for the Kinematica FM12 mixing head](image)

**Figure 4.2.9: Newton/Reynolds characteristic for the Kinematica FM12 mixing head**

4.2.5 Influence of cooling and rotor speed on overrun and product heating

The goal was to determine the maximum overrun for \( \text{N}_2 \) and \( \text{CO}_2 \) foams at given rotor speeds, keeping flow rate, product inlet temperature and pressure in the foaming head constant. This was done with and without cooling (0°C) of the mixing head. The results are shown in Figure 4.2.10 and Figure 4.2.11 as a function of the difference in temperature \( \Delta T \) between the outlet and the inlet temperature of the product. The inlet temperature was about 50°C.

Higher overruns were reached with \( \text{N}_2 \) gas compared to \( \text{CO}_2 \). Almost double the amount of \( \text{CO}_2 \) was needed to produce the same overrun compared with \( \text{N}_2 \) due to the higher solubility of \( \text{CO}_2 \) in the liquid phase. Rotor speed influences the dispersing force, the product heating \( \Delta T \) and the related product viscosity. For maximum overrun without cooling an optimum rotor speed around 1200 was found at a product heating \( \Delta T \) smaller than 15°C. Higher \( \Delta T \) lead to unacceptable fast coalescence due to the lower viscosity leading as well to a reduced overrun. The cooling of the mixing head shifted the curves to the lower product heating \( \Delta T \) and as well to higher overruns. The conclusions are that cooling to \( \Delta T \leq 15°C \) and a rotor speed in the range 1200-1800 rpm is essential to reach high overruns. The cooling of the foam in the mixer is very effective and negative \( \Delta T \) were found at low rotor speed (<1200rpm).
4.2 Foaming

4.2.6 Influence of rotor speed on bubble size distribution

The bubble size distribution in foams is a function of the dispersing acting stresses and the residence time in the mixer. For a given rotor speed the maximal bubble size is given by the critical Weber number for the system. To obtain PVP foams with different bubble size distribution, foams were produced with N₂ gas, varying the rotor speed. In this trials all other foaming parameters like overrun (200%), inlet temperature (44°C) and feed rate (12 l/h) were kept constant. Two foam samples were taken at each rotor speed and the bubble size distribution was measured. From each sample three different “populations” (70-150 bubbles/image) were measured. At low
4.2 Foaming

At rotation speeds (600 and 800 rpm) the foam was not homogenous and the bubble size distribution could not be measured. The results are shown in Table 4.2.1.

Table 4.2.1: Results from bubbles size measurements of foam produced at different rotor speeds

<table>
<thead>
<tr>
<th>Rpm</th>
<th>600</th>
<th>800</th>
<th>1000</th>
<th>1200</th>
<th>1400</th>
<th>1600</th>
<th>1800</th>
<th>2000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prod in [°C]</td>
<td>44.9</td>
<td>42.7</td>
<td>44.7</td>
<td>44.5</td>
<td>42.5</td>
<td>44.4</td>
<td>43.9</td>
<td>43.2</td>
</tr>
<tr>
<td>Prod out [°C]</td>
<td>49.2</td>
<td>38.1</td>
<td>44.7</td>
<td>67.4</td>
<td>49.5</td>
<td>68.5</td>
<td>69.2</td>
<td>70.7</td>
</tr>
<tr>
<td>Delta T</td>
<td>4.3</td>
<td>-4.6</td>
<td>0</td>
<td>22.9</td>
<td>7</td>
<td>24.1</td>
<td>15.3</td>
<td>27.5</td>
</tr>
<tr>
<td>Cooling in [°C]</td>
<td>49.3</td>
<td>33.8</td>
<td>34.9</td>
<td>33.5</td>
<td>48.6</td>
<td>25.4</td>
<td>17.4</td>
<td>14.3</td>
</tr>
<tr>
<td>Cooling out [°C]</td>
<td>49.4</td>
<td>34.4</td>
<td>35.3</td>
<td>35.2</td>
<td>48.7</td>
<td>27.7</td>
<td>20.3</td>
<td>17.6</td>
</tr>
<tr>
<td>Delta T</td>
<td>1</td>
<td>0.6</td>
<td>0.4</td>
<td>1.7</td>
<td>0.1</td>
<td>2.3</td>
<td>2.9</td>
<td>3.3</td>
</tr>
<tr>
<td>Tot Power [W]</td>
<td>122</td>
<td>335</td>
<td>614</td>
<td>454</td>
<td>562</td>
<td>584</td>
<td>660</td>
<td>710</td>
</tr>
<tr>
<td>Net Power [W]</td>
<td>80</td>
<td>277</td>
<td>537</td>
<td>337</td>
<td>384</td>
<td>384</td>
<td>390</td>
<td>430</td>
</tr>
<tr>
<td>Stand. Dev. [µm]</td>
<td>4.84</td>
<td>4.55</td>
<td>4.34</td>
<td>4.93</td>
<td>5.47</td>
<td>5.51</td>
<td>167</td>
<td>194</td>
</tr>
</tbody>
</table>

Surprisingly no significant difference was found in the mean bubble diameter (about 10 µm) and the standard deviation. A possible explanation is that higher rotor speed leads to higher temperatures (40°C at 800 rpm and 70°C at 2000 rpm), even though it was tried to keep the outlet temperature constant by cooling the mixing head. The higher temperature results in a lower viscosity, significantly reducing the stresses acting to disperse the gas bubbles. As can be seen from the viscosity measurements in Chapter 4.2.2, the viscosity of the PVP solution drops 10 times from about 30 Pa s to 3 Pa s in the range between 40 and 70°C. Higher temperatures lead also to higher re-coalescence rates of the gas bubbles in and after the foaming head. As a result the measured equilibrium bubble size stays constant. The standard deviation is rather high indicating a broad bubble size distribution.

4.2.7 Influence of rotor speed and time on foam stability

The trials were repeated to improve the accuracy of the bubble size distribution analytic and to measure as well the foam stability as a function of time. Foam samples were taken at 1000, 1400 and 1800 rpm as described for the prior trial. The foams in the sample holder were kept for 3 minutes at room temperature and then measured again. The idea was to observe the evolution of the foam structure after 3 minutes. These measurements give also an information about the foam stability with time. Under such conditions stable foams would show only little change in the bubble size distribution. Figure 4.2.12 shows two images of foams produced with N₂ from a 70% solids content solution of PVP at different rotor speeds.
4.2 Foaming

![Image: N₂ foam, 1000 rpm vs N₂ foam, 1800 rpm](image)

Figure 4.2.12: PVP foams produced at different rotor speeds

The following boxplots (Figure 4.2.13 and Figure 4.2.14) illustrate the statistical analysis of three populations of the measured bubble size distributions.

![Image: Boxplots of bubble diameters at different rpm after 0 and 3 minutes holding time](image)

Figure 4.2.13: Boxplots of bubble diameters at different rpm after 0 and 3 minutes holding time
Figure 4.2.13 shows that all the box plots have a positive skewness. The right and the left side of the box are the first and the third quartiles. The width of the box is then the interquartile range (IQR) and represents 50% of the data points. The black point in the center is the median. Because of the skewness observed, the mean diameter is not useful. The circles outside the dotted whiskers (= 1.5*IQR) indicate extreme diameters. As the extreme diameter values have a strong influence on the mean and the standard deviation, the natural logarithm was taken to redraw the boxplots. In Figure 4.2.14 it can be seen that the distributions are more symmetric and closer to a normal, bell shaped distribution.

![Boxplots of bubble diameters (logarithmic scale) at different rpm after time 0 and 3 min](image)

Figure 4.2.14: Boxplots of bubble diameters (logarithmic scale) at different rpm after time 0 and 3 min

The evolution of the bubble size distribution after a waiting time of 3 minutes in Figure 4.2.14 shows different behaviors at different rotor speed. For the foam
produced at 1800 rpm the median value shifts towards bigger diameters and the
interquartile range gets wider due to coalescence of the bubbles. For the foam
produced at 1400 rpm the median shifts towards bigger diameters. The interquartile
range also shifts toward higher values but its width stays constant indicating a slow
coarsening of the bubbles due to coalescence and Ostwald ripening. In the case of the
foam produced at 1000 rpm the median remained the same and the interquartile
increases to the two sides indicating that the distribution moved towards smaller
bubbles and bigger bubbles as well. This is an indication for a rapid Ostwald ripening
as the small bubbles get smaller and the bigger increase in size.
Although there is a big variability within the sample replicates the conclusion is the
following: there is no significant change in the bubble size distribution for different
rotor speeds in the range of 1000-1800 rpm (Figure 4.2.15). The problem of this data
set is that the reproducibility of the experiments was insufficient (see Rpm 1400;
Time 0 values in Figure 4.2.15). One of the obvious reasons for this was a leak in the
rotating joint that was found after the experiment. The gas leak did not allow a
constant control of the gas dosing, as part of the gas was lost through the leaking joint.
After three minutes the mean diameter of the foam bubbles increases slightly due to
coalescence and Ostwald ripening.

![Figure 4.2.15: Mean bubble diameter as a function of rotor speed after 0 and 3 minutes](image)

**Figure 4.2.15: Mean bubble diameter as a function of rotor speed after 0 and 3 minutes**

**Time evolution of the foam structure**

In this experiment the change in foam structure with time was characterized by
measuring the foam bubble diameter in the sample holder at room temperature after
given time intervals. The foam sample with N$_2$ was produced at 1200 rpm contained
X = 63% PVP and had an overrun of 297%. Pictures of the foam sample were taken
after 0, 5, 8, 10 and 75 minutes. Figure 4.2.16 shows the time evolution of the
bubbles. The bubble diameter values after 75 minutes were neglected because there
were only five bubbles in the picture, and therefore no statistically significant
diameter could be measured.
4.2 Foaming

PVP foam produced with N₂ gas at 1200 rpm. Solid content of the solution 63% and an overrun at time 0 min of 297%. The images were taken after 0, 5, 8, 10 and 75 minutes at room temperature.

Figure 4.2.16: Foam time evolution

Figure 4.2.17 shows the increase in mean bubble diameter and the standard deviation of the mean within ten minutes from 21.3 μm to 27.8 μm.
4.2 Foaming

4.2.8 Influence of pressure and gas on foam structure

In this trial foams were produced with two different back-pressures (1.5 and 3.5 bars) and two gases (N\textsubscript{2} and CO\textsubscript{2}). The mean bubble diameter of foam produced with CO\textsubscript{2} (Figure 4.2.19) was significantly larger than for the foam produced with N\textsubscript{2} (Figure 4.2.18). Larger bubbles of CO\textsubscript{2} foams can be explained by the faster coalescence and Ostwald ripening effects due to the much higher solubility of CO\textsubscript{2} and the big difference of CO\textsubscript{2} partial pressure between foam and atmosphere compared to foams with N\textsubscript{2} gas. Higher back pressure lead to decreased overrun at the outlet of the tube. The decreasing overrun with higher back-pressure could be due to a higher solubilization of the gas in the liquid phase.

Table 4.2.2: Bubble diameter and overrun at different back-pressures

<table>
<thead>
<tr>
<th>Pressure [bar]</th>
<th>N\textsubscript{2}</th>
<th>CO\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.5</td>
<td>3.5</td>
</tr>
<tr>
<td>Mean diam. [µm]</td>
<td>12.94</td>
<td>12.27</td>
</tr>
<tr>
<td>Stand. Dev. [µm]</td>
<td>6.16</td>
<td>5.61</td>
</tr>
<tr>
<td>Overrun [%]</td>
<td>260</td>
<td>198</td>
</tr>
<tr>
<td>Gas flow [l/h]</td>
<td>13.5</td>
<td>22.0</td>
</tr>
</tbody>
</table>

Figure 4.2.18 and Figure 4.2.19 show the differences in the bubble size distribution of the two foams produced with different gases with about the same overrun. It has to be remarked that the image analysis software did not work for the CO\textsubscript{2} foam due to the different image quality. Therefore the bubble diameters were measured “manually”.

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4.2 Foaming

Figure 4.2.18: PVP foam with N₂ gas, OR 198 %, 1200 rpm, back-pressure 3.5 bar, X=70 %

Figure 4.2.19: PVP foam with CO₂ gas, OR 203 %, 1200 rpm, back-pressure 3.5 bar, X=70 %
4.2.9 Determination of the critical Weber number \( \text{We}_{\text{crit}} \)

As mentioned previously, laminar flow conditions were found for the PVP solutions investigated here in the mixing head. Therefore the Weber number has to be calculated for laminar flow, dominated by viscous forces. The acting shear stresses \( \tau \) can be calculated from the viscosity function \( \eta(\dot{\gamma}) \) of the whipping fluid and the shear rate \( \dot{\gamma} = \pi n D/s \) according to Newton’s law \( \tau(\dot{\gamma}) = \eta(\dot{\gamma}) \cdot \dot{\gamma} \) (Eq. 2.2.9). \( n \) denotes the rotor speed in rpm, \( D \) is the rotor diameter and \( s \) is the axial gap between rotor and stator (Hanselmann, 1996). The VTF-equation was used to calculate the temperature dependent viscosity. The shear stress in the laminar flow field in the shear gap between rotor and stator pins results as:

\[
\tau(T, \dot{\gamma} = \text{const.}) = A \cdot e^{\frac{B}{T-T_0}} \cdot \frac{\pi \cdot n \cdot D}{s}
\]  
Eq. 4.2.2

After inserting the measured bubble size distributions and power input values resulting from the foam trial and the viscosity values and a \( C_1 \) value of 17000 (Eq. 4.2.1) into Eq. 2.2.14, the values for the critical \( \text{We} \)-number in Table 4.2.3 were obtained (for more details in the calculations see Ruepp, 1998).

<table>
<thead>
<tr>
<th>Rotor speed [1/min]</th>
<th>Xmax (3.6 bar) [m]</th>
<th>Power [Js/m]</th>
<th>Surface tension [N/m]</th>
<th>density [kg/m³]</th>
<th>shear Vol [m³]</th>
<th>Tau lam [N/m]</th>
<th>( \text{We}_{\text{crit}} ) [Pa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>0.0000176</td>
<td>120</td>
<td>0.048</td>
<td>1100</td>
<td>0.000092</td>
<td>46260.4</td>
<td>4.2</td>
</tr>
<tr>
<td>1400</td>
<td>0.0000170</td>
<td>152</td>
<td>0.048</td>
<td>1100</td>
<td>0.000092</td>
<td>52696.7</td>
<td>4.8</td>
</tr>
<tr>
<td>1800</td>
<td>0.0000168</td>
<td>187</td>
<td>0.048</td>
<td>1100</td>
<td>0.000092</td>
<td>55388.9</td>
<td>5.1</td>
</tr>
</tbody>
</table>

The obtained critical Weber numbers agree with the Weber critical numbers reported in the literature for similar viscosity ratios \( \lambda_v \) of \( 10^{-3}-10^{-4} \) (Grace, 1982) if it is considered that the viscosity in the foaming head is in the range of 100 Pa s (see Chapter 2.2.3.2).
4.3 Drying kinetics

4.3.1 Determination of physical properties

4.3.1.1 Sorption/de-sorption isotherms

Table 4.3.1 shows the water content $X_{\text{H}_2\text{O}}$ (wet basis) and $X_d$ (dry basis) measured by Karl Fischer Titration of the PVP powder humidified using different salt solutions.

<table>
<thead>
<tr>
<th></th>
<th>$K_2CO_3$</th>
<th>MgCl$_2$</th>
<th>CH$_3$COOK</th>
<th>LiCl</th>
<th>$K_2CO_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_w$</td>
<td>0.440</td>
<td>0.328</td>
<td>0.225</td>
<td>0.112</td>
<td>0.431</td>
</tr>
<tr>
<td>$X_{\text{H}_2\text{O}}$</td>
<td>0.14</td>
<td>0.99</td>
<td>0.068</td>
<td>0.039</td>
<td>0.16</td>
</tr>
<tr>
<td>$X_d$</td>
<td>0.16</td>
<td>0.11</td>
<td>0.07</td>
<td>0.04</td>
<td>0.19</td>
</tr>
</tbody>
</table>

The sorption isotherm for PVP powders is shown in Figure 4.3.1. A GAB model was fitted through the experimental values. The sorption values for PVP-K30 for 2 and 22°C are also plotted and show good agreement with the water content values for the humidified PVP samples used for the collapse determination.

![Sorption isotherm for humidified PVP k15 powder](image)

Figure 4.3.1: Sorption isotherm for humidified PVP k15 powder

For the calculation of the partial vapor pressure in the drying bed the de-sorption isotherms at different temperature were taken from MacKenzie (1972) (Figure 4.3.2).
4.3 Drying kinetics

A GAB model was used to fit the desorption isotherms at different temperatures for the drying calculation. The influence of temperature on the desorption isotherms is expressed by the combination of the GAB model with the temperature dependent constant C (Equation 2.3.5). The GAB values $K$ and $X_m$ are considered as constants. The literature values and the GAB models for $-40, -20, 2, 22 \, ^\circ\text{C}$ are shown in Figure 4.3.3. From the drying experiments an additional experimental value was added for the dried powder bed at $32 \, ^\circ\text{C}$ that corresponds to the completely dried powder ($X=0.6\%$) after several drying hours.

Figure 4.3.2: PVP Desorption isotherms from MacKenzie (1972). (The lines are to guide the eye)

Figure 4.3.3: GAB model fit for the desorption isotherms of PVP
4.3 Drying kinetics

The desorption isotherms show the typical reduced water binding capacity with higher temperatures. The GAB model fits the experimental data roughly. The main difficulty in obtaining a better fit for the whole drying temperature range lies in the fact that the values below 2°C are measured at the vapor partial pressure over ice. Therefore the values at temperatures below the freezing point of water show a less sigmoidal isotherm behavior compared to the values above 0°C (Figure 4.3.2). This makes it difficult to obtain a better fit with the GAB model, which generally for hygroscopic materials fits experimental values at higher temperatures very well. The GAB constants and heat of sorption obtained are shown in Table 4.3.2:

Table 4.3.2: GAB constants for the de-sorption isotherms of PVP

<table>
<thead>
<tr>
<th>Constant</th>
<th>Experimentally regression</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>0.567</td>
</tr>
<tr>
<td>(X_{fb})</td>
<td>0.373</td>
</tr>
<tr>
<td>(c^*)</td>
<td>0.001603</td>
</tr>
<tr>
<td>(Q_1-Q_m ) [J mol(^{-1})]</td>
<td>17352.8</td>
</tr>
</tbody>
</table>

4.3.1.2 Density and porosity of the dried powder samples

The dry PVP has a matrix density of 1.203 g/cm\(^3\) (Molyneux, 1984). The structure of PVP-C\(_2\)O\(_2\) and PVP-N\(_2\) foamed particles for two different overruns was characterized by measuring the porosities and the bulk densities as described in Chapter 3.3.4.4.

The CO\(_2\) foams have a more open porosity \(\varepsilon_{op}\) compared to the N\(_2\) ones, indicating that the foam produced with CO\(_2\) has a more open structure. Figure 4.3.4 and Figure 4.3.5 show the results obtained for the different powders.

![Figure 4.3.4: Comparison of densities and porosities of PVP-CO\(_2\) and PVP-N\(_2\) foams for different overruns in the dry state (particle size 1< x < 2 mm)
4.3 Drying kinetics

Matrix Helium Bulk Bulk Inter- Intra- Open Closed density density density porosity particle particle porosity porosity within a within a particle particle porosity within a particle porosity within a particle

Figure 4.3.5: Comparison of densities and porosities of PVP-CO2 and PVP-N2 foams for different overruns in the dry state (particle size 2< x < 3.15 mm)

N2 foams show more closed porosity values within a particle. This can be also observed from the SEM pictures (Figure 4.3.11 and Figure 4.3.12), where the CO2 foams show more cracks and “channels” in the matrix structure, which could account for the larger open porosity detected.

4.3.1.3 Powder particle size distribution

Table 4.3.3 shows the results of PVP-powders after drying using the CPA method. The results are expressed by applying the equation of Rosin, Rammler, Sperling and Bennett (RRSB) (see Chapter 3.3.4.5)

![Graph showing comparison of densities and porosities of PVP-CO2 and PVP-N2 foams.]

Table 4.3.3: Particle size analysis of dried PVP powder applying the RRSB-distribution equation

<table>
<thead>
<tr>
<th>Particle size [mm]</th>
<th>RRSB n</th>
<th>RRSB mean diameter [mm]</th>
<th>Specific Surface [cm²/cm³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVP-CO2 2-3.15</td>
<td>6.46</td>
<td>2.38</td>
<td>28.55</td>
</tr>
<tr>
<td>PVP-N2 2-3.15</td>
<td>4.73</td>
<td>2.26</td>
<td>31.57</td>
</tr>
<tr>
<td>PVP-CO2 1-2</td>
<td>6.39</td>
<td>1.76</td>
<td>37.81</td>
</tr>
<tr>
<td>PVP-N2 1-2</td>
<td>5.78</td>
<td>1.74</td>
<td>38.39</td>
</tr>
</tbody>
</table>

Table 4.3.3 shows the mean diameter of the different powders for the two fractions. There is a 25 % increase of the volume specific surface area for the fraction 1-2 mm compared to the fraction 2-3.15 mm. This increase in volume specific surface should increase the drying rates for the smaller particle size fraction as the evaporation area per unit volume in the particle is increased.
4.3 Drying kinetics

4.3.2 Drying kinetics

The temperature profiles and the water loss were recorded continuously during the drying experiments. The temperatures of the heating plate and in the powder bed at a height of 0 mm (powder tray), and at the mid-plane of each ring at 5, 15, 25, 35, 45, 55 and 65 mm are measured every 30 s. In all experiments with the powder bed, the temperature of the heating plate (40°C) and the pressure (0.5 mbar) were kept constant.

Figure 4.3.6 shows an example of a powder bed that was dried for 64 hours to a final water content of X = 0.6%.

The powder tray temperature approaches rapidly the temperature of the heating plate. The temperature inside the powder bed, on the bottom of the product (5 mm), follows the powder tray temperature closely. The temperatures measured at the other powder bed locations are initially influenced by a flashing effect. This effect is the result of sudden evaporation occurring until the temperature dependent equilibrium water activity equals the vapor partial pressure in the vacuum chamber. Later on, the temperature inside the powder bed increases very slowly indicating a very low heat transfer coefficient in the powder bed.

In order to reduce the experimental time and to obtain different water contents in the powder layers, the drying time was set to 12 hours for further trials. The drying was stopped by breaking the vacuum and cooling down the powder bed with liquid nitrogen.

4.3.2.1 Influence of foam structure resulting from CO₂ and N₂ gas

The drying kinetics for CO₂ and N₂ foams with different bubbles size distributions (Table 4.2.2) are shown in Figure 4.3.7 and Figure 4.3.8 respectively.
4.3 Drying kinetics

In order to compare the drying kinetics for the different foam structures, the drying rate of the whole bed is calculated and normalized to the dry matter content of the PVP matrix. The resulting curve shows the drying rate in mg water for 1 g of dry PVP per minute. With this calculation it is possible to compensate for the differences in starting weights of the samples. Figure 4.3.9 and Figure 4.3.10 show the drying rates for the two different foams and for the two different powder sizes (1-2 and 2-3 mm). The drying rates are compared between a solid content $1 - X$ of 0.65 and 0.8%.
4.3 Drying kinetics

Figure 4.3.9: Drying rates of N₂ and CO₂ foams, OR= 200%, particle size 1-2 mm

Figure 4.3.10: Drying rates of N₂ and CO₂ foams, OR=200%, particle size 2-3 mm

Figure 4.3.9 and Figure 4.3.10 show no significant difference in the drying rate for the different bubble size distributions resulting from the different foaming gases (N₂ and CO₂). This could be an indication that the heat transfer rate, rather than the difference in internal pore surface area, is the limiting factor for the drying rate. This can also be observed in Figure 4.3.7 and Figure 4.3.8 where both powders show similar temperature profiles. Additionally the SEM images (Figure 4.3.11 and Figure 4.3.12) and the powder porosity measurements show that the CO₂ foams have a more open structure compared to N₂. These cracks and open structures in the CO₂ foams may compensate for the lower specific surface area of the larger CO₂ foam bubbles.
4.3 Drying kinetics

Figure 4.3.11: SEM Picture PVP CO$_2$ foam, OR= 200%, particle size 1-2mm

Figure 4.3.12: SEM Picture PVP N$_2$ foam, OR= 200%, particle size 1-2 mm
4.3 Drying kinetics

4.3.2.2 Influence of powder size

Figure 4.3.13 and Figure 4.3.14 show the drying rates of PVP powders foamed with N\textsubscript{2} and CO\textsubscript{2} with particle size distributions between 1-2 and 2-3 mm.

The results confirm the expectation that smaller particles dry faster than larger ones, due to the larger volume specific surface area of the latter. This means as well that the smaller inter-particle pores in the 1-2 mm powder fraction compared to the 2-3 mm fraction do not restrict and thus compensates the improved mass transfer effect of the increased specific surface area.
4.3 Drying kinetics

4.3.2.3 Influence of different overruns

Figure 4.3.15 shows the drying rates of PVP powders foamed with N₂ with overruns of 106 and 200%.

![Drying rate N₂ foam 106% OR 1-2mm vs. N₂ foam 200% OR 1-2mm](image)

**Figure 4.3.15: PVP N₂ foams, OR = 106 and 200%, and particle size 1-2 mm**

The powder with higher overrun dries much faster compared to the low overrun one. The water molecules in the lower overrun sample have to diffuse through thicker walls to the open intra- and inter-particle pores. This leads to the expected slower drying rate.

4.3.3 Freeze-drying kinetics in the state diagram

The open symbols in Figure 4.3.16 shows the powder bed temperatures and solid contents for the first 5 layers (5, 15, 25, 35 and 45 mm height) of PVP powders after 12 hours drying time. The closed symbols show the mean temperature and the integral solid content for the whole bed.
The layer at 5 mm is the driest and the hottest. The other layers show the broad temperature distribution in the whole bed. The solid content indicates a steep temperature gradient across the powder bed as demonstrated in Figure 4.3.7 and Figure 4.3.8. The powder made out of the low overrun foam dries slower than the high overrun one as shown in Figure 4.3.15. Consequently the temperature and solid concentration points for the 106% OR foam are shifted to the left and down in the state diagram. The mean value for the temperature and solid content for the powders with different overrun also show this effect.

It is clear from Figure 4.3.16 that the drying is being done at temperatures much below the glass transition temperature T_g (DSC) and therefore far away from the collapse region for PVP powders.

The layer at 5 mm is being heated up at a rate of about 3.3 °C/hour. From the collapse measurement data (Chapter 4.1) this would result in a collapse temperature at about the T_g DSC value. From these experiments it can be concluded that the heating rate could be increased significantly by increasing the heating plate temperature or the pressure in the drying chamber to improve the heat transfer in the powder bed. However the time dependency of the temperature/solid content profiles in the powder bed layers have to be considered as well. Figure 4.3.16 indicates the state after 12 hours. From Figure 4.3.8 it is obvious that in the initial drying state the characteristic points in the state diagram are much closer to the glass transition curve.
4.4 Modeling results

4.4.1 Basic assumptions for the drying model
Classical heat and mass transfer mechanisms are the basis of the drying model used to describe the real vacuum drying process. The mass transfer is defined as the water and vapor diffusion through the powder bed, whereas conduction, convection and radiation are responsible for the heat transfer.
For the modeling, the drying process is considered as a one-dimensional heat and mass transfer, excluding the influence of the surrounding walls. The powder bed is heated at the bottom, and the water can only be liberated through/from the surface of the top section to the vacuum. Further assumptions are made to be able to build up a model for the drying process:
• homogeneous powder bed, with a similar structure and porosity throughout the whole bed,
• open structure or porosity, i.e., having pores with connection to the outside, implying constant pressure at all points during drying,
• diffusion coefficients independent of temperature.

4.4.2 Description of the model and details of the computations

4.4.2.1 Discretisation of the powder bed volume
The height of the powder bed is divided in volume slices: the top and bottom slices have a thickness of 1/100 of a millimeter and all slices in between a thickness of 1 mm. The finite volume method is applied. The water content X (dry basis) and enthalpy H in each section characterize the drying process.
The structure and porosity of the product has an important effect not only on the physical properties, but also on the kind of mass transfer. The mass transfer through a powder bed of foamed particles is much higher than in the pore-free product, because the vapor diffusivity through the pores is several magnitudes higher than the water diffusivity through a solid material. A gas bubble distribution in the particles will allow water to evaporate on the hotter side and condense on the colder side of the bubble at the same water content X. A bubble distribution with open pores will result in evaporation on one side, vapor diffusion through the pore and possible condensation at different points along the pore or even direct transportation to the top surface of the bed. Therefore the amount and size of bubbles and the size and “length” of pores, in which the vapor can diffuse, is of major interest.
Figure 4.4.1 shows a schematic section of the powder bed assuming that the powder particles are foamed spheres.
4.4 Modeling results

Figure 4.4.1: Schematic section a randomly packed powder bed with spherically foamed powder particles. \( \varepsilon \) denotes the different porosities

For the model, the total porosity of the bed \( \varepsilon_{\text{bed}} \) is computed from the known volume and the mass of the powder bed after the drying. \( \varepsilon_{\text{bed}} \) is used in the model to account for the different structure by the porosity of different powders in the heat and mass transfer equations. In the model, the porous structure is characterized by a so called “Mixed Coefficient” (MC) and a “Length of Vapor” (LV) (see Figure 4.4.2).

Figure 4.4.2: Model parameters “Length of Vapor” LV and Mixed Coefficient MC for the powder bed drying

The Mixed Coefficient gives the fraction of water molecules that condenses in the next slice. A Mixed Coefficient of 1 results in a complete condensation in the next slice, a Mixed Coefficient value of 0 results in an open structure with direct vapor transport through a complete pore system to the outside of the powder bed. Usual structures lead to a partial condensation of the vapor in the following slices. Therefore the Mixed Coefficient value is between the two extremes of 0 and 1. The Length of Vapor describes the way in which the vapor is able to diffuse. It is the factor giving the average length for vapor diffusion \( l_{\text{av}} \) compared to the direct vertical direction \( l_{\text{min}} \).
to the surface. A Length of Vapor value of 1 means that pores are straight cylinders, vertically oriented. A higher value than one means that there is some pore tortuosity that makes the effective distance (or pore length) longer than the direct “straight line” (Figure 4.4.2).

4.4.2.2 Heat and mass transfer in the powder bed

Figure 4.4.3 describes the basis of the model with its major heat and mass transfer mechanisms and relationships schematically:

Figure 4.4.3: Scheme of the drying model

The mass transfer mechanism from the center section is described in more detail as shown in Figure 4.4.4. $M_{\text{liq},m,m+1}$ is the water diffusion rate from section $m$ to section
4.4 Modeling results

The vapor diffusion rate $M_{vap}^m$ has to be separated in two parts: the one condensing in the next slice and the remaining vapor diffusion leaving the bed.

$$\begin{align*}
M_{vap}^m &= M_{vap}^m \cdot MC + M_{vap}^m \cdot (1 - MC) \\
M_{vap}^m &= S \cdot \frac{X_m - X_{m+1}}{l_{m,m+1}} \cdot D_w
\end{align*}$$

where $S$ is the surface area, $D_w$ the water diffusion coefficient and $l_{m,m+1}$ the distance between the centers of sections $m$ and $m+1$.

The vapor diffusion rates $M_{vap}$ between two layers of the product and to the outside is given by: the outside vapor concentration $c_0$, the vapor concentration $c_m$ in the section $m$, the distance $l_m$ from the actual section $m$ to the surface, the vapor diffusivity $D_v$ and the resistance factor “Length of Vapor” $LV$.

$$\begin{align*}
M_{vap} &= S \cdot \frac{c_m - c_{out}}{l_m \cdot LV} \cdot D_v \\
M_{vap\text{ out}} &= S \cdot \frac{c_m - c_{out}}{l_m \cdot LV} \cdot D_v \cdot (1 - MC)
\end{align*}$$

The vapor concentration $c_{v,m}$ is calculated from the partial vapor pressure $p_{v,m}$ in section $m$:

$$c_{v,m} = \frac{p_{v,m} \cdot M}{R \cdot T}$$

where $M$ is the molar mass of water, $R$ the ideal gas constant and $T$ the absolute temperature. For the outside vapor concentration $c_{out}$, the outside pressure $p_{out}$ and the outside temperature $T_{out}$ are taken into account by using (Eq. 4.4.4). The vapor...
4.4 Modeling results

concentration $c_{\text{out}}$ was corrected for the vapor entering the drying chamber through the micro leak valve. A gas flowmeter was installed to record the airflow rate at the electronically regulated leak valve.

Inside the powder bed, the partial vapor pressure is computed from the maximal vapor pressure $p_{\text{vmax}}$ and the water activity $a_w$, which results from the GAB desorption isotherm model (see Chapter 4.1.1). The change in water content $d_m$ in slice $m$ is calculated using the Mixed Coefficient as following:

$$\frac{dm}{dt} = M_{\text{liq},m-1,m} - M_{\text{liq},m,m+1} - M_{\text{vap},m+1,m} - M_{\text{vap},m,m+1} \cdot MC$$  \hspace{1cm} \text{Eq. 4.4.5}

In the bottom slice the Eq. 4.4.5 is reduced to the water and vapor transport in to the section above. The top slice does not contain the liquid water diffusion part from the environment.

The heat transfer in the center section, expressed as change of enthalpies, is driven by conduction, convection, evaporation and condensation, as shown in Figure 4.4.5.

The energy transfer via conduction between two slices (here $m-1$ and $m$) is based on the second law of Fourier (Eq. 2.3.9).

$$\dot{Q}_{\text{cond},m-1,m} = \lambda_{av} \cdot A \cdot \frac{\Delta T}{m-1,m}$$  \hspace{1cm} \text{Eq. 4.4.6}

where $\lambda_{av}$ is the average thermal conductivity and $\Delta T$ the temperature difference. The energy due to evaporation $\dot{Q}_{\text{evap},m}$ in section $m$ is calculated by

$$\dot{Q}_{\text{evap},m} = c_{\text{vap}} \cdot \dot{M}_{\text{vap},m}$$  \hspace{1cm} \text{Eq. 4.4.7}

where $c_{\text{vap}}$ is the specific evaporation energy of water. The temperature dependence of $c_{\text{vap}}$ is not taken into account, as it is small. The transported energy via liquid water diffusion between section $m-1$ and $m$ and reverse is expressed in $\dot{Q}_{\text{conv},m-1,m}$. 

Figure 4.4.5. Heat transfer model a the center layer

The energy transfer via conduction between two slices (here $m-1$ and $m$) is based on the second law of Fourier (Eq. 2.3.9).

$$\dot{Q}_{\text{cond},m-1,m} = \lambda_{av} \cdot A \cdot \frac{\Delta T}{m-1,m}$$  \hspace{1cm} \text{Eq. 4.4.6}

where $\lambda_{av}$ is the average thermal conductivity and $\Delta T$ the temperature difference. The energy due to evaporation $\dot{Q}_{\text{evap},m}$ in section $m$ is calculated by

$$\dot{Q}_{\text{evap},m} = c_{\text{vap}} \cdot \dot{M}_{\text{vap},m}$$  \hspace{1cm} \text{Eq. 4.4.7}

where $c_{\text{vap}}$ is the specific evaporation energy of water. The temperature dependence of $c_{\text{vap}}$ is not taken into account, as it is small. The transported energy via liquid water diffusion between section $m-1$ and $m$ and reverse is expressed in $\dot{Q}_{\text{conv},m-1,m}$. 

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\[ Q_{\text{conv} \, m-1,m} = M_{\text{liq} \, m-1,m} \cdot c_{\text{pw}} \cdot \Delta T_{m-1,m} \]  \hspace{1cm} \text{Eq. 4.4.8}

where \( c_{\text{pw}} \) is the heat capacity of water. Finally the overall enthalpy change in one slice in the center section (here \( m \)) is described by:

\[ \frac{dH_m}{dt} = Q_{\text{cond} \, m-1,m} - Q_{\text{cond} \, m,m+1} + Q_{\text{conv} \, m-1,m} - Q_{\text{conv} \, m,m+1} + MC \cdot Q_{\text{evap} \, m-1} - Q_{\text{evap} \, m} \]  \hspace{1cm} \text{Eq. 4.4.9}

For the bottom layer the same equation is applied excluding the condensation energy (\( Q_{\text{evap} \, m-1} \)) and convection energy (\( Q_{\text{conv} \, m-1,m} \)) from the lower part (heating plate). The top section is computed by Eq. 4.4.9, without the term for water convection (\( Q_{\text{conv} \, m,m+1} \)), but including the gain of energy due to radiation from Eq. 2.3.17.

The physical properties for the heat and mass transfer between two slices are usually calculated by the arithmetic average. However, the thermal conductivity \( \lambda_{\text{av}} \) is estimated from their reciprocal values as reported in Eq. 2.3.26.

As explained in Chapter 3.3.4.3, the thermal conductivity \( \lambda \) and the heat capacity \( C_p \) have been determined experimentally. The temperatures during the heating of the dry product powder bed have been recorded as shown in Figure 4.4.6.

![Figure 4.4.6: Heating experiment of the dry powder bed (CO2 foam powder, 200% OR, particle size 1-2 mm) for determination of the heat capacity and heat conductivity](image)

The heating plate was kept at a constant temperature of 40°C. The heat conductivity and heat capacity were then determined between each time step. The porosity, the average temperature and the water content were taken into account for the calculations. The water content was assumed to be constant at \( \delta = 0.6 \% \), which is
4.4 Modeling results

Based on the final dry powder bed measurements. Higher water contents with some residual water would lead to lower thermal conductivity values due to the required evaporation energy. The modeling results are shown in Figure 4.4.7.

![Figure 4.4.7: Modeling fit for the dry powder bed of PVP for the determination of the heat capacity and heat transfer coefficient](image)

The calculated values for $C_p$ was 1311 kJ/kg °C and for $\lambda$ was 0.03 W/m °C. Detailed information about the equations used, properties and constants are given in the appendix of this thesis. The heat and mass balance is controlled, to ensure the correct behavior of the whole system.

Finally the experimental data from the drying process have been used to estimate the two unknowns in the model: Mixed Coefficient (MC) and “Length of Vapor” (LV). Both of these parameters have clear physical meanings, but are difficult to determine experimentally.

4.4.3 Results and Discussion

The modeling work was more difficult than expected. The basic model developed for the description of the moisture and temperature distribution during the vacuum drying of a malted drink powder by Raederer (1997) had to be modified for a powder bed starting at temperatures below 0°C. The low temperatures and slow heat transfer rates caused problems for the calculations of the amount of water condensing in the next layer. This water condenses at the surface the particles and pores and has different properties compared to the water that has to diffuse from the inside of the particles. First modeling results for different powders are shown in this chapter but they are a first attempt for the determination of the modeling parameters Length of Vapor LV and Mixed Coefficient MC. The simple model assumptions will have to be extended for the calculation and simulation of the complex coupled heat and mass transfer at low temperatures and low water contents. It was particularly difficult to model the starting conditions for this system because the boundary conditions are not met for the first 30 minutes of the drying. This has to do with the loading conditions; like very
4.4 Modeling results

low powder temperature (below -40°C) and water condensation on the plate and the surfaces from the surrounding air during the loading of the sample into the dryer. Therefore, in a first approach, the model calculations were started after 1 hour of drying when more steady conditions were reached.

4.4.3.1 Influence of foam structure resulting from CO\textsubscript{2} and N\textsubscript{2} gas

The modeling results for CO\textsubscript{2} and N\textsubscript{2} foams with different bubbles size distributions (Table 4.2.2) are shown in Figure 4.4.8 and Figure 4.4.9.

![Figure 4.4.8: Modeling results for a CO\textsubscript{2}-PVP foam (mean bubble diameter = 67 \(\mu\text{m}\), OR = 200\%, particle size 1-2 mm)](image1)

![Figure 4.4.9: Modeling results for a N\textsubscript{2}-PVP foam (mean bubble diameter = 12.2 \(\mu\text{m}\), OR = 200\%, particle size 1-2 mm)](image2)
These first results gave a MC value of 0.9 for both foams (CO₂ and N₂) indicating that 90% of the evaporated water in one layer of the bed re-condenses in the next upper layer. Coupled with the low thermal conductivity this is an indication for the slow drying rates of the powder bed. It also confirms the results of the calculations of the drying rates (Chapter 4.3.2.1), that there is no significant difference in the drying rates for the two different bubble size distributions. Different calculations showed the MC is the main model parameter. Small variations in MC had a big influence on the calculated temperature and moisture curves. The calculated Length of Vapor LV for CO₂ foam was 3 and for N₂ foam 10. This preliminary results would also confirm the more open structure for CO₂ foam as indicated in Chapter 4.3.2.1.

4.4.3.2 Influence of powder particle size

The modeling results for CO₂ foams with different particle size fractions are shown in Figure 4.4.8 for the 1-2 mm fraction and in Figure 4.4.10 for the 2-3 mm fraction.

For the two fractions the MC value was again 0.9 and the LV value for the small fraction (1-2 mm) was 3 and for the bigger fraction (2-3 mm) was 4. This first result for the different powders does not agree with the drying kinetics results in Chapter 4.3.2.2. The reason for this could be from the way the mean porosity is calculated in the model. The porosity is calculated from the bed height and the total weight of the powder in a first approximation. As a result, the mean bed porosity during the drying trials has, for the fraction 1-2 mm a value of 0.74, and for the fraction 2-3 mm, a value of 0.755. The difference of the porosities is very small and does not take enough into account the difference in inter and intra particle porosity for the two fractions (see Chapter 4.3.1.2). Another difficulty in the determination of the porosity is the imprecision in the measurement of the powder bed height. The error is of the order of 5 mm. For the bed heights in the drying experiments (70-80 mm) results in a relative error of the order of 15% of the bed height. Additionally it has been observed that the height of the powder bed decreases during drying. This is due to the vibration of the
4.4 Modeling results

drying equipment (compressor) and has an influence on the packing of the bed particles and therefore influences the height of the bed. It would be of interest to dry beds with different heights to evaluate these effects. First observations indicate a reduction in height in the order of 10% of the total height at the beginning. The drying geometry will be modified to improve the measurement of the bed height.

4.4.3.3 Influence of different overruns
The drying rates of PVP powders foamed with N₂ are shown in Figure 4.4.9 for an overrun of 200% and in Figure 4.4.11 for an overrun of 106%

![Figure 4.4.11: Modeling results for a N₂-PVP foam, OR = 106%, particle size 1-2 mm](image)

The calculated values for the powder with 200% foam overrun are MC = 0.9 and LV = 10. For the powder with 106% overrun, MC is 0.997 and LV is 1. These results confirm the expected and measured (Chapter 4.3.2.3) differences in drying rates for different foam densities. The powder with higher overrun dries much faster compared to the low overrun one. The very high MC value of 0.997 indicates that 99.7% of the vapor leaving a layer condenses in the upper layer. This shows the strong dependence on MC for the very slow drying rate.

4.4.3.4 Moisture profile of the bed from the model calculations
From the calculated model parameters MC and LV it now possible to calculate the moisture profile for the different bed heights. First results are shown for a CO₂ foam in Figure 4.4.12. Using the critical collapse temperature/water content values (see Chapter 4.1.7) it is now possible for any given simulation condition to detect if collapse will occur.
4.4 Modeling results

Figure 4.4.12: Moisture profile during the drying of a powder bed of PVP CO₂ foam particles with 200% overrun

Figure 4.4.12 shows also the crossing over of the water content curves at the top of the powder bed (X H₂O at 55 and 65 mm). This effect is due to the heat input by radiation from the surroundings of the drying chamber to the top of the bed. This is also shown in the measured and calculated values of water contents at different bed heights in Figure 4.4.13. It can be seen that the model overestimates the water contents in the center of the bed. But the calculated water distribution profile agrees well with the experimental values.

Figure 4.4.13: Water content distribution at different powder bed heights measured and modeled for a CO₂-PVP foam, OR = 200%, particle size 1-2 mm
5 Conclusions

The aim of this thesis work was to determine the influence of microstructure on the drying kinetics of a foamed amorphous model food concentrate. The model system chosen for this work was the water-soluble polymer polyvinylpyrrolidone (PVP). The drying process was studied in a conventional freeze-drying equipment. As a difference to the classical freeze-drying process, the solution to be dried had a concentration above \( C_g' \) (maximally cryo-concentrated solution). As a result no ice forms in the freezing stage of the drying process. The solutions to be dried were foamed before the drying step to generate a porous structure for the ease of drying. The material behavior related to the process parameters was described in the State diagram. From the results and discussions the following conclusions can be drawn:

5.1 Material behavior related to the drying process in the State Diagram

For successful freeze drying the matrix to be dried has to keep it’s rigidity without collapse throughout the process. This rigidity can be described in terms of viscosity of the material. Freeze drying practice on ice containing solutions with \( C < C_g' \) shows that the temperature of the onset of de-cryo-concentration \( T_m' \) is the maximum temperature giving the needed rigidity to the material for successful freeze drying without collapse. Above \( C_g' \), the temperatures of collapse during freeze-drying are iso-viscosity lines parallel to the glass transition temperature \( T_g \). To maintain the porous structure without collapse, freeze-drying must be carried out under conditions where a specifically defined material related Deborah Number is \( \gg 1 \) (solid like state). Since both viscosity and related molecular relaxation time decrease sharply above \( T_g \), the drying time (= processing/observation time) must also be similarly reduced to maintain \( De \gg 1 \), e.g. by increasing drying rates for a given temperature profile.

The VTF and the WLF equations proved to be adequate to describe the temperature dependence of the viscosity of PVP near the glass transition temperature \( T_g \). When the viscosity results of the PVP solutions were plotted on a \( T_g \) scaled Arrhenius Plot, PVP K15 shows a typical “fragile” material viscosity behavior in the strong/fragile material classification proposed by Angell (1994). The viscosity of PVP as a function of temperature shows a strong curvature towards \( T_g \) and the viscosity value at the glass transition \( (10^{8.9} \text{ Pa s}) \) is several orders of magnitude lower than the value of \( 10^{18} \text{ Pa s} \) usually proposed in the literature for the viscosity at \( T_g \). The determined fragility parameters for PVP K15 solutions are \( D = 7.7 \) (\( D \rightarrow \infty \), for “strong” material behavior) and a corresponding value of \( m = 92 \) (\( m \rightarrow 16 \), for “strong” material behavior), indicating the fragile character of the material.

The glass transition temperature \( T_g \) was determined with DSC and DMTA. An extrapolation of the DMTA \( E'' \) peak temperature frequency dependence data to 0.0001 Hz was found to give a peak temperature equal to the glass transition temperature measured with DSC \((10^\circ \text{C/min})\). The concentration dependence was described using the Gordon & Taylor equation. \( T_g \) decreases rapidly with increasing moisture content. The glass transition temperature, stickiness temperature, collapse temperature with the corresponding viscosities of PVP K15 were plotted together as a function of solid content in a state diagram. The \( T_g' \) and the \( T_m' \) lines for solutions containing ice were derived from the DMTA measurements.
The description of the collapse phenomena from the stickiness and optical observation in the state diagram is a useful tool to study the structure stability as a function of the drying process parameters time and temperature. Conservative drying conditions would maintain material temperature $T$ below $T_g'$ and $T_g (C)$ at all times. However if heat and mass transfer rates can be increased, the freeze drying can follow a temperature path above $T_g'$ and $T_g (C)$. Freeze drying of “fragile” materials must, in both cases, always be done closer to (or below) the glass transition temperature, compared to freeze drying of “strong” materials. This is best illustrated in state diagrams for a “fragile” material (PVP) (Figure 5.1.1) and a “strong” material (Figure 5.1.2). The collapse zone is defined between the $10^6$-$10^8$ Pa s iso-viscosity curves.

Figure 5.1.1: State diagram indicating the freeze-drying path below the collapse zone for a “fragile” material (PVP K15)

Figure 5.1.2: State diagram indicating the freeze-drying path below the collapse zone for a “strong” material (Arrhenius temperature dependent viscosity)
Figure 5.1.1 shows that the freeze-drying temperature/concentration path has to be close to the glass transition temperature $T_g$ line to avoid collapse during the drying process. The collapse viscosity limits are between 5°C (viscosity = $10^8$ Pa s) and 15°C (viscosity = $10^6$ Pa s) above the glass transition temperature. Consequently a conservative slow heating rate has to be chosen to avoid structural collapse.

Figure 5.1.2 shows the freeze-drying temperature/concentration path for a “strong” material, where the viscosity has an Arrhenius temperature dependence (see also Figure 4.1.9). The product temperature during the drying can be 30°C ($10^8$ Pa s) to 50°C ($10^6$ Pa s) above the concentration dependent glass transition temperature.

Knowledge of the product stability conditions in the state diagram enables the design of a freeze-drying process with an optimum heating-rate profile, wherein the temperature-moisture-time protocol can be pre-programmed and controlled to maintain the temperature of the sample below its collapse temperature (Shalaev and Franks, 1995). This insures that the non-ice matrix remains rigid enough to support its own weight against rubbery viscous flow throughout the course of the ice-sublimation and desorption stages of the vacuum-drying process.

The “strong/fragile” material classification could also be helpful to determine process conditions for other food products and processes (e.g. agglomeration, concentration and crystallization) and powder stability during storage (e.g. “caking” and collapse) above the glass transition temperature.

**5.2 Foaming of highly concentrated amorphous solutions**

The effect of process parameters on the foaming performance of a new dynamic rotor-stator mixer was studied during foaming of highly concentrated solutions of PVP. The mixer geometry developed at the Laboratory of Food Process Engineering (Prof. E. Windhab) at the Federal Institute of Technology Zürich proved to be successful for foaming such highly viscous liquids. This whipping equipment allowed the continuous production of foams with controlled foam structure parameters.

Foam structure parameters like overrun, viscosity and bubble size distributions were determined as a function of rotor speed, foaming gas, pressure and temperature. By varying the solutions properties and process parameters, a range of Newton and Reynolds numbers giving a power characteristic $Ne = f(Re)$ for the whipping head specific rotor-stator geometry was obtained. Based on this characteristic, it was found that the PVP solutions were foamed in the laminar flow region, due to the high viscosities (>10 Pa s) of the solutions.

The bubble size distributions could be measured under a microscope with an image analysis program developed at the Nestlé Research Center (Mayor, 1998). Unexpectedly the measured bubble size distributions did not change significantly with rotor speed in the range between 1000 and 2000 rpm under condition of constant (non-maximum) overrun. Higher energy input lead to higher temperature and therefore lower viscosity and higher re-coalescence rates. Even though the shear rate is increased at higher rpm the resulting dispersing shear stress could remain about constant due to decreasing viscosity.

The two foaming gases (N$_2$ and CO$_2$) showed significant differences in bubble size distribution and foam stability (mean bubble diameter 12.3 μm for N$_2$ and 67.2 μm for
Conclusions

CO₂ foams). This finding allowed the production of powders with different microstructure for the drying trials.

The surface tension for PVP solutions with surfactant was measured at different concentrations and temperatures. The pendent drop method allowed the measurements of the equilibrium surface tension in the concentration and temperature range of the foaming conditions (70% solids and temperatures above 50°C).

The measured bubble diameters were correlated to the shear stress, under laminar flow conditions, by a critical Weber number. This critical Weber number, calculated from the experimental results, was around 5.

The results gained from this work give information on foaming performance and process parameters for the production of foams with different structures. Furthermore, they will be useful for scaling up the continuous whipping machine to a semi-industrial or industrial scale.

5.3 Drying kinetics as a function of structure parameters

The drying experiments showed the effect of structure of porous powders on the kinetics of drying.

The microstructure was characterized by measuring the bubble size distribution in foams made with different gases. Porosity, density measurements and SEM-images of the dried powder were also made.

Helium pycnometry showed a greater porosity in the foams gassed with CO₂ indicating a more open foam structure of the dried particles. The SEM-images showed many more cracks in the foamed particles made using CO₂ gas. The lack of cracks and small bubbles in the N₂ foams could possibly be due to the “insulating” qualities of this structure resulting in less internal tension during the freezing operation (in liquid nitrogen) after the foaming. The cracks in the CO₂ foams increase somewhat the evaporation surface area and provide channels for transporting the vapor out of the particles.

Unexpectedly these powders with different bubble size distributions showed no significant difference in the drying rate. An explanation could be that the drying rate is limited by the heat transfer in the powder bed. In this case the relatively small differences in internal structure are of little influence to the overall heat transfer between the particles in the bed.

The drying rate of smaller particles is found to be faster than for large particles. This is expected from the larger volume specific surface area of about 38 cm²/cm³ of the smaller powder size fraction (1-2 mm) compared to 30 cm²/cm³ for the 2-3.15 mm size fraction. The larger specific surface area increases the heat and the mass transfer in the bed.

The effect of the density of the powders (overrun) is remarkable. Powders with 200% overrun dry almost 50% faster compared to 100% overrun ones.

Plotting the drying kinetics in the state diagram shows that, for the given process parameters, the drying is performed at conditions well below the glass transition curve.
and therefore well below the collapse region for PVP powders. The heating rate could be increased significantly by increasing the plate temperature or the operating pressure in the drying chambers without the risk of powder collapse.

5.4 Modeling of the drying kinetics

Although there are first modeling results for the drying kinetics, there are still some difficulty in fitting the calculated curves to the experimental values. The heat and mass transfer phenomena are much more complex than expected for the drying process in this work. The model for example does not take into account possible heat transfer phenomena in radial direction and through the walls. The simple model in this work has to be developed further taking into account the problems described in Chapter 4.4.3 e.g. boundary conditions at the drying start and water condensation during the powder loading procedure. The physical properties, especially the desorption isotherms for lower temperatures, have to be better determined and taken into account in the model calculations. The results show that the description of the powder bed in terms of porosity and packing ratio is of crucial important for the description of the drying kinetics and modeling. More effort has to be made to better measure and incorporate these structure parameters in the drying modeling. The number of experiments has to be increased to better understand the transport phenomena in the bed. To further improve the modeling results more duplicates of the same drying trials have to be done, with accurate measurements of the bed height during the drying.

It will also be of great interest to change the bed heights (e.g. 30, 60 and 120 mm) in future experiments to test the model calculations. So far only experiment with similar heights (70-80 mm) were done.

From the obtained results it can be concluded that the model parameter Mixed Coefficient MC which describes the evaporated water fraction that condenses in the next upper slice has a major influence in the model calculation. The MC values range from 0.9-0.99 indicating that most of the evaporated water condenses in the upper slice. For higher overruns Raederer (1997) found MC values in the order of 0.2 for the vacuum drying of a malted drink solution. High MC values result in slow drying rates as is the case in drying experiments shown in this work. MC also indicates the effect of microstructure, e.g. overrun, on the drying kinetics. The second parameter Length of Vapor LV which describes a diffusion resistance factor has a less influence compared to the MC parameter for the existing model. The LV values range from 1-10 indicating also the effect of microstructure on the drying rates. Raederer (1997) found LV values in the order of 5.5 for the vacuum drying of a malted drink solution.

The resulting values for the different drying trials confirm the findings of the measured drying kinetics which showed little difference for different bubble and particle size distributions, but faster drying rates for higher foam overrun powders. From the calculated moisture profiles for the different bed heights it is now possible to determine the critical temperature/water content conditions to avoid collapse of the powder during the drying process.
6 References


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7 Appendix

7.1 Images Kinematica FM12 whipping equipment

Figure 7.1.1: Section of the Kinematica FM12 whipping head

Figure 7.1.2: View of the rotor-stator of the Kinematica FM12 whipping head

Figure 7.1.3: Stator (left) and rotor (right) of the Kinematica FM12 equipment
7 Appendix

7.2 Modeling program

Model BED

//
// Finite volume modelling for the drying of a PVP Powder Bed
// N is the number of slices.
// Top and Bottom slices are 1/100mm
// Internal slices are 1mm thick
//
// From Milo_crn:DaP 14 Aug 98; adapted by BWL: May-June 99
// Model with fixed Bed height and free porosity

N  as IntegerParameter;
O  as IntegerParameter(N+1);
M  as IntegerParameter(N-1);
L  as IntegerParameter(N-2);
NC as IntegerParameter;
IltoN as IntegerSet([1:N]);
I0toN as IntegerSet([0:N]);
I0to6 as IntegerSet([0:6]);
I2oN as IntegerSet([2:N]);
HtoNC as IntegerSet([1:NC]);
HtoM as IntegerSet([1:M]);
HtoO as IntegerSet([1:O]);
//
// *** Variable Name *********** Variable Type ********* Comments *

AirParam         as Notype(Fixed);  // Ponderation of the vanne air flux
ACCE             as ENTHALPY;    // [J] Accumulated energy
ACCWAT           as MASS;       // [kg] accumulated water
AW(ItoN)         as FRACTION;   // water activity (each layer)
CONCOUT          as CONCENTRATION;  // [kg/m3] external wapor concentration
CONCVAP(ItoN)    as CONCENTRATION;  // [kg/m3] vapor concentration (each layer)
CONCWAT(ItoN)    as CONCENTRATION;  // [kg/m3] water concentration (each layer)
CPPVP            as HCAPACITYFOOD(fixed);  // [J/(kg*C)] dry PVP heat capacity
CPWAT            as HCAPACITY(4183,fixed);  // [J/(kg*C)] water heat capacity
CVAP_Wat         as LATHEAT(2502777,fixed);  // [J/kg] latent heat of vaporisation
DIAM             as LENGTH(0.20,fixed);  // [m] Bed diameter
DIFFLIQ(ItoM)    as MASSFLOW;   // [kg/s] water mass flow
DIFFVAPOUT(ItoN) as MASSFLOW;   // [kg/s] vapor mass flow
DLIQ(ItoM)       as DIFFUSION;  // [m2/s] water diffusion coefficient
DLIQO1           as DIFFUSION(3.81971e-13,fixed); // [m2/s] coef def the DLIQ (C. Oksanen)
DLIQO2           as DIFFUSION(15.1049,fixed); // [m2/s] coef def the DLIQ (C. Oksanen)
DT(ItoN)         as TEMPERATUREC;  // [C] mean Temp between adjacent layers
DVAP(ItoN)       as DIFFUSION;  // [m2/s] vapor diffusion coefficient
DVAP1            as DIFFUSION(2.45644e-5,fixed); // [m2/s] coef defining the DVAP (A.Jung)
DVAP2            as DIFFUSION(1.949895,fixed); // [m2/s] coef defining the DVAP (A.Jung)
EFINAL           as ENTHALPY;   // [J] Final energy
EIN              as ENTHALPY;   // [J] Input energy
ELAYER(ItoN)     as ENTHALPY;   // [J] energy
EOUT             as ENTHALPY;   // [J] output energy
ETOT             as ENTHALPY;   // [J] Total energy
EXPNUM           as NOTYPE(fixed); // code number related to experiments

(communication with Exel data)
FORMFACT         as FRACTION(1,fixed); // [-] formfactor
GABA(ItoN)       as NOTYPE;    // [-] Desorption isotherm; G.A.B.

parameters and constants

GABBBI(ItoN)     as NOTYPE;    // [-] "
GABCBI(ItoN)     as NOTYPE;    // [-] "
GABC1            as NOTYPE(0.0016039,fixed);  // [-] "
GABC2            as NOTYPE(13.3252,892,fixed);  // [-] "
GABK             as NOTYPE(0.5764201,fixed);  // [-] "
GABXM            as NOTYPE(fixed);  // code number related to experimental

heating sources (communication with Exel data)
HEATPLATE        as NOTYPE(fixed);  // code number related to experimental
HEIGHTCAKE       as LENGTH;    // [m] Bed height
HEIGHTCAKEINIT   as LENGTH(fixed);  // [m] Initial bed height
as LENGTH; // [m] slice height
as H_CONDUCT; // [W/(m*C)] Heat conductivity
as H_CONDUCT(26e-3,fixed); // [W/(m*C)] air heat conductivity
as H_CONDUCT; // [W/(m*C)] average heat conductivity between adjacent layers
as H_CONDUCT; // [W/(m*C)] vapor/air mix heat conductivity
as H_CONDUCT; // [W/(m*C)] particle heat conductivity
as H_CONDUCT(fixed); // [W/(m*C)] dry unfoamed PVP heat conductivity
as H_CONDUCT; // [W/(m*C)] PVP + water heat conductivity
as LENGTH(0.57109,fixed); // [m] water heat conductivity
as LENGTH; // [m] distance from slice center to next slice center
as LENGTH; // [m] distance from slice center to bed surface
as NOTYPE(100, fixed); // [-] coefficient to define LENGTHVAP
as NOTYPE(100, fixed); // [-] Apparent length for vapor to diffuse
as NOTYPE(-1.27706e-7,fixed); // Coefficients defining LBDAMIX (from Aspen Plus)
as NOTYPE(-4.52398e-3,fixed); // Coefficients defining LBDAMIX (from Aspen Plus)
as NOTYPE(7.70989e-5,fixed); // Coefficients defining LBDAMIX (from Aspen Plus)
as NOTYPE(3.36684e-3,fixed); // Coefficients defining LBDAMIX (from Aspen Plus)
as MASS; // [kg] mass of bound water in bed
as MASS; // [kg] mass of bound water
as MASS; // [kg] Mass of dry PVP
as FRACTION; // Averaged porosity over the whole bed
as FLUX; // [kmol/min] Vannex air flux
as MASS(fixed); // [kg] Initial mass of wet bed
as FRACTION(fixed); // [-] Apparent percentage of evaporated water condensing in next slice
as MOLECWEIGHT(18e-3, fixed); // [kg/mol] water molecular weight
as MASS; // [kg] Initial water mass in bed
as MASS; // [kg] water mass
as MASS; // [kg] total mass
as MOLE; // air mole number in drying chamber
as MOLE; // vapor mole number from bed evaporation in drying chamber
as MOLE; // vapor mole number from vannex flux in drying chamber
as MOLE; // number of particle in a ring
as MOLE; // total gas mole number in drying chamber
as NOTYPE(3.141592654,fixed); // [-] number of particles in contact with the heating plate
as PRESSURE(fixed); // [N/m2] maximum vapor pressure in slice
as PRESSURE; // [N/m2] vapor pressure in drying chamber
as PRESSURE; // [N/m2] vapor pressure in drying chamber
as PRESSURE; // [N/m2] vapour mole fraction of the vannex flux
as PRESSURE; // number of particle in contact with the heating plate
as PRESSURE; // [N/m2] total pressure in the drying chamber
as PRESSURE; // [N/m2] vapor pressure
as HEATFLOW; // [J/s] Heat flow: Conduction part
as HEATFLOW; // [J/s] Heat flow: Convection part
as HEATFLOW; // [J/s] Heat flow: Evaporation part
as HEATFLOW; // [J/s] Heat flow: Radiation part
as HEATFLOW; // [J/s] Heat flow: Radiation part (top slice)
as HEATFLOW; // [J/s]
as GASCONST(8.31441,fixed); // [J/(K*mol)] Boltzmann constant
as DENSITY(1203, fixed); // [kg/m3] PVP dry and unfoamed density
as DENSITY(1000, fixed); // [kg/m3] water density
as DENSITY; // [kg/m3] initial wet bed density
as TEMPERATUREC(initial); // [°C] Temperature in C
as TEMPERATUREC; // [-] Averaged temperature between 2 adjacent slices
as TEMPERATUREK; // [K] Temperature in K
as TEMPERATUREC; // [-] Averaged temperature over the bed
Appendix

TPB(I0to6) as NOTYPE(fixed); // coefficient fitting the experimental Bottom heating plate behaviour
TPT(I0to6) as NOTYPE(fixed); // coefficient fitting the experimental Top heating plate behaviour
TPlateTop as TEMPERATUREC; // [°C] Temperature of the Top heating plate
TPlateBot as TEMPERATUREC; // [°C] Temperature of the Bottom heating plate
V(I0to6) as NOTYPE(fixed); // coefficient fitting the experimental Air flux behaviour

VOLCAKE as VOLUME; // [m³] bed volume
VOLCAKEINIT as VOLUME; // [m³] Initial bed volume
VOALLAYER(I0toN) as VOLUME; // [m³] slice volume
VOLOVEN as VOLUME(0.394668, fixed); // [m³] volume of the drying chamber
WATOUT as MASS; // [kg] Total mass of water evaporated from the bed
XWATBOUND as FRACTION; // Mass fraction of bound water
XWAT(I0toN) as FRACTION; // [-] Water content db
XWATINIT as FRACTION; // [-] Initial water content over whole bed
XWATMAX as FRACTION; // Maximum water content
XWATMEAN as FRACTION; // [-] Averaged water content over whole bed
YH20(I0toN) as FRACTION; // Vapor mass fraction in the free spaces of layer

--- Equations for experimentally fitted curves for Heat and Air flux ---

TPlateTop = TPT(6)*timeA6 + TPT(5)*timeA5 + TPT(4)*timeA4 + TPT(3)*timeA3 + TPT(2)*timeA2 + TPT(1)*timeA1 + TPT(0);
TPlateBot = TPB(6)*timeA6 + TPB(5)*timeA5 + TPB(4)*timeA4 + TPB(3)*timeA3 + TPB(2)*timeA2 + TPB(1)*timeA1 + TPB(0);
MesAirFlux/AirParam = V(6)*timeA6 + V(5)*timeA5 + V(4)*timeA4 + V(3)*timeA3 + V(2)*timeA2 + V(1)*timeA1 + V(0);

--- Mass ---

MWATINIT = (MINIT*XWATINIT)/(1+XWATINIT);
MDRY = MINIT-MWATINIT;
MBOUNDWAT = XWATBOUND*MDRY;
MPVPLAYER(I) = MDRY/(HEIGHTCAKEINIT/0.00001);
MPVPLAYER(N) = MDRY/(HEIGHTCAKEINIT/0.00001);
For i in [2:M] Do
  MPVPLAYER(i) = (MDRY-2*MPVPLAYER(1))/(N-2);
EndFor;
MBOUNDWLAYER = XWATBOUND*MPVPLAYER;
MTOTLAYER = MPVPLAYER+MWATLAYER+MBOUNDWLAYER;

--- Surface ---

SECTION = (DIAM*A2)/4*Pi;
POROSINTERP = (POROSITY-PARTPOROS)/(1-PARTPOROS);
SurfVoid1 = SECTION * POROSINTERP;
NC = RADIUS/PARTDIAM;
for i in [1:NC] Do
  NPART(i)=Pi*(DIAM-PARTDIAM*(i-1/2))/PARTDIAM;
endfor;
NPARTTOT=Sigma(NPART);
SurfCont1 = Sigma(NPART)*(Pi*PARTDIAM*A2)/4/2;
SurfCont1 = SECTION ;
SurfVoid1 = SECTION*POROSINTERP;
SurfContRad = SECTION * (1-POROSINTERP);
SurfContRad = SECTION;
SurfCont = SECTION*POROSINTERP;
SurfCont = SECTION*(1-POROSINTERP);

--- Volume; Height ---

HEIGHTCAKEINIT = VOLCAKE/SECTION;
RHOSTOT = MINIT/VOLCAKE;
VOALLAYER(I) = VOLCAKE/(HEIGHTCAKEINIT/0.00001);
VOALLAYER(N) = VOLCAKE/(HEIGHTCAKEINIT/0.00001);
For i in [2:M] Do
  VOALLAYER(i) = (VOLCAKE-VOALLAYER(1)*2)/(N-2);
EndFor;
HEIGHTLAYER(1) = 0.00001;
HEIGHTLAYER(N) = 0.00001;
For i in [2:M] Do
  HEIGHTLAYER(i) = (HEIGHTCAKEINIT-2*HEIGHTLAYER(1))/(N-2);
EndFor;
VOLLAYER = (MPVPLAYER/RHOPVP + MWATLAYER/RHOWATER + MBOUNDWLAYER/RHOWATER)/(1-POROSITY);
MEANPOROS = (Sigma(POROSITY)-POROSITY(l)-POROSITY(N))/(N-2);
// -Concentration
CONCWAT = MWATLAYER/VOLLAYER*(1-POROSITY);
XWAT = MWATLAYER/MPVPLAYER;
CONCVAP = POROSITY*PVAP*MW/(R*TK); // Cf. K. Thorvaldsson
// -Heat Transfert
// expressed as vol fraction (Choi & Okos)
1/LBDASOL = (1/RHOTOT)
  *{(RHOPVP/LBDAPVP)*(MPVPLAYER/MTOTLAYER)
    +(RHOWATER/LBDAWATER)*(MWATLAYER/MTOTLAYER)
    +(RHOWATER/LBDAWATER)*(MBOUNDWLAYER/MTOTLAYER));
// expressed as Maxwell model for porous material within a particle <==> with the particle porosity
// LBDAPART = (2*LBDASOL+LBDAAIR-2*PARTPOROS*(LBDASOL-LBDAAIR))*LBDASOL
// /A*2*LBDASOL+LBDAAIR+PARTPOROS*(LBDASOL-LBDAAIR));
// The free spaces intra and interparticles is a mix of vapor and air; We replace LBDAIR by LBDAMIX
// the relation between vapor mass fraction and LBDAMix at different temperature was established by Aspen Plus.
// LBDAMIX = A(T)*YH2O + B(T); and YH2O= vapor mass/total gas Mass; YH2O = PVAP/POUT*18e-3/28e-3
YH2O = PVAP/POUT*18e-3/28e-3;
LBDAMIX = (LM1*TK2+LM2*TK+LM3)*YH2O+(LMa*TK+LMb);
LBDAPART = (2*LBDASOL+LBDAMIX-2*PARTPOROS*(LBDASOL-LBDAMIX))*LBDASOL
// /A2*LBDASOL+LBDAMIX+PARTPOROS*(LBDASOL-LBDAMIX));
// 1/LBDA = (1/LBDAPART*(1.0-POROSINTERP)+1/LBDAAIR*(POROSINTERP));
1/LBDA = (1/LBDAPART*(1.0-POROSINTERP)+1/LBDAMIX*(POROSINTERP));
// -Properties in between each layer
// -Average temperature
TAV(1) = (TPlateBot+T(l))/2;
For i in [2:N] Do
  TAV(i) = (T(i-1)+T(i))/2;
EndFor;
// -Diffusion coefficient
DLIQ = DLIQO1*exp(DLIQ02*XWAT);
DVAP = (DVAP1 * (TAV+273.15)ADVAP2)/POUT;
// -Structure
LENGTH(1) = HEIGHTLAYER(1)/2+HEIGHTLAYER(2)/2;
LENGTH(0) = HEIGHTLAYER(1)/2;
For i in [2:L] Do
  LENGTH(i) = HEIGHTLAYER(2);
EndFor;
LENGTH(N) = HEIGHTLAYER(2);
LENGTH(1) = HEIGHTLAYER(0);
EndFor;
LENGTH(M) = HEIGHTLAYER(N)/2+HEIGHTLAYER(M)/2;
LENGTH(N) = HEIGHTLAYER(N)/2;
LENGTHV(1) = HEIGHTCAKEINIT;
For i in [2:N] Do
  LENGTHV(i) = LENGTHV(i-1)-HEIGHTLAYER(i-1);
EndFor;
LENGTHVAP = -(LENGTHVAP0-1)*XWAT/XWATMAX+LENGTHVAP0;
// -Heat transfert coefficient
For i in ItoN Do
  1/LBDAV(i) = (1/HEIGHTLAYER(i)+HEIGHTLAYER(i-1))
  *((HEIGHTLAYER(i))/LBDA(i)+HEIGHTLAYER(i-1)/LBDA(i-1));
EndFor;
// Temperature difference
DT(i) = TPlateBot-T(i);
For i in [2:N] Do
DT(i) = T(i-1)-T(i);
EndFor;

// Mass Water Change in each layer
massH2O1: MWATLAYER(1) = -DIFFLIQ(1)
* (CONCWAT(1)-CONCWAT(2))
+ DIFFVAPOUT(1)
* (CONCVAP(1)-CONCOUT)
* SurfVoid(1)
/ (LENGTHV(1)*LENGTHVAP(1));

// Internal Layers
For i in [2:M] Do
massH2O: MWATLAYER(i) = +DIFFLIQ(i-1)-DIFFLIQ(i)
* (CONCWAT(i)-CONCWAT(i+1))
+ DIFFVAPOUT(i)
* (CONCVAP(i)-CONCOUT)
* SurfVoid(i)
/ (LENGTHV(i)*LENGTHVAP(i));
EndFor;

// Top very thin Layer
massH2O:N: MWATLAYER(N) = +DIFFLIQ(M)
* (CONCWAT(M)-CONCWAT(M+1))
+ DIFFVAPOUT(M)
* (CONCVAP(M)-CONCOUT)
* SurfVoid(M)
/ (LENGTHV(M)*LENGTHVAP(M));

// No Condensation of internal vapor at the top layer
POUT=Ntot*(8.314*(TPlateTop+273.15))/VOLOVEN;
Ntot = Nair + NH2O + NhumExt;
$Nair = (1-PerHum)*MesAirFlux/(60*22.4) - ToPump *(Nair / Ntot);  // Air Flux converted in mole/s
$NhumExt = PerHum*MesAirFlux/(60*22.4) - ToPump *(NhumExt / Ntot);   // Air Flux converted in mole/s
ToPump = $WATOUT/18E-3 + MesAirFlux/(60*22.4);

CONCOUT = POUT*(NH2O+NhumExt) / Ntot*18E-3/(8.314*(TPlateTop+273.15));

DIFFVAPOUT(N) = (CONCVAP(N)-CONCOUT)
* SurfVoid(N)
/ (LENGTHV(N)*LENGTHVAP(N));

PH2O = (NH2O+NhumExt)*(8.314*(TPlateTop+273.15))/VOLOVEN;

// Total Energy
EFINAL = Sigma(ELAYER);
// --- Energy change for each layer ----------------------------------------
// --- Bottom very thin layer ---------------------------------------------
Energy1: $ELAYER(1) = -QEVAP(1) // Energy Transfer by Evaporation-Condensation
+QCONDUCT(1)-QCONDUCT(2) // Energy Transfer by Conduction
-QCONV(1); // Energy Transfer by Convection

//Conduction1: QCONDUCT(1) = LBDA(1)*SurfCont/LIGHT(0)*DT(1); // LENGTH(0) = HEIGHTLAYER(1)/2
Conduction1: QCONDUCT(1) = LBDA(1)*SurfCont/LIGHT(0)*DT(1); // LENGTH(0) = HEIGHTLAYER(1)/2

// Internal Layers
For i in [2:M] Do
Energy: $ELAYER(i) = -QCONV(i)+QCONV(i-1) // Energy Transfer by Convection
-QCONDUCT(i+1)+QCONDUCT(i) // Energy Transfer by Conduction
-QEVAP(i)+MIXCOEF*QEVAP(i-1); // Energy Transfer by Evaporation-Condensation
EndFor;

For i in [2:N] Do // Convection: QCONV(i) = DIFFLIQ(i)*CPWAT*DT(i+1);
Evaporation: QEVAP(i) = CVAP_Wat*DIFFVAPOUT(i);
EndFor;

For i in [1:M] Do
Evaporation: QEVAP(i) = CVAP_Wat*DIFFVAPOUT(N);
EndFor;

// Top Layer
// No Condensation of internal vapor at the top layer
EnergyN: $ELAYER(N) = +QCONV(M) // Energy Transfer by Evaporation-Condensation
+QCONDUCT(N) // Energy Transfer by Conduction
-QEVAP(N)+MIXCOEF*QEVAP(M) // Energy Transfer by Convection
+QRADN; // Energy Transfer by Radiation

Radiation: QRADN = FORMFACT*SurfContRad*5.67E-8*((TPlateTop+273.15)^4-TK(N)^4);
QRAD(N) = FORMFACT*SurfContRad*5.67E-8*((TPlateTop+273.15)^4-TK(N)^4);
QRAD = FORMFACT*SurfContRad*5.67E-8*((TPlateTop+273.15)^4-TK(N)^4);
QRAD(0) = ABS(FORMFACT*SurfContRad*5.67E-8*(TK(1)^4-TPlateBot+273.15)^4));

// --- GAB Sorption Isotherm -----------------------------------------------
TK = T*273.15;
GABC = GABC1*Exp(GABC2/(R*TK));
GABAA = XWAT*GABK*2-XWAT*GABK*2*GABC;
GABB = XWAT*GABK*GABC-2*XWAT*GABK-GABK*GABC*GABXM;
PVAP = PMAX*AW;
AW = (-GABB-Sqrt(ABS((GABB^2)-4*XWAT*GABAA)))/(2*GABAA);

// --- Vapor pressure -----------------------------------------------------
PMAX = 213.31*Exp(-6139.3*((1/(273.15+T))-3.8344e-3));
195 mBar at 60 C

// --- Temperature of each layer ------------------------------------------
Temperaturecalculation:

\[
\text{TK} = \frac{\text{ELAYER} \times (\text{MWATLAYER} \times \text{CPWAT} + \text{MBOUNDWLAYER} \times \text{CPWAT} + \text{MPVPLAYER} \times \text{CPPVP})}{\text{ELAYER} \times (\text{MWATLAYER} \times \text{CPWAT} + \text{MBOUNDWLAYER} \times \text{CPWAT} + \text{MPVPLAYER} \times \text{CPPVP})};
\]

--- Mean Average Water Content and Temperature -----------

MeanH2O: \( XWATMEAN = \frac{\Sigma(\text{MWATLAYER})}{\text{MDRY} + XWATBOUND} \)

MeanTemp: \( \text{TMEAN} = 273.15 + \frac{\Sigma(\text{ELAYER})}{\Sigma(\text{MWATLAYER} \times \text{CPWAT} + \text{MBOUNDWLAYER} \times \text{CPWAT} + \text{MDRY} \times \text{CPPVP})} \)

MassEvap: \( WATOUT = \text{DIFFVAPOUT}(N) + (1 - \text{MIXCOEF}) \times (\Sigma(\text{DIFFVAPOUT}) - \text{DIFFVAPOUT}(N)) \)

--- Balance Check -------------------------------

Mass

AccumulatedH2O: \( \text{ACCWAT} = \Sigma(\text{MWATLAYER}) + \text{MBOUNDWAT} + \text{WATOUT} \)

Heat

EnergyBalanceIn: \( \text{EIN} = \text{QCONDUCT}(1) + \text{QRADN} \)

EnergyBalanceOut: \( \text{EOUT} = \text{QEVAP}(N) + (1 - \text{MIXCOEF}) \times (\Sigma(\text{QEVAP}) - \text{QEVAP}(N)) \)

AccumulatedEnergy: \( \text{ACCE} = \Sigma(\text{ELAYER}) - \text{EIN} + \text{EOUT} \)

end;
CURRICULUM VITAE

Friedrich Witschi
born on March 23rd, 1968, Guayaquil, Ecuador
Citizen of Kirchlindach, BE, Switzerland

since 1999 Research Scientist, Nestlé R&D Center Kemptthal

1995-1999 Ph.D. thesis at the Laboratory of Food Process Engineering (Prof. E. Windhab), Swiss Federal Institute of Technology (ETH) Zürich and Process Research Group, Nestlé Research Center, Lausanne

1989-1995 Food Engineering Diploma at the ETH Zürich

Diploma thesis: “Process parameters influencing foaming properties of whey proteins”, Laboratory of Food Process Engineering (Prof. E. Windhab), ETH Zürich and Food Structure Group, Nestlé Research Center, Lausanne

Industrial Placements:
Nestlé R&D Center York, UK
Nestlé R&D Center Quito, Ecuador
Brewery Hürlimann, Zürich, Switzerland
Intermilch, Bern, Switzerland

1986-1989 Secondary School, Solothurn, Switzerland

1974-1986 Primary and Secondary School, Guayaquil, Ecuador