

## 1 Introduction

Spray drying is a drying technique used in a vast variety of industries [(Masters, 1985), (Mujumdar, 1995)] in which in one process step a particulate, dried material is obtained from a liquid feed. Rapid solvent evaporation assures that the thermal stress in the particles is low in comparison with other drying methods, like drum or belt drying. Therefore, despite a poor energetic efficiency in comparison to other drying methods, spray drying finds often application in the food industry in production of dairy products, coffee as well as fruit and vegetable juices.

The obtained powder can either be applied as a final product or be further processed. In some specific applications, as in case of skim milk in confectionery products, such dried food powders are applied directly in a powdered form. However, often products are used in a liquid state by mixing a powder with water.

Among important properties of powdered products are flowability, reconstitution behaviour, dust formation and powder bulk density. Powder flowability is important for precise powder dosage in packaging and in beverage systems. Good reconstitution behaviour is a prerequisite for easy application in a liquid form as well as digestion of powder. Due to dust explosion hazard, minimizing dust formation of powders assures safe powder handling. Higher powder bulk density minimizes a volume of a silo and a constant powder bulk density is necessary, if a volumetric dosage system is applied.

The above mentioned properties of powders depend on the properties of particles, such as moisture, particle size distribution and particle morphology. These properties of particles, which in the literature are also called primary properties of a powder (Kim et al., 2009b), are determined by properties of the liquid feed and by spray drying conditions. Alternatively, properties of a given powder can be optimized by such processes like agglomeration or granulation.

Many food products, which are dried by spray drying, are mixtures of multiple components. Spatial distribution of these components within a particle can also determine product properties, as in case of oxygen sensitive components or additives with unpleasant odour, which should be located in the centre of a particle. Location of specific components on particle surface can enhance or inhibit wetting of powders as well as have a negative effect on powder flowability.

In order to tailor properties of multicomponent powders to product requirements, it is important to understand the underlying processes, which lead to distribution of components within a particle. A relevant question is, if a surface composition can be controlled by drying conditions or feed composition. Another important question is, in what extend



the surface composition influences the properties of a spray dried particulate product. In answering these questions the link between the process and the properties of resulting powder remains in focus.

In this work a theoretical model is formulated, which describes drying and component transport within a drying drop. The model is applied to simulate profiles of two solutes, which differ in their molecular size, in a drop during drying and to predict the composition on the surface of a formed particle. The considered material is a dairy model-system, which contains two solutes – lactose and whey protein isolate, WPI – dissolved in water. Further insights on the relationship between the mass fraction of the solutes in the total solids and the drying rate are delivered by experimental investigation of the surface composition, powder wetting and flowability of powders produced by spray drying of the model-system.

After presentation of the fundamentals of the process and powder science, which are believed to be relevant for the scope of this work, a drying model of a single drop with two solutes is introduced. It is followed by presentation of used materials and experimental methods applied in characterization of powders. The next chapter reports the results of simulations and the following one presents the experimentally observed effects of the investigated parameters on the properties of the powders. The last chapter covers a synthetic discussion of the obtained results and conclusions with practical recommendations for a spray drying process.

### **1.1 General description of a spray drying process**

Spray drying is a process in which pumpable feed, like solutions, suspensions and pastes are atomized into drops and dried into particulate form. A schematic of a typical spray dryer is shown in Figure 1.1. The feed is pumped into a drying chamber and at the inlet atomized by a nozzle or a rotary atomizer into minute drops, which contact the hot drying medium. The typical drop size in spray drying is between 10 and 250  $\mu\text{m}$  (Mujumdar, 1995). A large contact surface between a feed material and a drying gas enables rapid solvent removal. At the outlet of the dryer a particulate product is obtained. During drying due to moisture evaporation the temperature of the drying medium decreases and its moisture content increases. In order to obtain desired properties of the product, minimize material losses, improve process efficiency and fulfil safety standards various designs of drying chambers and atomizing equipment were developed. The details of different spray dryer layouts are given, for example, by Masters (1985). Spray drying is applied in chemical, pharmaceutical and food industry. In the food industry it is used to production of diary powders, coffee and vegetable and fruit powders.

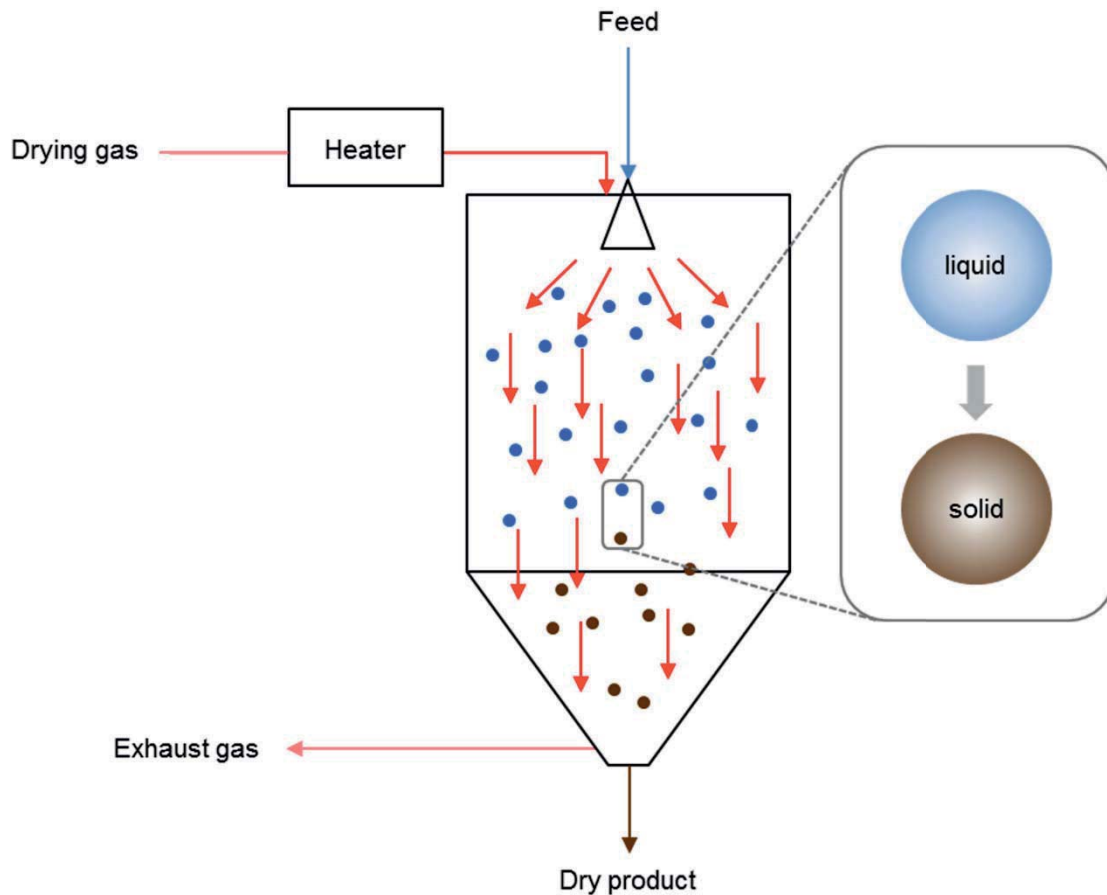


Figure 1.1 Schematic of a typical spray dryer.

### 1.1.1 Solid formation in spray drying

The knowledge of the physical fundamentals of solids formation in spray drying originates from observations of drying of single drops on hanging wire [(Furuta et al., 2007), (Chen and Lin, 2005), (Fu et al., 2011)], in magnetic field (Griffith et al., 2008) and acoustic levitator [(Schiffter and Lee, 2007), (Groenewold et al., 2002)], in towers (Vehring et al., 2007) and by taking powder samples along a spray drying tower (Zbicinski et al., 2002). The mechanism of solid formation depends on the nature of the material as well as the drying conditions. In the following as first the most basic scenario of particle formation is presented, afterwards few alternative scenarios, which lead to modified particle morphology, are named.

A drop produced by one of the atomization methods contacts drying medium in the spray drying tower. It is characteristic for spray drying feeds that the solvent content is high. In laboratory experiments initial water contents are between 70 and 90 wt. % [(Millqvist-Fureby et al., 1999), (Wang, 2010)], in industrial processes it reaches 50 wt. %.

Due to high amount of solvent in a drop and high temperature of the drying medium the partial pressure of the solvent on the surface of the drop is higher than the partial pressure of the solvent in the drying gas. The difference in the partial pressures of the solvent in

both phases is a driving force for solvent removal from the surface of a drop. As long as there is sufficient solvent on the surface the evaporation rate is constant, which corresponds to a linear decrease in moisture shown in Figure 1.2a. During this period a drop remains in a liquid state, or respectively as a suspension. The drop radius shrinks and solute or solid concentration, in case of suspensions, in the drop increases. At this stage, due to the heat removed by evaporation, a temperature of the drop reaches the adiabatic cooling temperature,  $T_{wtb}$ , (Figure 1.2b). This period of uninhibited solvent removal from a surface of a drop is called the first stage of drying.

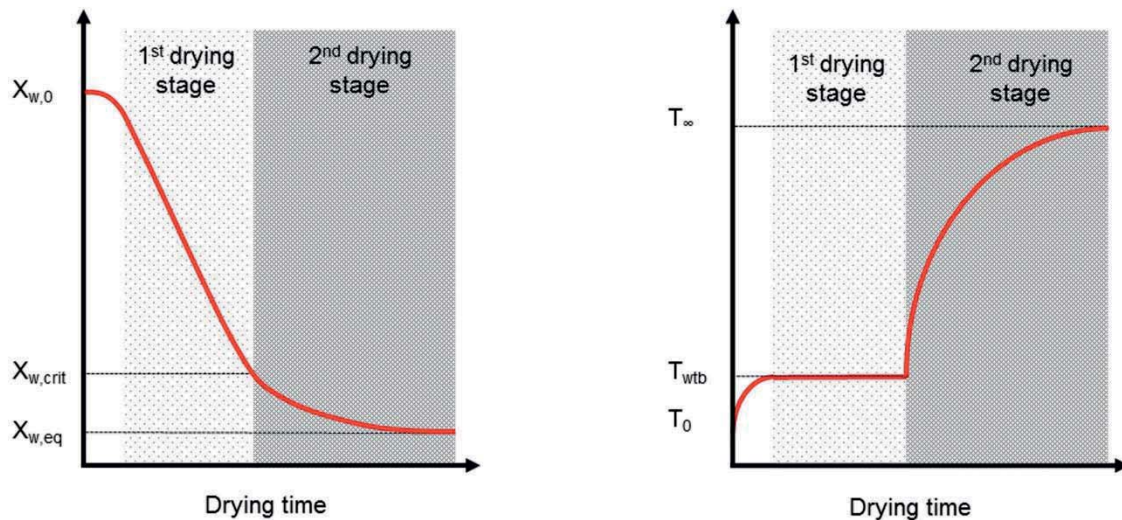


Figure 1.2 Typical change in a) drop or particle moisture content and b) temperature during drying.

As the solvent is removed, the solute accumulates in the vicinity of the surface. The concentration gradient between the surface and the core of a drop is levelled out by advective flux of solutes away from the surface towards the centre of a drop. If the mass transport is fast, the concentration of the solute or solids particles remains uniformly distributed in a volume of the drop. As drying progress, the increasing solute concentration results in a lower mobility of water molecules in the drop. This leads to a decreased solvent transport towards the surface and to a lower solvent evaporation rate. Particle moisture content from which the evaporation rate starts to decrease is described as the critical moisture content,  $X_{w,crit}$ . The decreasing solvent evaporation rate (Figure 1.2a) decreases the rate of heat removal from the drop. Therefore, in the second stage of drying the temperature of a drop increases (Figure 1.2b), approaching the drying gas temperature. Once the majority of the solvent is removed, a solid particle appears. The morphological changes, which correspond to this drying history, are pictured in Figure 1.3.

If solvent removal from the surface is faster than the mass transport of the solute away from the surface, the solute accumulates on the surface forming a porous shell or skin. This solid layer results in mass transport resistance to solvent transport, which leads to decreased drying rate and transition to second drying period at higher total water contents



in a drop. Once a solid layer, skin or shell, forms on the surface, a particle cannot uniformly shrink further (Tsotsas, 2012). As the process is very rapid, even crystallizing materials form amorphous particles (Vehring, 2008).

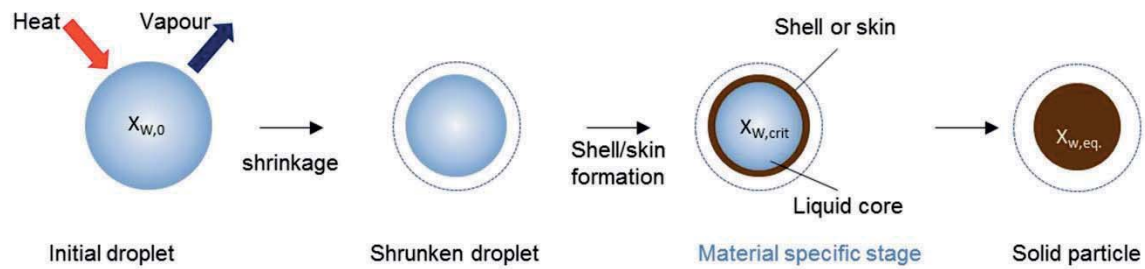


Figure 1.3 Development of particle morphology during particle formation.

The amount of moisture in the material at the end of drying results from an equilibrium between the partial pressure of water in the two phases, i.e. between the relative humidity of the drying gas and the water activity of dried material. The dependence between the equilibrium moisture content ( $X_{w,eq}$ ) and the water activity of a given material during drying is described by moisture desorption isotherm. An example of a moisture desorption isotherm of skimmed milk powder at 25°C, which was determined and fitted by Vuataz et al. (2002) to Brunauer-Emmett-Teller model is shown in Figure 1.4.

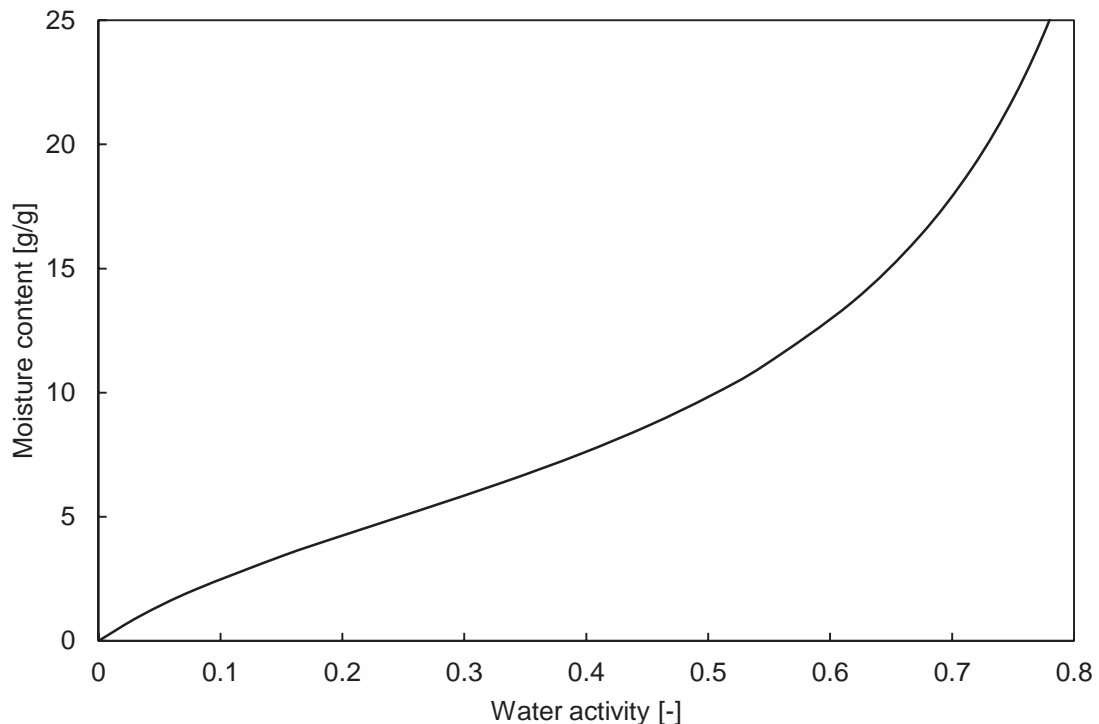


Figure 1.4 Desorption isotherm of skimmed milk powder at 25°C determined by Vuataz et al. (2002) and fitted to Brunauer-Emmett-Teller model.

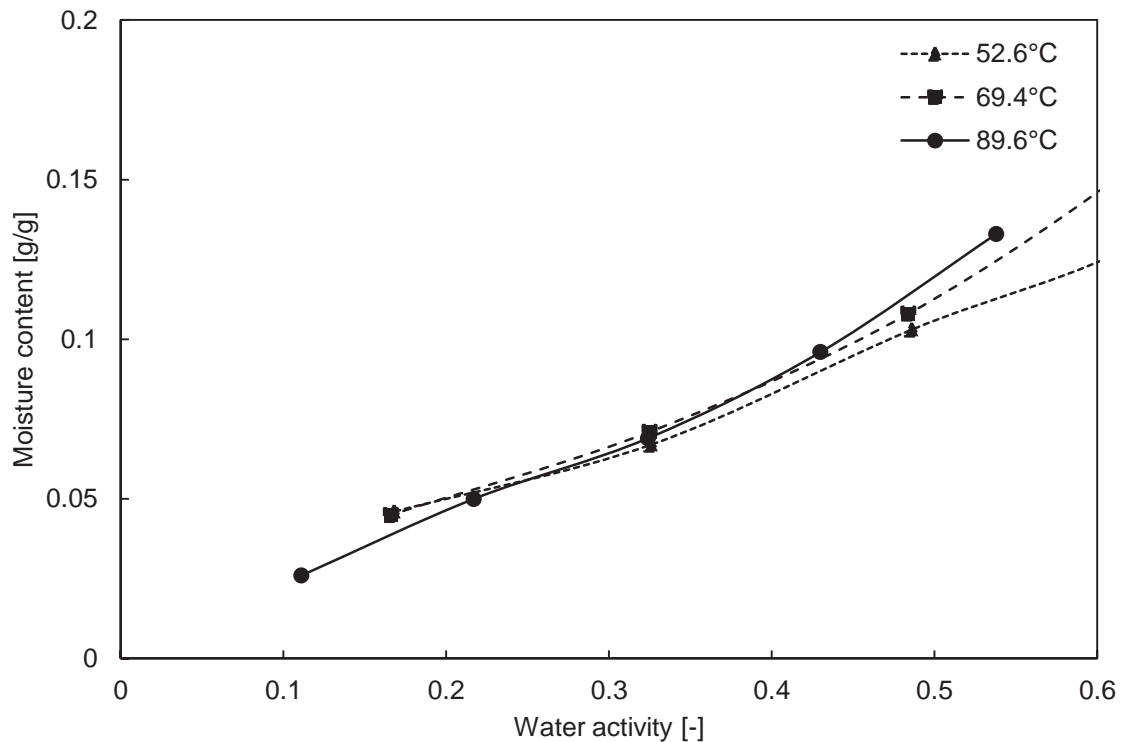


Figure 1.5 Moisture desorption isotherm of skimmed milk powder measured by Lin et al. (2005).

For many materials the equilibrium moisture content decreases with the increasing temperature (Tsotsas et al., 2000). Lin et al. (2005), however, have observed that the desorption isotherms of skimmed milk powder at temperatures above 50°C are characterized by an inversion point, so that at relative humidity above 20 % the equilibrium moisture in the material increases with the temperature. The desorption isotherms of skimmed milk powder measured by Lin et al. (2005) are shown in Figure 1.5.

### 1.1.2 Development of particle morphology

Depending on material properties and drying history the solidification of the outer layer of a drop can lead to formation of hollow, shuttered or wrinkled particles (Handscorn et al., 2009b). In a spray dryer there is some distribution in drying histories due to temperature, velocity and residence time distributions [(Mezhericher et al., 2012), (Schmitz-Schug et al., 2016)]. This can result in some distribution in morphology of spray dried particles.

## 1.2 The meaning of powder properties

Good quality of any powder product is determined by adjustment of the powder properties to the application. During powder production (Bhandari et al., 1997), conveying, packaging and mixing good product flowability is desired (Fitzpatrick et al., 2004). However, during powder tableting or pelleting a certain level of adhesion of particles to each other under a load is expected (Palzer, 2011). In powder agglomeration the adhesive behaviour of a powder is imposed by, for example, addition of a plasticizer, which locally



decreases the glass transition temperature of a particle (Palzer, 2009). For powders, which are used by dissolving in a solvent, like milk powder or coffee, good reconstitution properties are important. In case of some particles a controlled dissolution upon exposure to specific conditions is required. Mechanical properties of particles play a role in a release of certain flavour components (Gouin, 2004).

Among these, powder flowability, and caking as the opposite, as well as wetting are influenced by the properties of the surface as explained below. However, other characteristics like particle size and shape or submolecular structure of the material also impact flowability and wetting.

### ***1.2.1 Wetting and instant properties of powders***

Wetting is one of the steps of powder reconstitution and often the rate limiting step (Hogekamp and Schubert, 2003). The capillary forces play a dominating role during wetting. The Washburn equation (Eq. 1.1) can be used to describe the rate of capillary rise in a powder pore network (Forny et al., 2011). In Eq. 1.1  $\bar{r}$  is the mean pore diameter of the pores in the bulk material,  $l$  is the solvent penetration distance,  $\gamma$  the surface tension of the liquid,  $\eta$  its dynamic viscosity,  $c$ , the form factor and  $\theta$  the Young's contact angle. Therefore, the rate of wetting of a powder bulk is favoured for large capillaries, which correspond to large particles, and materials on which the contact angles are small.

$$\frac{l^2}{t} = \frac{\gamma \cdot c \cdot \bar{r} \cdot \cos\theta}{2\eta} \quad (1.1)$$

Contact angle delivers information about the strength of the interaction between a solid and the solvent. On an ideal, rigid, homogeneous surface a contact angle of a solvent is given by Young's equation (Eq. 1.2), which describes the interfacial energy balance [(Good, 1992), (Decker et al., 1999)]. For a given solvent the contact angle depends on the chemical composition of the solid. In Figure 1.6 a shape and a contact angle of a water drop on a hydrophobic and hydrophilic surface is shown. On a hydrophilic surface the contact angle of water drop is smaller, because the interaction with the liquid is stronger than on a hydrophobic surface.

Real surfaces are characterized by some roughness, which amplify the effects (Palzer, 2001). An apparent contact angle between such a surface and a contour of a sessile drop placed on the surface is not equal to the Young's contact angle (Lazghab et al., 2005). Nevertheless, it is used as an assessment of the strength of interaction between the solvent and the solids [(Puri et al., 2010), (Ji et al., 2016), (Susana et al., 2012), (Lerk et al., 1976)].

$$\gamma_{SL} - \gamma_{SV} - \gamma_{LV} \cos \theta = 0 \quad (1.2)$$

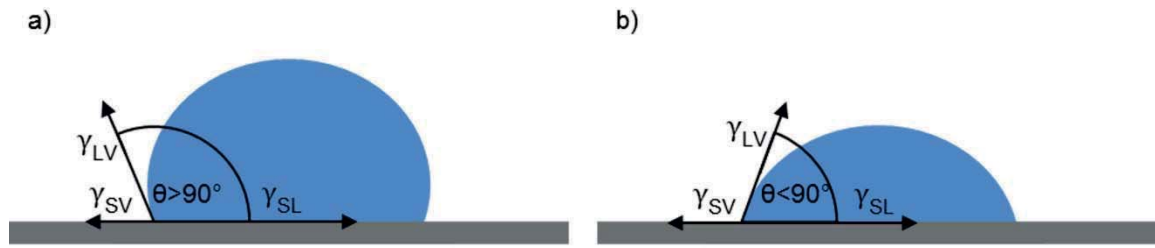


Figure 1.6 Young's contact angle of a test hydrophilic solvent drop on a) hydrophobic and b) hydrophilic surface, where  $\gamma_{SL}$  is the surface tension between the solid and liquid,  $\gamma_{SV}$  is the surface tension between the solid and vapour,  $\gamma_{LV}$  is the surface tension between the liquid and vapour.

Further powder properties which influence the rate of solvent penetration are: powder dissolution and particle swelling, which can lead to an increase in liquid viscosity or affect the pore size. The further steps of powder reconstitution are sinking, dispersion and dissolution (Hogekamp and Schubert, 2003). Sinkability is driven by a difference between the apparent density of the powder and solvent density. The sunken powder should disperse in order to provide large contact surface to accelerate dissolution. Analogically to the powder wetting, powder dispersion is influenced by the type of the solid-solvent interaction.

### 1.2.2 Flow properties of powders

Powder flow is a plastic deformation of the powder bulk due to movement of the individual particles against each other (Schulze, 2008). The degree of movement of the particles in a bulk depends on the strength of adhesive forces and friction between particles (Schulze, 2008).

Lifshitz:

$$F_{vdW} = \frac{h\omega}{32 \cdot \pi \cdot h_s^3} \cdot a^2 \quad (1.3)$$

Hamaker, for  $h_s < 150$  nm

$$F_{vdW} = \frac{H}{24 \cdot h_s^3} \cdot a^2 \quad (1.4)$$

The dominating adhesive force especially for the small and dry particles is the van der Waals force due to plastic and visco-elastic deformations of particles, which for two particles separated by a distance  $h_s$  can be described by Eq. 1.3 or Eq. 1.4 (Dopfer et al., 2013), in which  $a$  is the diameter of the circular contact area between the particles and  $h\omega$  is the Lifshitz-van der Waals constant and  $H$  the Hamaker constant. The magnitude of the van der Waals force depends on the size of the contact area and on the chemical composition of the surface, since the constants are related to the surface energy of the material of which the particles consist (Lifshitz, 1956, Hamaker, 1937).





Further adhesion mechanism relevant to powder flowability is formation of sinter bridges between particles (Hartmann and Palzer, 2011). Formation of the sinter bridges can be described with Frenkel's equation (Eq. 1.5) or equation given by Rumpf (Eq. 1.6.), (Hartmann and Palzer, 2011).

$$\left(\frac{h}{d}\right)^2 = \frac{1}{6} \cdot \frac{\gamma}{d} \cdot \frac{t_c}{\eta} \quad (1.5)$$

$$\left(\frac{h}{d}\right)^2 = \left(\frac{4}{5} \cdot \frac{\gamma}{d} + \frac{2 \cdot F_t}{5 \cdot \pi \cdot d^2}\right) \cdot \frac{t_c}{\eta} \quad (1.6)$$

In both equations  $h$  is the diameter of a sinter bridge,  $d$  is the particle diameter,  $t_c$  the contact time between the particles and  $F_t$  in Eq. 1.6 is the force with which the particles are contacted with each other. It can be seen that the size of a sinter bridge increases with time, the contact force and surface tension of the material as well as with decreasing material viscosity.

The change in viscosity of the surface or the whole particle concerns especially the amorphous materials. On contrary to crystalline structures, in which the molecules are arranged in a thermodynamically stable lattice, amorphous materials are formed by rapid removal of a solvent from the matrix and cooling, which results in unordered supramolecular structure called glass [(White and Cakebread, 1966), (Alexander and Judson King, 1985), (Vehring, 2008)]. In many particulate food materials the amorphous or semi-amorphous structure is advantageous (Palzer et al., 2012). Due to viscosity of about  $10^{12} - 10^{13}$  Pa·s (Schmelzer and Gutzow, 2011) of such materials the mechanical properties are like those of solids. However, due to moisture sorption properties the structure enables fast dissolution of the materials (Palzer et al., 2012).

$$T_g = \frac{(1 - X) \cdot T_{g,S} + k \cdot X \cdot T_{g,W}}{(1 - X) + k \cdot X} \quad (1.7)$$

The viscosity of amorphous materials depends strongly on the temperature and the solvent content, which affects molecular mobility (Roos and Karel, 1990). The relationship between the temperature, at which the viscosity of the materials suddenly drops by three orders of magnitude, i.e. the glass transition temperature  $T_g$ , and moisture content  $X$  of the materials is described by the Gordon-Taylor-equation (Gordon and Taylor, 1952) (Eq. 1.7), where  $T_{g,S}$  and  $T_{g,W}$  are the glass transition temperatures of the substance and water respectively and  $k$  is a constant characteristic for the pair substance-water.

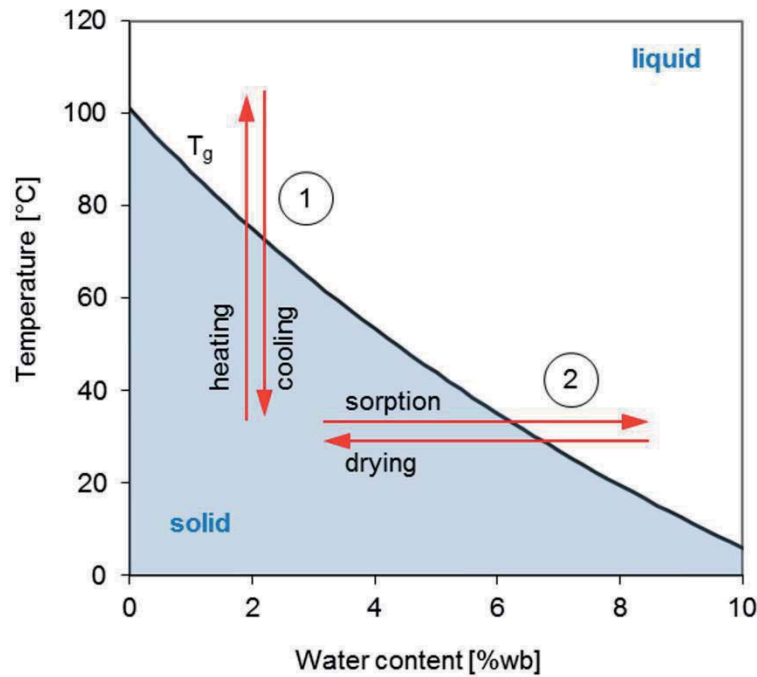


Figure 1.7 Typical dependency of glass transition temperature on powder moisture.

A typical glass transition curve can be seen in Figure 1.7. Above the glass transition temperature the material is in a liquid form and below it is solid. A transition from a solid to a liquid form can take place due to either exposure to increased temperature (path 1) or sorption of moisture (path 2). During spray drying the material follows path 2 in the first stage of drying. In the second stage of drying, if the temperature of the material increases, the material can liquefy and become sticky (path 1). When a powder is exposed to moisture, for example in the air, it can absorb the moisture and change from solid to a viscous rubber (path 2). Exposure to temperatures above the glass transition temperature at a given powder moisture results in a decreased viscosity of the surface, which can lead to formation of viscous bridges between particles [(Roos and Karel, 1991), (Lloyd et al., 1996), (Bhandari et al., 1997), (Downton, 1982)].

$$\log\left(\frac{\theta_{cr}}{\theta_g}\right) = \frac{-17.44 (T - T_g)}{51.6 + (T - T_g)} \quad (1.8)$$

The empirical Williams-Landel-Ferry (WLF) (Williams et al., 1955) equation describes the temperature dependency of mechanical relaxation time of amorphous polymers. Roos and Karel (Roos and Karel, 1990) showed that above the glass transition temperature the time to crystallization  $\theta_{cr}$  follows the WLF equation (Eq. 1.8), in which  $\theta_g$  is time to crystallization at glass transition temperature.