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A Distributed Parameter Model for the Drying of Multicomponent Aerosol and Sessile Droplets

Jakub M. Gac*, Leon Gradoń

Warsaw University of Technology, Faculty of Chemical and Process Engineering, ul. Waryńskiego 1, Warsaw, Poland
J.Gac@ichip.pw.edu.pl

The new distributed parameter model is formulated for the purpose of the investigation of a drying of suspended and sessile droplets of multi-component solutions. The main feature of this model is the division of a droplet/wet particle into the shells and formulating the mass and heat balances for each shell, which have a shape of spheres in a case of aerosol particles and a shape close to the cylinders in a case of sessile droplets. Presented model takes into account the crust formation during the second stage of drying. This effect is neglected in existing models of the phenomenon. The model predicts the dimension and a shape of particle or formed deposits. It also indicates the possibility of a segregation of components when their solubility and diffusion coefficients are different.

1. Introduction

The drying process is one of more important phenomena in chemical engineering. The widely investigated examples of this process are: drying in fluidized bed (Pěnička et al, 2012), drying of thin liquid film of solution (Wellner et al, 2012) or drying of single droplet of solution.

The dynamics of a drying of droplets both suspended as well as sessile is a very common phenomenon and thus has become a subject of growing interests in many experimental studies and theoretical considerations. The drying of a suspended droplet consisted of a solution or slurry is often applied as a well-known spray drying technique. This method allows obtaining small particles with desired shape and properties (Masters, 1980). The main advantage of this method is the uniformity of the shape and diameter of obtained particles. That is the reason for the wide usage of a spray drying in cases where the uniformity of shape, diameter and composition of particles has a crucial meaning, e.g. designing of medicaments for aerosol-therapy.

The drying of sessile droplet, on the other hand, could be important in consideration of the dynamics of deposited droplet, which may contain e.g. pathogenic bacteria or viruses (Parienta et al, 2011).

Another promising property of the spray-drying technique could be the segregation of components inside a particle during the drying of a droplet that contains these components. This process of segregation is important especially for drying of suspended droplets and may find applications e.g. in drug delivery (Takatsuka et al, 2007) or encapsulation process (Ferreira et al, 2007).

There is well recognized that the process of drying of a droplet consists of two stages (Mezhericher et al, 2007). During the first one, the evaporation takes place and the volume of a droplet decreases. If the suspended droplet is dried this is followed by the decrease of its radius while the shape of a droplet does not change and remains spherical. In opposite, the base radius of sessile droplet usually does not change during the drying process. It is caused by so-called triple line pinning, when the line of contact of three phases is attached to the solid surface. For sessile droplet we observe a decrease of its height and the contact angle instead. During the second stage of drying there a solid crust, in a case of a suspended droplet, or solid agglomerate in a case of a sessile droplet are formed. The formation of a solid crust usually begins from the outer layer of suspended droplet, while the concentration of solutes near the surface is the highest. For the sessile droplet, the agglomerates may have one of two forms. One of them is well known "stain ring" which has a form of a ring with radius equal to a base radius of a sessile droplet

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(Deegan et al, 1997). However, in some cases the agglomerate takes a form of a cone or pillar placed at the centre of initial droplet (Baldwin and Fairhurst, 2012).
The most of numerical models of droplet drying use the well-known numerical techniques, such as finite difference or finite element method, for solving of the equations of mass and heat balance (Mezhericher et al, 2007). These methods give quite good results, however they are often significantly time and memory consuming, while the very fine numerical mesh should be applied to achieve the desired accuracy. Another problem concerning with the methods mentioned above is a motion of boundaries of computational domain what is an effect of decrease of a droplet dimension during the drying. The moving boundary problems usually need more complicated numerical techniques, e.g. with dynamic mesh (Mezhericher et al, 2007). This is the reason why the mesh-free methods are extensively developed recently. The main group of these methods are so-called distributed parameter models (DPM) (Wang and Langrisch, 2009). According to the rules of these models, the dried droplet is divided onto a few parts, which volumes may change during the drying process. For every part, heat and mass balance equations are solved. These equations have now a form of a system of simple algebraic equations what allows avoiding many difficulties concerning the finite difference and finite element methods. However, most of DPM models present in literature do not take into account a solid crust formation (Parentia et al, 2011). After that, according to our knowledge, there is no DPM scheme for sessile droplet.
The objective of our study is to formulate the distributed parameter model (DPM) for a drying of suspended as well as sessile multicomponent droplet. By means of this model, we investigate the final composition of particles formed in the spray drying process and the composition of deposits formed during the evaporation of the sessile droplet. Particularly, we describe the influence of parameters of soluble components (their solubility and diffusion coefficients) on the shape and composition of particles and deposits.

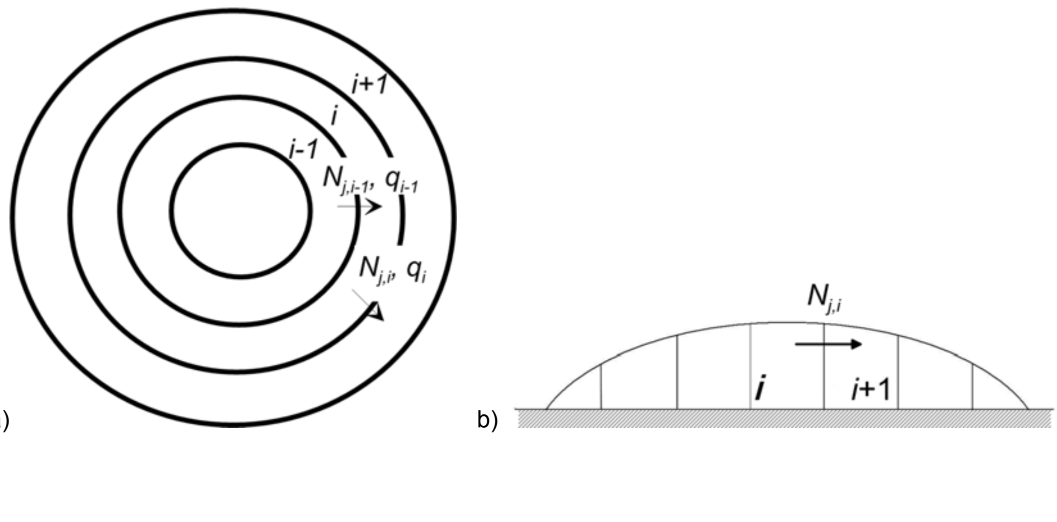
2. Numerical model

In this section, we present the mathematical and numerical formulation of the drying of a suspended as well as a sessile droplet.
The DPM model for a drying of suspended droplet has been formulated and described in details in our last paper (Gac and Gradoń, 2013). The main assumptions of this model are as follows:

- the droplet is spherical and has a spherical symmetry
- the droplet is small enough and the convection inside could be neglected; the heat and mass transfer appears through the conduction and diffusion only
- the particle formed in a result of a drying of the droplet has also a spherical symmetry.

According to the DPM, the droplet is divided into N spherical shells as it has been shown in Figure 1a. During the first stage of drying the number of shells does not change but the thickness of each shell decreases in time. The mass balance for each shell has a form:

$$\frac{dm_{j,i}}{dt} = 4\pi\left(\frac{i-1}{N}R_d\right)^2 N_{j,i-1} - 4\pi\left(\frac{i}{N}R_d\right)^2 N_{j,i} \quad (1)$$



a) b)

Figure 1: discrete parameter model for (a) suspended and (b) sessile droplets.

where $m_{j,i}$ denotes the mass of *j*-th substance in *i*-th shell. The mass flux of a substance *j* from shell *i* to shell *i+1* denoted as $N_{j,i}$ is given by:

$$N_{j,i} = \rho_{j,i} \frac{i}{N} \left| \frac{dR_d}{dt} \right| + J_{j,i} \tag{2}$$

In the above expression the first component arises from the change of a radius of a droplet and the radii of shells, while the second is a diffusive flux given by:

$$J_{j,i} = -\frac{ND_j}{R_d} \left(\rho_{j,i+1} - \rho_{j,i} \right) \tag{3}$$

The system of equations (1) for every shell and every substance can be easily solved e.g. by means of Euler scheme. Similar form has the heat balances:

$$m_i c_{p,d} \frac{dT_i}{dt} = 4\pi \left(\frac{i-1}{N} R_d \right)^2 q_{i-1} - 4\pi \left(\frac{i}{N} R_d \right)^2 q_i \tag{4}$$

where T_i is a temperature In *i*-th shell and the heat flux from shell *i* to *i*+1 q_i is given by:

$$q_i = -\frac{Nk_d}{R_d} \left(T_{i+1} - T_i \right) \tag{5}$$

The second drying stage starts when the concentration of one of the substances soluble exceeds its solubility. It usually takes place in the most outer shell firstly, and this shell forms a solid crust. Next, we assume that each shell in which the concentration of any substance exceeds its solubility becomes the part of solid crust. The equations of heat and mass balances for the shells in wet core have the same form as in the first drying stage. The only differences are in formulation of the boundary conditions (Gac and Gradoń, 2013).

Now, let turn us to the model of a drying of the sessile droplet.

The equations of DPM for the sessile droplet are obtained under the following assumptions:

- the droplet has the shape of spherical cup during the whole the drying process; the basal radius of a droplet is constant while the wetting angle may change (Cazabat and Guenna, 2010)
- the droplet and the formed deposits of the solid (stein ring) have the axial symmetry.

The droplet is divided into *N* shells, which shapes result from the cross-section of cylindrical ring and a spherical cup as it has been shown in Figure 1b. The number of shells does not change during the simulation of a process neither the radius of any shell do not change but the height of a shell changes as a result of evaporation. The evaporation mass flux of a solvent is given by means of the formula (Cazabat and Guenna, 2010):

$$N_{i,evap} = D_{vap} \frac{\rho_{vap,sat} - \rho_{vap,\infty}}{\rho_{liquid}} \frac{g(\vartheta)}{R_d} \left(1 - \left(\frac{r_i}{R_d} \right)^2 \right)^{-\lambda(\vartheta)} \tag{6}$$

where $g(\vartheta)$ and $\lambda(\vartheta)$ are the functions of the contact angle ϑ; their form can be found in (Cazabat and Guenna, 2010). The first stage procedure of every time step is computation of the new temporary volume of every shell as:

$$V_i^{temp} = V_i - N_{i,evap} \cdot S_{i,ext} \cdot \Delta t \tag{7}$$

where, $S_{i,ext}$ is a surface between the *i*-th shell and the ambient.

The sum of the temporary volumes of the shells is a new volume of a droplet. On the base of the value of this volume, the new value of contact angle ϑ^{new} and the new volumes of every shell V_i^{new} are computed. These volumes differ, in general, from the volumes given by equation (7). When this difference is known, the convective flux between the shells may be computed as:

$$N_{i,conv} = \frac{V_i^{temp} - V_i^{new}}{S_{i,i+1} \cdot \Delta t} \tag{8}$$

where , $S_{i,i+1}$ denotes the surface between *i*-th and *i+1*-st shell. Note that contrary to a suspended droplet the convective flux for a sessile droplet cannot be neglected (Cazabat and Guenna, 2010).
Now, the total mass flux of substance *j* between the shells *i* and *i+1* is given by the formula:

$$N_{j,i} = N_{i,conv} \cdot \rho_{j,i} + J_{j,i} \tag{9}$$

where, the diffusive mass flux is given by equation (3). For a sessile droplet we assume that the temperature of a droplet is constant during the drying process and thus the heat balance is not considered. We assume that, when a concentration of any substance in any shell exceeds its solubility, there a solid deposit appears in that shell. Subsequently, the concentration of this substance in the shell decreases to the value of its solubility. We further assume that due to the high solubility of solutes and relatively high density of a solid deposit its volume is small when compared to the shell volume. The height of deposit in every shell is assumed to be constant over the entire shell and the increase of this deposit in each time step is computed according to the formula:

$$\Delta h_{j,i} = \frac{(\rho_{j,i} - \rho_{j,\max})V_i}{\rho_{j,solid} \cdot S_{i,solid}} \tag{10}$$

where $\rho_{j,\max}$ denotes a solubility of component *j*, $\rho_{j,solid}$ is a density of solid substance *j* and $S_{i,solid}$ is a surface between *i*-th shell and solid base (note that while the base radius of a droplet does not change this surface is constant).
The simulations of a drying of suspended droplet are run until the volume concentration of water in any shell is greater than given minimal value. The simulation of a drying of sessile droplet stops when the volume of every shell is less than the assumed minimum value.

3. Results

The results of DPM simulations of a drying of multicomponent suspended droplet are described in details in our very last paper (Gac and Gradoń, 2013). We do not repeat these results, but we present only the main conclusions before we report the results obtained for the sessile droplet, which has not been presented anywhere yet.

Table 1: Physicochemical parameters of solvent used in simulations

Parameter	Value	Unit
Density of solvent (water), ρ_{liquid}	997	kg/m^3
Specific heat of solvent (water), c_p	4.19	kJ/kg/K
Heat of evaporation of solvent (water), L_t	2300	kJ/kg
Heat conductivity of solvent (water), k_d	0.58	W/m/K
Diffusion coefficient of solvent (water) vapour in air, D_{vap}	25.9	mm^2/s

In our simulations we have assumed that the solvent is water. The physicochemical properties of solvent have been given in table 1. The parameters of solutes (their solubility, diffusion coefficient and initial concentration) have been changed to investigate the drying of droplet containing various substances.

The effect of the component segregation may be observed as the result of a drying of suspended droplet when the diffusion coefficients of components are significantly different. The strength of this effect depends also on a solubility of the components in the solution. When this solubility is relatively high, a small particle is formed and the segregation of components does not appear or it is negligible. When the solubility of components is lower the segregation may occur. Two layers of particle are distinguished. In the most outer one the concentration of a component with lower value of the diffusion coefficient is higher than the second one while in the most inner layer the concentration of this component is lower.

Now, let us consider the drying of the sessile droplet with one soluble substance.

In Figure 2a we present the cross-section through the deposit formed during the drying of the sessile droplet. The diffusion coefficient and the solubility of a solute are equal to $7 \cdot 10^{-7}$ m^2/s and 100 kg/m^3, respectively. The basic radius of a droplet is equal to 25 μm. We recognize that the deposit has a form of the well known “stain ring” and is the highest near the border of a droplet. Quite different shape has a deposit presented in Figure 2b (the diffusion coefficient equal to $7 \cdot 10^{-7}$ m^2/s and the solubility equal to 50 kg/m^3). Now, the maximal height of a deposit is in the center of a droplet. Such “pillar-shaped” deposits have been observed experimentally e.g. during the drying of droplets of solutions of polymers (Baldwin and Fairhurst, 2012). The pillars observed in experiments are usually “slimmer” than those observed in our simulations while in real world the basic radius of the sessile droplet is not constant and starts to decrease in the late phase of drying.

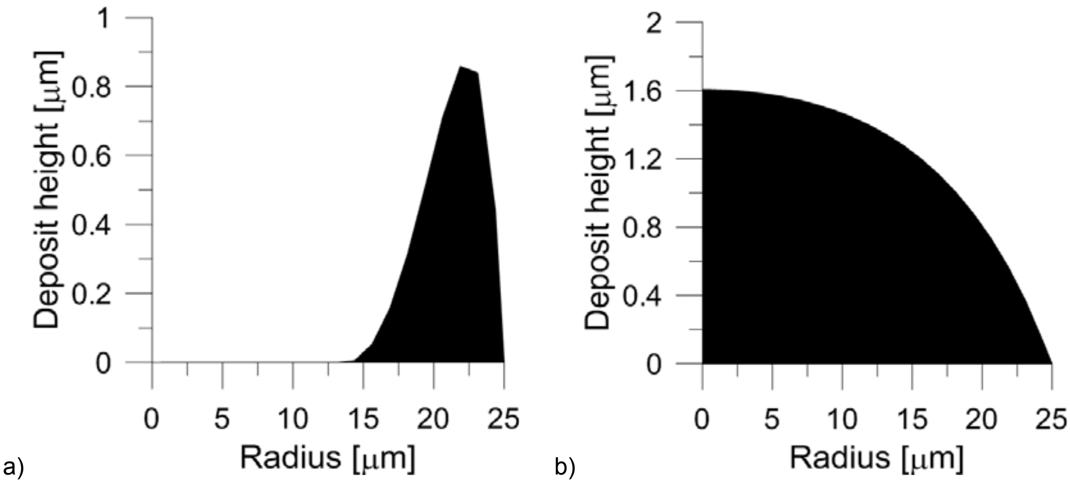


Figure 2: the final shape of a deposit formed as a result of drying of the sessile droplet for (a) high solubility and low diffusion coefficient and (b) low solubility and high diffusion coefficient of a solute.

We observe the partial segregation of deposited substances when both solutes dissolved in the sessile droplet. The deposit of a substance with higher diffusion coefficient and lower solubility appears mainly near the center of a droplet, while the deposit of a substance with lower diffusion coefficient and higher solubility forms a ring near the initial contact line of a droplet. Such results are obtained for the case when the influence of one substance onto the solubility of the other one is neglected. The general aspect of considered model will be of the subject of our further research.

4. Conclusions

By means of DPM method we have simulated the drying of suspended droplet with crust formation as well as a drying of the sessile droplet with deposit formation.

We have noticed that during the drying of suspended droplet consisted of a solution the segregation of components can take place if the components have significantly different values of the solubility and diffusion coefficients and particularly, the component with lower diffusion coefficient has higher solubility.

For the case of a drying of the sessile droplet the shape of formed deposits and the shape of the product are also influenced by the diffusion coefficient and the solubility of the solutes. If the coefficient is low and the solubility is relatively high, the deposit is formed as a well known “ring stain” on the perimeter of the dried droplet. Otherwise, the deposit has a form of a broader ring or even “pyramid” with an axis in the center of a dried droplet. If a few solutes are present in the droplet, the segregation takes place.

Although the simplicity of the presented model (which arises from the assumption of the symmetry of drying droplet) the results of our simulations are consistent with those obtained by means of other methods. That allows us to expect that the model may be successfully used to predict the final shape and composition of particles or deposits obtained by means of drying of suspended or the sessile droplets.

References

Baldwin K.A., Fairhurst D.J., 2012, The effects of molecular weight, evaporation rate and polymer concentration on pillar formation in drying poly(ethylene oxide) droplets, Colloids and Surfaces A: Physicochemical and Engineering Aspects, DOI: 10.1016/j.colsurfa.2012.10.049.

Cazabat A.-M., Guenna G., 2010, Evaporation of macroscopic sessile droplets, Soft Matter 6, 2591-2612, DOI: 10.1039/B924477H.

Deegan R. D., Bakajin O., Dupont T.F., Huber G., Nagel S. R., Witten T. A., 1997, Capillary flow as the cause of ring stains from dried liquid drops, Nature, 389, 827-829.

Ferrrreira I., Rocha S., Coehlo M., 2007, Encapsulation of antioxidants by spray-drying, Chemical Engineering Transactions, 11, 713-718.

Gac J.M., Gradoń L., 2013, A distributed parameter model for the spray drying of multicomponent droplets with a crust formation, Advanced Powder Technology 24, 324-330, DOI: 10.1016/j.apt.2012.08.004.

Masters K., 1980, Spray drying, Advances in Drying, 1, 269-298.

Mezhericher M., Levy A., Borde I., 2007, Theoretical drying model of single droplets containing insoluble or dissolved solids, Drying Technol. 25, 1035-1042, DOI: 10.1080/07373930701394902.

Pěnička M., Hoffman P., Fořt I., Bartoň J., 2012, Reduction of the Total Drying Time in Mixed Fluidized Layer, Chemical Engineering Transactions, 29, 475-480. DOI: 10.3303/CET1229080.

Parienta D., Morawska L., Johnson G.R., Ristovski Z.D., Hargreaves M., Mengersen K., Corbett S., Chao C.Y.H., Li Y., Katoshevski D., 2011, Theoretical analysis of the motion and evaporation of exhaled respiratory droplets of mixed composition, Journal of Aerosol Science 42, 1-10, DOI: 10.1016/j.jaerosci.2010.10.005.

Takatsuka S., Morita T., Horikiri Y., Yamahara H., Saji H., 2007, Absorption enhancement of poorly absorbed hydrophilic compounds from various mucosal sites by combination of mucolytic agent and non-ionic surfactant, International Journal of Pharmaceutics 338, 87-93, DOI: 10.1016/j.ijpharm.2007.01.027.

Wang S., Langrish T.A.G., 2009, A distributed parameter model for particles in the spray drying process, Advances Powder Technology 20, 220-226, DOI: 10.1016/j.apt.2009.03.004.

Wellner N., Siebeneck K., Scholl S., 2012, Falling Film Evaporator: Drying of Ionic Liquids with Low Thermal Stress, 29, 571-576. DOI: 10.3303/CET1229096.