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# Concentration fields in evaporating droplets

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## Abstract

An analytical solution of the problem of diffusional mass transport inside a spherical binary mixture droplet is presented. The droplet evaporates according to the $d^2$-law. Mass fraction profiles of the mixture components are obtained as series expansions in confluent hypergeometric, Legendre and sine/cosine functions. The analytical description is valid for arbitrary ratio of the rate of shrinkage of the sphere surface to the diffusion coefficient in the liquid phase. The results allow for a prediction of the morphology of the dried particles, i.e., whether hollow or solid spheres result from the drying process. The field of application of the results presented is spray drying of solutions of solid substances.
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*Keywords:* Analytical; Droplet; Drying

## 1. Introduction

Technical processes like spray drying and air/fuel mixture formation rely on the evaporation of liquid components from droplets in a hot gaseous environment. In the former process, the dry solute is the goal of the process, while in the latter the gaseous mixture of air and fuel vapor is desired. In both cases, the droplet liquid undergoes a temporal change in composition due to the liquid evaporation, which may lead to the formation of concentration gradients inside the droplet. It has been recognized quite some time ago that in spray drying the mass transfer processes inside the droplet are the key to understanding the formation of dry particles with different morphology. Duffie and Marshall [1] looked at the influences of the drying and liquid feed temperatures, initial solute concentration and material properties on the resulting dry particles. They investigated aqueous solutions of salts like NaCl, $KNO_3$, $NH_4NO_3$ and others, solutions of dyes, milk, and corn syrup. An important result of their investigations was that increased drying temperatures lead to a decrease of the bulk density of the dry particulate matter due to increased particle sizes. Variations in the liquid feed temperature, in contrast, have only marginal influence on the drying result. In [2,3] we find the factors listed that may lead to the formation of hollow spheres in spray drying: the formation of a surface film of dry solute on the droplet (as it is the case with, e.g., aqueous $NaSiO_3$ and $C_{12}H_{22}O_{11}$ solutions), which keeps the particle size widely constant during the drying process and may finally rupture as the second drying stage starts; large drying rates as compared to the diffusive mass transport of solute in the droplet, so that hollow shells are formed; and finally the capillary effects of the solid surface, once it is formed, which can force the liquid solution towards the surface and lead to an under-pressure inside the particle. Sano and Keey [4] developed a drying model for

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**Nomenclature**

| | |
|---|---|
| $a$ | droplet radius (m) |
| $a$, $b$ | parameter of Kummer's function (–) |
| $a_0$ | initial droplet radius (m) |
| $A$ | droplet surface ($\mathrm{m}^2$) |
| $B_\mathrm{M}$ | Spalding mass transfer number (–) |
| $C_j$ | expansion coefficient (–) |
| $D$ | diffusion coefficient ($\mathrm{m}^2$/s) |
| $G$ | non-dimensional diffusion coefficient (–) |
| $\dot{m}_i$ | evaporation rate of component $i$ (kg/s) |
| $\dot{m}_{\mathrm{f},i}$ | evaporation mass flux of component $i$ (kg/($\mathrm{m}^2$s)) |
| $M$ | confluent hypergeometric function of the first kind (–) |
| $m$, $n$ | integer separation numbers (–) |
| $p$ | exponent (–) |
| $r$ | radial coordinate (m) |
| $Sh^*$ | modified Sherwood number (–) |
| $t$ | time (s) |
| $U$ | confluent hypergeometric function of the second kind (–) |
| $Y_i$ | mass fraction of mixture component $i$ (–) |
| $\overline{Y}_{20}$ | volume-average mass fraction of solute (–) |
| $Y_{\mathrm{sat},2}$ | mass fraction of solute at saturation (–) |
| *Greek symbols* | |
| $\alpha$ | non-dimensional rate of shrinkage of the droplet surface (–) |
| $\tilde{\alpha}$ | rate of shrinkage of the droplet surface ($\mathrm{m}^2$/s) |
| $\varepsilon$ | porosity (–) |
| $\vartheta$ | polar angle in spherical coordinates (rad) |
| $\lambda_j$ | eigenvalue (–) |
| $\xi$ | non-dimensional radial coordinate (–) |
| $\rho_\mathrm{l}$ | liquid density (kg/$\mathrm{m}^3$) |
| $\varphi$ | azimuthal angle in spherical coordinates (rad) |

predicting the formation of hollow particles in the drying of skim milk. These authors identified the increase of the vapor pressure at the beginning of the second drying stage as the reason for the inflation of the dried particles. Ford [5] presented a model for the drying of aqueous NaCl solution droplets, which includes the diffusional transport of the solute in the liquid, the formation of crystallization nuclei, the growth of the crystals, and the formation and growth of a solid crust on the surface of the drying droplet. In the modeling of the solid crust, a constant porosity of $\varepsilon = 0.7$ is assumed, which is typical for a dense packaging of monodispersed spheres. The result of Ford's calculations is a morphology chart for the dry particles, which specifies the internal structure of the particles (i.e., hollow or solid spheres) as a function of initial droplet radius, drying temperature, drying air humidity, and initial salt concentration. Elapsed times to the formation of the solid crust are also given. The typical time to crust formation for NaCl solution droplets is 90 ms for an initial droplet diameter of 20 μm, initial salt concentration of 200 kg/$\mathrm{m}^3$, a drying temperature of 80 °C, and zero ambient air humidity. Yarin, Brenn and coworkers [6,7] investigated this behavior of aqueous NaCl solution droplets using an acoustic levitator. These authors identified a characteristic parameter in the non-dimensional diffusion equation for mass transport of the solute in the liquid, which may be used for characterizing the drying regimes with solid and hollow sphere formation.

It is the aim of the present work to provide an analytical solution for the concentration fields in the droplet as a function of time and space during evaporation in order to predict the tendencies of the droplets to form hollow or solid dry particles. The solution is valid for cases with linear decrease of the droplet surface area with time. The mathematical function developed is valid for arbitrary ratio of surface shrinkage rate to diffusion coefficient of the solute in the liquid and predicts the formation of high solute concentrations at the surface of the sphere for high drying rates accurately.

## 2. Mathematical description

We treat the problem of evaporation of a spherical droplet consisting of a binary mixture of a liquid (called the solvent) and a dissolved solid substance with very low vapor pressure (called the solute). The evaporation rate is, among others, determined by the Sherwood number imposed by the convective situation of the droplet in its host medium. The mass transfer inside the droplet, however, is considered to be controlled by diffusion and by the shrinkage of the droplet surface, i.e., we do not consider recirculating motions inside the droplet. The problem is therefore governed by the continuity and energy equations. Liquids like the ones relevant for spray drying exhibit Lewis numbers of $\mathrm{O}(10^2)$, which means that the temperature relaxation goes much faster than mass diffusion. We therefore assume flat temperature profiles in the droplet and concentrate exclusively on the calculation of the concentration profiles in the liquid [8]. The droplet temperature as a function of time must of course be determined for an evaluation of the equations we develop here. In our calculations we determine it as the wet-bulb temperature of water at the ambient temperature and relative humidity chosen.

### 2.1. Definition of the problem

For the droplet liquid at rest, the continuity equation for each component of the binary liquid mixture reduces to the diffusion equation. We therefore start from the diffusion equation for the mass fraction $Y_i$ of a mixture component $i$ in the droplet. Since the droplet shape is assumed to be spherical all the time, it makes sense to formulate the Laplace operator on the right-hand side of the diffusion equation in the spherical coordinates $r$, $\vartheta$, and $\varphi$. The diffusion equation for the substance $i$ in the binary mixture droplet, formulated in the mass fraction $Y_i$, reads

$$\frac{\partial Y_i}{\partial t} = D\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial Y_i}{\partial r}\right) + \frac{1}{r^2 \sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial Y_i}{\partial\vartheta}\right) + \frac{1}{r^2\sin^2\vartheta}\frac{\partial^2 Y_i}{\partial\varphi^2}\right], \tag{1}$$

where $D$ is the binary diffusion coefficient in the liquid. In this equation, subscript $i = 1$ will be used for the solvent, and $i = 2$ for the solute. The boundary condition is that the mass fraction $Y_i(r = a(t))$ at the droplet surface be determined by equation

$$-D\frac{\partial Y_i}{\partial r} - \frac{\mathrm{d}a}{\mathrm{d}t}Y_i = \frac{\dot{m}_{\mathrm{f},i}}{\rho_1} \quad \text{at } r = a(t) \text{ for all times } t, \tag{2}$$

where $a$ is the time-dependent droplet radius, $\rho_1$ is the liquid density and $\dot{m}_{\mathrm{f},i}$ the mass flux of substance $i$ across the droplet surface. The latter may be a function of the angles $\vartheta$ and $\varphi$, but it may be formulated as the ratio $\dot{m}_i/A$ of the evaporation rate of component $i$ and the droplet surface $A$ in the case that there is no dependency on these angles. It is furthermore zero for the dissolved solid substance, which is assumed to be non-evaporating here. For the solvent, the evaporation rate is determined by the convective situation of the droplet in the ambient gaseous medium. Further to this boundary condition, the solution of Eq. (1) must satisfy the regularity condition that the radial derivative of the mass fraction profile vanishes at the droplet center, i.e., that

$$\frac{\partial Y_i}{\partial r} = 0 \quad \text{at } r = 0 \text{ for all times } t \tag{3}$$

and the initial condition that the mass fraction profile of substance $i$ in the droplet at time $t = 0$ (which must also satisfy the boundary and regularity conditions, of course) be given as a function

$$Y_i(t = 0, r) = Y_{i0}(r) \quad \text{for all } r \text{ at time } t = 0. \tag{4}$$

The spatial domain on which the problem is to be solved, i.e., the volume of the spherical droplet, is time-dependent. We therefore choose a similarity approach for solving the differential equation and transform it according to $t_1 = t$, $\xi = r/a(t)$ into the form

$$a^2\frac{\partial Y_i}{\partial t} = \frac{\mathrm{d}a^2}{\mathrm{d}t}\frac{\xi}{2}\frac{\partial Y_i}{\partial\xi} + \frac{D}{\xi^2}\frac{\partial}{\partial\xi}\left(\xi^2\frac{\partial Y_i}{\partial\xi}\right) + \frac{D}{\xi^2}\left[\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial Y_i}{\partial\vartheta}\right) + \frac{1}{\sin^2\vartheta}\frac{\partial^2 Y_i}{\partial\varphi^2}\right], \tag{5}$$

where we have dropped the subscript 1 from the time $t_1$ [6]. The boundary, regularity, and initial conditions transform accordingly. The boundary condition (2) now reads

$$-D\frac{\partial Y_i}{\partial\xi} - \frac{\tilde{\alpha}}{2}Y_i = \frac{a(t)\dot{m}_{\mathrm{f},i}}{\rho_1} \quad \text{at } \xi = 1 \text{ for all times } t, \tag{6}$$

where we have denoted the rate of shrinkage $\mathrm{d}a^2/\mathrm{d}t$ by $\tilde{\alpha}$. The regularity condition (3) now reads $\partial Y_i/\partial\xi = 0$ at $\xi = 0$, and the initial condition (4) becomes

$$Y_i(t = 0, \xi) = Y_{i0}(\xi) \quad \text{for all } \xi \text{ at time } t = 0. \tag{7}$$

We now render the whole problem non-dimensional with the droplet lifetime $t_1$ defined as

$$t_1 = \frac{a_0^2}{\tilde{\alpha}}\left[\left(\frac{\overline{Y}_{20}}{(1-\overline{Y}_{20})\rho_{s2}/\rho_1 + \overline{Y}_{20}}\right)^{2/3} - 1\right], \tag{8}$$

and the initial droplet radius $a_0$. Here we denote the mean initial mass fraction of solute in the droplet by $\overline{Y}_{20}$, the solid density by $\rho_{s2}$, and the solvent density by $\rho_1$. The droplet lifetime as defined by equation (8) is obtained under the assumption that, at the end of the drying process, the remaining particle has the density $\rho_{s2}$ of the compact solid substance, which is the longest possible lifetime. Using these reference quantities, we obtain the non-dimensional form of the differential equation (5) as

$$\bar{a}^2\frac{\partial Y_i}{\partial\tau} = \alpha\frac{\xi}{2}\frac{\partial Y_i}{\partial\xi} + \frac{G}{\xi^2}\frac{\partial}{\partial\xi}\left(\xi^2\frac{\partial Y_i}{\partial\xi}\right) + \frac{G}{\xi^2}\left[\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial Y_i}{\partial\vartheta}\right) + \frac{1}{\sin^2\vartheta}\frac{\partial^2 Y_i}{\partial\varphi^2}\right], \tag{9}$$

where

$$\bar{a} = \frac{a}{a_0}, \quad \tau = \frac{t}{t_1}, \quad \alpha = \tilde{\alpha}\frac{t_1}{a_0^2}, \quad G = D\frac{t_1}{a_0^2}.$$

The boundary condition (6) is rewritten and yields

$$-\frac{\partial Y_i}{\partial\xi} - \frac{\alpha}{2G}Y_i = \frac{a(\tau)\dot{m}_{\mathrm{f},i}}{D\rho_1} \quad \text{at } \xi = 1 \text{ for all times } \tau, \tag{10}$$

and the initial condition becomes

$$Y_i(\tau = 0, \xi) = Y_{i0}(\xi) \quad \text{for all } \xi \text{ at time } \tau = 0. \tag{11}$$

### 2.2. Analytical solution of the problem

We see that the differential equation (9) is separable in the case that the (non-dimensional) shrinkage rate of the droplet surface $\alpha$ is time-independent, i.e., if the droplet evaporates according to the so-called $d^2$-law. The droplet surface as a function of time then reads $A = A_0 + 4\pi\tilde{\alpha}t$, which is in non-dimensional form $\bar{a}^2 = 1 + \alpha\tau$. With the separation approach $Y_i(\tau, \xi, \vartheta, \varphi) = T(\tau)\cdot F(\xi)\cdot H(\vartheta)\cdot X(\varphi)$ we obtain the ordinary differential equations

$$\begin{aligned}\frac{\bar{a}^2}{G}\frac{T'}{T} &= \left(\frac{\xi}{2}\frac{\alpha}{G}+\frac{2}{\xi}\right)\frac{F'}{F}+\frac{F''}{F}\\ &\quad+\frac{1}{\xi^2}\left[\frac{1}{\sin\vartheta}\frac{1}{H}\frac{\mathrm{d}}{\mathrm{d}\vartheta}(\sin\vartheta\cdot H')+\frac{1}{\sin^2\vartheta}\frac{X''}{X}\right]\\ &:= -\lambda_j\frac{\alpha}{G},\end{aligned} \tag{12}$$

where primes denote derivatives w.r.t. the independent variables, and $\lambda_j$ is the separation constant. The differential equation for the function $T(\tau)$ is readily solved to yield

$$T(\tau) = C_\tau(1+\alpha\tau)^{-\lambda_j}, \tag{13}$$

where $C_\tau$ is a constant. The remaining differential equation for the functions of the non-dimensional radial coordinate $\xi$ and the angles $\vartheta$ and $\varphi$ is further separated to yield

$$\begin{aligned}&\xi^2\left[\left(\frac{\xi}{2}\frac{\alpha}{G}+\frac{2}{\xi}\right)\frac{F'}{F}+\frac{F''}{F}+\lambda_j\frac{\alpha}{G}\right]\\ &\quad= -\frac{1}{\sin\vartheta}\frac{1}{H}\frac{\mathrm{d}}{\mathrm{d}\vartheta}(\sin\vartheta\cdot H')-\frac{1}{\sin^2\vartheta}\frac{X''}{X}\\ &\quad:= n(n+1),\end{aligned} \tag{14}$$

where $n$ is an integer number. From this equation we obtain the differential equation

$$\xi^2F''+\left(\frac{\alpha}{2G}\xi^2+2\right)\xi F'+\left[\lambda_j\frac{\alpha}{G}\xi^2-n(n+1)\right]F=0 \tag{15}$$

in the non-dimensional radial coordinate $\xi$. Further separation of Eq. (14) yields the two differential equations

$$-\sin\vartheta\frac{1}{H}\frac{\mathrm{d}}{\mathrm{d}\vartheta}(\sin\vartheta\cdot H')-n(n+1)\sin^2\vartheta=\frac{X''}{X}:=-m^2 \tag{16}$$

with the integer number $m$. From these equations we obtain

$$\frac{1}{\sin\vartheta}\frac{\mathrm{d}}{\mathrm{d}\vartheta}(\sin\vartheta\cdot H')+\left[n(n+1)-\frac{m^2}{\sin^2\vartheta}\right]H=0 \tag{17}$$

and

$$X''+m^2X=0 \tag{18}$$

as the differential equations governing the shape of the mass fraction profiles in the directions of the angles $\vartheta$ and $\varphi$. In the separation, the number $m$ must be zero or an integer number, and the number $n$ must satisfy the relation $n \geqslant m$. Equation (17) is Legendre's differential equation with the general solution

$$H(\cos\vartheta) = C_1P_n^m(\cos\vartheta)+C_2Q_n^m(\cos\vartheta), \tag{19}$$

where the $P_n^m$ and $Q_n^m$ are the Legendre functions of the first and second kind, respectively, and $C_1$, $C_2$ are constants. Since we expect a finite solution at the poles of the sphere, we must exclude the functions of the second kind from the solution by setting $C_2 = 0$. Eq. (18) is a harmonic differential equation with the general solution

$$X(\varphi) = D_1\cos m\varphi + D_2\sin m\varphi, \tag{20}$$

where $D_1$, $D_2$ are constants.

Solving the differential equation (15) in the non-dimensional radial coordinate requires some more effort. Equation is of the type 2.215 in the book by Kamke [9], and it belongs to the group of hypergeometric ordinary differential equations. The equation may be transformed by

$$F(\xi) = \mu^k\cdot\zeta(\mu), \tag{21}$$

with $\mu = \xi^2$, to yield the new form

$$\mu\zeta''+\left(\frac{\alpha}{4G}\mu+\frac{3}{2}+2k\right)\zeta'+(k+\lambda_j)\frac{\alpha}{4G}\zeta=0. \tag{22}$$

In the transformation (21), the exponent $k$ is to be determined as a solution of the equation

$$4k^2+2k-n(n+1)=0, \tag{23}$$

which yields the results $k_1 = n/2$ and $k_2 = -(n+1)/2$. A further transformation of (22) by $\zeta(\mu) = Z(x)$ with $x = \gamma\mu$ (where $\gamma$ is a constant) leads to the final form of the differential equation, which reads

$$xZ''+\left(-x+\frac{3}{2}+2k\right)Z'-(k+\lambda_j)Z=0, \tag{24}$$

where we had to take $\gamma = -\alpha/(4G)$. Eq. (24) is readily identified as the confluent hypergeometric equation [10]. After transformation back into the function $F(\xi)$, we have the general solution of (15) reading

$$\begin{aligned}F(\xi) = \xi^{2k}\Big[&E_1\cdot M\left(\lambda_j+k,\frac{3}{2}+2k,\gamma\xi^2\right)\\ &+E_2\cdot U\left(\lambda_j+k,\frac{3}{2}+2k,\gamma\xi^2\right)\Big],\end{aligned} \tag{25}$$

where $E_1$, $E_2$ are constants. The functions $M$ and $U$ are confluent hypergeometric functions of the first and second kind, respectively. The function of the first kind is also called Kummer's function. The two functions are defined as follows [10]:

$$\begin{aligned}M(a,b,x) = 1+\frac{a}{b}x+\frac{a(a+1)}{b(b+1)}\frac{x^2}{2!}\\ +\frac{a(a+1)(a+2)}{b(b+1)(b+2)}\frac{x^3}{3!}+\cdots.\end{aligned} \tag{26}$$

$$U(a,b,x)=\frac{\pi}{\sin\pi b}\left[\frac{M(a,b,x)}{\Gamma(1+a-b)\cdot\Gamma(b)}-x^{1-b}\frac{M(1+a-b,2-b,x)}{\Gamma(a)\cdot\Gamma(2-b)}\right]. \tag{27}$$

With these functions, the general solution (25) reads

$$\begin{aligned}F(\xi)=&\,E_1\cdot\xi^{2k}M\left(\lambda_j+k,\frac{3}{2}+2k,-\frac{\alpha}{4G}\xi^2\right)\\&+E_2\cdot\frac{\pi}{\sin\left[\pi\left(\frac{3}{2}+2k\right)\right]}\\&\cdot\left[\xi^{2k}\frac{M\left(\lambda_j+k,\frac{3}{2}+2k,-\frac{\alpha}{4G}\xi^2\right)}{\Gamma\left(1+\lambda_j-\frac{3}{2}-k\right)\cdot\Gamma\left(\frac{3}{2}+2k\right)}\right.\\&\left.-\left(-\frac{\alpha}{4G}\right)^{-\frac{1}{2}-2k}\frac{1}{\xi}\frac{M\left(\lambda_j-\frac{1}{2}-k,\frac{1}{2}-2k,-\frac{\alpha}{4G}\xi^2\right)}{\Gamma\left(\lambda_j+k\right)\cdot\Gamma\left(\frac{1}{2}-2k\right)}\right].\end{aligned} \tag{28}$$

An inspection of Eq. (28) reveals that the function $U$ with the coefficient $E_2$ diverges as $\xi\to 0$, i.e., at the droplet center. This part of the solution must therefore be excluded by setting $E_2 = 0$. Furthermore we see that, in order that the term with $E_1$ does not diverge at the droplet center, we must select positive values of $k$ or zero, i.e., the solution $k = n/2$ of Eq. (23). We therefore obtain as the general solution of the differential equation (15) the function

$$F(\xi)=C_\xi\xi^n M\left(\lambda_j+\frac{n}{2},\frac{3}{2}+n,-\frac{\alpha}{4G}\xi^2\right). \tag{29}$$

We can now compose an eigensolution of the diffusion equation (9), according to our separation approach, from the functions given by Eqs. (13), (19), (20), and (29) in the form

$$\begin{aligned}Y_{i,j}(\tau,\xi)=&\,(1+\alpha\tau)^{-\lambda_j}\cdot[C_{1nm,j}\cos m\varphi+C_{2nm,j}\sin m\varphi]\\&\cdot\xi^n P_n^m(\cos\vartheta)\cdot M\left(\lambda_j+\frac{n}{2},\frac{3}{2}+n,-\frac{\alpha}{4G}\xi^2\right)\end{aligned} \tag{30}$$

and obtain the general solution of the equation as the linear combination

$$\begin{aligned}Y_i(\tau,\xi)=&\sum_j\sum_{n,m}(1+\alpha\tau)^{-\lambda_j}\\&\cdot[C_{1nm,j}\cos m\varphi+C_{2nm,j}\sin m\varphi]\\&\cdot\xi^n P_n^m(\cos\vartheta)\cdot M\left(\lambda_j+\frac{n}{2},\frac{3}{2}+n,-\frac{\alpha}{4G}\xi^2\right)\end{aligned} \tag{31}$$

of all these eigensolutions. An inspection of Eq. (31) reveals that the functions satisfy the regularity condition at the droplet center.

For treating a most realistic case, we assume the profiles of the mixture component mass fractions to be radially symmetric by setting $n = m = 0$. This simplification turns Eq. (31) into the form

$$Y_i(\tau,\xi)=\sum_j C_j(1+\alpha\tau)^{-\lambda_j}\cdot M\left(\lambda_j,\frac{3}{2},-\frac{\alpha}{4G}\xi^2\right), \tag{32}$$

which describes the mass fraction profiles in the sphere. The coefficients $C_j$ in this series expansion are determined by satisfying the initial condition (11). The boundary condition (10) must be satisfied by all eigensolutions separately, i.e., by all Kummer's functions in (32). This boundary condition is particularly simple for the non-evaporating solute $i = 2$, since it is homogeneous in this case. Formulating this condition by substituting the summand of (32) into the boundary condition (10), we obtain for $\dot{m}_2=0$ the requirement that

$$M'\left(\lambda_j,\frac{3}{2},x\right)-M\left(\lambda_j,\frac{3}{2},x\right)=0\quad\text{at }\xi=1. \tag{33}$$

In this equation, the prime denotes the derivative of the function $M$ w.r.t. the third argument $x=-\alpha\xi^2/(4G)$. Making use of the identity [10]

$$(j-i)M(i,j+1,x)=j[M(i,j,x)-M'(i,j,x)], \tag{34}$$

we see that Eq. (33) can be satisfied by letting

$$\lambda_0=\frac{3}{2}\quad\text{or for }M\left(\lambda_j,\frac{5}{2},-\frac{\alpha}{4G}\right)=0 \tag{35}$$

i.e., we obtain solutions of our problem by choosing the eigenvalues $\lambda_j$ as 3/2 (for $j = 0$) or such that the value of the quantity $-\alpha/(4G)$ becomes the $j$th zero ($j > 0$) of the function $M$ in (35). These zeros are computed following a procedure given by Abramowitz and Stegun [10].

The expansion coefficients $C_j$ in (32) must be determined such that the expansion (32) represents the initial distribution of the mass fraction $Y_{i0}(\xi)$ in the droplet at $\tau = 0$. For doing this, we need an orthogonality relation for the eigenfunctions of the problem. Inspection of the ordinary differential equation (15) for our special case $n = 0$ reveals that the quantity $-\alpha\lambda_j/G$ is an eigenvalue of the differential operator

$$\frac{\partial^2}{\partial\xi^2}+\left(\frac{\alpha}{2G}\xi+\frac{2}{\xi}\right)\frac{\partial}{\partial\xi}. \tag{36}$$

This operator is not symmetric with respect to the formation of scalar products in Hilbert spaces, so that we cannot expect the eigenfunctions satisfying the differential equation (15) to be orthogonal, nor can we expect that the system of functions in (32) be complete nor that the eigenvalues be real. However, trying to convert the operator into a symmetrical form by multiplying the differential equation (15) for $n = 0$ with a function $q$, i.e., requiring that

$$qF''+q\left(\frac{\alpha}{2G}\xi+\frac{2}{\xi}\right)F'=\frac{\partial}{\partial\xi}\left(q\frac{\partial F}{\partial\xi}\right)=-\lambda_j\frac{\alpha}{G}qF, \tag{37}$$

we find that we can make the differential operator symmetrical. This requires appropriate determination of the function $q$, for which we obtain a differential equation by differentiating the central part of (37) and comparing the terms obtained with the left-hand part [11]. This comparison leads to a differential equation for the function $q$, which has the solution

$$q(\xi) = \xi^2 \mathrm{e}^{\alpha\xi^2/(4G)}. \tag{38}$$

Since this procedure worked just with a multiplication of the original ordinary differential equation (15) (for $n = 0$) with a function $q$, the solution (29) with $n = 0$ remains valid, and, in order to obtain the coefficients $C_j$ in the expansion (32), we can now make use of the orthogonality of two functions $M$ when multiplied by the function $q$ given by (38). This means that we can now calculate the coefficients $C_j$ such that the expansion (32) represents the initial distribution $Y_{20}(\xi)$ of the mass fraction of the solute in the droplet liquid. The equation for the $C_j$ reads

$$C_j = \frac{\int_{\xi=0}^{1} qY_{20}(\xi)M(\lambda_j, 3/2, -\alpha\xi^2/(4G))\,\mathrm{d}\xi}{\int_{\xi=0}^{1} qM(\lambda_j, 3/2, -\alpha\xi^2/(4G)) \cdot M(\lambda_j, 3/2, -\alpha\xi^2/(4G))\,\mathrm{d}\xi}. \tag{39}$$

With this equation, the problem of diffusional mass transport of the solute inside the droplet is solved for the special case of radial symmetry of the concentration fields. With the field of the mass fraction $Y_2(\tau,\xi)$ of the solute known, we can easily calculate the field $Y_1(\tau,\xi)$ of the solvent as $Y_1(\tau,\xi) = 1 - Y_2(\tau,\xi)$.

## 3. Evaluation of the equations and example calculations

We evaluate the equations found in the preceding section assuming that the initial distribution of the solute mass fraction may be described as a polynomial of the form

$$Y_{20}(\xi) = a_0 + a_p\xi^p. \tag{40}$$

This is the simplest initial mass fraction distribution which may satisfy both the boundary condition at $\xi = 1$ and the regularity condition at the droplet center. The coefficients in (40) are determined by the boundary condition and by the requirement that the integral of the distribution $Y_{20}(\xi)$ over the droplet volume must yield $\overline{Y}_{20}$ times the initial droplet volume, which is a known quantity for the liquid solution at the beginning of the drying process. The coefficients read

$$a_0 = \overline{Y}_{20}\frac{p + \frac{\alpha}{2G}}{p + \frac{p}{p+3}\frac{\alpha}{2G}} \quad \text{and} \quad a_p = -\overline{Y}_{20}\frac{\frac{\alpha}{2G}}{p + \frac{p}{p+3}\frac{\alpha}{2G}}. \tag{41}$$

In these equations, $\overline{Y}_{20}$ is the overall mean mass fraction of solute in the droplet at $\tau = 0$. For the exponent $p$ we will take the value of 5 in our calculations below. Having chosen a set of input data $a_0$, $\overline{Y}_{20}$, $D$ and $\tilde{\alpha}$, we first compute the eigenvalues $\lambda_j$ from (35) and the expansion coefficients $C_j$ from (39), and then compute the values of the function (32) at various times $0 \leqslant \tau \leqslant 1$ and non-dimensional radial positions $0 \leqslant \xi \leqslant 1$, varying the ratio $\tilde{\alpha}/D$ of the rate of droplet shrinkage to the diffusion coefficient of the solute in the solvent (or of the corresponding non-dimensional quantities $\alpha$ and $G$). For the rate of droplet shrinkage we take typical values obtained in our levitator experiments [6] in order to ensure realistic cases. The diffusion coefficient we take as concentration-independent, which is a valid assumption for a wide range of concentrations. The rate of shrinkage may be associated with the Sherwood number of mass transfer across the droplet surface and with other relevant parameters according to the equation

$$\alpha = \frac{\rho_{\mathrm{g}}}{\rho_1}\frac{D_{\mathrm{g}}}{D}GSh^* \ln(1 + B_{\mathrm{M}}), \tag{42}$$

where $\rho_{\mathrm{g}}$ is a mean gas density around the droplet, $\rho_1$ is the liquid solvent density, $D_{\mathrm{g}}$ the diffusion coefficient of the evaporated solvent in the ambient air, $Sh^*$ a modified Sherwood number as introduced in [12], and $B_{\mathrm{M}}$ the Spalding mass transfer number. This equation quantifies the change of the Sherwood number with time to be realized according to the temporal change of $B_{\mathrm{M}}$ due to the increasing concentration of solute near the surface of the droplet during the drying process. A similar equation was developed in [7]. In that paper, however, the convective mass transfer of liquid vapor from the droplet surface was caused by an acoustic streaming flow. The Sherwood number had therefore to be modeled accordingly.

As an example we calculate the drying of droplets of an aqueous sodium chloride solution at two different rates of droplet shrinkage $\alpha$. We take $\alpha$ as constant, as assumed in our theory, choosing different ratios of $\alpha/G$ far below and far above 1. The following two figures show the computational results achieved by evaluating Eq. (32) together with (35) and (39), using the above procedure. It turned out that a maximum number of 10 terms in the expansion (32) is sufficient to have an accurate description of the mass fraction profiles. The curves in the two figures are profiles for different non-dimensional times, starting with the initial states $\tau = 0$. The uppermost curves in the figures show the situation where the saturation concentration $Y_{\mathrm{sat},2}$ is reached at the surface of the droplet for the first time. The data shown in Fig. 1 belong to the case of a low evaporation rate and show flat concentration profiles, as expected, since the diffusive transport of solute in the droplet liquid has enough time in this case to redistribute the solute from the surface of the droplet towards its center during solvent evaporation. The profiles in Fig. 2, in contrast, are found for a relatively high evaporation rate of the solvent. Consequently, larger gradients of the mass fraction of the solute are seen. The profiles show a clear tendency of the drying droplets to turn into hollow

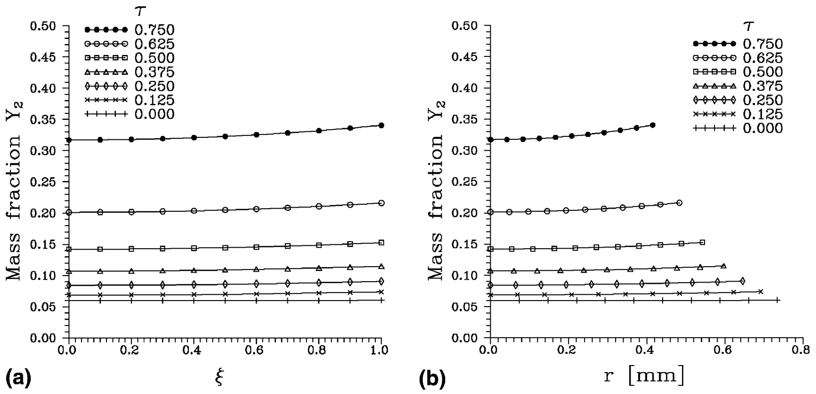

Fig. 1. Evolution of the mass fraction $Y_2$ of solute in a drying droplet of a sodium chloride solution as a function (a)—of the non-dimensional radial coordinate $\xi$, (b)—of the dimensional radial coordinate, showing the shrinkage of the droplet with time. Data: $\rho_1 = 1000\,\text{kg/m}^3$, $\rho_{s2} = 2165\,\text{kg/m}^3$, $\tilde{\alpha} = -0.46 \times 10^{-9}\ \text{m}^2/\text{s}$, $D = 1.61 \times 10^{-9}\ \text{m}^2/\text{s}$, $\overline{Y}_{20} = 0.06$, $Y_{\text{sat},2} = 0.2629$, $a_0 = 0.734\,\text{mm}$. Diffusion coefficient and saturation mass fraction correspond to a droplet wet bulb temperature of 8 °C, i.e., to an ambient air temperature of 20 °C and a relative humidity of 4.7%. The value of the exponent $p$ in the initial distribution is 5.

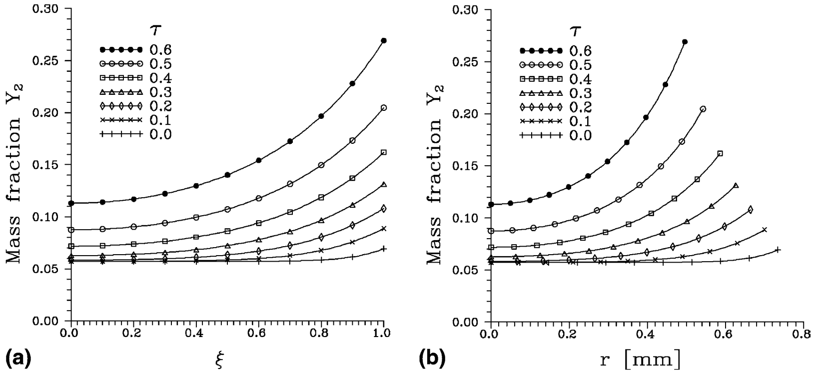

Fig. 2. Evolution of the mass fraction $Y_2$ of solute in a drying droplet of a sodium chloride solution as a function (a) – of the non-dimensional radial coordinate $\xi$, (b) – of the dimensional radial coordinate, showing the shrinkage of the droplet with time. Data: $\rho_1 = 1000\,\text{kg/m}^3$, $\rho_{s2} = 2165\,\text{kg/m}^3$, $\tilde{\alpha} = -5.64 \times 10^{-9}\ \text{m}^2/\text{s}$, $D = 1.61 \times 10^{-9}\ \text{m}^2/\text{s}$, $\overline{Y}_{20} = 0.06$, $Y_{\text{sat},2} = 0.2629$, $a_0 = 0.734\,\text{mm}$. Diffusion coefficient and saturation mass fraction correspond to a droplet wet bulb temperature of 8 °C, i.e., to an ambient air temperature of 20 °C and a relative humidity of 4.7%. The value of the exponent $p$ in the initial distribution is 5.

spherical shells for the high evaporation rate, while the low evaporation rate clearly leaves enough time for producing solid spheres. Another effect is that the time elapsed until saturation is reached at the droplet surface is longer for the lower evaporation rate. The analytical solution of the diffusion equation is seen to yield physically plausible results.

## 4. Conclusions

An analytical solution of the diffusion equation on a spherical domain with moving boundary is developed in order to quantify the diffusive transport of the components of a binary mixture inside a droplet during evaporation of the solvent. The diffusion equation governing the problem is solved using a separation approach for the special case of time-independent rate of shrinkage of the droplet, i.e., for a droplet drying according to the $d^2$-law. The dependency of the solute concentration on the radial coordinate is found to be given by Kummer's functions, which belong to the group of confluent hypergeometric functions, while the dependencies on the angles $\vartheta$ and $\varphi$ in spherical coordinates are given by Legendre and sine or cosine functions, respectively. The solution presented for the special case that the mass fractions of the mixture components depend on the radial coordinate only is valid for arbitrary values of the ratio of rate of droplet shrinkage to diffusion coefficient in the droplet liquid. An investigation of the analytical function for typical drying situations reveals the expected behavior, i.e., the formation of large concentration gradients in the droplet at high evaporation rates, and flat concentration profiles for slow drying. Times elapsed until the state of saturation is reached are quantified. Other phenomena in drying like precipitation and crust formation are not included in the calculations.

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