

Drying of a liquid droplet suspended in its own vapour

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Abstract

In this work we consider the spray drying of colloidal solutions or sols, a process that leads to the production of nanoporous powders, which are of importance in numerous manufacturing applications. In this paper an initial model of this process is formulated by considering the evaporation of a liquid droplet suspended in its own vapour. Mass, momentum, and energy balances are given for the liquid and vapour phases of the problem. Perturbation analysis is applied to the system, showing that the system is effectively isobaric, and it is shown that surface tension may be neglected. The subsequent moving boundary problem is solved numerically and the results of this process are presented.

Contents

1	Introduction	2
2	Model Development	3
2.1	Model Equations	3
2.2	Perturbation Analysis	5
3	Numerical Techniques	7
4	Results and Conclusions	8

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1 Introduction

The spray drying of colloidal solutions, or sols, is of importance in numerous manufacturing applications [1]. One such application is the production of nanoporous ceramic powders. Our overall aim is to develop models of this process in order to determine how changes in the chemistry within individual sol droplets, and in the drying conditions, alter the morphology and characteristics of the resulting powders. In this paper we present an initial model for the spray drying process in which we consider a liquid droplet evaporating within an environment of its own vapour.

A number of simplified models of spray drying have been considered in the literature. Sirignano [2] discusses the processes of droplet evaporation in the context of fuel combustion. Whilst he formulates quite complex models of the process, he makes little mention of such evaporation concepts as vapor pressure or surface tension. Van der Lijn [3] models the spray drying of liquid foods. He does, however, make numerous oversimplifications, including neglecting the thermal distributions in the droplet. Sano and Keey [4] consider the formation of hollow sphere morphologies during the spray drying of sol droplets. It is assumed *a priori*, however, that a bubble will form inside the droplet without proof that this is the cause of the hollow sphere phenomenon.

The spray drying of sols involves four distinct phases. First, the atomised colloidal solution is released into the drying chamber. Once in the chamber, the droplets evaporate until colloid at the surface solidifies to form a crust. Third; liquid is evaporated through the crust and this causes the crust to thicken. Finally, when most of the liquid has been evaporated, the microsphere is heated until it exits the drying chamber. This process can lead to a variety of morphologies, the most desirable being a solid sphere. Less desirable morphologies include tori and hollow spheres.

As noted earlier, in this paper we simplify the above drying process to one in which a single droplet, containing liquid, but no colloid, is being dried in a quiescent atmosphere that contains only the liquid in vapour form. This allows the consideration of only the first two drying phases mentioned above, with the second phase continuing until the droplet is fully evaporated. There are two reasons for modelling this simplified process. First, it provides confirmation of the equations that will be used in the more complex models that follow from this work, and second, it allows contemplation of the method by which the moving boundary can be managed numerically.

We now consider the derivation of the model equations describing this process.

2 Model Development

Model Assumptions: In order to facilitate the development of a mathematical model that describes the physical system introduced above, the following simplifying assumptions have been made:

1. The liquid phase is incompressible.
2. The gas phase is ideal, inviscid, and infinite.
3. Both the liquid and gas phases are homogeneous/pure.
4. There are no outside forces acting upon the system.
5. The entire system is spherically symmetric.
6. The gas phase has significantly lower density than the liquid phase.
7. Each phase is initially in equilibrium internally.

As a result of the above assumptions, the following equations can be formulated.

2.1 Model Equations

Inside the droplet: Given Assumption 1, the density of the liquid phase is constant, and the liquid phase velocity is zero. Therefore, the heat balance equation within the droplet is [5]

$$\rho_l \hat{C}_l \frac{\partial T_l}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \lambda_l \frac{\partial T_l}{\partial r} \right), \quad (1)$$

where ρ is the density, \hat{C} is the constant volume specific heat, T is the temperature, λ is the thermal conductivity, r is the radial coordinate, and t is the temporal coordinate. The subscript l indicates that the variable is in the liquid phase.

Initially, by Assumption 7, the temperature within the droplet is uniformly at T_0 . Furthermore, at the centre of the droplet, symmetry requires that

$$\frac{\partial T_l}{\partial r} = 0. \quad (2)$$

Outside the droplet: Noting Assumption 2, the ideal gas law may be applied, namely [6],

$$p_v = C_v \bar{R} T_v, \quad (3)$$

where p is the pressure, C is the concentration, and \bar{R} is the universal gas constant. The subscript v indicates that the variable is in the vapour phase.

Noting Assumption 3, a material balance outside the droplet yields [5]

$$\frac{DC_v}{Dt} = -\frac{C_v}{r^2} \frac{\partial}{\partial r} (r^2 u_v), \quad (4)$$

where u is the radial velocity, and $\frac{D}{Dt}$ represents the material derivative [6].

Conservation of momentum in the gas phase [5] can be simplified using the continuity equation, Assumption 2 and Assumption 4 to give

$$C_v \frac{Du_v}{Dt} = -\frac{1}{m_m} \frac{\partial p_v}{\partial r}, \quad (5)$$

where m_m is the molar mass of the substance.

The spherically symmetric energy balance equation is [5]

$$m_m C_v \hat{C}_v \frac{DT_v}{Dt} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \lambda_v \frac{\partial T_v}{\partial r} \right) - \frac{p_v}{r^2} \frac{\partial}{\partial r} (r^2 u_v). \quad (6)$$

Initially, the concentration, the temperature, and the velocity of the gas are assumed to be uniformly C_∞ , T_∞ , and 0, respectively. Furthermore, at a sufficiently large distance from the droplet, the temperature and concentration are assumed to be T_∞ and C_∞ , respectively, for all times.

At the surface of the droplet: The liquid and gas phases are in thermal contact at the surface, and thus continuity of temperature applies [7]. That is,

$$T_v = T_l \quad (7)$$

at the surface of the droplet.

All thermal energy conducted into the droplet from the gas is used for either sensible heating of the droplet, or the supply of the latent heat energy to evaporating material. As such, the heat flux surface condition can be formulated as [8]

$$\lambda \frac{\partial T_v}{\partial r} = \lambda_l \frac{\partial T_l}{\partial r} - L \rho_l \dot{R}, \quad (8)$$

where L is the latent heat of vaporisation of the material and $\dot{R} \equiv \frac{dR}{dt}$, where $R(t)$ is the outer radius of the droplet at time t .

For mass conservation at the interface, the mass flux out of the liquid phase must equal the mass flux into the gas phase. This can be represented algebraically as [8]

$$C_v(u_v - \dot{R}) = -\frac{\rho_l \dot{R}}{m_m}. \quad (9)$$

The pressure at the surface of the droplet, due to Assumption 6, is found by generalising the Clapeyron equation to unequal pressures [9]. This gives

$$\frac{1}{\rho_l} \frac{dp_l}{dt} - \frac{1}{m_m C_v} \frac{dp_v}{dt} = -\frac{L}{T_v} \frac{dT_v}{dt}, \quad (10)$$

where the full time derivative is

$$\frac{d}{dt} \equiv \frac{\partial}{\partial t} + \dot{R} \frac{\partial}{\partial r}.$$

Considering the balance of forces occurring at the surface leads to an equation giving the difference between the gas and liquid pressures at the surface [8]

$$p_v = p_l - \frac{\sigma}{R} + \rho_l \dot{R} u_v, \quad (11)$$

where σ is the surface tension, which is a known function of time.

Initially, the droplet radius is R_0 .

2.2 Perturbation Analysis

Nondimensionalisation: We nondimensionalise the system using the following equations

$$\begin{aligned} t &= t_0 \tilde{t}, & r &= R_0 \tilde{r}, & C_v &= C_\infty \tilde{C}_v, \\ u_v &= \frac{R_0}{t_0} \tilde{u}_v, & T_l &= T_0 \tilde{T}_l, & T_v &= T_\infty \tilde{T}_v, \\ R(t) &= R_0 \tilde{R}(\tilde{t}), & \dot{R} &= \frac{R_0}{t_0} \tilde{R}', & p_l &= C_\infty \bar{R} T_\infty \tilde{p}_l. \end{aligned}$$

All constants in these equations are known except t_0 , which will be chosen in the present work to represent the timescale of evaporation. This choice, however, is not unique. Applying these equations leads to the following system (neglecting the tilde notation for simplicity - all variables from here are dimensionless):

At $t = 0$,

$$\begin{aligned} T_l &= 1, & T_v &= 1, \\ C_v &= 1, & u_v &= 0. \end{aligned} \quad (12)$$

At $r = 0$,

$$\frac{\partial T_l}{\partial r} = 0. \quad (13)$$

For $0 < r < R(t)$,

$$\frac{\partial T_l}{\partial t} = \nu_1 \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial T_l}{\partial r} \right). \quad (14)$$

At $r = R(t)$,

$$T_v = \nu_5 T_l, \quad (15)$$

$$\frac{\partial T_v}{\partial r} = \nu_6 \frac{\partial T_l}{\partial r} - \nu_7 \dot{R}, \quad (16)$$

$$C_v(u_v - \dot{R}) = -\nu_8 \dot{R}, \quad (17)$$

$$\frac{dp_l}{dt} = \nu_8 \frac{1}{C_v} \frac{d(C_v T_v)}{dt} - \nu_9 \frac{1}{T_v} \frac{dT_v}{dt}, \quad (18)$$

$$C_v T_v = p_l - \nu_{10} \frac{\sigma}{R} + \nu_{11} \dot{R} u_v. \quad (19)$$

For $r > R(t)$,

$$\frac{DC_v}{Dt} = -\frac{C_v}{r^2} \frac{\partial}{\partial r} (r^2 u_v), \quad (20)$$

$$C_v \frac{Du_v}{Dt} = -\nu_2 \frac{\partial}{\partial r} (C_v T_v), \quad (21)$$

$$C_v \frac{DT_v}{Dt} = \nu_3 \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial T_v}{\partial r} \right) - \nu_4 \frac{C_v T_v}{r^2} \frac{\partial}{\partial r} (r^2 u_v). \quad (22)$$

As $r \rightarrow \infty$,

$$T_v \rightarrow 1, \quad (23)$$

$$C_v \rightarrow 1. \quad (24)$$

Finally, $R(0) = 1$.

The exact form of the dimensionless parameters ν_1 through ν_{11} in the above equations is given elsewhere [10].

Perturbation Analysis: From here, we consider the material in question to be water. The remaining constants are taken to be within the ranges $273.15 \text{ K} \leq T_0 \leq 423.15 \text{ K}$, $323.15 \text{ K} \leq T_\infty \leq 423.15 \text{ K}$, $1 \text{ mol} \leq C_\infty \leq 20 \text{ mol}$, and $1 \mu\text{m} \leq R_0 \leq 100 \mu\text{m}$. Additionally, t_0 is taken to be the value that sets $\nu_7 = 1$. As mentioned earlier, this means that t_0 represents the time scale of evaporation of the droplet.

This then leads to the following ranges for the dimensionless parameters

$$\begin{aligned}
46 \leq \nu_1 \leq 72 & & 2.2 \cdot 10^{10} \leq \nu_2 \leq 2.8 \cdot 10^{14} & & 7900 \leq \nu_3 \leq 2.1 \cdot 10^5 \\
0.247 \leq \nu_4 \leq 0.247 & & 0.6 \leq \nu_5 \leq 1.3 & & 23.4 \leq \nu_6 \leq 47.5 \\
2800 \leq \nu_8 \leq 5.6 \cdot 10^4 & & 3 \cdot 10^4 \leq \nu_9 \leq 8 \cdot 10^5 & & 0.01 \leq \nu_{10} \leq 31.3 \\
& & 9.8 \cdot 10^{-12} \leq \nu_{11} \leq 2.6 \cdot 10^{-6} & &
\end{aligned}$$

It can be concluded that $1/\nu_2$ is a very small parameter, representing the ratio of kinetic energy density to pressure, and can be neglected in a first order perturbation expansion. Neglecting $1/\nu_2$ in Equation 21 and matching with Equations 23 and 24, we find that

$$C_v T_v = 1. \quad (25)$$

This result implies that the system is effectively isobaric. Furthermore, we note from Equation 21 that neglecting $1/\nu_2$ elicits a temporal boundary layer in u_v , however, the analysis of this effect will not be considered here.

Applying Equation 25 to Equations 20 and 22 and equating gives

$$\frac{\partial T_v}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 u_v T_v) = \frac{2\nu_3}{1 + \nu_4} \frac{T_v}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial T_v}{\partial r} \right). \quad (26)$$

Substituting Equation 25 into Equation 18 and integrating in time gives, at $r = R(t)$,

$$p_l = 1 - \nu_9 \log \frac{T_v}{T_k}, \quad (27)$$

where T_k is the value of T_v which sets $p_l = 1$. Substituting Equation 25 into 19 and matching with 27 gives

$$\log \frac{T_v}{T_k} = -\frac{\nu_{10}}{\nu_9} \frac{\sigma}{R} + \frac{\nu_{11}}{\nu_9} \dot{R} u_v. \quad (28)$$

Equations 14, 26, and 28, with associated boundary and initial conditions 12, 13, 15, 16, and 17, constitute our simplified model for drying a liquid droplet in its own vapour.

3 Numerical Techniques

In solving this system of equations we first transform the equations inside the droplet using $r = xR(t)$, where $0 < x < 1$, as this fixes the surface of the droplet at $x = 1$. Outside the droplet, we apply $r = x + R(t)$, where

$0 < x < x_{max}$, as this fixes the surface of the droplet at $x = 1$ while ensuring that grid evolution does not cause loss of data at distances away from the droplet at late times. The resulting equations are then discretised using a control volume method. The non-linear term in Equation 26 is linearised by supposing that the temperature is approximately uniform across the control volume, and applying a Newton scheme to the system to ensure realistic convergence.

The algorithm used in solving the system was implemented in Matlab and is as follows:

```

Initialise Variables
while  $t < t_{max}$  and  $R(t) > 0$  do
  while Convergence has not occurred do
    Determine  $T_l$  distribution (using discrete form of equation 14)
    Determine  $T_v$  distribution (using discrete form of equation 28)
    Approximate  $\dot{R}$  (using equation 16)
    Determine  $u_v$  distribution (using discrete form of equation 26)
    Find error due to the lagging of  $u_v$  and  $\dot{R}$  for convergence criteria
  end while
  Take time step ( $t \leftarrow t + \Delta t$ )
end while

```

4 Results and Conclusions

Figures 1(a) and (b) show the early and long time evolution, respectively, of the size of a water droplet initially at 350 K as it is dried in an atmosphere of its own vapour initially at a concentration $C_\infty = 20 \text{ mol m}^{-3}$, in which $T_\infty = 368 \text{ K}$. Initially, the temperature of the liquid at the surface of the droplet, T_l , is considerably lower than the temperature, T_v , of the vapour surrounding it and this induces the boundary layer effect observed in Figure 1(a) in which the droplet undergoes condensation at early times before evaporation takes place. This effect, although not overly significant in the current simulation, can become pronounced under more extreme drying conditions and/or for different liquids, and has been observed experimentally [11].

Figures 1(a) and (b) also depict a second set of results in which the surface tension, σ , of the water droplet has been set to zero. The two simulations ($\sigma \neq 0$ and $\sigma = 0$) are indistinguishable, and we found this to be true for a wide range of initial temperatures, initial vapour concentrations, and initial droplet radii. This demonstrates that surface tension plays a negligible role in the evaporation of water droplets in their own vapour.

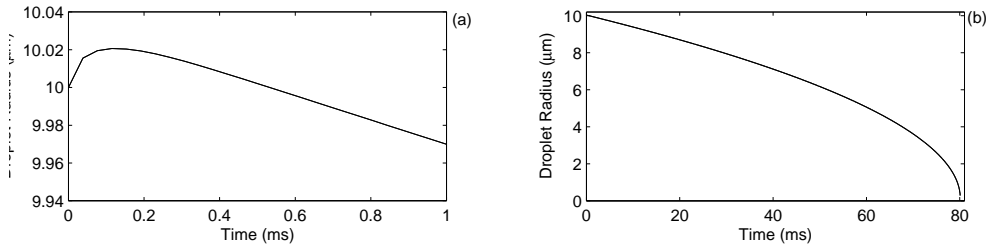


Figure 1: Graphs of water droplet radius vs. time for (a) early times and (b) long times.

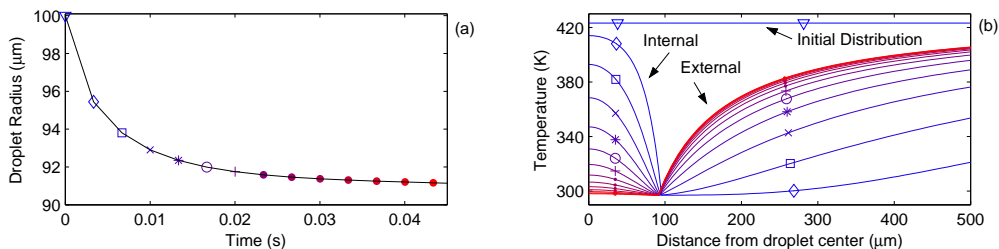


Figure 2: Graphs of early time (a) water droplet radius and (b) temperature distributions.

Godsave [12] observed, empirically, that the radius of a drying liquid droplet is generally of the form $R(t)^2 = R_0^2 - \beta t$, where β is the evaporation constant and R_0 is the initial droplet radius. Least squares fitting of the data in Figure 1(b) to this function produces a very close match (RMS error of less than 0.2%) for a β value of $0.0013 \text{ mm}^2 \text{ s}^{-1}$, thus suggesting that our model may produce results close to those observed experimentally. A more direct comparison of the model with relevant experimental data is currently being considered by the authors.

Figures 2(a) and (b) show the evolution of droplet radius and temperature distribution, respectively, at early times, for a water droplet with $T_0 = T_\infty = 423 \text{ K}$ and $C_\infty = 1 \text{ mol m}^{-3}$. In contrast with the condensation effect observed in Figure 1(a), we see that in Figure 2(a) the droplet evaporates rapidly. The temperature, T_l , for the liquid is approximated by the dimensioned form of Equation 28, which after noting that σ and ν_{11} are negligible becomes $T_l \approx \tilde{T}_k T_\infty$. In the simulation in Figure 2, the initial temperature of the droplet is much higher than that predicted by this relation, and as such the liquid temperature drops rapidly during the early stages of drying as shown in Figure 2(b). The heat associated with this loss in temperature is used to evaporate the droplet, leading to the profile shown in Figure 2(a).

In conclusion, we note that we have developed a model for the drying of a

liquid droplet in its own vapour. The computational algorithm described in Section 3 has successfully implemented the moving boundary aspect of the problem, and as such the same technique may be applicable to more complex models. We demonstrated using perturbation techniques that the system can be considered to be isobaric, and surface tension was shown to be negligible. The model was found to agree with empirical observations of experimental data.

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