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Abstract: Hydrogen extraction from nature is a time-consuming and energy-intensive procedure. Most of the current methods of extracting H_2 are not eco-friendly, and the thermochemical copperchlorine (Cu-Cl) cycle is a promising alternative since the ingredients are continuously recycled within the cycle without discharging pollutants into the atmosphere. In this study, the heat recovered from molten cuprous chloride (CuCl) salt produced in one of the reactors and quenched in a water bath is analyzed numerically to determine the amount of thermal energy that can be recovered and improve the efficiency of the Cu-Cl cycle. The quenching cell is simulated in an inert atmosphere since CuCl is highly reactive in the presence of oxygen. The interactions of various diameters of CuCl droplets within nitrogen (N₂) are numerically modeled in COMSOL Multiphysics. Silver chloride (AgCl) is also used in this study to validate the phase-change process. It was discovered in this study that during the free fall, the outer surface of the molten droplets solidifies, and the phase change of droplets slowly propagates radially inwards, which slows down the energy dissipation. It was also determined that the average internal temperature of the droplet does not change substantially with droplet diameter or quenching height. Based on this study, the net energy recovered after quenching was calculated to be around 23 kJ during 1 kg of H₂ production.

Keywords: heat capacity; phase changing material (PCM); hydrogen production; thermochemical cycles; silver chloride; cuprous chloride; numerical analysis; heat recovery; liquid-to-solid phase change

1. Introduction

The human population's needs are increasingly becoming more energy dependent than ever. To reduce the carbon footprint and to cater to the energy needs, alternative renewable methods of energy conversion and fuel production are adopted. Hydrogen (H_2) is a clean fuel with high energy density; hence, it offers a promising avenue to address the world's energy problem. However, H_2 cannot be found in its elemental form in nature, so it must be extracted from hydrogen-rich compounds. Currently, the majority of hydrogen used originates from reforming processes [1-3]. The thermochemical Cu-Cl cycle is one of the clean hydrogen production methods and a viable solution to producing fuel in high quantities. Naterer et al. [4–8] and Lewis et al. [9] have extensively researched the operation and feasibility of the Cu-Cl cycle in which water is decomposed into its constituents via a sequence of reactions performed internally using intermediate copper and chloride compounds. There are two main advantages of this cycle: 1. all the chemicals are recycled in a closed internal loop on a continuous basis, and 2. the operational temperature is much lower than the other thermochemical cycles [8,10], being approximately 530 °C. In the first step of the cycle, the CuCl is mixed with hydrochloric acid (HCl_(aq)) at stoichiometric proportions to produce hydrogen, as shown in Figure 1. At step 4 of this cycle, the CuCl is regenerated by decomposition of CuO·CuCl₂ at 530 $^{\circ}$ C in the decomposition reactor. The regenerated CuCl is in the molten state, which after being cooled to 90 °C is dissolved in aqueous HCl to form the analyte solution of the electrolysis step (Equation (1)), the



Citation: Jianu, O.A.; Rajasekaran, B. Transient Thermo-Fluid Analysis of Free Falling CuCl and AgCl Droplets with Liquid-to-Solid Phase Change. *Energies* **2022**, *15*, 4628. https:// doi.org/10.3390/en15134628

Academic Editor: David Chiaramonti

Received: 29 May 2022 Accepted: 22 June 2022 Published: 24 June 2022

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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). step in which H₂ is being produced. The temperature of molten CuCl obtained from the decomposition reactor ranges from 430 to 530 °C. To recover energy from molten CuCl, obtained from step 4, the CuCl is directly quenched into water. The quenching in water is necessary, as gaseous $HCl_{(aq)}$ from the hydrolysis reactor (step 3 in Figure 1) is added, forming the aqueous HCl_(aq) solution required for CuCl dissolution. By recovering heat during the quenching of CuCl, the thermal efficiency of the cycle is increased, making the cycle a suitable hydrogen production method. Ghandehariun [11] used pinch analysis to determine the maximum recoverable heat from CuCl. Based on the existing industrial process on molten materials, Ghandehariun [11–14] extensively studied heat recovery from molten salts for several configurations and found that direct contact using steam or air as a coolant to be the most favorable method. Manan et al. [15] carried out an experiment on quenching CuCl directly into $HCl_{(aq)}$ at room temperature on different configurations and reported that quenching in HCl was not favorable due to its vapor formation as it could enter the decomposition reactor, causing safety concerns. Jianu et al. [16–18] comprehensively researched the dissolution of CuCl and developed correlations of the ternary system in the Cu-Cl cycle. The CuCl was found to be predominantly immiscible in water in the absence of HCl [18]. Based on Ghandehariun [11–14], Manan [15] and Jianu's [16–18] findings, the best way to recover maximum heat is to quench CuCl directly in water with inert N_2 atmosphere. The quenched water is used in the electrolysis step, as shown in Figure 1.



Figure 1. Stoichiometric chart of the Cu-Cl cycle (adopted from [4-8]).

The amount of water for quenching is calculated based on the stoichiometric proportion in step 3. The quenching process of molten CuCl involves a liquid to solid phase change since the temperature of molten CuCl is close to its phase change temperature. Calvet [19] numerically studied the phase change process of a PCM by intensifying the effective thermal conductivity of the PCM using COMSOL Multiphysics [20]. Jalal [21] used COMSOL Multiphysics to study the forced convection cooling on packaged vents. Mayank [22] examined the effect of conduction on a PCM in a spherical and cylindrical vessel during a phase change process using COMSOL Multiphysics with a fixed temperature boundary. Azad [23] performed both numerical and experimental studies to investigate the effects of heating temperature on the phase change of a PCM with natural convection.

Eduard [24] analyzed the temperature gradients inside the PCM capsules using an energy equation model, and their results were validated with the experimental results. Nabeel [25] performed analytical, numerical and experimental investigations for thermal energy storage by melting and ensuing convection of PCM in various shaped enclosures. After a profound analysis of the above studies, a new numerical model is developed to examine the CuCl and N₂ interactions.

2. Description of Methodology

Quenching CuCl in water can be separated into two major parts: a. CuCl free falls through an inert atmosphere, and b. a CuCl droplet enters the water contained in a cell. As CuCl is highly reactive in the presence of oxygen (O_2) and forms more stable complexes, the quench cell is purged with an inert N_2 atmosphere to ensure an oxygen-free environment. In this study, the interaction between N_2 and the CuCl droplet in free fall is modeled numerically using COMSOL Multiphysics to determine the amount of heat lost by the droplet to the N_2 environment. The main objective of this model is to determine the amount of energy transferred to the water after the CuCl loses heat during the free-fall.

2.1. Assumptions

The following assumptions are made to simplify the numerical model and reduce computation time:

- 1. N₂ is considered to be an ideal incompressible fluid, as the numerical simulation is primarily focused on evaluating heat interactions between N₂ and the droplet.
- 2. To reduce the complexity, the shape of the droplet is assumed to be spherical, and its shape does not change with time [14,26]. Furthermore, it is assumed that the bubble retains its spherical shape, and any forces acting on the bubble will not deform it since the outer layer solidifies in less than a second, as justified in the results section.
- 3. To have consistent thermophysical properties throughout the simulation, the droplet is presumed to be homogeneous and will be a function of temperature both in its molten and solid-state.
- 4. A preliminary study with varying density and constant volume revealed that approximate change in mass is less than 2% for the desired time range. The volume change is the same as mass change, as the volume is proportional to the mass. As the volume change is negligible, the moving mesh method in COMSOL Multiphysics is not applied here, which could lead to undesired results, and it is computationally expensive. Abiding by the law of mass conservation, the density is taken as an average value between solid and liquid phases.
- 5. According to the conservation of mass as in Equation (1), mixing within the droplet is caused by density changes with respect to time.

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho u) = 0 \tag{1}$$

However, since the density is taken as constant due to insignificant volume change in the droplet, the internal velocity (u) becomes zero as in Equation (1), thereby there is no mixing within the droplet.

2.2. Numerical Model

A 2D axisymmetric geometry is adopted to model the interactions between droplet and N₂, as shown in Figure 2. An axisymmetric approach was selected to reduce the finite element calculations during simulation. The droplet is placed in the center of the N₂ domain, where N₂ enters at the bottom and exits at the top of the domain. The basic measurements of the domain are tabulated in Table 1. To simulate a free-falling droplet, N₂ is made to flow relative to the fixed droplet. The relative acceleration of N_2 is calculated using Equation (2).

$$a_d - \frac{Drag + F_g}{m_d} = 0 \tag{2}$$

$$C_d = \frac{24}{Re} + \frac{2.6\left(\frac{Re}{5.0}\right)}{1 + \left(\frac{Re}{5.0}\right)^{1.52}} + \frac{0.411 * \left(\frac{Re}{2.63 * 10^5}\right)^{-7.94}}{1 + \left(\frac{Re}{2.63 * 10^5}\right)^{-8.00}} + \frac{0.25 * \frac{Re}{10^6}}{1 + \frac{Re}{10^6}}$$
(3)

$$Drag = \frac{1}{2}\rho V^2 A C_d \tag{4}$$

$$Re = \frac{\rho DV}{\mu} \tag{5}$$

where a_d is the acceleration of the droplet as it is free-falling through the N₂ atmosphere (m/s²), F_g is the force due to gravity on the droplet (N), and C_d is the coefficient of drag (Equation (3)) [27], the drag is calculated using Equation (4), Re is the Reynolds number (Equation (5)), ρ is the density of N₂ (kg/m³), V is the velocity of N₂ (m/s), and μ is the dynamic viscosity of N₂ (Pa·s).



Figure 2. The 2D model geometry of the model with the droplet and the N_2 domain with their inflow and outflow directions.

The velocity profile of the droplet was determined by solving the above equations numerically in COMSOL Multiphysics. As the N_2 flow starts from the state of rest, numerical analysis is modeled to transition from laminar to turbulent flow by constant monitoring of Re using probes. The overall simulation time is capped at one second, as the free fall

distance covered by the droplet by that time is around 5 m, and it will be impractical for a lab scale model.

Description	Name	Value
Radius of droplet	R _d	0.0025, 0.005, 0.01 (m)
Width of the domain	width	0.006, 0.01, 0.02 (m)
Height of the domain	height	0.027, 0.045, 0.09 (m)
Initial temperature of the droplet (AgCl)	T _{i,d}	745, 740, 740 (K)
Temperature of the N ₂	T _f	298.15 (K)
Density of CuCl	ρ_{CuCl}	$4038.075 (kg/m^3)$
Melting point of CuCl	T _m , _{CuCl}	700 (K)
Latent heat of CuCl	L _m , _{CuCl}	71.51587 (J/g)
Density of AgCl	ρ_{AgCl}	5179 (kg/m ³)
Melting point of AgCl	$T_{m,AgCl}$	727 (K)
Latent heat of AgCl	L _m , AgCl	92,105 (J/kg)

Table 1. Geometric dimensions and thermophysical properties of the model.

2.2.1. Momentum Equation

The nitrogen is treated as a Newtonian fluid, and then the incompressible form of the Naiver–Stokes equation in a coordinate free representation is expressed as in Equation (6).

$$\frac{D\vec{V}}{Dt} = \vec{g} - \frac{\nabla P}{\rho} + \nu \nabla^2 \vec{V}$$
(6)

 \overrightarrow{V} is the velocity of the N₂ in (m/s), \overrightarrow{g} represents the gravitational acceleration (m/s²), ν represents the kinematic viscosity (m²/s), ρ is the density of the N₂ (kg/m³), P represents the pressure and V_∞ is the free-stream velocity. The walls of the droplet are taken as a no-slip boundary. For a stationary wall, that means that V = 0 and $V = V_{\infty}$ at infinity. As there is no mixing inside the droplet, the Naiver–Stokes equation is applied only for the N₂ domain.

As the N_2 flow reaches the turbulent regime, the Reynolds-averaged Navier–Stokes (RANS) is used for conservation of momentum. Menter's shear-stress transport (SST) two-equation model with realizability constraints is adopted to capture the turbulence effects, as it can resolve the flow all the way down to the wall [28].

2.2.2. Energy Equation

For modeling the interactions between the droplet and the N_2 , the energy equation is applied for both the droplet and N_2 domain. The conservation of energy is expressed as

$$\rho C_p \frac{\partial T}{\partial t} + \rho C_p u \cdot \nabla \mathbf{T} + \nabla \cdot \mathbf{q} = 0 \tag{7}$$

$$q = -k\nabla T \tag{8}$$

where ρ is the density and C_p is the thermal capacity. The thermal conductivity, k, describes the relationship between the heat flux vector q and the temperature gradient ∇T in $q = -k\nabla T$, which is Fourier's Law of heat conduction. As it was determined that there is no mixing inside the droplet, energy change due to the viscous dissipation can be neglected. As the droplet does not react with N₂, for the numerical simulation, the boundaries of the droplet can be treated as a wall, which implies that heat transfer occurs across the boundaries of the droplet, and there is no mass transfer across it. Rate of conduction in the droplet and the rate of convection by the N₂ are equal at the boundaries of the droplet.

$$Q_{Conduction} = Q_{Convection} \tag{9}$$

$$-k(T)\frac{\partial T}{\partial r} = h(T_s - T_{\infty})$$
(10)

2.3. Thermophysical Properties

The specific heat capacity is a critical property for the heat recovery study. Rajasekaran and Jianu [29] developed a model that predicts the variation of specific heat capacity with temperature using distinctive physical approaches at different temperatures, as shown in Figure 2. This model was developed based on the existing electromotive force (EMF) and thermal data from various literature. In their model, the specific heat results of AgCl and CuCl were compared, as the AgCl and CuCl have similar material properties. [29]

The solid to liquid phase transition temperature of AgCl is 727 K. For AgCl, the thermal conductivity (k) and the dynamic viscosity (μ) are given by Equations (11) and (12) [30–32]:

$$k_{AgCl} = 296 \mathrm{T}^{-1} \tag{11}$$

$$\mu_{AgCl} = \mathbf{A} + \mathbf{BT} + \mathbf{CT}^2 + \mathbf{DT}^3 \tag{12}$$

where A = 6.91305, B = -0.447411×10^{-2} , C = -6.49368×10^{-6} , D = 5.41584×10^{-9} . Zamfirescu [33] reported that CuCl can be considered as a molecular liquid above its melting point. Due to the absence of experimental data on CuCl, the low temperature molecular liquid's empirical relations are used for dynamic viscosity and thermal conductivity for CuCl as given in Equations (13) and (14) [34]:

$$\mu_{CuCl} = 0.365 \exp\left(-6.95 + \frac{1418}{T}\right) \tag{13}$$

$$k_{CuCl} = \frac{0.19(1 - T_r)^{0.38}}{T_r^{1/6}}$$
(14)

where T_r is the reduced temperature ($T_r = T/T_c$) and T_c is the critical temperature.

2.4. Mesh Study

Meshing is a process where the geometry is broken into smaller elements and the governing differential equations are applied for all the elements. In any numerical analysis, the governing equations quantify the physical phenomenon, in this case, fluid flow and heat transfer, and as the equations are being solved numerically on each individual element for the entire computational domain, its accuracy highly depends on the number of elements in the computational domain. Though increasing the mesh density might result in accurate results, it comes with the cost of a longer computational time.

There are different types of meshing elements, and each has its own advantages and disadvantages. In this model, a triangular meshing model is adopted as the domain is irregular. The mesh density was maximized in the areas where the material undergoes a phase transition, as shown in Figure 3. In COMSOL Multiphysics, the quality of mesh can be analyzed using mesh statistics. Here, 3 computational domains are used for 3 different droplet sizes. The mesh structure remains the same for both AgCl and CuCl for the same droplet size, as given in Table 2.

Table 2. M	esh statistics.
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Radius of Droplet (R _d)	No. of Elements	Mesh Area (m ²)	Average Element Quality
0.01	1,762,171	0.0018	0.94
0.005	222,846	$4.5 imes10^{-4}$	0.94
0.0025	25,949	$1.65 imes10^{-4}$	0.87



Figure 3. The mesh structure for a droplet radius of 0.0025 m.

3. Simulation Results

3.1. Free Fall

Initially, the droplet's acceleration is equal to the gravitational acceleration. The acceleration of the droplet is affected due to the buoyant and drag force. The buoyant forces are neglected since the volume of the droplet is small; hence, the buoyant force is negligible compared to the drag force and force of gravity. Since the coefficient of drag (C_d) is a function of velocity, the drag force increases with velocity. Ghandehariun [12–14] evaluated the drag force by assuming C_d to be a constant, whereas in this study, the drag force Equations (3)–(5) were implemented into COMSOL; hence, C_d is not constant in this study. Thus, the accuracy of this numerical model is increased.

3.2. Phase Change Inside a Droplet

Figures 4–9 illustrate the temperature profile and velocity distribution of the droplet and the N₂ domain, where the velocity distribution is represented with colored streamlines, with arrows representing flow directions, and the color of the arrow represents the velocity of the flow. For the velocity distribution lines, red represents a higher velocity, and blue represents lower velocities. The temperature profile is represented as a field across the domain where red and blue represent higher and lower temperatures, respectively. It can be noted that the temperature distribution inside the droplet is not radially symmetric. This is due to the phase change of the molten salt as it loses heat to the surroundings. Since there is a variation in the flow velocity over the spherical surface, the solidification process does not only occur in the radial direction because the heat transfer process is three-dimensional. The flow of N_2 accelerates as we move along the surface of the sphere, and the flow reaches its near maximum velocity halfway through the surface. The interface that separates the solid and liquid, represented as a white line, propagates radially inwards as the solidification occurs. The heat transfer rates are higher at the lower end of the droplet due to the higher velocity of N_2 , whereas at the upper end of the droplet, the heat transfer rates are slower due to the reduced velocity and recirculation of N_2 above the droplet.



Figure 4. Temperature distribution of N_2 and the droplet (AgCl) domain with a droplet radius of 0.0025 m.



Figure 5. Temperature distribution of N_2 and the droplet (AgCl) domain with a droplet radius of 0.005 m.



Figure 6. Temperature distribution of N_2 and the droplet (AgCl) domain with a droplet radius of 0.01 m.



Figure 7. Temperature distribution of N_2 and the droplet (CuCl) domain with a droplet radius of 0.0025 m.





Figure 8. Temperature distribution of N_2 and the droplet (CuCl) domain with a droplet radius of 0.005 m.



Figure 9. Temperature distribution of N_2 and the droplet (CuCl) domain with a droplet radius of 0.01 m.

The initial temperature of the AgCl and CuCl droplets is 740 and 723 K, respectively. Consequently, the phase change for the 0.01 m droplet begins at 0.2 s and 0.17 s for CuCl and AgCl, respectively. When comparing the AgCl and CuCl droplets of identical diameters (Figures 4 and 7, respectively), it is evident that the change from the liquid to solid phase occurs much faster in AgCl compared to CuCl. The AgCl's higher thermal conductivity, almost double compared to CuCl at their respective phase-change temperatures, increases the thermal diffusivity of AgCl significantly, which, in turn, increases the heat transfer rates of AgCl. The lower thermal diffusivity of CuCl facilitates energy retention, which can be used for heat recovery.

3.3. Effects of Diameter

From the above Figures 4–6, it is evident that the phase change process is much slower as the diameter of the droplet increases. Since the heat transfer rate is proportional to the radius of the droplet, larger droplets will have higher heat transfer rates. Though the heat transfer rates are greater for larger droplets, it takes longer to cool due to the higher energy content in large droplets compared to smaller ones. Furthermore, the outer surface of the droplet solidifies in 0.02–0.3 s for all sizes of the droplets, which corroborates with our assumption of droplets being spherical in shape.

4. Heat Recovery Study

The quenching height in a quench cell is defined as the distance between the droplet's contact with the water surface and the droplet's origin, which the droplet travels in free-fall. At the end of the free fall, the droplets are not in thermal equilibrium with the water in the quench cell; hence, heat from the droplets is transferred to the water, thereby increasing its temperature. The required temperature for step 1, as shown in Figure 1, is approximately 90 °C. The rise in temperature of the water, from 80 °C, is determined using Equation (13). The effective temperature of the droplet is evaluated from the simulated results at the droplet's contact point with the water surface. The effective temperature is taken as constant for all the droplets for the specific quenching height. The number of droplets (N) is calculated based on the stoichiometric proportions and droplet volume. By maintaining stoichiometric proportions of CuCl, the number of droplets (N) will be a rational number in most cases. To determine the accurate final temperature of the water, the decimal part in the N is converted as a whole droplet with the decimal fraction of the volume. For example, the N for the droplet with a radius of 0.0025 m is 370.8740. The volume of the last droplet is taken as 0.8740 of the other droplets. The heat capacity and effective temperature of that droplet are assumed to be the same as the other droplets for the diameter considered. Figure 10 illustrates the rise in temperature of the water from 353 K, at a quenching height of 20 cm, for three different droplet diameters.

$$m_w C_{p,w} \Delta T = m_d C_{p,d} \Delta T \tag{15}$$

The final temperature of the droplet increases with the increase in droplet diameters, but the variation is not significant, as shown in Table 3. This is mainly due to the smaller quenching height and the phase change process. Generally, increasing the quenching height should lower the final temperature of the droplet; however, in this case, as the droplet free-falls through the N_2 , it cools and undergoes a phase change process. During the phase change process, the temperature of the droplet remains almost constant. Therefore, the average temperature of the droplet drops until the phase change and remains relatively constant as it solidifies.

The focus of previous literature was to classify various methodologies for heat recovery and the properties of CuCl. This study uses those literature studies to build a better model and estimates the amount of energy that can be recovered. It was determined that approximately 23 kJ of energy is recovered from the molten salt during the production of 1 kg of H₂, which, in turn, increased the temperature of the water.



Figure 10. Temperature increase in water by CuCl droplets for the quenching height of 20 cm.

Table 3. Properties of droplets for the quenching height at 20 cm for 1 kg of H_2 production.

Droplet Radius (m)	No. of Droplets (N)	Mass of Each Droplet (kg)	Final Temperature of Water (K)	Net Energy Recovered (kJ)
0.0025	371	0.0003	372.09	22.919
0.005	47	0.0021	372.46	23.367
0.01	6	0.0169	372.78	23.754

5. Conclusions

Literature reviews [11–18] show that quenching in water is the best method for recovering heat from molten CuCl in the thermochemical Cu-Cl cycle for hydrogen production. The molten CuCl and AgCl drip into small droplets, and the droplets are allowed to free fall in the inert N₂ atmosphere for up to one second. The AgCl and CuCl droplets of three different diameters were numerically modeled in COMSOL Multiphysics, and their thermal interactions with N_2 were studied. The outer surface of the droplet begins to solidify from 0.02 to 0.3 s for various droplet sizes, and the phase change propagates inward at different rates due to the non-uniform velocity around the droplet. It was determined that the heat transfer rates are significantly higher in AgCl compared to CuCl for identical droplet diameters since AgCl has higher thermal diffusivity. Based on the simulated numerical model, heat recovery analysis on quenched CuCl droplets shows the final temperature of the water increases from 353 to 372 K, and the water's final temperature does not change significantly with droplet diameter and the quenching height. This lower temperature variation on the droplets is caused by the phase change process, which begins as soon as the droplet free falls. This translates to 23 kJ of energy being recovered for every 1 kg of H₂ produced, thus increasing the overall efficiency of the thermochemical Cu-Cl cycle.

Author Contributions: Conceptualization, O.A.J.; Data curation, B.R.; Formal analysis, B.R.; Funding acquisition, O.A.J.; Methodology, B.R.; Project administration, O.A.J.; Resources, O.A.J.; Software, B.R.; Supervision, O.A.J.; Writing—original draft, B.R.; Writing—review & editing, O.A.J. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by NSERC Discovery.

Acknowledgments: The authors would like to acknowledge the University of Windsor and the Natural Science and Engineering Research Council (NSERC) for the financial support to enable this study.

Conflicts of Interest: The authors declare no conflict of interest.

Nomenclature

Cp	Specific heat (J/molK)
g	Gravitational acceleration (m/s ²)
H	Enthalpy (J/kg)
k	Thermal conductivity (W/mK)
L	Latent heat (J/kg)
V	Velocity (m/s)
р	pressure (N/m^2)
R _d	Radius of the droplet (m)
t	Time (s)
Т	Temperature (K)
T _i	Initial temperature
T _f	Final temperature
T _m	Melting temperature
T_{∞}	Temperature at infinite
Greek Symbols	
ρ	Density (kg/m ³)
μ	Dynamic viscosity (kg/ms)
ν	kinematic viscosity (m ² /s)
α	Thermal diffusion coefficient (m ² /s)
Subscripts	
i	initial
m	melting
с	critical
d	droplet

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