Report - Processes of freezing and thawing of porous media

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Contents

Abstract

This report studies different experiments and mathematical models of water and soil freezing. Soil freezing has important effects in order to understand deformation of grounds, such as for instance the roads in winter. The model is based on Stefan problem which is a particular type of free boundary problem. Several experiments and models with water, sand and gas are performed and then modelled with the use of COMSOL 3.3 in order to visualize the freezing evolution.

1 Introduction

In order to study the behavior of soil freezing, a free boundary problem is considered. This problem can be simplified as the following Stefan problem for $x \geq 0$ and $t > 0$:

$$\begin{aligned}
&\rho C_p \frac{\partial T}{\partial t}(x,t) = \nabla(\kappa \nabla T(x,t)) + Q && \text{(heat conduction equation)} \quad (1)\\
&\kappa \frac{\partial T}{\partial \eta}(x,t)\Big|_S - \kappa \frac{\partial T}{\partial \eta}(x,t)\Big|_L = Lv && \text{(Stefan condition)}\\
&T(x,0) = T_0 && \text{(boundary condition)}\\
&T(0,t) = T(t_0) && \text{(initial condition)}
\end{aligned}$$

where

$$\begin{aligned}
&\rho : \text{ density}\\
&C_p : \text{ heat capacity}\\
&\kappa : \text{ thermal conductivity}\\
&Q : \text{ heat source}\\
&\text{L} : \text{latent heat}
\end{aligned}$$

The problem describes the evolution of the boundary between solid phase and liquid phase and can be represented Figure 1.

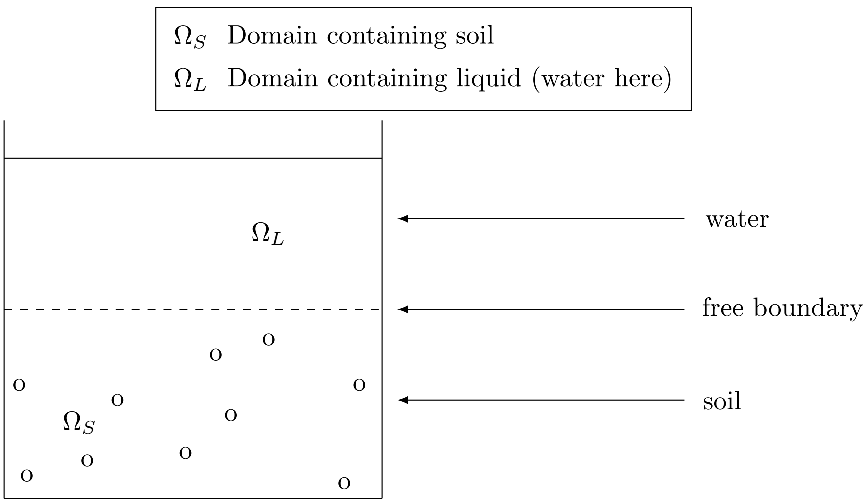


Figure 1: Illustration of the problem

In the case of Stefan problem, the boundary between liquid and solid phases can move in time, this boundary is called free boundary. For example in the case of regions where there is permafrost (ground that remains frozen), if permafrost melts the free boundary goes up and if it freezes the free boundary goes down.

However, two types of geometry has to be distinguished.

- Homogeneous geometry, where the volume of water freezing or thawing is studied
- Heterogeneous geometry, where the volume filled by sand and water in pores is studied

1.1 Homogeneous geometry

In the case of no phase change, i.e. when we consider only water or only ice, we compute the *internal energy* as

$$U(x,t) = \int_{T^*}^{T(x,t)} \rho C_p \, dT$$

In the case of phase change, i.e. if we have both ice and water, we compute the *enthalpy* as

$$H(x,t) = \underbrace{U(x,t)}_{\text{internal energy}} + L \cdot \mathcal{H}(T(x,t)) \tag{2}$$

where L is the latent heat and $\mathcal{H}$ is the Heaviside function defined as

$$\mathcal{H}(T(x,t)) = \begin{cases} 1 & \text{for} \quad T(x,t) > T^* \\ 0 & \text{for} \quad T(x,t) < T^* \end{cases} \tag{3}$$

where T^* is the temperature at the melting point, namely $T^* = 273$ Kelvin in case of pure water and $T^* = 276.8$ Kelvin in case of heavy water.

1.2 Heterogeneous geometry

The heat conduction equation (1) in this case is rewritten as

$$C_p \frac{\partial T}{\partial t}(x,t) + L \frac{\partial \theta}{\partial t}(T(x,t)) = \nabla(\kappa \nabla T(x,t))$$

where the power function θ is defined as

$$\theta(T(x,t)) = \eta \phi(T(x,t))$$

where

$$\phi(T(x,t)) = \begin{cases} 1 & \text{if} \quad T(x,t) \geq T^* \\ \left| \dfrac{T^*}{T(x,t)} \right|^b & \text{if} \quad T(x,t) < T^* \end{cases}$$

and η is the porosity.

2 Freezing of pure water $H_2 0$

2.1 Natural experiments

2.1.1 Beforehand computations

- **Energy needed to go from liquid state (25°C) to solid state (0°C) :**

Denote Q_1 as the energy needed to go from liquid state to solid state. This energy can be computed as

$$Q_1 = V \cdot L$$

where $V = 0.5$ L is the volume of water inside the bottle and $L = 334$ kJ/kg is the latent heat. Q_1 is therefore computed as

$$Q_1 = 0.5 \cdot 334 = 167 \text{ kJ}$$

- **Amount of energy needed to freeze 0.5 litter of water from 25 °C to 0 °C :**

The heat capacity of ice is given by $C = \dfrac{\Delta Q}{\Delta T} = 2.1$ kJ/°C, where ΔQ represents the amount of energy that is needed to freeze 0.5 litter of water from 25 °C to 0 °C and ΔT represents the change of temperature. Thus we can compute

$$\begin{aligned} \Delta Q &= C \cdot \Delta T \\ &= 2.1 \cdot 25 \text{ kJ} \\ &= 52.5 \text{ kJ} \end{aligned}$$

- **Time needed for the ice to be frozen**

It is difficult to deduce the time needed for the ice to freeze from the previous computations. Therefore, one can obtain such a result by checking the freezing power of the refrigerator. The freezer that is used can freeze 14 kg of water in 24 hours, which means that about 48 minutes are needed in order for 0.5 kg of water to be frozen, supposing that the temperature inside the freezer is −18 °C. Those results are not fully satisfactory when it comes to mathematical modelling and experiment as it will be discussed below.

2.1.2 Experiments and results

The experiment consists on placing a plastic bottle of 0.5 liters of water into the freezer to observe the time it takes to freeze.

After about 1 hour and a half to 2 hours, some ice starts to appear when shaking the bottle, but the water is not totally frozen. It takes about 3 hour and a half in order for the water in the bottle to be completely frozen, which is a lot more than in the computations section 2.1.1 above. One of the reasons could be that the temperature inside the freezer is not exactly at −18 °C. This can also be due to the fact that the bottle is made of plastic, which enables the water to keep warmer for a longer time. This is experimented by freezing the same amount of water (0.5 liters) in an open container and in a plastic bottle. The results can be observed Table 1. The cooling is a little bit faster in the open container than in the plastic bottle.

Time (in minutes)	Observation (bottle)	Observation (open container)
0	put it in the freezer	put it in the freezer
40	water	ice on the sides of the container
80	water	frozen only at the surface but water inside
120	starting to freeze	not totally frozen
150	not totally frozen	not totally frozen
180	not totally frozen	frozen
210	frozen	frozen

Table 1: Comparison of the cooling in a plastic bottle and in an open container

2.2 Experimental modelling

Consider the first derivative of the enthalpy (2) in respect to time :

$$\begin{aligned}\frac{\partial H}{\partial t}(x,t) &= \frac{\partial U}{\partial t}(x,t) + L \cdot \frac{\partial \mathcal{H}}{\partial T}(T(x,t)) \\ &= \rho C_p \frac{\partial T}{\partial t}(x,t) + L \cdot \frac{\partial \mathcal{H}}{\partial T}(T(x,t)) \\ &= \rho C_p \frac{\partial T}{\partial t}(x,t) + L \cdot \frac{\partial \mathcal{H}}{\partial T}(T(x,t) - T^*)\frac{\partial T}{\partial t}(x,t) \\ &= \nabla(\kappa \nabla T(x,t)) + Q\end{aligned}$$

where

$$Q = -L \cdot \frac{\partial \mathcal{H}}{\partial T}(T(x,t) - T^*)\frac{\partial T}{\partial t}(x,t) \tag{4}$$

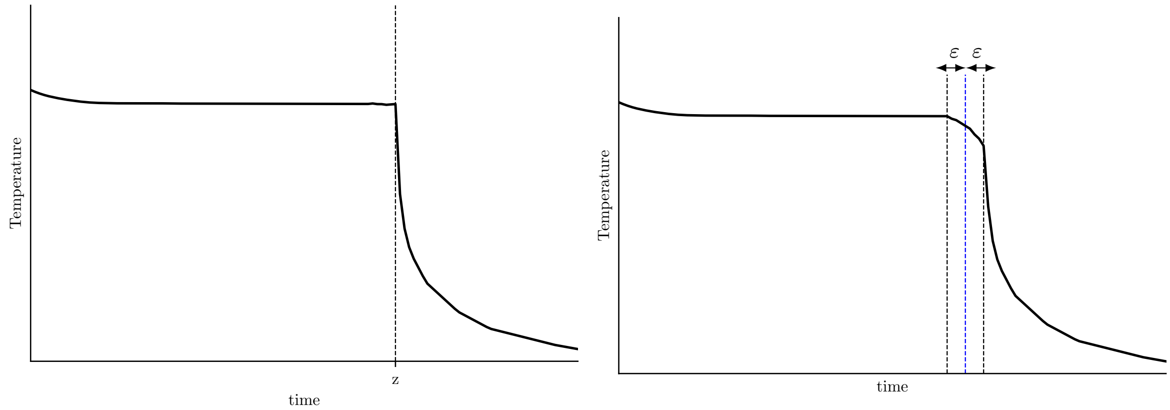
and by regularization it follows that

$$\begin{aligned}\frac{\partial U}{\partial t}(x,t) &= \rho C_p \frac{\partial T}{\partial t}(x,t) \\ &= \nabla(\kappa \nabla T(x,t)) - L \cdot \frac{\partial \mathcal{H}_\varepsilon}{\partial T}(T(x,t) - T^*)\frac{\partial T}{\partial t}(x,t)\end{aligned}$$

where ε is the scale of the regularization. The new regularized heat conduction equation can be written as

$$\rho C_p \frac{\partial T}{\partial t}(x,t) = \nabla(\kappa \nabla T(x,t)) - L \cdot \frac{\partial \mathcal{H}_\varepsilon}{\partial T}(T(x,t) - T^*)\frac{\partial T}{\partial t}(x,t)$$

The function $\mathcal{H}$ is represented Figure 2a. Regularization is needed for this function in order to insure existence properties at all points especially at the point z. The regularization function is denoted by $\mathcal{H}_\varepsilon$ and is constructed by substituting the function $\mathcal{H}$ by a smooth function on the interval $[-\varepsilon, +\varepsilon]$. See the illustration Figure 2b.



(a) Graph of the function $\mathcal{H}$

(b) Graph of the function $\mathcal{H}_\varepsilon$

Figure 2: Regularization of the Heaviside function $\mathcal{H}$

The freezing process is modelled with the use of Comsol 3.3, that solves the heat conduction equation (1) using the Finite Element Method. The water bottle is represented more simply in 3D as a cylinder of volume $V = 0.5$ L which is equivalent to a volume $V = 0.0005$ m^3, or in 2D as a rectangle. Let the radius of the cylinder be $r = 0.04$ m, therefore the height will be $H = \frac{1}{\pi} \cdot 0.3125 \approx 0.09947$ m. The 3D model is however more demanding in terms of computation time when the regularization parameter ε is small. Therefore, the bottle is modelled with Comsol 3.3 in 2D as a rectangle of size 0.08×0.09947 m. The rectangle is represented by symmetry in Comsol 3.3. The boundary condition is set at a temperature of $T_0 = 255$ Kelvin which corresponds to -18 °C (the temperature inside the freezer) and the initial condition to $T(t_0) = 300$ Kelvin which corresponds to the initial temperature of the water in the bottle. The heat source Q from equation (4) is computed using the regularized Heaviside function $\mathcal{H}_\varepsilon$:

$$Q = -L \cdot \frac{\partial \mathcal{H}_\varepsilon}{\partial T}(T(x,t) - T^*)\frac{\partial T}{\partial t}(x,t)$$

where $L = 334000$ J/kg denotes the latent heat of fusion for the ice.

In Comsol 3.3, the derivative of the Heaviside function is defined as $\texttt{fldc2hs}(T - 273)$. Thus, the heat source parameter Q is set to zero and the heat capacity becomes

$$C_p = C_p + L \cdot \texttt{fldc2hs}(T - 273, \varepsilon) \tag{5}$$

where C_p is computed using the fact that the units of the latent heat L and the heat capacity C_p are both in [J/kg] which gives

$$\rho(C_p + L\frac{\partial \mathcal{H}}{\partial T}(T(x,t) - T^*))\frac{\partial T}{\partial t}(x,t) = \nabla(\kappa \nabla T(x,t))$$

and using the heat conduction equation (1) it leads to

$$\begin{aligned} C_p &= \frac{1}{\rho\frac{\partial T}{\partial t}}\nabla(\kappa\nabla T) + \underbrace{\frac{1}{\rho\frac{\partial T}{\partial t}}Q}_{=0} \\ &= \frac{1}{\rho\frac{\partial T}{\partial t}}\rho(C_p + L\frac{\partial \mathcal{H}}{\partial T}(T - T^*))\frac{\partial T}{\partial t} \\ &= C_p + L\frac{\partial \mathcal{H}}{\partial T}(T - T^*) \end{aligned}$$

where ε represents the scale of the regularization and is taken as small as possible.

The other parameters used in the case of water are displayed in Table 2.

Density ρ	997 kg/m^3
Heat capacity C_p	4200 J/kg·K
Thermal conductivity κ	0.5918 W/m·K

Table 2: Parameter values for water

The time needed to cool the water up to 0 °C is computed using different types of meshes. It should take about 3 hours and a half for the water to freeze, which is in accordance with the results obtained during the experiment with the water bottle. The time in COMSOL 3.3 is computed between 0 and 10600 seconds, with a time step of 100 seconds. In this case, the maximum temperature obtained is 273.442 Kelvins, which means that the water is frozen.

The different results of the maximum temperature obtained for different meshes after 10600 seconds (about 3 hours and a half) of cooling can be observed Table 3.

Mesh	**Maximum temperature**
Extra fine	273.344 K
Finer	273.718 K
Fine	274.211 K
Normal	273.442 K
Coarse	258.714 K
Coarser	256.618 K
Extra coarse	255.66 K
Extremely coarse	255.448 K

Table 3: Freezing for different types of meshes

Videos of the cooling process computed with different meshes can be watched as follows :

- Finer mesh : `https://youtu.be/oWznctWiYmo`
- Normal mesh : `https://youtu.be/57Ub-C_GxhE`
- Coarser mesh : `https://youtu.be/4J4dDTokCDc`

The same time computation and the same parameters as above are used. Only half of the rectangle is visible in the videos since the model has been represented by symmetry.

For those computations, the regularization parameter used to calculate the heat capacity in equation (5) is $\varepsilon = 0.1$. The graphs of the data obtained from the values of the temperatures exported from COMSOL 3.3 at the point $(0, 0.05)$ for different time values between 0 and 16000 seconds with a time step of 100 seconds can be viewed Figure 3.

3 Freezing of porous media

3.1 Experiment with water and sand

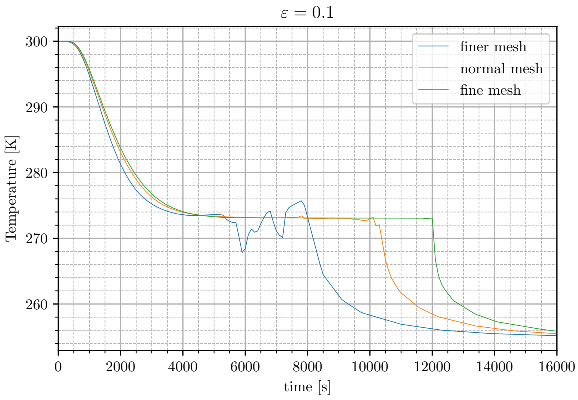
3.1.1 Computation of porosity using experimental sand ST 06/12 PAP

Several different experiments are performed. The first one consists on freezing a certain amount of sand ST 06/12 PAP with water in order to observe the expansion of ice. This is done by adding 16 mL of sand ST 06/12 PAP of diameter 0.94 µm to a test tube that is then filled again by water up to the same level as sand. The water that should be added in order to reach the same level as sand is 6.2 mL. The experimental process can be seen Figure 4.

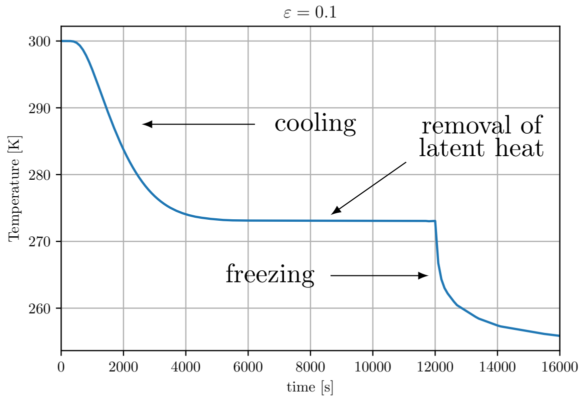
The results observed during the experiment are displayed Table 4.

The total volume of water and sand in the tube is

$$\begin{aligned} V &= V_W + V_S \\ &= 22.2 \text{ mL} \end{aligned}$$



(a) Freezing evolution with different types of meshes



(b) Freezing evolution with finer mesh

Figure 3: Freezing evolution of water

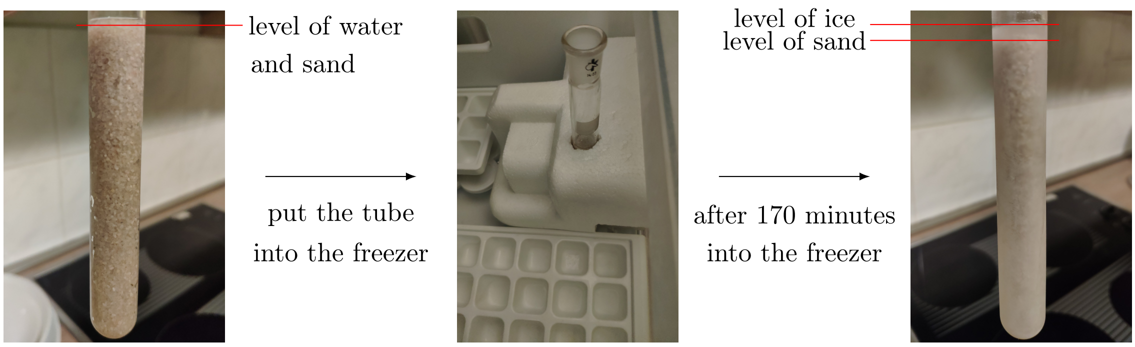


Figure 4: Experimental setup

where $V_W = 6.2$ mL represents the volume of water and $V_S = 16$ mL the volume of sand.

From the volume of water and sand in the tube, it is possible to compute the porosity of the sand as

$$\begin{aligned}\phi &= \frac{V_W}{V} \\ &= \frac{6.2}{22.2} = 0.279 \approx 0.3\end{aligned}$$

3.1.2 Cup experiment with pink sandstone from Vosges mountains

An other experiment consists on freezing other types of wet sand in order to observe the behavior after freezing. This is done with different types of pink sandstone from the Vosges mountains. The results are obtained Figure 5.

In the case of pink sandstone with smaller diameter of grains, see Figure 5a, the sand becomes dry and some cracks appear after freezing, whereas in the case of pink sandstone with larger diameter of grains, see Figure 5b, the result is more interesting after thawing where it is observed that some grains have moved. This experiment was also made before with an other type of sand [1].

It is also observed that the size of the grains have an impact on the relocation of the grains after freezing and thawing. The freezing and thawing process was made several times without moving the grains between previous and next freezing and the grains were moving following the same patterns.

3.2 Experimental modelling

The test tube is represented as a cylinder of volume $V = 22.2$ mL, which is equivalent to a volume $V = 0.0000222$ m^3. It is again computationally easier to implement the model in 2D in COMSOL 3.3.

Time (in minutes)	Level of sand (in mL)	Level of ice (in mL)
0	16	16
30	16	16.5
70	16	17
105	15.6	17
170	15.6	17

Table 4: Evolution of sand and ice

(a) Smaller diameter grains

(b) Larger diameter grains

Figure 5: Freezing and thawing experiment with pink sandstone

Suppose the radius of the cylinder to be $r = 0.01$ m, therefore the height will be $H = \frac{1}{\pi} \cdot 0.222 \approx 0.0707$ m, which gives a rectangle of size 0.02×0.0707 m. The values of density, heat capacity and thermal conductivity are displayed Table 5.

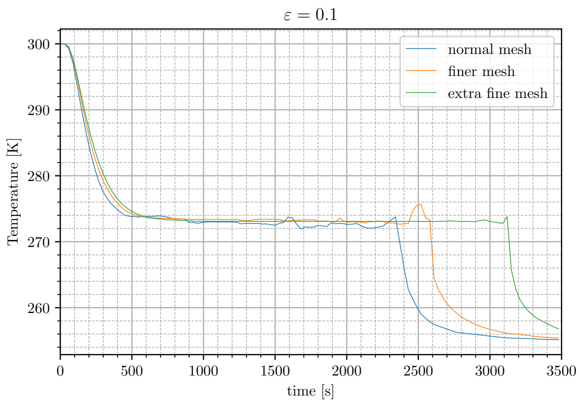
Density ρ	2039 kg/m^3
Heat capacity C_p	1500 J/kg·K
Thermal conductivity κ	0.25 W/m·K

Table 5: Parameter values for wet sand

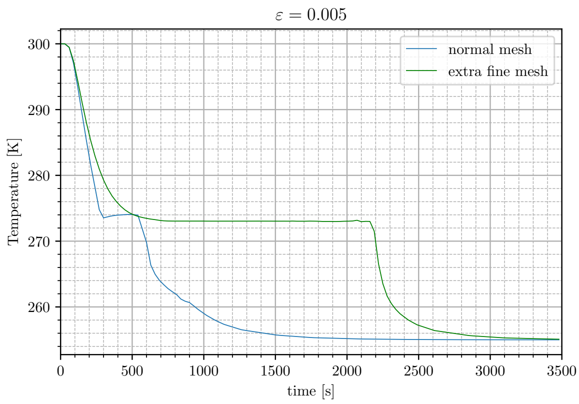
The boundary and initial conditions are set as in section 2.2. When setting the heat source Q to zero and computing the heat capacity C_p using the Heaviside function as shown in equation (5) we observe the results Figure 6.

The regularization scale is taken as $\varepsilon = 0.1$ and the simulation is run for about 1 hour, more precisely 3500 seconds, with a time step of 30 seconds.

However, this regularization is not fully satisfactory even for very fine meshes since Figure 6 shows some disturbance in the curve of freezing evolution even with extra fine mesh. Moreover, the porosity is not taken into account.



(a) Freezing evolution with $\varepsilon = 0.1$



(b) Freezing evolution with $\varepsilon = 0.05$

Figure 6: Freezing evolution of wet sand with different types of meshes

In order to fix it, the power function

$$\begin{aligned}\theta(T(x,t)) &= \eta\phi(T(x,t)) \\ &= \begin{cases} \eta & \text{if} \quad T(x,t) \geq T^* \\ \eta\left|\dfrac{T^*}{T(x,t)}\right|^b & \text{if} \quad T(x,t) < T^* \end{cases}\end{aligned}$$

is used, where $\eta \approx 0.3$ is the soil porosity computed section 3.1.1, ϕ is the liquid water fraction and b is a positive constant taken as $b = 0.5$ here. See [2], [3] and [4] for more information.

The heat conduction equation (1) is rewritten as

$$C_p\frac{\partial T}{\partial t}(x,t) + L\frac{\partial \theta}{\partial t}(T(x,t)) = \nabla(\kappa\nabla T(x,t))$$

where

$$\begin{aligned}Q &= -L\frac{\partial \theta}{\partial t}(T(x,t)) \\ &= -L\eta\frac{\partial \phi}{\partial t}(T(x,t))\end{aligned}$$

In Comsol 3.3 the values for the heat source Q is set to zero and the heat capacity is set as

$$C_p = C_p + L * a * \texttt{flc1hs}(T^* - T, \varepsilon) * abs(T^*)\hat{\ }b * b * abs(T)\hat{\ }(-b-1)$$

where $a = 1$ and $\texttt{flc1hs}(T, \varepsilon)$ denotes the Heaviside function (3) with regularization of $\varepsilon = 0.00001$.

The model is obtained with the values computed from common soil types in Alaska [3] displayed Table 6.

Boundary condition (T_0)	-0.1 °C
Depressed melting point (T^*)	-0.01 °C
Latent heat (L)	$2.5 \cdot 10^6$ J/kg
Switch (a)	1
Initial temperature ($T(t_0)$)	0.2 °C
Thermal conductivity (κ)	2.2 W/m·°C
Heat capacity (C_p)	$4.2 \cdot 10^6$ J/kg·°C

Table 6: Parameter values for heterogeneous geometry model

In the Comsol 3.3 model, the cooling process is studied between 0.2 °C and -0.1 °C during about 15 minutes (1000 seconds) and a timestep of 5 seconds. This model is a bit different from the experiment with the tube Figure 4 since it is not possible to see the plateau of the release of latent heat if the cooling process is studied between 27 °C and −18 °C. This should be due to the fact that this plateau is extremely small and can therefore only be observed for temperatures gap close to the melting point value, which is −0.01 °C in this case. The graph of the cooling process between 0.2 °C and −0.1 °C is displayed Figure 7.

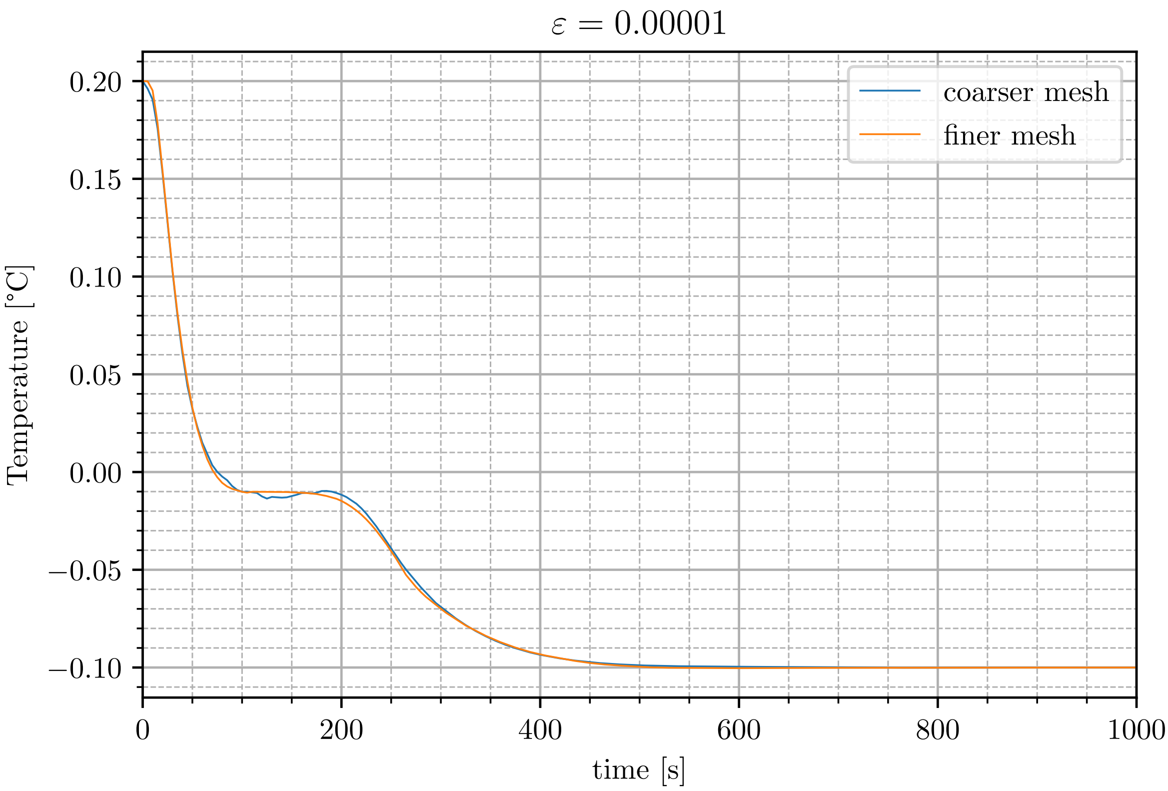


Figure 7: Freezing evolution of wet sand with different types of meshes

4 Freezing of water with gas

4.1 Experiments

Is the gas released from ice ?

A simple experiment with a 50 cL *Perrier* sparkling water has been made.

1. The bottle of *Perrier* is put into the freezer without opening it
2. When the sparkling water is frozen, the bottle is opened in order to see if some gas is released
3. The bottle is closed again an thawed
4. When the ice is totally thawed, the bottle is opened again to see if some gas is released

Unlike pure mineral water, the freezing of sparkling water takes longer time. The results are displayed Table 7.

As a result when opening the bottle after 5 hours in the freezer (the water is still not totally frozen), the gas goes out and the water freezes instantaneously.

After 10 hours in the freezer, the water is totally frozen. No gas (or nearly no gas) is going out when opening the bottle and the ice has expanded up to the cap. See `https://youtu.be/SeN-wov-Jsw`.

The thawing process, however, is faster than the freezing. After 5 hours, the ice is totally melted and the result obtained after opening the bottle can be seen at `https://youtu.be/cFtkSg1dRAY`. Most of the gas is released and therefore it can be concluded that gas was kept on the ice. Moreover,

Time (in minutes)	Observation
0	put in the freezer
60	water
150	water
210	partially frozen (starts to freeze from the bottom, some water at the top)
240	partially frozen (starts to freeze from the bottom, some water at the top)
300	partially frozen (starts to freeze from the bottom, some water at the top)
600	frozen

Table 7: Freezing time of sparkling water

if one tries to drink the water after this experiment, the water is not as sparkling as it was before the experiment.

In order to observe or not gas bubbles contained in the frozen Perrier water, a new sealed bottle is frozen for 25 hours and a half and the ice is then taken out from the bottle. Videos of the result can be watch at `https://youtu.be/IBT3H4oXO5Y` and `https://youtu.be/-HS2oz8vDi0`. Gas bubbles kept in the ice are observed, furthermore, noise of the gas going out while water is thawing can be heard.

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