Desorption Properties of porous media: Aerogel and Safety of Hydrogen Fuel Storage.

by

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Abstract

Fuel tanks filled with organic aerogel might increase the safety level of hydrogen storage for hydrogen combustion vehicles. Aerogel, a material with high porosity and good thermal insulation, readily adsorbs liquid and might prevent a rapid change in temperature and catastrophic release of fuel in the event of an accident. This project modeled how chunks of aerogel retained liquids in a burning environment and built a simulation model to match the experimental data for methane. The model was a sphere of organic aerogel initially saturated with liquid methane and held at a fixed high temperature on the surface. The model simulated the heat conducting into the aerogel sphere, evaporating liquid methane and hence increasing pressure. At the same time gas particles diffused out due to the pressure gradient. The liquid weight as a function of time is compared with the experiments. The simulation has allowed us to obtain a characteristic time scale that would apply not only to methane but also other gases. The result would help us evaluate the feasibility of aerogel filled hydrogen fuel tanks.

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Chapter 1

Introduction

1.1 Hydrogen Fuel and Aerogel

Hydrogen is seen as a major energy carrier for the future. It is a clean source of power which creates only water after combustion. Hydrogen can be stored in gaseous forms, in liquid forms, in metal hydride or in porous systems. The latter two are safer but the technologies are not as mature. Since hydrogen is gaseous under ambient conditions, how to pack sufficient amount of hydrogen becomes a problem. Compression and liquefaction help improve the amount stored in a fixed volume. However, more important than sufficient storage is the safety of storage because hydrogen is explosive. This project studies the safety of liquid hydrogen stored in aerogel.

Aerogel is a synthetic material first created in 1931. Samuel S. Kister of Stanford University found a way to dry gelatinous substances without collapsing the structure [2]. Hence aerogel is a porous material of which as much as 99.8 percent of the volume is empty space. Aerogel can be made of inorganic or organic material such as silica, aluminum oxide or carbon. The aerogel chunks studied in this project are made of phenol-furfural and are black [3].

Aerogel has several applications. NASA used silica aerogel to collect stardust. Since the structure of aerogel provides the best cushion, aerogel can slow down the stardust without destroying the particles. In addition, silica aerogel is transparent and it helps to find the stardust particles. Aerogel has a large surface area and can serve as catalysts. Moreover, Aerogel's low thermal conductivity leads to the invention of aerogel container, which insulates heat better than Styrofoam containers. This project investigates applying the properties of aerogel, nanometer-sized pores of aerogel and low thermal conductivity, to make safer liquid hydrogen storage devices.

1.2 Summary of Work

This thesis is divided into four big chapters, the mechanism of fluid desroption in porous media under a temperature and a pressure gradient, the computational simulations, experiments, and simulation and experiment comparison. Instead of hydrogen, this project works with liquid methane because it is readily available and safer than hydrogen. If not specially indicated, all the constants are constants of methane which are listed in Appendix A.

The two questions Chapter 2 answers are: how are particles stored in aerogel and how do particles leave the aerogel. Given a specific temperature and pressure, under equilibrium, the methane isotherm shows the amount of liquid stored in aerogel. Diffusion and conduction are introduced to explain particle movement and temperature changes. The heat that conducts in evaporates liquid particles and raise the pressure. Then particles diffuse out due to a pressure gradient. The isotherm, diffusing equation, diffusing coefficient, conduction equation and thermal conductivities are introduced and discussed in Chapter 2.

With the diffusion and conduction equations, the equations used to describe the system are derived. A constant high temperature at the surface represents the flame. The computational simulations are programmed in Mathcad. First a one dimensional model is developed and then Moving Boundary Model is introduced. Two analytically solvable problems are studied in Chapter 3 to gain more insight of the system. Finally the three dimensional model is built and the results are presented.

The simulation results are compared with the experimental results in Chapter 4. The set up and the result of the experiment is presented. The effective length of each sample is found to obtain the characteristic time. The relationship between length and disorption time was derived in Chapter 3 and can be observed in the experimental result. The simulation do not exactly matches with the experimental results. One possible explanation about the temperature distribution on the surface of the sample is raised. Chapter 5 further studies the temperature effects on the simulation model.

At the end the results have allowed us to obtain a characteristic time scale that would apply not only to methane but also other gases. The result would help us evaluate the feasibility of aerogel filled hydrogen fuel tanks.

Chapter 2

Theory

The theory chapter is divided into two sections. The first section discusses how methane is stored in aerogel. The second section presents how methane is driven out of aerogel. Diffusion equations describe how particles move and conductions describe how heat flows. Two sets of equations are coupled together and control the rate of methane leaving aerogel which will be further discussed in Chapter Three.

2.1 Distribution of Liquid and Gas inside Aerogel - Isotherm

In this section, how the methane is stored in aerogel is studied. The pore here is modeled as a hollow spheres as illustrated in Figure 2.1. A pore has pore size a, and a layer of liquid methane with thickness d is adsorbed on the surface of the pore. The thickness of the liquid is related with pressure. When a pore is



Figure 2.1: A pore in the aerogel. The pores in aerogel are modeled as hollow spheres with radius a. The grey color represents the organic material surrounding the pore. The pore has radius a and a layer of liquid with thickness d is adsorbed on the inner surface of the pore.

filled with liquid the pressure is called the saturation pressure P_{sat} . The saturation pressure depends on temperature and the following equation is fit to the data from NIST. Figure 2.1 plots the saturation pressure as a function of time.

$$P_{sat}(T) = 1059.2 \exp\left(\frac{-1039.38}{T}\right)$$
 MPa

When the pressure is lower than the saturation pressure, the chemical potential helps with finding the thickness of the liquid layer. When equilibrium is reached, the chemical potential is the same throughout the pores. Thus the gas has chemical potential μ_{gas} and it can be expressed as: [5].

$$\mu_{gas} = \mu_0 + kT \ln(\frac{P}{P_{sat}}) \qquad \mu_0 = \text{saturated chemical potential}$$
(2.1)

The chemical potential of the liquid consists of two parts, one from the surface tension and one from van der Waals attraction force. The pressure difference



Figure 2.2: Methane's saturation pressure v.s Temperature. The function is fit to the saturation pressure data from NIST Chemistry WebBook. When the temperature is at 112.3 K the pressure is 0.1 MPa (1 atm).

across a curvature is $\Delta P = \frac{-2\gamma}{R}$, where γ is the surface tension (0.01346 N/m for methane), and R is the radius of the curvature. Thus the chemical potential per liquid particle due to surface tension is written as $\Delta \mu_s$. z_1^3 is the volume each liquid particle occupies $(z_1^3 = \frac{\rho}{m})$.

$$\Delta \mu_s = -\frac{2\gamma z_1^3}{a-d}$$

The chemical potential contributed from the van der Waals attraction is derived from the inter-particle force, or potential $u = \frac{-\alpha}{r^6}$ [6]. The van der Waals force acting on one particle distance d away from the surface is found by integrating through the entire solid. The energy is:

$$-\frac{4}{3}\pi\alpha\frac{a^3}{d^3}\cdot\frac{1}{(2a-d)^3}$$

This expression is simplified by defining $k T_v$ the lowering energy by adsorbing one particle onto a flat surface $(a \to \infty)$. The van der Waals temperature T_v is about 1500 K.

$$-kT_v\left(\frac{z_1}{d}\right)^3 = -\frac{4}{3}\pi\alpha\frac{1}{8d^3} \qquad (a \to \infty)$$

Then the chemical potential contributed from the van der Waals attraction is:

$$\Delta \mu_v = -\frac{kT_v \, z_1^3}{d^3} \cdot \frac{8a^3}{(2a-d)^3}$$

Define dimensionless quantity $z = \frac{d}{a}$ and $p = \frac{P}{P_{sat}}$. The the liquid particle has chemical potential:

$$\mu_{liq} = \mu_0 - \frac{k T_v z_1^3}{a^3} \cdot \frac{8}{z^3 (2-z)^3} - \frac{2 \gamma z_1^3}{a (1-z)}$$
(2.2)

When it is in equilibrium, the chemical potential of the gas and the liquid are equal. Thus the isotherm is found by equating μ_{gas} and μ_{liq} and then solve for the pressure.

$$Ta = \frac{8T_v z_1^3}{a^3} \qquad Tb = \frac{2\gamma z_1^3}{a k}$$

$$p(T, z) = \exp\left[-\frac{Ta}{T}\frac{1}{z^3(2-z)^3} - \frac{Tb}{T}\frac{1}{1-z}\right]$$
(2.3)



Figure 2.3: Isotherm for methane in aerogel with pore size a = 100 nm at 112.3 K. The critical pressure is 0.997 when the red line curves back. For adsorption, when the pressure is above the critical pressure, the tension in the liquid pulls liquid in and the pore is saturated. Therefore, for p greater than 0.997, z equals to 1 as the dash line indicates.

The isotherm (2.3) tells us how much liquid is stored in a single pore for a given pressure and temperature. When the pore size is 100 nm and the temperature is at methane's boiling temperature 112.3 K, the isotherm is plotted in Figure 2.1. For p smaller than 0.987, z is smaller 0.05 and for p greater than 0.987, z is saturated to 1. This means that the pore is almost empty unless the pressure is close to the saturation pressure. When the temperature is higher than the boiling

temperature, the saturation pressure is a fast growing function. So it requires a even higher pressure to fill up the pores. This result will be very important when we are simplifying the simulation model.

2.2 Diffusion and Conduction

2.2.1 Diffusion Equations

Given a concentration difference, particles move from high to low concentration. Diffusion is a result of random motions of particles but under the hypothesis that the rate of transfer is proportional to the concentration gradient measured, the process can be described mathematically [7]. In one dimension:

$$J = -D\frac{\partial n}{\partial x} \tag{2.4}$$

$$\frac{\partial n}{\partial t} = -\frac{\partial J}{\partial x} \tag{2.5}$$

(2.4) and (2.5) are the equations for one dimensional model where J is the flux, rate transfer per unit area. D is called the diffusion coefficient, n is the concentration of diffusing substance, and x and t are the spatial and time coordinates respectively.

If the diffusion coefficient is uniform everywhere, then the equation becomes $\frac{\partial n}{\partial t} = D \frac{\partial^2 J}{\partial x^2} \text{ to which } n(x,t) = \left(A\cos(kx) + B\sin(kx)\right)e^{-\lambda^2 t} \text{ is a solution [8]}.$



Figure 2.4: A tube inside aerogel with pore size a; adsorbed liquid thickness z and length L.

However, most of the time the diffusion coefficient is not a fixed constant. In a long cylinder with radius r, assuming the flow is laminar, then Poiseuille's law (2.6) describes how fluid flows [9]. \dot{V} is the volume flow rate and η is the viscosity of the fluid. The diffusion coefficient can be derived from Poiseuille's law.

$$\dot{V} = \frac{\pi r^4}{8\eta} \frac{\partial p}{\partial x}$$
 Poiseuille's Law (2.6)

In the following case, the number flow rate is derived for a cylinder with a layer of liquid adsorbed on the wall (Figure 2.4). And the diffusion coefficient is then defined.

Gas Diffusion Coefficient

$$\dot{V}_{gas} = \frac{\pi (a-z)^4}{8\eta_q} \frac{\partial p}{\partial x} \qquad \eta_g = \text{gas viscosity}$$

From the ideal gas law:

$$n_{gas} = \frac{N}{V} = \frac{p}{kT}$$
$$\frac{\partial n}{\partial x} = \frac{\partial n}{\partial p} \frac{\partial p}{\partial x} = \frac{1}{kT} \frac{\partial p}{\partial x}$$
$$N = \frac{p}{kT} V$$
$$\dot{N}_{gas} = \frac{p}{kT} \dot{V}_{gas}$$
$$= \frac{p}{kT} \frac{\pi (a-z)^4}{8\eta_g} \frac{\partial p}{\partial x}$$
$$= \frac{\pi p (a-z)^4}{8\eta_g} \frac{\partial n}{\partial x}$$

Flux J is \dot{N} divided by the area πa^2 Thus

$$J_{gas} = \frac{\dot{N}}{\pi a^2} = \frac{p}{8\eta_g} \frac{(a-z)^4}{a^2} \frac{\partial n}{\partial x}$$

Compared with (2.4), the diffusion coefficient is

$$D_{gas}(p) = \frac{p}{8\eta_g} \frac{(a-z)^4}{a^2}$$
(2.7)

Liquid Diffusion Coefficient

The diffusion coefficient for liquid is a little bit more complicated. For laminar flow, the velocity of fluid at the cylinder wall has zero speed. The flow has greater velocity as it is further away from the cylinder wall. The viscosity force is proportional to the velocity difference. The volume flow rate is calculated by finding the speed at each place. The force created by viscosity between two sheets of flow with area A in Figure 2.5 is

$$F = \eta A \frac{\nu_2 - \nu_1}{\Delta r}$$



Figure 2.5: Two layers of liquid flow with velocity v_1 and v_2 . The layers have area A had distance Δr in between. The figure on the right is an illustration of cylindrical layers of flow.

$$F(r) = \eta 2\pi r L \frac{\partial \nu}{\partial r}$$
 for the cylindrical model

Furthermore the total net force is zero. That is

$$F(r+\partial r) - F(r) + PA = 0 \qquad A = 2\pi r dr \quad P = \frac{dp}{dx}L$$
$$2\pi\eta L \frac{\partial}{\partial r} \left(r\frac{\partial\nu}{\partial r}\right)_{0}^{+} + 2\pi r L \frac{\partial p}{\partial x} = 0$$

Solve for ν then

$$\nu(r) = \frac{-1}{4\eta} \frac{\partial p}{\partial x} r^2 + c_1 \ln r + c_2$$

Plug in the boundary condition given by the aerogel tube, Figure 2.4

$$\nu(a) = 0; \qquad F(b) = 0$$

to find the constants c_1 and c_2 .

$$c_1 = \frac{1}{2\eta} \frac{\partial p}{\partial x} b^2$$
$$c_2 = \left(\frac{1}{\eta} \frac{\partial p}{\partial x}\right) \left(\frac{a^2}{2} - \frac{b^2}{2} \ln a\right)$$

Therefore ν becomes:

$$\nu(r) = \frac{1}{2\eta} \frac{\partial p}{\partial x} \left(\frac{(a^2 - r^2)}{2} + b^2 \ln(\frac{r}{a}) \right)$$
(2.8)

Integrate $\nu(r)$ from b to a to get \dot{V}

$$\dot{V}_{liq} = \int_b^a \nu(r) 2\pi r dr \tag{2.9}$$

With b = a - z and liquid viscosity η_l , the integral becomes

$$\dot{V}_{liq} = \frac{\pi}{8\eta_l} \frac{\partial p}{\partial x} a^4 \left(1 - 4\left(\frac{a-z}{a}\right)^2 + 3\left(\frac{a-z}{a}\right)^4 - 4\left(\frac{a-z}{a}\right)^4 \ln\left(\frac{a-z}{a}\right) \right) \quad (2.10)$$

What is needed is the flux ($J = \frac{\dot{N}}{\pi a^2}$) and $\dot{N} = \frac{\rho}{m}\dot{V}$ for liquid. And again, changing $\frac{\partial p}{\partial x}$ to $\frac{\partial n}{\partial x}$ by $\frac{\partial n}{\partial x} = \frac{1}{kT}\frac{\partial p}{\partial x}$, we got

$$J_{liq} = \frac{kT\rho}{8\eta_l m} a^2 \left(1 - 4\left(\frac{a-z}{a}\right)^2 + 3\left(\frac{a-z}{a}\right)^4 - 4\left(\frac{a-z}{a}\right)^4 \ln\left(\frac{a-z}{a}\right)\right) \frac{\partial n}{\partial x} \quad (2.11)$$

$$D_{liq} = \frac{kT\rho}{8\eta_l m} a^2 \left(1 - 4\left(\frac{a-z}{a}\right)^2 + 3\left(\frac{a-z}{a}\right)^4 - 4\left(\frac{a-z}{a}\right)^4 \ln\left(\frac{a-z}{a}\right) \right) \quad (2.12)$$

The diffusion coefficients of liquid and gas methane as a function of pressure is shown in Figure 2.6. It is worthwhile mentioned that D_{liq} depends on pressure only because the thickness of the liquid layer is pressure dependent.

The total diffusion coefficient of particles is calculated from the sum of liquid component and gas component. $D = D_{gas} + D_{liq}$ With the diffusion coefficient, one can numerically simulate the diffusion rate. This will be further discussed in Chapter 3.2.2.

2.2.2 Conduction Equations

Heat conduction is no different than particle diffusion [7]. It is described by conduction equations which is similar to diffusion equations. Heat flux J_Q



Figure 2.6: Diffusion coefficients for liquid and gas methane in the aerogel tube.

is proportional to temperature gradients and the heat change rate is described as:

$$J_Q = -K \frac{\partial T}{\partial x} \tag{2.13}$$

$$\frac{\Delta Q}{\Delta t}\frac{1}{V} = c\rho\frac{\partial T}{\partial t} = K\frac{\partial^2 T}{\partial x^2}$$
(2.14)

c and ρ are heat capacity and density of the material. K is called the thermal conductivity. The thermal conductivity is a function of temperature K(T). Figure 2.7 is the heat conductivity of methane. In the simulations, the value for heat conductivities of methane are fit to the NIST data.

gas methane	$K_g(T) = 4.008 \cdot 10^{-6} \cdot T^{1.552} + 0.00648 $ W/mk	Ś
liquid methane	$K_l = 0.186$ W/mK	
aerogel	$K_a = 0.003$ W/mK	

Table 2.1: Thermal conductivity for methane gas, methane liquid and aerogel.



Figure 2.7: Thermal conductivity for methane gas at different temperature (pressure equals to 1 atm). The function is fit to the data in NIST Chemistry WebBook.

Heat conducts in not only through methane (liquid and gas) but also through aerogel. The following discusses how to describe heat flow through a combination of aerogel and gas methane, $K_g \oplus K_a$. Only $K_g \oplus K_a$ is discussed because from the previous discussion in Chapter 2.1 we know the pores are either empty or totally filled. We would also need the thermal conductivity of liquid methane plus aerogel but not the three together. $K_l \oplus K_a$ has the same formula as $K_g \oplus K_a$ with K_g replaced by K_l .

Figure 2.8 illustrates how we simulate pores as cubes of size l^3 evenly spaced and imbedded in aerogel chunks. Figure 2.8 C is the decomposition of the components. First a space filled with gas is being parallel placed with a piece of aerogel. The effective conductivity is K_{e1} and then this piece is in series with the second aerogel chunk with conductivity of the organic material $K_{e2} = K_o$.

Effective conductivity of n pieces of material with area $A_1, A_2, A_3 \dots A_n$ and



Figure 2.8: The model for finding combined thermal conductivity. (a) is the 1-D illustration of the model structure. (b) One basic unit has length l. The empty cubic volume has length l'. (c) Decompose the basic unit into two parts which have thermal conductivity K_{e1} and K_{e2} . The length for the first part L1 is l' and L2 is (l - l')The area A1 is $l^2 - l'^2$, A2 is l'^2

conductivity $K_1, K_2, K_3 \dots K_n$ parallel placed together is given by [7]:

$$A_{total}K_{total} = A_1K_1 + A_2K_2 + A_3K_3 + \dots + A_nK_n \qquad \text{parallel} \qquad (2.15)$$

On the other hand if it is n pieces of materal with thickness $L_1, L_2, L_3 \dots L_n$ in series, the effective conductivity is

$$\frac{L_{total}}{K_{total}} = \frac{L_1}{K_1} + \frac{L_2}{K_2} + \frac{L_3}{K_3} + \dots + \frac{L_n}{K_n} \qquad \text{series}$$
(2.16)

Thus, (2.15) and (2.16) help us to find the effective conductivity as following:

$$\begin{cases} K_{e1} = K_o \left(\frac{l^2 - l'^2}{l^2}\right) + K_g \frac{l'^2}{l^2} \\ K_{e2} = K_o \\ \frac{l}{K_{eff}} = \frac{l'}{K_{e1}} + \frac{l - l'}{K_{e2}} \\ f = \left(\frac{l'}{l}\right)^3 \text{ filling fraction} \end{cases}$$

Then the effective conductivity is

$$K_{eff} = \frac{K_{e1}K_{e2}}{K_{e2}f^{1/3} + K_{e1}(1 - f^{1/3})}$$
(2.17)

The last step here is to find K_o , thermal conductivity of organic material, from the thermal conductivity of aerogel. The conductivity of aerogel, $K_a = 0.003$ W/mK, is measured in vacuum. In other words K_a equals to K_{eff} when pressure is zero ($K_g = 0$) Plug in $K_g = 0$ into (2.17) and solve for K_o .

$$K_o = K_a \frac{1 + f - f^{2/3}}{1 - f^{2/3}}$$

Finally we found the expression of the effective conductivity as a function of filling fraction, conductivity of methane gas and conductivity of aerogel.

$$K_{eff} = \frac{K_a^2 \cdot \left(1 + f - f^{2/3}\right)^2 + K_g \cdot K_a \cdot f^{2/3} \cdot \left(1 + f - f^{2/3}\right)}{K_a \cdot \left(1 + f - f^{2/3}\right) \cdot f^{1/3} + \left(1 - f^{1/3}\right) \left(1 - f^{2/3}\right) \left(K_a \cdot \left(1 + f - f^{2/3}\right) + K_g \cdot f^{2/3}\right)}$$
(2.18)



Figure 2.9: Effective thermal conductivity Keff at different filling fraction f. One is calculated at temperature T = 112K. The other is at 800 K. Ka is aerogel thermal conductivity. Kg is the methane gas thermal conductivity, also at two different temperatures, 112 K and 800 K.

Figure 2.9 is the plot of thermal conductivities of aerogel, methane gas and the combination of the two. When the filling fraction is zero (that is no pores, no empty spaces in aerogel), the effective conductivity is just that of aerogel. And when the filling fraction is close to one, the effective conductivity becomes the sum of the gas and aerogel conductivities.

Now we know the mathematical formulas to describe the particle diffusion and heat conduction. The final piece before we can do the simulation is the heat involved when liquid particles evaporate and become gas particles. That is the latent heat L_v

$$\Delta Q = L_v \cdot \Delta N_{liq \to qas} = mc\Delta T$$

Evaporated particles show up in both particle diffusion equation and heat con-

duction equation. This is what makes particle diffusion and heat conduction equations couple together and hard to solve analytically. If the diffusion coefficient and thermal conductivity are constants independent of concentration and temperature, analytical solutions can be found [7].

Involving temperature dependent conductivity and pressure dependent diffusion coefficient, the system in this thesis is more complicated. Furthermore the system involves two sets of diffusion gas and liquid diffusion, which only make analytical solutions infeasible. In the next chapter simulations methods and results will be presented.

Chapter 3

Simulations

Chapter Three presents how to simulate the rate of methane loss in a spherical piece of aerogel originally soaked with liquid methane at methane's boiling temperature with the outer surface exposed to a high temperature (800K). The equations to describe the system are derived in 3.1. And then some simplification is made: Each pore is either filled with only gas or only liquid. The gas diffusion is the dominant diffusion process so the liquid diffusion process is neglected. Then the mathematical discriptions and results of the simplified system are presented in 3.2. Finally these results are compared to the experimental data in the next chapter.

3.1 Simulations I - Equations

The goal of this section is to describe the system with equations. The key concepts are the conservation of energy, conservation of particles and the isotherm.



Figure 3.1: One dimensional model. Aerogel has length L, pore size a and the liquid layer thickness isd.

Originally a spherical chunk of aerogel is saturated with liquid methane at 112 K, the methane's boiling temperature, T_b . A constant high temperature (800 K) is applied to the aerogel surface and represents the flame. The particles diffuse out in gas and liquid form. In the mean time, liquid methane can evaporate or the gas can condense depending on the heat available. There are three ways to change the temperature. First, heat can conduct in through aerogel, gas and liquid to raise the temperature. Second, temperature can change when the hot or cold gas and liquid particles move. Finally, through evaporation or condensation, the temperature also changes. The assumption made here is that local equilibrium is achieved so the isotherm is always valid [10].

Now lets write the equations down for a one dimensional model (Figure 3.1). Let subscripts a g l and evap represents alongel, gas, liquid and evaporated particles. n is the number density. J and J_Q are the particle flux and heat flux respectively.

Conservation of particle leads to:

$$\frac{\partial n_g}{\partial t} = -\frac{\partial J_g}{\partial x} + \frac{\partial n_{evap}}{\partial t}$$
(3.1)

$$\frac{\partial n_l}{\partial t} = -\frac{\partial J_l}{\partial x} - \frac{\partial n_{evap}}{\partial t}$$
(3.2)

Conservation of energy gives:

$$\frac{1}{V}\frac{\partial Q}{\partial t} = (\rho_a c_a + \rho_l c_l + \rho_g c_g \frac{\partial T}{\partial t}) = -\frac{\partial}{\partial x}(J_{Qa} + J_{Ql} + J_{Qg}) - L_v \frac{\partial n_{evap}}{\partial t} - \rho_g c_g v_g \frac{\partial T}{\partial x} - \rho_l c_l v_l \frac{\partial T}{\partial x}$$
(3.3)

The latter two terms represent the heat flow caused by the cold or hot particle diffusing to regions at a different temperature. v is the velocity of the particle can be found from the flux relation J = nv Rewrite the density ρ to be mass times number density then $\rho cv \frac{\partial T}{\partial x}$ becomes $mcJ\frac{\partial T}{\partial x}$

However, three equations are not sufficient to solve for four unknowns, n_g , n_l , n_{evap} and the temperature T. Thus, isotherm is employed in equilibrium constraint, which contributes two more equations. Isotherm is a function z(p,T) which tells us the thickness of the liquid layer z at any pressure and temperature.

$$dn_g = \left(\frac{\partial n_g}{\partial z}\right) dz + \left(\frac{\partial n_g}{\partial T}\right) dT \tag{3.4}$$

$$dn_l = \left(\frac{\partial n_l}{\partial z}\right) dz + \left(\frac{\partial n_l}{\partial T}\right) dT \tag{3.5}$$

Here the isotherm $p(T, z)/P_{sat} = \exp\left(\frac{-A}{T \cdot z^3 \cdot (2-z)^3} - \frac{B}{T \cdot (1-z)}\right)$ (ref eq) is derived from the spherical model but is used on the cylindrical tube model which the diffusion constant is derived based on (Figure 3.1). n_g is the number density of the gas particles in the cylindrical tube. From ideal gas law $(N_g = \frac{PV}{kT})$ we know $n_g = \frac{N_g}{V_{sample}} = \frac{p \cdot P_{sat} L \pi (a-d)^2}{kT} \frac{1}{V_{sample}}$. $V_{sapmple}$ equals to $L \pi a^2 / f$ for each tube and let normalized thickness z be $z = \frac{d}{a}$. Call this number density function I_g and it becomes

$$I_g(T,z) = \frac{p(T,z) \cdot P_{sat}(T)}{kTf} (1-z)^2$$
(3.6)

As for liquid, the number density N_l is $N_l = \frac{V_l \rho}{m} = \frac{V_l}{z_1^3}$, $z_1^3 = \frac{m}{\rho}$ the volume of one liquid particle. Then number density function I_l becomes

$$I_{l} = \frac{N_{l}}{V_{sample}} = \frac{1}{z_{1}^{3}} (L\pi a^{2} - L\pi (a - d)^{2}) \frac{1}{V_{sample}}$$
$$= \frac{1}{z_{1}^{3} f} (1 - (1 - z)^{2}) = \frac{1}{z_{1}^{3} f} (2z - z^{2})$$

$$I_l(z) = \frac{1}{z_1^3 f} (2z - z^2)$$
(3.7)

In (3.4) and (3.5) need $\frac{\partial n_g}{\partial z}$, $\frac{\partial n_g}{\partial T}$, $\frac{\partial n_l}{\partial z}$, and $\frac{\partial n_l}{\partial T}$. Therefore, we take (3.6) and (3.7) and find their partial differentiations, I_{gz} , I_{gT} , I_{lz} , and I_{lT} . Notice that I_{lT} is zero. The number density of liquid is independent of the temperature.

The way to solve or numerically simulate the system of equations $(3.1) \sim$ (3.5) is to separate terms with dt to one side of the equation. Thus these equation becomes

$$\begin{aligned} (I_{gz}dz + I_{gT}dT - dn_g)/dt &= 0 \\ (I_{lz}dz + 0dT - dn_l)/dt &= 0 \\ (dn_g - dn_{evap})/dt &= -\frac{\partial J_g}{\partial x} = \frac{\partial}{\partial x} \left(D_{gas} \frac{\partial n_g}{\partial x} \right) \\ (dn_l + dn_{evap})/dt &= -\frac{\partial J_l}{\partial x} = \frac{\partial}{\partial x} \left(D_{liq} \frac{\partial n_l}{\partial x} \right) \\ \left((\rho_a c_a + \rho_l c_l + \rho_g c_g) dT + L_v dn_{evap} \right)/dt &= -\frac{d}{dx} (J_{Qa} + J_{Ql} + J_{Qg}) - \rho_g c_g v_g \frac{dT}{dx} - \rho_l c_l v_l \frac{dT}{dx} \\ &= \sum K \frac{d^2 T}{dx^2} + m C_g D_{gas} \frac{dn_g}{dx} \frac{dT}{dx} + m C_l D_{liq} \frac{dn_l}{dx} \frac{dT}{dx} \end{aligned}$$

Finally, turn these equations into a matrix and times the inverse matrix of the coefficients on both sides. Then we have the information we need to find out z, T, n_g, n_l and n_{evap} with a proper time step dt. However, notice that I_{gz}, I_{lz} and I_{gt} are functions of T and z which add to the complicity of the inverse matrix. In the following $\sum \rho c$ and $\sum K$ represents $\rho_a c_a + \rho_l c_l + \rho_g c_g$ and $K_a \oplus K_l \oplus K_g$ respectively. The \oplus is the thermal conductivity addition discussed in Chapter 2.2.2.

$$\begin{pmatrix} I_{gz} & I_{gT} & -1 & 0 & 0 \\ I_{lz} & 0 & 0 & -1 & 0 \\ 0 & 0 & 1 & 0 & -1 \\ 0 & 0 & 0 & 1 & 1 \\ 0 & \sum \rho c & 0 & 0 & L_v \end{pmatrix} \begin{pmatrix} dz \\ dT \\ dn_g \\ dn_l \\ dn_{evap} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ \frac{d}{dx}(D_{gas}\frac{dn_g}{dx}) \\ \frac{d}{dx}(D_{liq}\frac{dn_l}{dx}) \\ \sum K\frac{d^2T}{dx^2} + m\frac{dT}{dx}(C_g D_{gas}\frac{dn_g}{dx} + C_l D_{liq}\frac{dn_l}{dx}) \end{pmatrix} dt$$

$$\begin{pmatrix} dz \\ dT \\ dn_g \\ dn_l \\ dn_{evap} \end{pmatrix} = \begin{pmatrix} I_{gz} & I_{gT} & -1 & 0 & 0 \\ I_{lz} & 0 & 0 & -1 & 0 \\ 0 & 0 & 1 & 0 & -1 \\ 0 & 0 & 0 & 1 & 1 \\ 0 & \sum \rho c & 0 & 0 & L_v \end{pmatrix}^{-1} \begin{pmatrix} 0 & 0 \\ 0 & 0 \\ \frac{d}{dx}(D_{gas}\frac{dn_g}{dx}) \\ \frac{d}{dx}(D_{liq}\frac{dn_l}{dx}) \\ \sum K\frac{d^2T}{dx^2} + m\frac{dT}{dx}(C_g D_{gas}\frac{dn_g}{dx} + C_l D_{liq}\frac{dn_l}{dx}) \end{pmatrix} dt$$

$$(3.8)$$

The programming is done through Mathcad (Appendix D). The initial condition is set to be the whole piece of aerogel saturated with liquid methane at methane's boiling temperature. It turned out the program ran slowly and failed to converge when the temperature outside of the aerogel is hotter than 117 K (5K more than the boiling temperature.) These studies helped us understand how the system work but a less complex way to carry out the simulation is needed.

3.2 Simulations II - Moving boundary Model

The isotherm (Figure 2.1) implies that the pores in aerogel are almost empty as long as the pressure is less than 98 % of the saturation pressure. This motivates us to set up the moving boundary model (Figure 3.2). Moving boundary models are generally applied to the cases which have discontinuous diffusion coefficients [7]. For example, in some cases the diffusion rate drops to zero when reaching to some specific concentration. As the name suggests, the moving boundary model has a boundary beyond which the aerogel is saturated with liquid and before which no liquid exists. Only the gas particles diffuse and the source of gas particles come from liquid evaporation at the boundary.

The system is simplified into two regions. In the gas region, the heat conducts in and gas particles diffuse out. At the boundary, liquid particles evaporate and the temperature adjusts according to the heat flux in and the latent heat loss. The boundary recedes after liquid particles at the boundary all evaporate. Finally in the liquid region, only the heat conducts in and no particle moves. The liquid region is set to have uniform temperature. The pressure in the liquid part is always maintained at the saturation pressure of the liquid temperature. In



Figure 3.2: One aerogel tube in the moving boundary model.

other words if there is liquid then the pressure is always at the saturated pressure P_{sat} . Thus by using the boundary moving model, not only is the diffusion problem simplified, the isotherm equation is also omitted.

We started from studying a one dimensional model and also study two problems that can be analytically solved to gain more insight into the model. Then the simulation is run on a three dimensional model which has radial symmetry. The results of the 3-D simulation are compared to the experimental data in Chapter 4.

3.2.1 1-D Model

For the simulation in 3.1 we need to keep track of z, T, n_g , n_l and n_{evap} . Now the thickness of liquid z is zero in the gas region and one in the liquid region. Similarly n_l is zero in the gas region and saturated in the liquid region. Therefore we no longer need to know z and n_l . Instead only the boundary position is needed.

Т

To find the temperature T, (3.3) is still valid and can be further simplified. In the gas region, the terms involving liquid are ignored.

$$(\rho_a c_a + \rho_g c_g \frac{dT}{dt}) = (K_a \oplus K_g) \frac{d^2 T}{dx^2} - \rho_g c_g v_g \frac{dT}{dx}$$

 $K_a \oplus K_g$ is exactly K_{eff} (2.18) found in Chapter 2. Also $\rho_g c_g$ is ignored because the density of gas it is much smaller than the density of aerogel. By ignoring $\rho_a c_a$ it helps to speed up the calculation since the density of the gas ρ_a is not a fixed constant. Therefore to simulate the temperature in the gas region, the equation we use is

$$dT = \left(K_{eff}\frac{d^2T}{dx^2} + mc_g D_{gas}\frac{dn_g}{dx}\frac{dT}{dx}\right)\frac{dt}{\rho_a c_a}$$
(3.9)

The temperature at the boundary is obtained differently because the liquid ist set to have infinite heat conduction, and the temperature in the liquid part is uniform. Thus heat flux from the gas part comes in and heats up the whole liquid region.

$$\Delta T = \frac{J_Q A \Delta t}{M_{\text{total liquid mass}} c_l + M_{\text{aerogel}} c_a}$$
$$= \frac{J_Q A \Delta t}{(\rho_l c_l + \rho_a c_a) A (L - b)}$$
$$= \frac{J_Q \Delta t}{(\rho_l c_l + \rho_a c_a) (L - b)}$$

The evaporation only happens at the boundary. The number of particles evaporated is set to be the number of gas particles diffusing out of the boundary. The heat lost by evaporation then cools down the liquid.

$$n_{evap}A\Delta x = -J_gA\Delta t$$
$$\Delta T = -L_v n_{evap} = L_v D_{gas} \frac{dn_g}{dx} \frac{\Delta t}{(\rho_l c_l + \rho_a c_a)(L-b)}$$

Hence the temperature change at the boundary is

$$dT_b = \left(-K_{eff}\frac{dT}{dx}\Big|_b - L_v D_{gas}\frac{dn_g}{dx}\Big|_b\right)\frac{dt}{(\rho_a c_a + \rho_l c_l)(L-b)}$$
(3.10)

 n_g

The last thing needed to be taken care of is the gas number density n_g , but this is no different than the diffusion equation (3.1). Again n_{evap} is zero in the gas region. At the boundary the gas number density depends on the pressure which is set to be the saturate pressure at the temperature. Therefore the conduction equation which controls the temperature still couples with the diffusion equation and can affect the diffusion rate.

Gas diffusion equation is $dn_g = \frac{d}{dx}(D_{gas}\frac{dn_g}{dx}) \cdot dt$. Now the diffusion constant D_{gas} is simply $D_{gas} = -\frac{pa^2}{8\eta_g}$. Different than stated in (2.7) since the liquid thickness z is always zero. Furthermore since in the diffusion equation, D_{gas} is a function of pressure we changed $\frac{dn_g}{dx}$ in to $\frac{1}{kT}\frac{dp}{dx}$ by the ideal gas law to make dn_g a function of pressure too. The ideal gas law is always valid in the gas region to so we only need to keep track of either n_g or p. By doing this, it is easier to program the simulation.

To conclude, the simulation flow is summarized in Table 3.1. The computer code is in Appendix C for reference.

Table 3.1: Equations for simulating 1-D moving boundary model		
boundary is at b		
Gas	$dn_g = \frac{d}{dx} \left(\frac{D_{gas}}{kT} \frac{dp}{dx} \right) \cdot dt$	
	$dn_l = 0$	
	$dT = \left(K_{eff}\frac{d^2T}{dx^2} + mc_g\frac{D_{gas}}{kT}\frac{dp}{dx}\frac{dT}{dx}\right)\frac{1}{\rho_a c_a} \cdot dt$	
	p = nkT	
Boundary	$n_g = \frac{p}{kT}$	
	$dn_l = -n_{evap} = \frac{D_{gas}}{kT} \frac{dn_g}{dx} \Big _b \frac{1}{dx} \cdot dt$	
	$dT = \left(-K_{eff} \frac{dT}{dx} \Big _{b} - L_{v} \frac{D_{gas}}{kT} \frac{dp}{dx} \Big _{b} \frac{1}{dx} \right) \frac{1}{(\rho_{a}c_{a} + \rho_{l}c_{l})(L-b)} \cdot dt$	
	$p = P_{sat}(T)$	
Liquid	$n_g = n_g _{boundary}$	
	$dn_l = 0$	
	$dT = dT _{boundary}$	
	$p = p _{boundary}$	

 Table 3.1: Equations for simulating 1-D moving boundary model



Figure 3.3: 1-D moving boundary model result. Position of the boundary as a function of time. Red line is the simulation (the total length L = 5cm is divided into twenty divisions so the boundary moves like steps. Blue line is the function fit to the simulation result.

Results

Figure 3.3 shows that a five cm long one dimensional model takes 16790 seconds to empty out the liquid methane. And the boundary position is proportional to square root of time. The fact that the boundary position is proportional to square root of time deserves further discussion. In the next section two analytical solvable problems are presented to find the relationship between time and the position of the boundary, or the relationship between length L and the time it takes to empty.

3.2.2 1-D Pure Diffusion Analytical Solutions

Two cases are analytically solved in Chapter 3.2.2 and 3.2.3. 1) Diffusion Limit Model and 2) Conduction Limit Model. It turned out the boundary moves as a square root function of time if there is only pure diffusion. The result coincides with the result of the simulation. This result also implies that the times scales as the square of the length so a tube of aerogel twice as long as this one will take four times longer to empty. In the Diffusion Limit Model, there is only diffusion caused by a fixed pressure difference inside and outside the aerogel with no temperature change in the system. In other words the heat needed to evaporate the liquid is arbitrarily taken to be zero. Therefore the diffusion rate controls the boundary moving rate. In case 2) Conduction Limit Model, whatever evaporates diffused out immediately. The time it takes to conduct the heat in to evaporate all the liquid is studied. Again the liquid conductivity is set to be infinite so the whole liquid region is at the same temperature.

Figure 3.4 is the illustration of the Diffusion Limit Model. The pressure outside the aerogel is P_0 and the pressure in the liquid region is P_s , the saturated pressure at the given temperature. Initially the whole aerogel is saturated with liquid so the boundary is at x = 0. The first step is to find \dot{N} in one aerogel tube. Assuming the volume of the sample is V = AL. The total number of aerogel tubes in the system is $\frac{ALf}{\pi a^2 L}$, where f is the filling fraction and a is the pore size. Then we can figure out the total number diffusion rate in the system and find the boundary position as a function of time.

From Poiseuille's Law and the ideal gas law, one can find N.

$$\dot{V} = -\frac{\pi a^4}{8\eta} \frac{dp}{dx}$$
 Poiseuille's Law



Figure 3.4: One dimensional pure diffusion model. The aerogel has area A and length L. Heat and gas particles only conducts or diffuses in from the open end x = 0. Pressure outside the aerogel is Po and inside is at saturation pressure Psat. Po and Psat are fixed constants.

$$\dot{N} = \dot{V} \frac{p}{kT}$$
$$\frac{dp}{dx} = -\frac{8\eta}{\pi a^4} \frac{kT}{p} \dot{N}$$

Integrate from the open end to x, and then we get \dot{N} when the boundary is at x.

$$\int_{p_0}^{p_s} p dp = \int_0^x -\frac{8\eta kT}{\pi a^4} \dot{N} dx$$
$$\dot{N} = -\frac{\pi a^4}{16\eta kT} \frac{p_s^2 - p_0^2}{x}$$
$$\dot{N}_{total} = -\frac{\pi a^4}{16\eta kT} \frac{p_s^2 - p_0^2}{x} \cdot \frac{Af}{\pi a^2}$$

Then we can find the rate of boundary moving \dot{x} . Let z_1^3 be the volume of one liquid particle $(z_1^3 = \frac{m}{\rho})$.

$$\dot{x} = -\dot{N}_{total} \frac{z_1^3}{Af}$$

$$\frac{dx}{dt} = \frac{z_1^3 a^2}{16\eta kT} \frac{p_s^2 - p_0^2}{x}$$

Let $\beta = \frac{z_1^2 a^2}{16\eta kT} (p_s^2 - p_0^2)$ and integrate from time zero to time t_b , the time it takes move the boundary from 0 to x_b .

$$\int_0^{x_b} x dx = \int_0^{t_b} \beta dt$$
$$\frac{x_b^2}{2} = \beta t_b$$

$$x(t) = \sqrt{2\beta t} \qquad \beta = \frac{z_1^3 a^2}{16\eta kT} (p_s^2 - p_0^2)$$
(3.11)

It turns out the boundary moves as a square root function of time if there is only pure diffusion. The result coincides with the result of the simulation. This result also implies that the times scales as the square of the length so a tube of aerogel twice as long as this one will take four times longer to empty. The next step is to study the other limit, Conduction Limit Model and find the correlation between the length and time.

3.2.3 1-D Pure Conduction Analytical Solutions

Conduction is similar to diffusion, so the result also has the similar property. However, conduction problem is a little more complicate. Figure 3.5 illustrates the model. Initially the aerogel is saturated with liquid and is at its boiling temperature. Outside of aerogel is maintained a temperature T_0 . Heat can conduct into aerogel to 1) evaporate the liquid, 2) heat up the gas and, 3) heat up the liquid. Therefore this is more complicate than pure diffusion case. However, if we assume all the heat that conducts into aerogel only evaporate the liquid then we can show that this no different than the diffusion problem.



Figure 3.5: One dimensional pure conduction model. The aerogel has area A and length L. Heat and gas particles only conducts or diffuse in from the open end x = 0. Temperature outside the aerogel is To and inside is at boiling temperature Tb. To and Tb are fixed constants.

Heat evaporates liquid

 \dot{N}, \dot{N}_{total} and \dot{x} are needed to solve the problem. At the boundary the heat flux is

$$J_Q = \frac{dQ}{dt}\frac{1}{A} = -K\frac{dT}{dx}$$
$$\dot{Q} = -KA\frac{T_b - T_0}{x}$$

$$\dot{N} = \frac{Q}{L_v} = \frac{KA}{L_v} \frac{T_0 - T_b}{x}$$
 (3.12)

$$\begin{split} \dot{N}_{total} &= \dot{N} \frac{Af}{\pi a^2} \\ \dot{x} &= \dot{N}_{total} \frac{z_1^3}{Af} = \frac{K z_1^3}{L_v f} \frac{T_0 - T_b}{x} \end{split}$$

Let β^* be

$$\beta^* = \frac{Kz_1^3}{L_v f} (T_0 - T_b)$$

Then the solution to this problem is the same as the solution for the Diffusion Limit Case (3.11)

$$x(t) = \sqrt{2\beta^* t} \qquad \beta^* = \frac{K z_1^3}{L_v f} (T_0 - T_b)$$
 (3.13)

Heat evaporates liquid and heats up gas particles

Now we assume the heat conducts in not only to evaporate the liquid but also to heat up the gas. The liquid temperature still remains at the boiling temperature T_b . Assume the particle diffusing rate \dot{N} is a constant. From the heat conduction and boundary condition, \dot{N} can be found. Let the heat conducting in (2.14) equal to the heat used to heat up gas particles and solve for T.

$$\dot{Q}_1 = K \frac{d^2 T}{dx^2} A dx \qquad \text{heat conduction}$$
$$\dot{Q}_2 = m c_g \dot{N} dT = m c_g \dot{N} \frac{dT}{dx} dx \qquad \text{heating up gas}$$
$$Q_1 + Q_2 = 0$$
$$\frac{d^2 T}{dx^2} = -\frac{m c \dot{N}}{A K} \frac{dT}{dx}$$
$$T(x) = -c_1 \frac{K A}{m c \dot{N}} \exp(-\frac{m c \dot{N}}{K A} x) + c_0$$

The boundary condition gives

$$T(0) = T_0 \qquad -c_1 \frac{KA}{mc\dot{N}} + c_0 = T_0 \qquad (3.14)$$

$$T(x_b) = T_b \qquad -c_1 \frac{KA}{mc\dot{N}} \exp(-\frac{mcN}{KA}x_b) + c_0 = T_b$$
 (3.15)

•

At the boundary the heat matches with the heat for evaporation.

$$\dot{Q}|_b = L_v \dot{N}|_b$$

 \dot{Q} at the boundary is $J_Q A = -KA \frac{dT}{dx}$

$$L_v \dot{N} = -KA \frac{dT}{dx}\Big|_{x_b} = -KAc_1 \exp(-\frac{mcN}{KAx_b})$$
(3.16)

Finally, use (3.14) \sim (3.16) to find \dot{N}

$$\dot{N} = \frac{AK}{mcx_b} \ln\left(1 + \frac{mc}{L_v}(T_0 - T_b)\right) \tag{3.17}$$

To double check the answer, let $T_0 \to T_b$ then $\ln\left(1 + \frac{mc}{L_v}(T_0 - T_b)\right) \to \frac{mc}{L_v}(T_0 - T_b)$ which makes \dot{N} the same as the pervious part (3.12). In the pervious part there is no gas heating which can also be interpreted as the gas temperature is closed to the surface temperature.

It is desired to write (3.17) with a constant K^* so that \dot{N} is of the same format as (3.12). If we can do so then the solution to this model is also of the form $x(t) = \sqrt{2\beta t}$

$$\dot{N} = K^* \frac{A}{L_v} \frac{T_0 - T_b}{x}$$

$$K^* = \frac{KL_v}{mc(T_0 - T_b)} \ln\left(1 + \frac{mc}{L_v}(T_0 - T_b)\right)$$

$$x(t) = \sqrt{2\beta^{**}t} \qquad \beta^{**} = \frac{K^* z_1^3}{L_v f}(T_0 - T_b)$$
(3.18)

There is one more condition to be considered to complete this section. That

is the heat conducs in to heat up the gas and when it reaches the boundary, it not only evaporates the liquid but also heats up the liquid. Then the liquid part is no longer at a fixed temperature T_b . This will change the particle diffusing rate \dot{N} . Then the temperature change at the boundary and moving boundary make the problem complicated. We cannot predict if the boundary moving rate will still scale exactly as the square root of time. With one more variable T_b , unless one more condition is specified, the problem is not analytically solvable.

To conclude this section, we found that the time it takes to empty the liquid usually is proportional to the square of the sample length. This feature is also found in the 1-D model in 3.2.1.

$$x = \sqrt{2\beta t}$$
 $Time = \frac{L^2}{2\beta}$

Furthermore, by comparing $\frac{1}{\beta}$ and $\frac{1}{\beta^*}$, we can find which is the slower process. $\frac{1}{\beta}$ is of the 10⁷ order and $\frac{1}{\beta^*}$ is of the 10⁹. Therefore diffusion is a faster process and conduction is the slower one which dominates the time it takes to empty liquid out.

3.2.4 3-D Model

The 3-D model is an aerogel sphere with 5 cm radius. The temperature is 800 K uniformly throughout the surface. The model is radial symmetric, so the boundary position, temperature and pressure at the same distance from the center are the same. Therefore the simulation is similar to the 1-D model only with the partial differential changed to gradient and divergence. In this section, some tricks to make the simulation more efficient are introduced. And finally the results of the simulations are presented and discussed.



Figure 3.6: Three dimensional model. A spherical aerogel with radius 5 cm.

In thee dimensions, the flux and diffusion equations become

$$\vec{J} = -D\vec{\nabla}n$$
$$\frac{\partial n}{\partial t} = -\vec{\nabla}\cdot\vec{J}$$

Since the model is radial symmetric, there are only radial terms in the equation.

$$J_r = -D\frac{\partial n}{\partial r}$$
$$\frac{\partial n}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 D\frac{\partial n}{\partial r}\right)$$

Dimensionless Simulation

It is time to discuss how to program the simulation. First it is desired to make the simulation in a scaled space and time so the simulation runs on dimensionless quantities. From scaling the unit out, the fact that time scales as length square can also be found here. Table 3.1 has all the equations needed to be worked on.

First, define dimensionless variables $\tau \ z, \ \tilde{p}, \ \tilde{T}, \ \tilde{n}, \ \text{and} \ \tilde{\eta}.$



Figure 3.7: The indices in the simulation. r is the radius and z is the spatial variable. J and J_Q are gas particle flux and heat flux respectively.

$$\begin{split} r &= (L-z) \frac{L}{N} & \text{The radius is divided into N steps.} \\ z \text{ is the indix from } 0 \sim N \text{ (Figure 3.7)} \\ p &= \tilde{p} P_0 & \text{Pressure } P_0 = 1atm = 101300 \text{ Pa} \\ T &= \tilde{T} T_0 & \text{Temperature } T_0 = 293 \text{ K room temperature} \\ n_g &= \tilde{n} n_{NTP} & \text{Gas number density } n_{NTP} = \frac{P_0}{kT_0} = 2.5 \times 10^{25} \, \#/m^3 \\ \eta(T) &= \tilde{\eta}(T_0) \eta_0 & \text{Gas viscosity } \eta_0 = \eta(T_0) = 1.105 \times 10^{-5} Pa \, s \\ \eta(T) &= \frac{4.725 \cdot 10^{-9} \cdot T^{1.622}}{1 + T/89.051} Pa \, s \\ K_{eff}(T) &= \tilde{K}(T_0) K_0 & \text{Effective thermal conductivity } K_0 = K_{eff}(T_0) \\ D_{gas} &= \tilde{D} D_0 & \text{Diffusion constant } D_0 = \frac{P_0 a^2}{8\eta_0} \text{ ; } \tilde{D} = \frac{\tilde{p}}{\tilde{\eta}} \\ t &= \tau \cdot \gamma & \text{Time } \gamma \text{ is the time scale.} \end{split}$$

Start with the gas particle diffusing equation and rewrite with dimensionless variables. Notice that when changing $\frac{d}{dr}$ to $\frac{d}{dz}$ there is a -1 coming from $\frac{dr}{dz}$ =

-1.

$$dn_g = \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{D_{gas}}{kT} \frac{dp}{dr} \right) \cdot dt$$
$$n_{NTP} d\tilde{n} = \frac{1}{r^2} \frac{d}{dz \frac{L}{N}} \left(r^2 \frac{D_0 \tilde{p}}{\tilde{\eta} k T_0 \tilde{T}} \frac{P_0 d\tilde{p}}{dz \frac{L}{N}} \right) \cdot d\tau \gamma$$

Equate the constants on both sides and then we get the rescaled function.

$$d\tilde{n} = \frac{1}{z^2} \frac{d}{dz} \left(z^2 \frac{\tilde{p}}{\tilde{\eta}\tilde{T}} \frac{d\tilde{p}}{dz} \right) \cdot d\tau$$
(3.19)

$$\gamma = \frac{L^2}{D_0 N^2} \tag{3.20}$$

Since (3.19) runs simulation on arbitrary size of aerogel, the real time to empty the aerogel only depends on γ . For example, if an initial condition takes 100 time steps to empty out the liquid inside the real time is $100\gamma = 100 \frac{L^2}{D_0 N^2}$ and thus a 10 cm aerogel sphere takes four times longer to empty than a 5 cm aerogel sphere. The time scales as square of the length is very important.

Next is the conduction equation, which the same method is applied.

$$d\tilde{T} = \left(c_1 \cdot \frac{1}{z^2} \frac{d}{dz} \left(z^2 \tilde{K} \frac{d\tilde{T}}{dz}\right) + c_2 \cdot \frac{\tilde{p}}{\tilde{\eta}\tilde{T}} \frac{d\tilde{p}}{dz} \frac{d\tilde{T}}{dz}\right) \cdot d\tau$$
(3.21)

$$c_{1} = \frac{K_{0}}{D_{0} \rho_{a} c_{a}} \qquad c_{2} = \frac{m c_{g} n_{NTP}}{\rho_{a} c_{a}}$$
(3.22)

One needs to take care of the temperature equation at the boundary carefully because the model is spherical. The energy change per time $\frac{dQ}{dt}$ is $(volume \cdot (\rho c) \frac{dT}{dt})$. The heat out of the boundary by conduction is $(J_Q \cdot area)$ and by evaporation is $(L_v n_{evap} \cdot area \, dx)$.

$$(\rho_a c_a + \rho_l c_l) \frac{4}{3} \pi r^3 \cdot \frac{dT_b}{dt} = -K_e f f \frac{dT}{dr} \Big|_b \cdot 4\pi r^2 - L_v \frac{D_{gas}}{kT} \frac{dp}{dr} \frac{4\pi r^2 dr}{dr}$$
$$d\tilde{T} \Big|_b = \left(c_3 \tilde{K} \frac{d\tilde{T}}{dz} + c_4 \frac{\tilde{p}}{\tilde{\eta}\tilde{T}} \frac{d\tilde{p}}{dz} \right) \cdot \frac{1}{N-z} \cdot d\tau$$
(3.23)

$$c_{3} = \frac{3 K_{0}}{(\rho_{a} c_{a} + \rho_{l} c_{l}) D_{0}} \qquad c_{4} = \frac{3 n_{NTP} L_{v}}{T_{0} (\rho_{a} c_{a} + \rho_{l} c_{l})}$$
(3.24)

Therefore Table 3.1 becomes Table 3.2 in a three dimensional system. For simplicity the ~ is omitted. The simulaiton is run in Mathcad and the program is included in Appendix B.

Table 3.2: Equations for simulating 3-D moving boundary model			
The spatial index z runs from 0 to N. 0 is the open end.			
Boundary is at b; b starts at $z = 2$.			
Gas	$dn_g = \frac{1}{z^2} \frac{d}{dz} \left(z^2 \frac{p}{\eta T} \frac{dp}{dz} \right) \cdot d\tau$	$t_{real} = \gamma \cdot \tau$	
	$dn_l = 0$	$\gamma = \frac{L^2}{D_0 N^2}$	
	$dT = \left(c_1 \cdot \frac{1}{z^2} \frac{d}{dz} \left(z^2 K \frac{dT}{dz}\right) + c_2 \cdot \frac{p}{\eta T} \frac{dp}{dz} \frac{dT}{dz}\right) \cdot d\tau$	$c_1 = \frac{K_0}{D_0 \rho_a c_a}$	
	p = nkT	$c_2 = \frac{m c_g n_{NTP}}{\rho_a c_a}$	
Boundary	$n_g = \frac{p}{kT}$		
	$dn_l = -n_{evap} = \frac{p}{\eta T} \frac{dp}{dz} \frac{1}{dz} \cdot d\tau$		
	$dT _{b} = \left(c_{3}K\frac{dT}{z} + c_{4}\frac{p}{\eta T}\frac{dp}{dz}\right) \cdot \frac{1}{N-z} \cdot d\tau$	$c_3 = \frac{3 K_0}{(\rho_a c_a + \rho_l c_l) D_0}$	
	$p = P_{sat}(T)/p_0$	$c_4 = \frac{3 n_{NTP} L_v}{T_0 \left(\rho_a c_a + \rho_l c_l\right)}$	
Liquid	$n_g = n_g _{boundary}$		
	$dn_l = 0$		
	$dT = dT _{boundary}$		
	$p = p _{boundary}$		

The entire simulation is then dimensionless. The constants c_1 , c_2 , c_3 , and c_4 are all dimensionless. We can run the simulation once and scaled it for different sizes of aerogel through the time constant γ . On the other hand, what can slow the simulation are the pore size a and the number of spatial steps N. a is in the term of diffusion constant D_0 , so a bigger pore size not only makes the time step

small but also make the heat conduction terms c_1 and c_3 smaller relative to the diffusion term. (The coefficient for the diffusion term is 1.) In this thesis, the pore size is set to be 100 nm.

There is nothing we can do with the pore size a but we can run a trick to make the time to run the simulation depends less on N. For a good and more accurate simulation result, the steps should be as small as possible. However, the time it takes to run the same simulation for N = 10 and N = 100 is 10^2 times more. To improve on this, a second index M is going to be introduced in the next subsection.

Speed Up The Simulation

To speed up the simulation, the length of the gas part is always divided into M steps. For example, let M be 10. The whole radius is divided into 50 steps (N = 50), one step Δr is $\frac{L}{N}$ wide. When the boundary is at z = 2, one simulation step in the gas region is $\frac{2\Delta r}{M} = \frac{L}{N} \cdot \frac{2}{M}$ wide, which is smaller than Δr . Then when the boundary is at z = 30, one simulation step in the gas region is $\frac{L}{N} \cdot \frac{30}{M}$, which equals to $3\Delta r$.

There are two reasons why a second index is good. First of all, the most furious reactions happens at the beginning of the simulation, when the temperature in aerogel is 700 K lower than the surface. Before the second index is introduced, this is when the simulation is done by the least number of steps, since the gas region is small. Therefore, if at the beginning gas region is divided into smaller steps, the simulation can be more accurate. On the other hand, when the boundary is further away from the surface, the temperature and the pressure distribution are approaching their steady states. The diffusion and conduction slow down. Before the second index is introduced, the simulation is running through a lot of steps when not much is happening.

If the gas region is only divided into M steps, the simulation runs more efficient. Since the main parts in the simulation are the gas region and the boundary, it is better to have good step sizes for the gas region. The only things change in the liquid part is the pressure and the temperature, but these two quantities are the same as at the boundary. Therefore by keeping track where the boundary is and the pressure and the temperature at the boundary, we have all the information of the liquid region.

The array size this simulation needs is M+2. i = 0 represents the surface. $i = 1 \sim M$ are the gas region. And i = M + 1 is the boundary. In each ith array there is another array with size 6. The second array keep tracks of the real time, boundary position, temperature, pressure and the gas and liquid number densities. The Mathcad program is provided in Appendix B.

The time constant γ changes whenever the step size changes, but the result obtained by this method can still scale to different length L. The results are presented in the next subsection.

Simulation Results

Initial Conditions: A sphere of 5 cm radius aerogel saturated with liquid methane at 112.3 K.

External Conditions: Pressure at the surface is fixed at 1atm. Temperature at the surfaces is fixed at 800 K.



Figure 3.8: 3-D simulation result: Boundary position v.s. time. 0 is the open end and 5 is the center. It takes 6749 seconds to empty the liquid methane.

Simulation Result: Figure 3.8 to Figure 3.16. It takes 6749 seconds to empty the liquid methane. The temperature in the liquid raises about 22 K during the first 60 seconds and remains there with little fluctuations.

The boundary moves similarly to the rectangular model at the beginning, proportional to the square root of time. But at the end it speeds up and becomes proportional to the cubes of time (Figure 3.8). Then we convert the boundary curve to the liquid weight curve which is scaled to its initial weight. Although it takes 1.8 hours to empty the liquid methane, at the first hour the aerogel already loses 90% of the liquid. (Figure 3.9)

Figure 3.10 gives a good idea of what happens in the aerogel. The temperature quickly heats up to 133 K and remains there. This means after te first 60 seconds the heat which conducts to the boundary only evaporates the liquid.



Figure 3.9: 3-D simulation result: Liquid weight v.s. time. The liquid methane weight is scaled to its initial weight. At 840 seconds, 50% of the liquid remains. At 2520 seconds, 20% of the liquid remains. At 3600 seconds, 10% of the liquid remains.

And a balance between heat conduction and particle diffusion is reached. Every time the boundary shifts, the system equilibrates the pressure and temperature distribution. This explains the fluctuations on the temperature curve. Figure 3.11 shows in the first 5 minutes of the simulation, the boundary movement matches with the peaks of the temperature.

Figure 3.12 and Figure 3.13 further show the temperature and pressure distribution in the M scaled spatial steps of the gas region. For time at 2000, 3000 and 4000 seconds, the pressure and temperature changes are small. Only after 5000 seconds, when the boundary is at 3.5 cm away from the surface and the boundary starts to quickly move toward the center (proportional to time cube), the pressure in the gas region quickly drops. Figure 3.14 and Figure 3.15 are the temperature and pressure profile scaled to the real spatial steps. We can see



Figure 3.10: 3-D simulation result: Liquid temperature v.s. time. At 60 seconds, the temperature reaches 133.58 K and fluctuates between 134.29 K and 132.24 K.



Figure 3.11: 3-D simulation result: Liquid temperature and boundary position v.s. time for the first 300 seconds of the simulation. The fluctuation period matches with when the boundary moves.

how the aerogel heats up and how the pressure inside changes as the boundary moves.



Figure 3.12: 3-D simulation result: Temperature Profile. Temperature distributions at different times show the change throughout time inside the gas region. The gas region length is rescaled so M = 11 is the gas-liquid boundary.

Despite the fact that the liquid temperature raises only 22 degrees, which is still more than 600 degrees colder than the surface, the pressure inside the liquid is at the saturation pressure of that temperature. Therefore, saturation pressure around 133 K is more than 4 atm. We doubt if aerogel can sustain a big pressure that is 4 atm. In the following a different simulation is run with the aerogel 3 μm pore size instead of 0.1 μm . The new simulation results in a small pressure increase inside the aerogel (Figure 3.17). This pore size is determined by comparing the gas diffusion coefficient in Adam Papallos thesis, *Aerogel: A Study in Elastic Moduli and Diffusion* [3]. In Adams thesis the gas diffusion constant is

$$D_{adam} = 7.2P \times 10^{-8} + 5.67 \times 10^{-4} \quad m^2/s$$

By equating the coefficient of P with the coefficient of our gas diffusion constant



Figure 3.13: 3-D simulation result: Pressure Profile. Pressure distributions at different times show the change throughout time inside the gas region. The gas region length is rescaled so M = 11 is the gas-liquid boundary.

 $\frac{a^2}{8n}$, a equals to 3.18 μm . ($\eta = 17.62 \quad \mu Pa \ s @ 294 \ K, 1 \ atm$)

With a bigger pore size, diffusion is much faster and the internal pressure is smaller. A change in the pore size, however, changes the time scale. A simulation with a = 3um takes 900 times longer than the simulation with a = 0.1um.

Luckily we learned in Chapter 3.3 that the aerogel drying process is dominant by the conduction rate so the faster diffusion rate has little impact on the simulation except for the internal pressure distribution. The simulation result shows that with $a = 3\mu m$ it takes the same amount of time (6750 seconds) to empty the liquid. The boundary moving rate turns out to be identical with the simulation on pore size being 100 nm. On the other hand, the liquid temperature rises at most 0.21 degree and the corresponding saturation pressure is only 1.017 atm.

Unfortunately the internal pressure cannot determine the actual pores size. The pores in aerogel need not to be spherical and be of a uniform size. The pore



Figure 3.14: 3-D simulation result: Temperature Profile. Temperature distributions at five different times are put together to show the change throughout time at different position inside aerogel. The dots on each curve indicate the boundary positions. At x = 0, T is the fixed surface temperature 800K.



Figure 3.15: 3-D simulation result: Pressure Profile. Pressure distributions at five different times are put together to show the change throughout time at different position inside aerogel. The dots on each curve indicate the boundary positions. At the surface, pressure is fixed at 1 atm.



Figure 3.16: 3-D simulation result: Liquid Pressure v.s. time. This result is obtained by calculating the saturation pressure of the liquid temperature (Figure 3.10). The pressure fluctuates between 4.03 atm and 4.56 atm.

size in our simulation represents an effective pore size that describes the system. How well the pores connect to other pores is also included in this effective pore size in the simulation. Therefore, we cannot determine the size of the pores by just comparing the diffusion constants or by comparing the pressures.



Figure 3.17: Pore size 3 μm simulation result: Liquid pressure and temprature v.s. time. The temperature fluctuates between 112.33 K and 112.51 K. The pressure fluctuates between 1.002 atm and 1.017 atm.

The most important result of the simulation is the liquid weight curve because this can be compared with the experiment. In the experiment the weight of the aerogel is recorded while the aerogel is burning. By comparing the two curves, we can tell how well the simulation describes the system.

Chapter 4

Experiments

4.1 Setup of the Experiments

The experiments used six aerogel samples with different sizes and shapes. Two were placed on a plate and the other four were hung. Figure 4.2 is an illustration of the samples.

Apparatus:

A balance with an arm 10 times the distance than the other arm was setup. The short arm was connected to a force meter. The force meter measured between 0 and 10 N and it was connected to the computer which recorded time and force. The long arm was used to hang the aerogel sample.

Preparation of the methane soaked aerogel sample:

A cold bath of liquid nitrogen was prepared. A chunk of aerogel was placed in a test tube which was connected to methane gas. Then the test tube was lowered into the cold bath and the methane gas started condensing. When liquid methane



Figure 4.1: The apparatus and a burning aerogel. The aerogel was burning on the long arm of a balance which was connected to the force meter.

completely covered the aerogel chunk, the sample was ready.

The methane soaked aerogel was hung on the apparatus through a long hook. The sample was set on fire while the force meter recorded the time and weight loss. The experiment ended when the flam went out and the piece of aerogel started smoldering.

4.2 Results of the Experiments

The results are presented as a plot of scaled weight versus time in Figure 4.3. The weight difference between the beginning and the end of the experiment is set to be the total liquid weight which is the denominator of the scaled weight. The weight at each time minus the weight at the end is the remaining liquid weight, also the numerator of the scaled weight.

The time each sample took to burn is indicated in Figure 4.2. Since each sample has a different size and a different shape, the burn off time is expected to be different. The fact that time scales with the square of the length helps with comparing the data. In a spherical model, the time it takes to burn is proportional to the radius square. The characteristic length of other geometry is studied in order to compare the data sets. This length is called the effective length, L_{eff} .

The effective length is defined by the analytical solutions to the diffusion problem with a constant diffusion coefficient D.

$$\frac{\partial n}{\partial t} = D\nabla^2 n \tag{4.1}$$

The solution for a sphere with radius R with boundary condition $\psi_0(R) = 0$ is:

$$\Psi(r,t) = \phi(t) \,\psi(r) \qquad \phi_0(t) = e^{-\lambda_0 t} \qquad \psi_0(r) = \frac{\sin(k_0 r)}{k_0 r}$$
$$\lambda_0 = k_0^2 D = \frac{\pi^2 D}{R^2}$$

The characteristic time scale τ in this solution is $\frac{1}{\lambda_0}$, so define the effective length square L_{eff}^2 for a spherical model to be R^2 , which is proportional to $\frac{1}{\lambda_0}$.

The solution for a rectangular block model with sides L_x , L_y and L_z has λ_0 equaling to $D\pi^2 \left(\frac{1}{L_x^2} + \frac{1}{L_y^2} + \frac{1}{L_z^2}\right)$. The effective length is $\left(\frac{1}{L_x^2} + \frac{1}{L_y^2} + \frac{1}{L_z^2}\right)^{\frac{-1}{2}}$. If one side is much shorter then the other two, the time scale is dominant by the shortest length. This is intuitive because it is the easiest to diffuse out from the shortest path.

Finally, the solution for a cylinder with radius S and length L has λ_0 equaling to $D\pi^2 \left(\frac{x_0^2}{\pi^2 S^2} + \frac{1}{L^2}\right)$ where x_0 is the first zero in the zero-th order Bessel function, $x_0 = 2.43$. So the effective length is $\left(\frac{x_0^2}{\pi^2 S^2} + \frac{1}{L^2}\right)^{\frac{-1}{2}}$ With this information, the effective length of each sample is calculated. The time of each data is divided by their effective length square so the data sets can be compared.

The burn off results are shown in Figure 4.3. Sample 1 and Sample 6 are burned from a plate while the others are directly hung from the arm of the balance. The noise of the data is caused by the sample swinging while the data was taken. It is not easy to take data with low noise because the long hook swung after the samples were placed. Once the aerogel sample was removed from the cold bath, the methane started evaporating and the water molecules started condensing onto the aerogel surface, so there is no time to wait for the swinging to stop. The experimental result for Sample 1 is obtained by video taping Sample 1 burning



Figure 4.2: Aerogel samples. The sizes of the aerogel samples are indicated next to each graph. Leff is the effective length of the sample and τ is the time each sample took to burn.

on a scale with a can separating the scale and the flame. Therefore there was no swinging which caused the noise. However, it was not efficient to transcribe the reading of the scale from the recording of the video camera.

The results for Sample 3, 4 and 5 match relatively well with one another. Since the noise on Sample 2 and 6 are big and the result for Sample 1 is obtained by another method, the average curve is taken by the average of Sample 3, 4, and 5 with the scaled time. The average effective length is 0.92 cm. The average burning scaled time is 186 seconds/ $Leff^2$.

To compare with the simulation, the average data and the simulation data were plotted on Figure 4.4. The results match until the weight is 40% of its original. Afterwards the simulation weight losses much slower than the experiment. If compared by scaling time with the total time, then the weight losing rate of the simulation is faster than that of the experiment at the beginning.



Figure 4.3: Burn off results of six samples. The fraction of the total liquid weight and time were plotted. The samples' shapes and sizes are indicated in Figure 4.2. The results for sample 1, 2 and 6 are in A. and the results for 3, 4 and 5 are in B.

There are discrepancies between the experimental result and the simulation. Few things might affect the experimental results. First, the preparation affects the result due to the methane evaporation and the water molecules in the air started condensation onto the aerogel after the sample was removed from the cold bath. Although this only cost at most 30 seconds, it was already 20% of the time burn off time. Second, the edges of the aerogel samples began smoldering before the end of the experiments. When the aerogel itself started smoldering, the weight differences recorded were not purely from the loss of liquid methane. The above two are explanation to the discrepancies between the simulation and experimental results. We could eliminate theses two causes by other experimental setups. On the other hand, there is one consideration that could be included in the simulation. This might help obtain a model that better describes the system.

The simulation is run under a uniform temperature on the surface. When the aerogel is burning, however, the temperature around the surface is not expected to be the same. If there is a temperature distribution on the surface, the liquid inside the aerogel will have different temperatures. Then the pressure inside the liquid is not uniform. The pressure difference might cause the liquid to move and changed the simulation result. In the next chapter, we are going to discuss how the temperature distribution on the surface affects the boundary moving rate.



Figure 4.4: Averaged experimental data plot and simulation data plot. The y-axis is the liquid weight over the initial liquid weight. In A the x-axis is the time divided by L_{eff}^2 . The average data ends at effective time being 186 and the simulation ends at effective time bein 269. In B the time is scaled to the total burn off time.

Chapter 5

Discussion

This chapter is about two features found after comparing the simulation with the experimental result. First is the length square relationship with the desorption time. The second is about the discrepancies between the simulation and experimental results. More experiments and simulation models have been done to address the latter issue.

5.1 Relationship between Time and Length

The feature that the desorption time scales with the length square has showed up in the simulation result of the 1-D Boundary Moving Model, and in the analytical solutions to the Pure Diffusion Model and Pure Conduction Model. In the 3-D model, the time constant γ is also a function of the length square. Thus, if the experimental results also support this feature, we can easily find the burn off time of a different chunk of aerogel.



Figure 5.1: Burn off time v.s. Effective Length. The burn off time of the samples and their effective lengths are plotted in this graph. The dash line is the function $t(x) = a \cdot x^2$, where a is an constant. The prediction that the time scales with the square of the length matches well with the experimental results.

Comparing the burn off data by finding the effective length turns out to be successful. Figure 4.3 successfully put all the data sets together by scaling the time with the effective length square. Furthermore, Figure 5.1 plots the burn off time and the effective length of each sample to compare with the prediction $t(x) = a \cdot x^2$. t is the burn off time, x is the effective length (cm) and a is a constant. a equals to 180.7 fits the curve. (a is 170.6 if trying to fit to all data points, a is 180.7 if excluding Sample 1 and 6 which were burnt on a plate.) To conclude, the feature that the time is proportional to the length square is also found in the experiment.

5.2 Temperature Distribution on the Surface

Because the simulation results and the experimental results have some discrepancies, we think the temperature difference on the surface might be crucial. The temperature differences on the surface cause the differences in liquid temperature at the boundary. Thus the saturation pressure at the liquid is different. With pressure differences the liquid can flow around and the liquid boundary moves by means other than evaporation.

5.2.1 Improved 1-D Model

The 1-D moving boundary model is studied again. Figure 5.2 is an illustration of Liquid Moving Model. The model is the similar to the boundary moving model in Chapter 3 but there are two open ends, x = 0 and x = L. The two ends are applied with different surface temperatures. Furthermore, the liquid thermal conductivity is considered in this model so the temperature in the liquid region



Figure 5.2: One aerogel tube in 1-D Moving Boundary Model. This model has two open ends, x = 0 and L, and two boundaries, x_L and x_R . The gas particles diffuse out through the two ends. The open ends have two different temperatures. The heat conducts in through the two ends as well. The number of liquid particles at the boundaries can decrease or increase by evaporation or by viscous flow.

is not uniform. The combined aerogel and liquid thermal conductivity $K_l \oplus K_a$ is obtained by the same way as $K_g \oplus K_a$ (Chapter 2.2.2).

This model has two boundaries, X_L and X_R . The gas particles in two gas regions only diffuse out through the open end that is closer to the region. At the boundary the liquid particles can evaporate or move toward the boundary which has lower pressure.

The Poiseuille's law (2.6) is used to calculate the liquid flux as it is used to calculate the gas particle flux. The pressure difference in (5.1) is the difference of the pressure at two boundaries and the distance is the length of the liquid region $X_R - X_L$

$$J_{liq} = \frac{\rho_l a^2}{m \, 8\eta_l} \frac{\partial p}{\partial x} \tag{5.1}$$
With this information the simulation is built. Detail of the programming is shown in Appendix E. The results are shown from Figure 5.3 to Figure 5.5. If there is no temperature difference at the cold and hot open end, the liquid does not move. The simulation performs as if two 1-D Moving Boundary Models sticked back to back. In Figure 5.3, the red line shows that if the temperatures on both open ends are the same, the boundary ends at the center of the sample (2.5 cm). Figure 5.3 shows that when there is a 50-degree difference, the desorption takes longer than when there is no temperature difference. But when the temperature difference is 100 K, it takes shorter amount time to desorb.



Figure 5.3: Three sets of boundary position v.s time. 0 cm is the open end with colder external temperature. 5 cm is the open end with 800 K. The red line represents the boundary of the simulation with both ends have temperature 800K. The liquid does not move so the last boundary is at the center of the aerogel sample. The blue line is with the colder end at 750 K. It takes longer than the red one and the boundary ends closer to the cold end. The green line is with the colder end at 700 K. It takes shorter time than the red one.



Figure 5.4: Total time and the last boundary position v.s the cold end temperature. The simulation runs from 112.3 to 800 K to show the relationship between the desorption time and the cold end temperature. It also shows the relationship between the ending boundary position and the cold end temperature. The dash line at 0.375 cm is the initial boundary at the cold end.

The explanation to this is that when there is a small temperature difference, the pressure difference at the two liquid boundaries is small, so little of the liquid is pushed to the cold boundary. At the same time since one end is colder, the desorption takes longer. Therefore the total time the sample takes to dry is longer then the case with no temperature difference at the boundary. In the other case, when the temperature difference is big, the rate of liquid being pushed to the boundary compensates for the rate of evaporating. The total time the sample takes to dry is then shorter. This result is confirmed in Figure 5.4. In Figure 5.4 the temperature at the cold end runs from 112.3 to 800 K while the hot end is always 800 K. For one end at 112.3 K, it only takes 40 % of the time of the case with no temperature difference. The liquid boundary is pushed against the cold open end. From the simulation we know that besides a transition temperature that is close to the hot end temperature, the desorption rate is much faster.



Figure 5.5: Liquid weight v.s time. The results of two simulations in which the temperatures of the cold ends are 800 K and 700 K. The weight is presented as Weight/Total Weight. In A the red line ends at 4446 seconds, and the blue line ends at 3713 seconds. In B the time is scaled to the ending time each simulation.

The one dimensional Liquid Moving Model says that if there is a big temperature difference, the burn off time will be shorter. This might explains why the desorption time in the 3-D simulation in Chapter 3 is longer than the real experiment. Figure 5.5 compares the liquid weight curve with two cases, the cold end temperature being 800 and 700 K. Comparing Figure 5.5 with Figure 4.4, the experimental result, the similarity in the shapes of the curves are obvious. However this is a one dimensional model. This model is hard to carry out for a three dimensional sphere because the radial symmetry is lost so the simulation needs to calculate through each coordinate in the three dimensional place. To conclude, if there is a temperature distribution on the surface, the rate of weight loss will be greatly affected.

5.2.2 Surface Temperature Experiment

A small experiment was conducted to understand the temperature distribution on the surface of a burning aerogel. A thermal couple was placed at the tip of an aerogel sample saturated with liquid methane. All but one side of the sample were wrapped with aluminum foil to protect the thermal couple. While burning, the sample was rotated to sideward and to point upward every few seconds. The voltage across the thermal couple jumped when the sample rotated. The sample was even pointed downwards a few times before the flame went out. The voltage was then converted to temperature shown in Figure 5.6. This experiment shows that the temperature on the side is hotter than the top, and the bottom is probably the hottest. The temperature difference between at the sides and on the top can be as big as 120 degrees.

Surprisingly is that the temperature at the surface gains slowly instead of maintaining around a high temperature. This experiment not only shows the temperature distribution on the surface but also points out that the temperature at the surface is not fixed. Future research models should take into account of the time dependent temperature at the surface.



Figure 5.6: Surface Temperature Measurement. The burning aerogel sample was rotated every couple second to point up (\uparrow) or right (\rightarrow) . Close to the end the sample was also pointed downward (\downarrow) . The drop of temperature at the end was because the flame went out. This graph indicates that the temperature is higher close to the bottom of the surface.

Chapter 6

Conclusion

This thesis had done both theoretical and experimental work on the properties of desorption in porous media under a pressure and a temperature gradient. Organic aerogel and methane were studied in this thesis. Diffusion and conduction are the main concept to understand the desorption process. With the isotherm of liquid adsorption in spherical pores, simulation models are built to describe the system. A few variations of models have been studied and the results were compared to the experiments. The experiments took chunks of liquid methane soaked aerogel samples and monitored the weight while the samples were burning. Furthermore the temperature distribution at the surface of the aerogel sample was measured in order to improve the simulation model. Future research needs to focus on the time dependent surface temperature.

The results of the simulation and the experimental results both show that the total desorption time is proportional to the square of the sample's effective length. For a spherical sample the effective length is the radius. There are, however, discrepancies between the simulation and the experimental results. The liquid weight losing rate is slower than the experimental result at the end of the burning. The experiments take shorter time than the simulation. This leads to further investigation of a temperature differences on the surface, which turn out to have a significant impact on the result. The temperature distribution results in the liquid being pushed to the colder part, but because the liquid remains close to the burning surface, it evaporates faster.

The simulation result states that a five cm radius spherical aerogel saturated with liquid methane takes 1.88 hours (6750 seconds) to burn. On the other hand, it takes 1.25 hours (4500 seconds) to burn by the prediction using experimental result. The goal of this project is to extend the results to liquid hydrogen. Under the same condition, simulation result with hydrogen states that it takes 25.4 minutes (1525 seconds) to burn. This result indicates that storing hydrogen in aerogel chunks prevents explosion and thus the aerogel filled hydrogen fuel tank is a good suggestion to improve the safety of hydrogen storage.

Furthermore, this study goes beyond aerogel. The parameters used to describe a porous material in the simulations are pore size, filling fraction, density, heat capacity, and thermal conductivity. If these parameters of any porous material are known, the simulation models apply. To conclude, this thesis has done a general study of desorption properties of porous media, with the models and experiments carried out on organic aerogel and methane. This thesis also answers the original question, whether or not filling aerogel into hydrogen fuel tank can increase the safety level of hydrogen storage. And the answer is yes!

Appendix A

Constants

Aerogel

$\rho_a = 140$	kg/m^3	density
$c_a = 1700$	J/kg K	heat capacity
$k_a = 0.003$	W/m K	thermal conductivity

Methane

$T_b = 112.3$	K	boiling temperature $@$ 1 atm
$m = 26.672 \cdot 10^{-27}$	kg	mass per particle
$\rho = 422.4$	kg/m^3	liquid density
$z_1 = 3.98 \cdot 10^{-10}$	m	liquid particle size $(z_1^3=m/\rho)$
$\gamma = 0.01346$	N/m	surface tension
$T_v = 1500$	K	van der Waals temperature
$L_v = 1.362 \cdot 10^{-3}$	J	latent heat per particle
$\eta_l = 121.34$	μPas	liquid viscosity @ T_b
		$\eta_l(T) = 204.52 \cdot \left(\frac{T}{90.694}\right)^{-2.648}$
$\eta_g = 4.38$	μPas	gas viscosity
		$\eta_g(T) = \frac{4.725 \cdot 10^{-3} \cdot T^{1.622}}{1 + \frac{T}{89.051}}$
$c_l = 3480$	J/kg K	liquid heat capacity @ T_b
$c_g = 2218$	J/kg K	gas heat capacity @ T_b
$K_l = 0.186$	w/m K	liquid thermal conductivity @ T_b
		$K_l(T) = 0.341 - 0.001412 \cdot T$
$K_g = 0.011$	w/m K	gas thermal conductivity @ T_b
	$K_g(T) =$	$= 4.008 \cdot 10^{-6} \cdot T^{1.552} + 6.48 \cdot 10^{-3}$

Appendix B

Mathcad Program - Simulation II: 3-D Boundary Moving Model

3-D Spherical Simulation of moving boundary model. The second index $1 \sim M$ is for the Gas region.

Spherical Simulation Radius of the sample (m) $L_{\rm M} = 0.05$ pour size (m) filling fraction $a := 0.1 \cdot 10^{-6}$ N := 50 M := 10 f := 0.8 $k := 1.38 \cdot 10^{-23}$ Aerogel Properties ca := 1700 ρ a := 140 ρ aca := 2.38 \times 10⁵ ka := 0.003 Methane Properties Tb := 112.3 $m = 16 \cdot 1.667 \cdot 10^{-27}$ $Lv := 5.1083 \cdot 10^{5} \cdot m$ kl := 0.186 $p1c1 := 422.4 \cdot 3480 \cdot f$ cg := 2218 PO := 101300 Pa T0 := 293 К $psat(t) := \frac{10^{6} \cdot 1059.2 \cdot e}{\frac{10^{6} \cdot 1059.2 \cdot e}{P0}}$ $nNTP := \frac{P0}{k \cdot T0}$ $\mathrm{nNTP}=2.505\times10^{25}$

$$\eta_{0} := \frac{4.725 \cdot 10^{-9} \cdot T0^{1.622}}{1 + \frac{T0}{89.051}} \qquad \qquad \eta(t) := \frac{4.725 \cdot 10^{-9} \cdot (t \cdot T0)^{1.622}}{1 + \frac{t \cdot T0}{89.051}} \cdot \frac{1}{\eta_{0}}$$

kakg0 := 0.03046

$$kg(t) := 4.008 \cdot 10^{-6} (t \cdot T0)^{1.552} + 6.48 \times 10^{-3}$$

$$kakg(t) := \frac{ka^{2} \cdot \left(\frac{2}{1+f-f}^{3}\right)^{2} + kg(t) \cdot ka \cdot f^{\frac{2}{3}} \cdot \left(\frac{2}{1+f-f^{\frac{3}{3}}}\right)}{ka \cdot \left(\frac{2}{1+f-f^{\frac{3}{3}}}\right) \cdot f^{\frac{3}{3}} + \left(\frac{1}{1-f^{\frac{3}{3}}}\right) \left(\frac{2}{1-f^{\frac{3}{3}}}\right) \cdot \left[\frac{2}{ka \cdot \left(1+f-f^{\frac{3}{3}}\right) + kg(t) \cdot f^{\frac{3}{3}}}\right]} \cdot \frac{1}{kakg0}$$

Constants

$$D0 := \frac{a^2 \cdot P0}{8 \cdot \eta 0}$$

$$D0 = 1.146 \times 10^{-5}$$

$$const1 := \frac{kakg0}{D0paca}$$

$$const2 := \frac{nNTP \cdot m \cdot cg}{paca}$$

$$const2 = 6.227 \times 10^{-3}$$

$$const3 := \frac{3kakg0}{(plcl + paca) \cdot D0}$$

$$const3 = 5.637 \times 10^{-3}$$

$$const4 := \frac{3nNTP \cdot Lv}{T0 \cdot (plcl + paca)}$$

$$const4 = 2.472 \times 10^{-3}$$

$$timescale0 := \left(\frac{L}{N}\right)^2 \cdot \frac{1}{D0}$$

$$timescale0 = 0.087$$

Simulate from n until the real time reaches "otalTime" with time step dtime

 $bt(boundary, TempIn, TempOut, dtime, TimeInterval, TimeTotal) := \begin{tabular}{||C|} C \leftarrow IC(boundary, TempIn, TempOut) \end{tabular}$

t ← 0

The main code, sets the initial condition and evolve until the time reaches "TimeTotal". Report back the time, boundary position, liquid temperature and the liquid number density at the boundary

$$\begin{split} \mathbf{i} &\leftarrow \mathbf{0} \\ \mathbf{b}_0 &\leftarrow \left(\mathbf{c}^{\left(1\right)}\right)_1 \cdot \frac{\mathbf{L}}{\mathbf{N}} \\ \mathbf{n}_0 &\leftarrow \mathbf{0} \\ \mathbf{T}_{\mathbf{b}_0} &\leftarrow \left(\mathbf{c}^{\left(\mathbf{M}+1\right)}\right)_4 \cdot \mathbf{T} \mathbf{0} \\ \mathbf{n}_0 &\leftarrow \left(\mathbf{c}^{\left(\mathbf{M}+1\right)}\right)_3 \\ \text{while } \mathbf{t} \leq \mathsf{Time Total} \\ \mathbf{i} &\leftarrow \mathbf{i} + 1 \\ \mathbf{C} &\leftarrow \mathsf{simulation}(\mathbf{C}, \mathbf{t} + \mathsf{Time Interval}, \mathsf{dtime}) \\ \mathbf{t} &\leftarrow \left(\mathbf{c}^{\left(1\right)}\right)_0 \\ \mathbf{b}_i &\leftarrow \left(\mathbf{c}^{\left(1\right)}\right)_1 \cdot \frac{\mathbf{L}}{\mathbf{N}} \\ \mathbf{n}_i &\leftarrow \left(\mathbf{c}^{\left(\mathbf{M}+1\right)}\right)_3 \\ \mathbf{T}_i &\leftarrow \left(\mathbf{c}^{\left(\mathbf{M}+1\right)}\right)_4 \cdot \mathsf{T} \mathbf{0} \\ \mathbf{t}_i &\leftarrow \mathsf{t} \cdot \mathsf{timescale0} \\ \\ \mathsf{break} \quad \mathsf{if} \quad \left(\mathbf{c}^{\left(0\right)}\right)_1 > \mathbf{N} \\ \begin{pmatrix} \mathbf{n} \\ \mathbf{b} \\ \mathsf{Tb} \\ \mathsf{nl} \end{pmatrix} \end{split}$$

Initial Conditions

$$\begin{split} \mathrm{IC}(\mathsf{b},\mathrm{Tin},\mathrm{Tout}) \coloneqq & \operatorname{time} \leftarrow 0 \\ & \mathrm{for} \quad i \in 0 \\ & \mathrm{T}_i \leftarrow \frac{\mathrm{Tout}}{\mathrm{T}_0} \\ & \mathrm{p}_i \leftarrow 1 \\ & \mathrm{ng}_i \leftarrow \frac{\mathrm{P}_i}{\mathrm{T}_i} \cdot \mathrm{f} \\ & \mathrm{for} \quad i \in \mathrm{M} + 1 \\ & \mathrm{T}_i \leftarrow \frac{\mathrm{Tin}}{\mathrm{T}_0} \\ & \mathrm{p}_i \leftarrow \mathrm{psal}(\mathrm{T}_i) \\ & \mathrm{ng}_i \leftarrow \frac{\mathrm{P}_i}{\mathrm{T}_i} \cdot \mathrm{f} \\ & \mathrm{nl}_i \leftarrow \frac{1.58 \cdot 10^{28} \cdot \mathrm{f}}{\mathrm{nNTP}} \\ & \mathrm{for} \quad i \in 1 \dots \mathrm{M} \\ & \mathrm{nl}_i \leftarrow 0 \\ & \mathrm{T}_i \leftarrow \frac{\mathrm{Tout}}{\mathrm{T}_0} - \frac{\mathrm{i}}{\mathrm{M} + 1} \cdot \frac{\mathrm{Tout} - \mathrm{Tin}}{\mathrm{T}_0} \\ & \mathrm{p}_i \leftarrow \mathrm{p}_0 - \frac{\mathrm{i}}{\mathrm{M} + 1} \cdot (\mathrm{P}_0 - \mathrm{P}_{\mathrm{M} + 1}) \\ & \mathrm{ng}_i \leftarrow \frac{\mathrm{P}_i}{\mathrm{T}_i} \cdot \mathrm{f} \\ & \mathrm{for} \quad i \in 0 \dots \mathrm{M} + 1 \\ & \mathrm{R}^{(j)} \leftarrow \begin{pmatrix} \mathrm{time} \\ \mathrm{b} \\ \mathrm{ng}_i \\ \mathrm{nl}_i \\ \mathrm{T}_i \\ \mathrm{p}_i \end{pmatrix} \\ & \mathrm{R} \end{split}$$

from boundary=b-1 to b the infomation in the M gas region steps has to be recalculated

$$\begin{split} & \text{for } i \in M+1 \\ & \text{Iml}_i \leftarrow \frac{1.58 \cdot 10^{28} \cdot f}{n \text{NTP}} + n \text{I}_i \\ & \text{nT}_i \leftarrow \text{T}_i \\ & \text{nT}_i \leftarrow \text{T}_i \\ & \text{np}_i \leftarrow \text{p}_i \\ & \text{mg}_i \leftarrow \text{ng}_i \\ & \text{for } i \in 0...M+1 \\ & \text{R}^{(i)} \leftarrow \begin{pmatrix} \text{time} \\ & \text{nevvb} \\ & \text{mg}_i \\ & \text{ml}_i \\ & \text{nT}_i \\ & \text{np}_i \end{pmatrix} \\ & \text{R} \end{split}$$

Evolve from "n" until the real times reaches "time" or until the boundary moves.

$$\begin{split} \mathsf{DC}(\mathbf{n}, \mathsf{time}, \mathsf{dt}) & \coloneqq & \text{for } i \in \mathbb{O}. \ \mathsf{M} + 1 \\ & \left(\begin{array}{c} \mathsf{startTime} \\ \mathbf{b} \\ \mathsf{reg}_i \\ \mathbf{n}_i \\ \mathbf{T}_i \\ \mathbf{p}_i \end{array} \right) & \leftarrow & \mathsf{n}^{(j)} \\ & \texttt{timeScale} \leftarrow \left(\frac{\mathbf{b}}{\mathbf{M}} \right)^2 \\ & \texttt{endTime} \leftarrow \mathsf{startTime} \\ & \texttt{vhile} \ \texttt{endTime} \leftarrow \mathsf{startTime} \\ & \texttt{for } i \in 0 \dots \mathbf{M} \\ & \int_{\mathbf{I}} \leftarrow \frac{1}{\mathbf{v} \left(\frac{\mathsf{T}_{i+1} + \mathsf{T}_i}{2} \right) \cdot \left(\mathsf{T}_{i+1} + \mathsf{T}_i \right) \cdot \left(\mathsf{P}_{i+1} - \mathsf{P}_i \right) \\ & \texttt{for } i \in 1, 2 \dots \mathbf{M} \\ & \int_{\mathbf{I}} \mathsf{for } i \in 1, 2 \dots \mathbf{M} \\ & \int_{\mathbf{I}} \mathsf{drg}_i \leftarrow \left[\frac{-2J_{i-1}}{(\mathsf{N}+1) \cdot \frac{\mathsf{M}}{\mathsf{b}-i}} + \left(J_i - J_{i-1} \right) \right] \mathsf{dt} \\ & \int_{\mathbf{I}} \mathsf{drg}_i \leftarrow \left[\mathsf{constl} \left\{ \frac{-2J_{i-1}}{(\mathsf{N}+1) \cdot \frac{\mathsf{M}}{\mathsf{b}-i}} + \left(\mathsf{IT}_i - \mathsf{IT}_{i-1} \right) \right] + \mathsf{const2} J_{i-1} \left(\mathsf{T}_i - \mathsf{T}_{i-1} \right) \right] \mathsf{dt} \\ & \int_{\mathbf{I}} \mathsf{for } i \in \mathsf{M} + 1 \\ & \int_{\mathbf{I}} \mathsf{drg}_i \leftarrow -J_{i-1} \mathsf{dt} \\ & \int_{\mathbf{I}} \mathsf{dT}_i \leftarrow \frac{1}{(\mathsf{N}+1) \cdot \frac{\mathsf{M}}{\mathsf{b}} - \mathsf{M}} \cdot \left(-\mathsf{const3} \cdot \mathsf{JT}_{i-1} - \mathsf{const4} \cdot \mathsf{J}_{i-1} \right) \cdot \mathsf{dt} \end{split}$$

$$\mathbb{R}^{(i)} \leftarrow \mathbb{R}^{i} + \mathbb{I}^{i} + \mathbb{I}^{I$$

Simulation results

$$B := bt \left(2,112.3,800,0.05,\frac{60}{timescale0},\frac{6800}{timescale0}\right)$$

index := 0.. rows(B₀) - 1

s -7

Boundary position (cm) v.s. time (seconds)



ends at t = 6749 seconds

$$w_{index} \coloneqq \frac{4}{3} \cdot n \cdot \left[L - \left(B_1 \right)_{index} \right]^3 \cdot \frac{1.58 \cdot 10^{28} \cdot f}{nNTP} + 4 \cdot n \cdot \left[L - \left(B_1 \right)_{index} \right]^2 \cdot \frac{L}{N} \cdot \left(B_3 \right)_{index}$$

Liquid weight (%) v.s. Time (s)





Liquid pressure (atm) v.s. Time (s)

Liquid temperature (K) v.s. Time (s)



Appendix C

Mathcad Program - Simulation II: 1-D Boundary Moving Model

1-D rectangular model

pour size (m)	filling fraction	size of the sample (m)	N:= 20
a:= 0.1·10 ⁻⁶	f := 0.8	L := 0.05	
$D0 := \frac{a^2 \cdot p_0}{8 \cdot \eta_0}$	do = 1.146 × 10	o ⁻⁵	
constl := <u>kakg0</u> D0paca	const1 = 0.011	l	
$const2 := \frac{nNTP \cdot m \cdot cg}{paca}$	const2 = 6.227	7×10 ⁻³	
const3 :=	const3 = 1.879	9×10 ⁻³	
const4 := $\frac{nNTP \cdot Lv}{T0 \cdot (\rho lcl + \rho aca)}$	const4 = 8.239	9×10 ⁻⁴	
timescale0 := $\left(\frac{L}{N}\right)^2 \cdot \frac{1}{D0}$	timescale0	- 0.545	

The main code, sets the initial condition and evolve until the real time reaches "TimeTotal"Report back the time, boundary position, liquid temperature and the liquid number density at the boundary

btism(boundary, TempIn, TempOut, dtime, TimeInterval, Time Total) := S + IC(boundary, TempIn, TempOut)

$$\begin{aligned} & \leftarrow 0 \\ & t_0 \leftarrow \left(s^{(0)} \right)_0 \cdot \frac{L}{N} \\ & t_0 \leftarrow 0 \\ & Tb_0 \leftarrow \left(s^{(N-1)} \right)_3 \cdot T0 \\ & al_0 \leftarrow \left(s^{(N-1)} \right)_2 \\ & \text{while } t \leq \text{Time Total} \\ & \text{i} \leftarrow i + 1 \\ & \text{S} \leftarrow DC(S, \text{Time Interval}, \text{dtime}) \\ & t \leftarrow t + \text{Time Interval} \\ & b_i \leftarrow \left(s^{(1)} \right)_0 \cdot \frac{L}{N} \\ & nl_i \leftarrow \left[s^{(S^{(1)})} \right]_2 \\ & Tb_i \leftarrow \left(s^{(N-1)} \right)_3 \cdot T0 \\ & nt_i \leftarrow t \cdot \text{timescale0} \\ & \text{break} \quad \text{if } b_i > N \\ & \begin{pmatrix} n \\ b \\ Tb \\ nl \end{pmatrix} \end{aligned}$$

Initial conditions

$$\begin{split} \mathrm{IC}(\mathrm{b},\mathrm{Tin},\mathrm{Tout}) \coloneqq & \quad \text{for } i \in \mathbf{0} \\ & \quad \mathrm{nl}_i \leftarrow \mathbf{0} \\ & \quad \mathrm{T}_i \leftarrow \frac{\mathrm{Tout}}{\mathrm{T0}} \\ & \quad \mathrm{p}_i \leftarrow \mathbf{1} \\ & \quad \mathrm{ng}_i \leftarrow \frac{\mathrm{P}_i}{\mathrm{T}_i} \cdot \mathbf{f} \\ & \quad \text{for } i \in \mathrm{b.} \ \mathrm{N} \\ & \quad \mathrm{T}_i \leftarrow \frac{\mathrm{Tb}}{\mathrm{T0}} \\ & \quad \mathrm{p}_i \leftarrow \mathrm{psst}(\mathrm{T}_i) \\ & \quad \mathrm{ng}_i \leftarrow \frac{\mathrm{P}_i}{\mathrm{T}_i} \cdot \mathbf{f} \\ & \quad \mathrm{nl}_i \leftarrow \frac{1.58 \cdot \mathrm{10}^{28} \cdot \mathbf{f}}{\mathrm{nNTP}} \\ & \quad \text{for } i \in \mathrm{1...b-1} \\ & \quad \mathrm{nl}_i \leftarrow \mathbf{0} \\ & \quad \mathrm{T}_i \leftarrow \frac{\mathrm{Tin}}{\mathrm{T0}} \\ & \quad \mathrm{p}_i \leftarrow \mathrm{psst}(\mathrm{T}_i) \\ & \quad \mathrm{p}_i \leftarrow \mathrm{psst}(\mathrm{T}_i) \\ & \quad \mathrm{ng}_i \leftarrow \frac{\mathrm{P}_i}{\mathrm{T}_i} \cdot \mathbf{f} \\ & \quad \text{for } i \in \mathrm{0...N} \\ & \quad \mathrm{R}^{(i)} \leftarrow \begin{pmatrix} \mathrm{b} \\ \mathrm{ng}_i \\ & \quad \mathrm{nl}_i \\ & \quad \mathrm{T}_i \\ & \quad \mathrm{p}_i \end{pmatrix} \\ & \quad \mathrm{R} \\ \end{split}$$

Evolve for a given condition "n" until the scaled time reaches "time"

$$\begin{split} \mathrm{DC}(\mathbf{n}, \mathrm{time}, \mathbf{d}) &:= \|\mathbf{N} \leftarrow \mathrm{ok}(\mathbf{n}) - 1 \\ & \text{for } i \in \mathbf{0} . \ \mathbf{N} \\ & \left(\begin{array}{c} \mathbf{b} \\ \mathbf{n}_{\mathbf{k}_{\mathbf{j}}} \\ \mathbf{n}_{\mathbf{i}} \\ \mathbf{p}_{\mathbf{i}} \end{array} \right) \\ & \mathbf{u} \leftarrow \mathbf{0} \\ & \text{while } \mathbf{u} < \mathrm{time} \\ & \mathbf{p}_{\mathbf{i}} \\ & \mathbf{p}_{\mathbf{i}} \end{array} \\ & \mathbf{u} \leftarrow \mathbf{0} \\ & \text{while } \mathbf{u} < \mathrm{time} \\ & \| \mathbf{f}_{\mathbf{r}} i \in \mathbf{0}, 1... \mathbf{b} - 1 \\ & \| \mathbf{f}_{\mathbf{r}} i \in \mathbf{0}, 1... \mathbf{b} - 1 \\ & \| \mathbf{f}_{\mathbf{r}} i \in \mathbf{0}, 1... \mathbf{b} - 1 \\ & \| \mathbf{f}_{\mathbf{r}} i \in \mathbf{0}, 1... \mathbf{b} - 1 \\ & \| \mathbf{f}_{\mathbf{r}} i \in \mathbf{0}, 1... \mathbf{b} - 1 \\ & \| \mathbf{f}_{\mathbf{r}} i \in \mathbf{0}, 1... \mathbf{b} - 1 \\ & \| \mathbf{f}_{\mathbf{r}} i \in \mathbf{0}, 1... \mathbf{b} - 1 \\ & \| \mathbf{f}_{\mathbf{r}} i \in \mathbf{0}, 1... \mathbf{b} - 1 \\ & \| \mathbf{f}_{\mathbf{r}} i \in [\mathbf{1}_{2} ... \mathbf{0}_{-1}] \\ & \| \mathbf{f}_{\mathbf{r}} i \in \mathbf{0}, 1... \mathbf{f}_{\mathbf{r}} \right) \\ & \| \mathbf{f}_{\mathbf{r}} i \in \mathbf{b} \\ & \| \mathbf{f}_{\mathbf{r}} i \in \mathbf{1}_{j-1} dt \\ & \| \mathbf{f}_{\mathbf{r}} \mathbf{f} \mathbf{f}_{\mathbf{r}} \mathbf{f}_{\mathbf{r$$

Appendix C. Mathcad Program - Simulation II: 1-D Boundary Moving Model 88

 $\frac{60}{\text{timescale0}} = 110.056$

 $\begin{aligned} \mathbf{i} &:= 0.. \ N \qquad & \underbrace{dt}_{i} &:= 0.07 \\ & \text{Tinterval} &:= 110 \end{aligned}$ $\mathbf{b} &:= \ btism(2,112.3,800, dt, \ Tinterval, 280 \cdot \ Tinterval) \\ & \text{index} &:= 0.. \ 280 \qquad \qquad \mathbf{h}(\mathbf{x}) &:= \frac{\sqrt{\mathbf{x}}}{130} \cdot 5 \qquad \qquad \mathbf{t} &:= 0, 1.. \ 16000 \end{aligned}$

Boundary position (cm) v.s. time (seconds)



Liquid temperature (K) v.s. Time (s)



Appendix D

Mathcad Program - Simulation I: 1-D Model





$$\begin{array}{c|c} & -\frac{-1039.38}{t} \\ pst(t) := 10^6 \cdot 1059.2 * & \\ \hline \\ R_{\rm s}^{\rm (st, zz)} := & \left| \begin{array}{c} {\rm N} \leftarrow rows(t) - 1 \\ {\rm for } i \in 0..N \\ & {\rm I}_1 \leftarrow {\rm exp} \right| \\ \hline {\rm T}_1 \leftarrow {\rm I}_1 \\ & {\rm p}_1 \leftarrow \exp \! \left[\frac{-A}{T_1 \left({\rm x}_1 \right)^3 {\rm s}_2} \left[1 - \left({\rm x}_1 \right)^3 \right]^{\frac{1}{2}} \left[1 + {\rm st} \left({\rm x}_1 \right)^3 \right] \right] \\ \end{array} \right] \\ \label{eq:constraints} \\ {\rm IC}({\rm Nn}, zz, z0, tt, t0, realp0) := & \left| \begin{array}{c} {\rm N} \leftarrow {\rm Nn} \\ {\rm for } i \in 0..N \\ & {\rm x}_1 \leftarrow zz \\ {\rm x}_0 \leftarrow z0 \\ {\rm T}_1 \leftarrow {\rm tt} \\ {\rm T}_0 \leftarrow {\rm to} \\ {\rm p} \leftarrow {\rm P}({\rm T}, z) \\ {\rm for } i \in 0..N \\ {\rm pr}_1 \leftarrow {\rm p}_1 {\rm pst} \left({\rm T}_1 \right) \\ {\rm pr}_0 \leftarrow {\rm realp0} \\ {\rm for } i \in 0..N \\ & {\rm ng}_1 \leftarrow \frac{{\rm re}_1 \left(1 - {\rm x}_1 \right)^3}{6.02 \cdot 10^{23}} \\ {\rm nl}_1 \leftarrow \frac{1}{21^3} \left[\left({\rm x}_1 \right)^3 - 3 \left({\rm x}_1 \right)^2 + 3 {\rm x}_1 \right] \\ & {\rm nev}_1 \leftarrow 0 \\ {\rm nev}_0 \leftarrow 0 \\ & {\rm nev}_0 \leftarrow 0 \\ & {\rm nev}_1 \leftarrow 0 \\ {\rm nev}_1 \\ {\rm R} \\ \\ \end{array} \right] \\ {\rm R} \end{array}$$

$$\begin{split} \mathbb{D}(\mathbb{C}^{2}, \mathrm{d}) &:= & \left| \mathbf{N} \leftarrow \operatorname{rows}(\mathbb{C}^{2}) - 1 \\ & \text{for } i = 0 \dots \mathbf{N} \\ & \left(\begin{array}{c} \mathbf{x}_{1} \\ \mathbf{x}_{1} \\ \mathbf{n}_{2} \\ \mathbf{n}_{1} \\ \mathbf{n} \mathbf{er}_{1} \end{array} \right) \\ & \mathbf{p} \leftarrow \mathbb{P}(\mathbf{T}, \mathbf{x}) \\ & \text{for } i = 0 \dots \mathbf{N} \\ & \mathbf{p}_{1} \leftarrow \mathbb{P}(\mathbf{T}, \mathbf{x}) \\ & \text{for } i = 0 \dots \mathbf{N} \\ & \mathbf{p}_{1} \leftarrow \mathbb{P}(\mathbf{T}, \mathbf{x}) \\ & \text{for } i = 1 \dots \mathbf{N} \\ & \mathbf{p}_{1} \leftarrow \mathbb{P}(\mathbf{x}) \\ & \text{for } i = 1 \dots \mathbf{N} \\ & \left| \mathbf{15}\mathbf{T}_{1} \leftarrow \frac{(1 - \mathbf{x}_{1})^{3}}{\mathbf{k}(\mathbf{T}_{1})^{3}} \cdot \mathbf{rr}_{1} \left[\frac{\mathbf{A}}{\mathbf{e}(\mathbf{x}_{1})^{3}} \left[1 - (\mathbf{x}_{1})^{3} \right]^{\frac{1}{3}} \left[1 + \mathbf{x}'(\mathbf{x}_{1})^{3} \right] + 1039 \ 38 - \mathbf{T}_{1} \right] \frac{\mathbf{f}}{\mathbf{6} \ 0.02 \ 10^{23}} \\ & \left| \mathbf{15}\mathbf{T}_{1} \leftarrow \frac{(1 - \mathbf{x}_{1})^{2}}{\mathbf{k}(\mathbf{T}_{1})^{2}} \cdot \mathbf{rr}_{1} \left[\frac{\mathbf{A}}{\mathbf{e}(\mathbf{x}_{1})^{3}} \left[1 - (\mathbf{x}_{1})^{3} \right]^{\frac{1}{3}} \left[\left[\frac{3 - 2(\mathbf{x}_{1})^{3}}{(\mathbf{x}_{1})^{3} - (\mathbf{x}_{1})^{4}} \right] \left[1 + \mathbf{x}'(\mathbf{x}_{1})^{3} \right] - 3 \cdot \mathbf{x}^{\frac{1}{3}} \right] (1 - \mathbf{x}_{1}) - 3 \right] \frac{\mathbf{f}}{\mathbf{6} \ 0.02 \ 10^{23}} \\ & \left| \mathbf{15}\mathbf{Z}_{1} \leftarrow \mathbf{rr}_{1} \frac{(1 - \mathbf{x}_{1})^{2}}{\mathbf{k} \cdot \mathbf{T}_{1}} \left[\frac{\mathbf{A}}{\mathbf{e}(\mathbf{T}_{1}, \mathbf{x}_{1})} \left[1 + (\mathbf{x}_{1})^{3} \right] \left[1 + \mathbf{x}'(\mathbf{x}_{1})^{3} \right] - 3 \cdot \mathbf{x}^{\frac{1}{3}} \right] (1 - \mathbf{x}_{1}) - 3 \right] \frac{\mathbf{f}}{\mathbf{6} \ 0.02 \ 10^{23}} \\ & \left| \mathbf{15}\mathbf{Z}_{1} \leftarrow \mathbf{rr}_{1} \frac{1}{\mathbf{x}^{2}} \left[3(\mathbf{x}_{1})^{2} - \mathbf{6} \cdot \mathbf{x}_{1} + 3 \right] \frac{\mathbf{f}}{\mathbf{6} \ 0.02 \ 10^{23}} \\ & \mathbf{p}_{1} \leftarrow \mathbf{p} \ e_{1} \left(\mathbf{r} \ e_{1} + \mathbf{rr}_{1} \cdot \mathbf{rr}_{2} \right) e_{1} \left(\mathbf{r} \ e_{1} + \mathbf{rr}_{1} \cdot \mathbf{rr}_{2} \right) e_{1} \\ & \left| \mathbf{D}\mathbf{G}_{1} \leftarrow \frac{\mathbf{a}^{2}}{\mathbf{g}} \left[\frac{\mathbf{pr}_{1}}{\mathbf{rr}_{1} \cdot \mathbf{rr}_{1}} \left[1 - \mathbf{rr}_{1} \right]^{4} \right] \\ & \mathbf{D}\mathbf{I}_{1} \leftarrow \frac{\mathbf{a}^{2}}{\mathbf{g}} \left[\frac{\mathbf{k} \cdot \mathbf{T}_{1}}{\mathbf{rr}_{1} \cdot \mathbf{rr}_{1}} \left[1 - \mathbf{rr}_{1} \right]^{3} + 3(1 - \mathbf{rr}_{1})^{4} - 4(1 - \mathbf{rr}_{1})^{4} \cdot \mathbf{h}(1 - \mathbf{rr}_{1}) \right] \\ \end{array} \right| \end{aligned}$$

$$\begin{bmatrix} \operatorname{fir} \ i \in 1.. \ N-1 \\ \begin{pmatrix} dz_i \\ dT_i \\ dmg_i \\ dmw_i \end{pmatrix} \leftarrow \begin{bmatrix} \operatorname{IGZ}_i \ \operatorname{IGT}_i & -1 & 0 & 0 \\ \Pi Z_i & 0 & 0 & -1 & 0 \\ 0 & 0 & 1 & 0 & -1 \\ 0 & 0 & 0 & 1 & 1 \\ 0 & \rho c_i & 0 & 0 & L \\ \end{pmatrix}^{-1} \\ \begin{pmatrix} dmw_i \\ dmw_i \end{pmatrix} \leftarrow \begin{bmatrix} 0 \\ 0 \\ 0 \\ \rho c_i \\ \rho c_i$$

$$\begin{split} & d\boldsymbol{x}_{N} \leftarrow d\boldsymbol{x}_{N-1} \\ & d\boldsymbol{T}_{N} \leftarrow d\boldsymbol{T}_{N-1} \\ & d\boldsymbol{n} \boldsymbol{g}_{N} \leftarrow d\boldsymbol{n} \boldsymbol{g}_{N-1} \\ & d\boldsymbol{n} \boldsymbol{l}_{N} \leftarrow d\boldsymbol{n} \boldsymbol{l}_{N-1} \\ & d\boldsymbol{n} \boldsymbol{l}_{N} \leftarrow d\boldsymbol{n} \boldsymbol{n}_{N-1} \\ & d\boldsymbol{n} \boldsymbol{e} \boldsymbol{v}_{N} \leftarrow d\boldsymbol{n} \boldsymbol{e} \boldsymbol{v}_{N-1} \\ & for \quad i \in 1.. N \\ & \boldsymbol{R}_{i} \leftarrow \begin{pmatrix} d\boldsymbol{x}_{i} \\ & d\boldsymbol{n} \boldsymbol{g}_{i} \\ & d\boldsymbol{n} \boldsymbol{g}_{i} \\ & d\boldsymbol{n} \boldsymbol{l}_{i} \\ & d\boldsymbol{n} \boldsymbol{e} \boldsymbol{v}_{i} \end{pmatrix} \\ & \boldsymbol{R} \end{split}$$

Appendix E

Mathcad Program - 1-D Moving Liquid Model

1 - D Moving Liquid Model

pour size – 6	filling fraction	Size of the sample (m)	N:= 40	
a := 0.1.10 m	f := 0.8	L:= 0.05		
kakib := 0.10728	kl(t) := 0.341	– 0.001412t·T0		
	fit to the data	from NIST. note if T>243K, kI<0		
kakl(t) :=	$ka^{2}\left(\frac{2}{1+f-f^{3}}\right)^{2}$	$\frac{2}{4 + kl(t) \cdot ka \cdot f^{3}} \left(\frac{2}{1 + f - f^{3}} \right)$		
$ ka \cdot \left(\frac{2}{1+f-f^3}\right) \cdot \frac{1}{f^3} + \left(\frac{1}{1-f^3}\right) \left(\frac{2}{1-f^3}\right) \cdot \left\lfloor ka \cdot \left(\frac{2}{1+f-f^3}\right) + kl(t) \cdot \frac{2}{f^3} \right\rfloor \right] kaklb $				
$D0 := \frac{a^2 \cdot P0}{8 \cdot \eta 0 \cdot k \cdot 293}$	D0 = 2.8	35 × 10 ¹⁵		
$const1 := \frac{nNTP}{D0 \cdot P0}$	kakg0 paca cos	nst1 = 0.011		
$const2 := \frac{nNTP}{pac}$	m-cg co: :a	$nst2 = 6.227 \times 10^{-3}$		
const3 := $rac{nNTP}{D0 \cdot P0}$	kakg0 pici + paca cor	nst3 = 1.879 × 10 ⁻³		
const4 := $rac{nN}{T0\cdot(ho1}$	TP·La co: cl + paca)	$nst4 = 8.239 \times 10^{-4}$		
const5 := $\frac{pl}{m} \cdot \frac{a^2}{8 \cdot r}$	2 <u>f</u> co: 10 D0	nst5 = 609.447		

const6 := $\frac{nNTP}{D0 \cdot P0} \cdot \frac{kaklb}{plcl + paca}$ const6 = 6.618×10^{-3}

timescale0 :=
$$\left(\frac{L}{N}\right)^2 \cdot \frac{nNTP}{D0 \cdot P0}$$
 timescale0 = 0.136 $nll0 := \frac{\rho l}{m} \cdot \frac{f}{nNTP}$

The main code, sets the initial condition and iterate DC until the real time reaches "TimeTotal" Report back the time, boundary position, liquid temperature and the liquid number density at the boundaries for every "TimeInterval".

btism(bl, br, T1, Tr, dtime, TimeInterval, TimeTotal) :=

S

$$\begin{split} \mathbf{S} &\leftarrow \mathrm{IC}(\mathrm{bl},\mathrm{br},\mathrm{TI},\mathrm{TI}) \\ \mathbf{t} &\leftarrow 0 \\ \mathbf{i} &\leftarrow 0 \\ \mathbf{t}_0 &\leftarrow 0 \\ \mathbf{b}_0 &\leftarrow \left(\mathbf{S}^{(1)}\right)_0 \cdot \frac{\mathrm{L}}{\mathrm{N}} \\ \mathbf{b}_{T_0} &\leftarrow \left[\mathbf{S}^{(2)}\right)_0 \cdot \frac{\mathrm{L}}{\mathrm{N}} \\ \mathbf{T}_0 &\leftarrow \left[\mathbf{S}^{(\left(\varsigma(1)\right)_0}\right]_3, \mathrm{TO} \\ \mathbf{T}_0 &\leftarrow \left[\mathbf{S}^{\left(\left(\varsigma(1)\right)_0}\right]_3, \mathrm{TO} \\ \mathbf{n}_0 &\leftarrow \left[\mathbf{S}^{\left(\left(\varsigma(1)\right)_0}\right]_2 \\ \mathbf{n}_0 &\leftarrow \left[\mathbf{S}^{\left(\left(\varsigma(1)\right)_0}\right]_2 \\ \mathbf{n}_0 &\leftarrow \left[\mathbf{S}^{\left(\left(\varsigma(1)\right)_0}\right]_2 \\ \mathbf{n}_1 &\leftarrow \left[\mathbf{S}^{\left(\left(\varsigma(1)\right)_0}\right]_3, \mathrm{TO} \\ \mathbf{n}_1 &\leftarrow \left[\mathbf{S}^{\left(\left(\varsigma(1)\right)_0}\right]_3, \mathrm{TO} \\ \mathbf{n}_1 &\leftarrow \left[\mathbf{S}^{\left(\left(\varsigma(1)\right)_0}\right]_2 \\ \mathbf{n}_1 &\leftarrow \left[\mathbf{S}^{$$

Initial Condition, bl br are the bondary position of the left and right boundary. In the simulaitons bl = 3 br = N-3 $\,$

IC(b1,br,T1,Tr) :=	time $\leftarrow 0$	
	for $i \in 0$	
	$n_{i}^{l} \leftarrow 0$	
	$T_i \leftarrow \frac{T1}{T0}$	fori∈0 (time)
	$\mathbf{p}_i \leftarrow 1$	ng
	$\mathbf{ng}_{i} \leftarrow \frac{\mathbf{p}_{i}}{T_{\cdot}} \mathbf{f}$	$R^{(j)} \leftarrow \frac{nl_i}{r}$
	for $i \in 1N - 1$	¹ i
	$n_i \leftarrow 0$	(^P i)
	Т. ← <mark>ТЪ</mark>	(61)
	1 T0 n \leftarrow nsat(T.)	ng _i
		$\textbf{R}^{(j)} \leftarrow \begin{bmatrix} \textbf{nl}_{i} \\ \textbf{i} \end{bmatrix}$
	$ng_i \leftarrow \frac{r_i}{T_i} \cdot f$	Т _і
	for i∈ bl br	(p _i)
	$\operatorname{nl}_i \leftarrow \operatorname{nll}_i$	for i∈2
	for $i \in \mathbb{N}$	ng.
	$nl_i \leftarrow 0$ _ Tr	$R^{(j)} \leftarrow \begin{array}{c} nl \\ nl \\ i \end{array}$
	$T_i \leftarrow \overline{T0}$	Т _і
	$p_i \leftarrow 1$	(p _i)
	$ng_i \leftarrow \frac{p_i}{r} \cdot f$	for $i \in 3 N$
		$\begin{pmatrix} -1 \\ ng_i \end{pmatrix}$
		$R^{(i)} \leftarrow \begin{bmatrix} nl_i \\ i \end{bmatrix}$
		T _i
		p _i
		R

Start from a given condition "n" and iterate with time step "dt" until the time reaches "time"

```
DC(n, time, dt) := N \leftarrow cols(n) - 1
                                                                             for i \in 0.. N
                                                                                    \left( \begin{array}{c} {data_i} \\ {ng_i} \\ {nl_i} \\ {T_i} \end{array} \right) \leftarrow n^{\langle j \rangle} 
                                                                                           \mathbf{p}_{\mathbf{i}}
                                                                            startTime ← data<sub>n</sub>
                                                                            bl ← data<sub>1</sub>
                                                                           br \leftarrow data_{\gamma}
                                                                            endTime ← startTime
                                                                           while endTime < time
                                                                                          break if br = bl
                                                                                          otherwise
                                                                                                     1eft
                                                                                                   for i \in 0, 1 \dots b1 - 1
                                                                                  \begin{aligned} & \text{for } i \in 0, 1 \dots bl-1 \\ & J_i \leftarrow \frac{1}{\eta \left(\frac{T_{i+1} + T_i}{2}\right)} \cdot \frac{p_{i+1} + p_i}{T_{i+1} + T_i} \cdot \left(p_{i+1} - p_i\right) \\ & J_i \leftarrow \frac{1}{\eta \left(\frac{T_{i+1} + T_i}{2}\right)} \cdot \left(T_{i+1} - T_i\right) \\ & J_i \leftarrow \frac{1}{\eta \left(\frac{T_{i+1} + T_i}{2}\right)} \cdot \left(T_{i+1} - T_i\right) \\ & \text{for } i \in 1, 2 \dots bl-1 \\ & \text{dng}_i \leftarrow \left(J_i - J_{i-1}\right) \cdot dt \\ & \text{dT}_i \leftarrow \begin{bmatrix} \text{constl} \cdot \left(J_i - J_{i-1}\right) + \text{const2} \cdot J_{i-1} \cdot \left(T_i - T_{i-1}\right) \end{bmatrix} \cdot dt \end{aligned}
```

$$\begin{array}{l} \mbox{night} \\ \mbox{for } i \in {\rm br.} \ {\rm N} - 1 \\ \\ \\ \mbox{J}_{i} \leftarrow \frac{-1}{\eta \left(\frac{T_{i+1} + T_{i}}{2} \right)} \cdot \frac{p_{i+1} + p_{i}}{T_{i+1} + T_{i}} \cdot \left(p_{i+1} - p_{i} \right) \\ \\ \\ \mbox{J}_{i} \leftarrow -kakg \left(\frac{T_{i+1} + T_{i}}{2} \right) \cdot \left(T_{i+1} - T_{i} \right) \\ \mbox{for } i \in {\rm br} + 1 .. \ {\rm N} - 1 \\ \\ \\ \mbox{dng}_{i} \leftarrow - \left(J_{i} - J_{i-1} \right) \cdot dt \\ \\ \mbox{dT}_{i} \leftarrow \left[- {\rm constl} \cdot \left(JT_{i} - JT_{i-1} \right) - {\rm const2} \cdot J_{i} \left(T_{i+1} - T_{i} \right) \right] \cdot dt \\ \\ \mbox{dng}_{bl} \leftarrow - J_{bl-1} \cdot dt \\ \\ \mbox{dng}_{bl} \leftarrow - J_{bl-1} \cdot dt \\ \\ \mbox{for } i \in {\rm bl.} \ {\rm br} - 1 \\ \\ \mbox{JT}_{i} \leftarrow kakd \left(\frac{T_{i+1} + T_{i}}{2} \right) \cdot \left(T_{i+1} - T_{i} \right) \\ \\ \mbox{for } i \in {\rm bl.} \ {\rm br} - 1 \\ \\ \mbox{dT}_{bl} \leftarrow \left({\rm const6} \cdot JT_{bl} - {\rm const3} \cdot JT_{bl-1} - {\rm const4} \cdot J_{bl-1} \right) \cdot dt \\ \\ \mbox{dT}_{bl} \leftarrow \left({\rm const6} \cdot JT_{bl} - {\rm const3} \cdot JT_{bl-1} - {\rm const4} \cdot J_{br} \right) \cdot dt \\ \\ \mbox{dT}_{i} \leftarrow {\rm const6} \cdot \left(JT_{i} - JT_{i-1} \right) \cdot dt \\ \\ \mbox{otherwise} \\ \\ \mbox{dT}_{bl} \leftarrow \left({\rm const6} \cdot JT_{bl} - {\rm const3} \cdot JT_{bl-1} - {\rm const4} \cdot J_{bl-1} \right) \cdot dt \\ \\ \mbox{dT}_{bl} \leftarrow \left({\rm const6} \cdot JT_{bl} - {\rm const3} \cdot JT_{bl-1} - {\rm const4} \cdot J_{bl-1} \right) \cdot dt \\ \\ \mbox{dT}_{bl} \leftarrow \left({\rm const6} \cdot JT_{bl} - {\rm const3} \cdot JT_{bl-1} - {\rm const4} \cdot J_{bl-1} \right) \cdot dt \\ \\ \mbox{dT}_{bl} \leftarrow \left({\rm const6} \cdot JT_{bl} - {\rm const3} \cdot JT_{bl-1} - {\rm const4} \cdot J_{bl-1} \right) \cdot dt \\ \\ \mbox{dtherwise} \\ \\ \mbox{dt}_{bl} \leftarrow \left({\rm const3} \cdot JT_{bl} - {\rm const6} \cdot JT_{bl-1} - {\rm const4} \cdot J_{bl} \right) \cdot dt \\ \\ \mbox{dnl} \leftarrow {\rm const5} \cdot \frac{1}{\eta | \left(T_{bl} \right)} \cdot \frac{{\rm Pbr} - P_{bl}}{{\rm br} - {\rm bl}} \cdot dt \\ \end{array} \right.$$
$$\begin{array}{|c|c|c|c|} & \operatorname{NG} \\ & \operatorname{for} \quad i \in 1, 2.. \, \mathrm{bl} \\ & & \operatorname{ng}_i \leftarrow \operatorname{ng}_i + \operatorname{dng}_i \\ & & \operatorname{T}_i \leftarrow \operatorname{T}_i + \operatorname{dT}_i \\ & & \operatorname{p}_i \leftarrow \frac{\operatorname{ng}_i \cdot \operatorname{T}_i}{\mathrm{f}} \\ & & \operatorname{for} \quad i \in \mathrm{br}.. \, \mathrm{N-1} \\ & & \operatorname{ng}_i \leftarrow \operatorname{ng}_i + \operatorname{dng}_i \\ & & \operatorname{T}_i \leftarrow \operatorname{T}_i + \operatorname{dT}_i \\ & & \operatorname{p}_i \leftarrow \frac{\operatorname{ng}_i \cdot \operatorname{T}_i}{\mathrm{f}} \\ & & \operatorname{nl}_{\mathrm{bl}} \leftarrow \operatorname{nl}_{\mathrm{bl}} + \operatorname{dng}_{\mathrm{bl}} + \operatorname{dnl} \\ & & \operatorname{nl}_{\mathrm{br}} \leftarrow \operatorname{nl}_{\mathrm{br}} + \operatorname{dng}_{\mathrm{br}} - \operatorname{dnl} \\ & & \operatorname{for} \quad i \in \mathrm{bl} + 1 \ldots \mathrm{br} - 1 \\ & & \operatorname{T}_i \leftarrow \operatorname{T}_i + \operatorname{dT}_i \\ & & \operatorname{p}_i \leftarrow \operatorname{psat}(\operatorname{T}_i) \\ & & & \operatorname{ng}_i \leftarrow \frac{\operatorname{P}_i}{\mathrm{T}_i} \cdot \mathrm{f} \\ & & & \operatorname{for} \quad i \in \mathrm{bl} \\ & & & \operatorname{T}_i \leftarrow \operatorname{T}_{\mathrm{bl}} \\ & & & \operatorname{p}_i \leftarrow \operatorname{psat}(\operatorname{T}_i) \\ & & & \operatorname{ng}_i \leftarrow \frac{\operatorname{P}_i}{\mathrm{T}_i} \cdot \mathrm{f} \\ & & & \operatorname{for} \quad i \in \mathrm{br} \\ & & & & \operatorname{T}_i \leftarrow \operatorname{T}_{\mathrm{br}} \\ & & & & \operatorname{p}_i \leftarrow \operatorname{psat}(\operatorname{T}_i) \\ & & & & \operatorname{ng}_i \leftarrow \frac{\operatorname{P}_i}{\mathrm{T}_i} \cdot \mathrm{f} \\ & & & & \operatorname{ng}_i \leftarrow \frac{\operatorname{P}_i}{\mathrm{T}_i} \cdot \mathrm{f} \end{array}$$

When the left boundary equals to the right boundary position, instead of DC(n,time,dt), DCbrbl(n,time,dt) is executed. Since the left and right boundary are at the same position, the liquid viscous flow stops.

```
DCbrbl(n, time, dt) := N \leftarrow cols(n) - 1
                                                                                                    for i \in U. N

\begin{pmatrix} data_i \\ ng_i \\ nl_i \\ T_i \\ p_i \end{pmatrix} \leftarrow n^{\langle j \rangle}
                                                                                                            \mathsf{startTime} \leftarrow \mathsf{data}_\mathsf{N}
                                                                                                             bl ← data,
                                                                                                            br \leftarrow data_2
                                                                                                             endTime \leftarrow startTime
                                                                                                             while endTime < time
                                                                                             \begin{split} & \text{left} \\ & \text{for } i \in 0, 1 \dots \text{bl} - 1 \\ & J_i \leftarrow \frac{1}{\eta \left( \frac{T_{i+1} + T_i}{2} \right)} \cdot \frac{p_{i+1} + p_i}{T_{i+1} + T_i} \cdot \left( p_{i+1} - p_i \right) \\ & J_i \leftarrow \text{kakg} \left( \frac{T_{i+1} + T_i}{2} \right) \cdot \left( T_{i+1} - T_i \right) \\ & J_i \leftarrow \text{kakg} \left( \frac{T_{i+1} + T_i}{2} \right) \cdot \left( T_{i+1} - T_i \right) \\ & \text{for } i \in 1, 2 \dots \text{bl} - 1 \\ & \text{dng}_i \leftarrow \left( J_i - J_{i-1} \right) \cdot \text{dt} \\ & \text{dT}_i \leftarrow \left[ \text{constl} \cdot \left( JT_i - JT_{i-1} \right) + \text{const2} \cdot J_{i-1} \cdot \left( T_i - T_{i-1} \right) \right] \cdot \text{dt} \end{split}
```

$$\begin{split} & \text{right} \\ & \text{for } i \in \text{br.} \ \text{N} - 1 \\ & J_i \leftarrow \frac{-1}{\eta \left(\frac{T_{i+1} + T_i}{2}\right)} \cdot \frac{P_{i+1} + P_i}{T_{i+1} + T_i} \cdot \left(P_{i+1} - P_i\right) \\ & JT_i \leftarrow -\text{kakg} \left(\frac{T_{i+1} + T_i}{2}\right) \cdot \left(T_{i+1} - T_i\right) \\ & \text{for } i \in \text{br} + 1 \dots \text{N} - 1 \\ & \text{dng}_i \leftarrow -\left(J_i - J_{i-1}\right) \cdot \text{dt} \\ & \text{dT}_i \leftarrow \left[-\text{constl} \cdot \left(JT_i - JT_{i-1}\right) - \text{const2} \cdot J_i \left(T_{i+1} - T_i\right)\right] \cdot \text{dt} \\ & \text{for } i \in \text{br} \\ & \text{dng}_i \leftarrow -\left(J_{i-1} + J_i\right) \cdot \text{dt} \\ & \text{dT}_i \leftarrow \left[-\text{const3} \cdot \left(JT_{i-1} + JT_i\right) - \text{const4} \cdot \left(J_{i-1} + J_i\right)\right] \cdot \text{dt} \\ & \text{NG} \\ & \text{for } i \in 1, 2 \dots \text{N} - 1 \\ & \begin{array}{c} \text{ng}_i \leftarrow \text{ng}_i + \text{dng}_i \\ & T_i \leftarrow T_i + \text{dT}_i \\ & P_i \leftarrow \frac{\text{ng}_i T_i}{f} \\ & \text{nl}_{br} \leftarrow \text{nl}_{br} + \text{dng}_{br} \\ & \text{for } i \in \text{br} \\ & \begin{array}{c} \text{data}_0 \leftarrow \text{endTime} \\ & \text{data}_1 \leftarrow \text{bl} \\ & \text{data}_2 \leftarrow \text{br} \\ & \text{for } i \in 0 \dots \text{N} \\ & \begin{array}{c} \text{for } i \in 0 \dots \text{N} \\ & \text{for } i \in 0 \dots \text{N} \\ & \begin{array}{c} \text{data}_1 \leftarrow \text{bl} \\ & \text{data}_2 \leftarrow \text{br} \\ & \text{for } i \in 0 \dots \text{N} \\ & \begin{array}{c} \text{data}_1 \leftarrow \text{bl} \\ & \text{data}_2 \leftarrow \text{br} \\ & \text{for } i \in 0 \dots \text{N} \\ & \begin{array}{c} \text{data}_1 \\ & \text{rig}_i \\ & \text{nl}_i \\ & T_i \\ & P_i \end{array} \right) \\ & \text{R} \\ \end{array} \right. \end{aligned}$$









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