SIMULATION OF CELL GROWTH
IN HIGH-PRESSURE FOAM INJECTION MOLDING

by

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for the degree of Master of Applied Science
Department of Mechanical and Industrial Engineering
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ABSTRACT

In this work, visualized experiments were conducted to reveal the fundamental mechanisms of nucleation and growth using high-pressure foam injection molding (HP-FIM) with and without mold opening (MO) using a real-time in-situ visualization system. Results from both molding methods showed significant differences in nucleation and growth behavior and final foam morphology when different packing pressures were applied. A simulation strategy is proposed to predict the bubble growth profile in both HP-FIM and HP-FIM + MO. The simulation is composed of three main components 1. The Cell model, 2. Material and transport properties which are functions of temperature, pressure, and blowing agent concentration, 3. The Simha-Somcynsky equation of state. Simulation was conducted on both molding methods. The predicted growth profiles for both trials were in quantitative agreement with experimental findings. Sensitivity analysis was also conducted, the resulted growth profiles under different conditions were in qualitative agreement with the literatures.
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LIST OF SYMBOLS

Symbols:

- $r$: Radial distance in spherical coordinates
- $\theta$: Polar angle in spherical coordinates
- $t$: time
- $R$: Radius
- $V$: Velocity
- $P$: Pressure
- $C$: Concentration
- $\tau$: Shear stress
- $\gamma$: Surface tension
- $\eta_0$: Zero-shear viscosity
- $\lambda$: Relaxation time
- $\rho$: Density
- $D$: Diffusivity
- $K_h$: Henry’s law constant

Subscripts:

- $bub$: Bubble
- $shell$: Shell
- $r, rr$: In radial direction
- $\theta$: In tangent direction
- $0$: Initial condition ($t = 0$)
INTRODUCTION

1.1. Preamble

From packaging and cushioning to acoustic and thermal insulation, polymer foams, as a relatively young but rising sector of polymer industry, have influenced us in every aspect of our life. The rapid growth of foaming industry not only thanks to the broad application of foamed plastic products but also is attributed the environmentally friendly nature of foams as a result of material saving. In the early 1980s, microcellular foams were developed by Dr. Nam Suh, et al. in Massachusetts Institute of Technology (MIT) [1]. Excelling traditional foams in multiple departments, Microcellular foams can be manufactured by a variety of techniques, such as bead foaming, batch foaming, extrusion foaming, foam injection molding and etc.
Foam injection molding (FIM) parts are utilized in many industries such as automotive, construction, aerospace, sports and etc. Light-weighting, geometry accuracy, short production cycles and etc., countless advantages brings FIM a substantial amount of attention from industry and academia. Nonetheless, there is limited knowledge of what is actually going on in the mold due to the non-steady-state foaming environment.

Visualization as a means of characterization enables the real-time access to the mold cavity during foaming. It is commonly adopted to verify computer simulations on known foaming mechanisms and to identify unknown mechanisms. With the aid of visualization, more trustable simulation software can be developed to guide successful foam product design and cost-effective mold design.

1.2. Polymeric foams

Foams are everywhere. They are not only artificially manufactured using engineering materials, but also found naturally in woods [2], bones [3], and etc., shown in Figure 1-1.

Based on cell size and cell density, as shown in Table 1-1, they can be categorized based on cell size or cell density, and expansion ratio or foam density [1]. Developed in MIT [1], microcellular foams are characterized as having improved qualities of impact strength [4] [5], toughness [4], fracture strength [6], high fatigue life [6], thermal stability [7], low dielectric constant [8] as well as thermal and acoustical insulation [9].

Based on cell structure, foams can also be divided into closed-celled foams and open-celled foams as depicted in Figure 1-2. As shown, in closed cell foams, cells are separated by cell walls. They can be made from low to high expansion foams. Due to their superior
mechanical properties, they are commonly seen in structural applications, packaging, and insulation. Due to distinct cell-wall opening mechanism, open-celled foams feature interconnected pores. They usually have relatively high expansion ratio, thus they are mostly applied in acoustic abortion and liquid-liquid or liquid-particle separation (filtration). It is worth to mention that when expansion gets critically high, no visible foam walls remain in the foam, leaving only struts and nodes. This particular structure is called reticulated foams.

Table 1-1 Classification of polymeric foams

<table>
<thead>
<tr>
<th>Cell size and cell density</th>
<th>Foam density and expansion ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Conventional foam</strong></td>
<td></td>
</tr>
<tr>
<td>Cell size &gt; 100 um</td>
<td>High density</td>
</tr>
<tr>
<td>Cell density &lt; $10^6$ cells/cm$^3$</td>
<td>Expansion &lt; 4 fold</td>
</tr>
<tr>
<td><strong>Fine-celled foam</strong></td>
<td></td>
</tr>
<tr>
<td>$10 &lt;$ Cell size &lt; 100 um</td>
<td>Medium density</td>
</tr>
<tr>
<td>$10^6 &lt;$ Cell density &lt; $10^9$ cells/cm$^3$</td>
<td>4 fold &lt; Expansion &lt; 10 fold</td>
</tr>
<tr>
<td><strong>Microcellular foam</strong></td>
<td></td>
</tr>
<tr>
<td>1 um &lt; Cell size &lt; 10 um</td>
<td>Low density</td>
</tr>
<tr>
<td>$10^9 &lt;$ Cell density &lt; $10^{12}$ cells/cm$^3$</td>
<td>10 fold &lt; Expansion &lt; 40 fold</td>
</tr>
<tr>
<td><strong>Nanocellular</strong></td>
<td></td>
</tr>
<tr>
<td>Cell size &lt; 1 um</td>
<td>Ultra-low density</td>
</tr>
<tr>
<td>$10^{12}$ cells/cm$^3 &lt;$ Cell density</td>
<td>40 fold &lt; Expansion</td>
</tr>
</tbody>
</table>
1.3. Plastic foam manufacturing processes

Foaming processes are typically of 3 types: 1. Batch process (e.g. bead foaming), 2. Semi-continuous process (e.g. foam injection molding), 3. Continuous processes (e.g. extrusion foaming).

As illustrated in Figure 1-3, foaming consists of 4 fundamental steps:

i. Preparation of homogeneous polymer melt/gas mixture;

ii. Cell nucleation induced by thermodynamic instability;

iii. Cell growth;

iv. Stabilization of foam structures.

Figure 1-3 Schematic of the fundamental steps during foaming
1.4. Objective of the thesis

This work aims to provide an insight into the fundamental mechanisms in cell nucleation and growth in foam injection molding process via experimental research and theoretical modelling. It is completed in pursuance of facilitating the polymer foaming industry in more efficient optimization of the foam injection molding processing parameters, more consistent control over the injected foam morphology (i.e. structure uniformity and cell size), thus achieving desired properties.

A bubble growth simulation strategy will be proposed based on Figure 1-4. The model will be comprised of an accurate equation of state to calculate PVT parameters, a set of experimentally verified material and transport property models, and an improved well know growth model.

![Figure 1-4 Schematic overview of the model](image)

1.5. Research strategy

Figure 1-5 demonstrates the research strategy adopted for this work. All simulation are based and guided by experimental results. Iteration of the simulation was performed when the prediction does not match with experimental results.
Figure 1-5 Schematic of the overall research strategy
1.6. Overview of the thesis

Chapter 1 delivers an introduction to foaming techniques with an emphasis on the foam injection molding process. In addition, an overview of the proposed cell nucleation and growth model is presented. Objective and outline of this work can also be found in this chapter.

Chapter 2 presents a thorough literature survey on the topic of foam injection molding, fundamentals of cell nucleation and growth. A number of the most cited literatures in cell growth are tabulated in the end in terms of some of the most critical aspects involved in modelling and solving the growth process.

Chapter 3 entails the visualized FIM experiments conducted with Dr. Vahid Shaayegan, along with characterized results and discussion on foaming behavior in both high-pressure FIM and high-pressure FIM with mold opening.

Chapter 4 proposed a strategy which adopts a well-accepted bubble growth model that is able to accurately describe the diffusion phenomenon in a multi-bubble growth environment. Based on this model, the proposed strategy extends the capability of the model by adding transient material and transport properties and accurate equation of state for both the pure gaseous phase and the polymer/gas mixture phase.

Chapter 5 summarizes this work and provide some possible direction in the future endeavor in this area.
Chapter 2

LITURATURE REVIEW AND THEORETICAL BACKGROUND

2.1. Introduction

This chapter provide an overview of foam injection molding fundamentals and relevant molding technologies. Furthermore, an introduction of classical nucleation theory (CNT) is presented followed with its applications in Moreover, this chapter also summarizes the theoretical and experimental researches in the field of bubble nucleation and growth phenomena in polymeric foaming process. With the aid of experimental results accomplished from various researchers, the validity of the numerous proposed theories, mathematic models,
simulation strategies and numerical implementation are validated. In the end, a thorough comparison between existing models in bubble growth phenomena are compared.

2.2. Fundamental steps of foam injection molding

Foam injection molding machines are typically composed of an injection unit, a molding unit, a control unit and a gas unit, as depicted in Figure 2-1. In addition to the fundamental foaming steps outlined in Section 1.3. Plastic foam manufacturing processes, FIM adds a molding (i.e. shaping) stage to the processing cycle. Depending on particular molding technologies, the molding stage can occur at different stages of foaming procedures.

![Figure 2-1 Schematic of FIM machine (based on reciprocating screw design)](image)

2.2.1. Chemical and physical blowing agents

In FIM, blowing agent (BA) (i.e. volatiles) can be added to the system by either chemical blowing agents (CBA) or physical blowing agents (PBA).

CBA gives off gas, commonly CO₂ or N₂ at a decomposition temperature leaving behind
salt residues in the melt. Application of CBA requires no additional equipment upgrade which is suitable for lab-scale or pilot-scale experiments to test the ‘foam-ability’ certain materials and etc. However, it suffers from an obvious drawback which is the limitation in BA concentration. Production of low density, high expansion foams become difficult. Moreover, without the aid of fillers, it is difficult to obtain high cell density.

On the other hand, PBA is capable of producing foam of low to high expansion, closed cell to open cell structure. Its versatility is due to the large range of gas concentration that can be injected into the melt. However, to achieve accurate control of gas dosing, special equipment needs to be attached to the injection machine and modification is required as shown in Figure 2-1, which will inevitably increase the cost of the system. Nonetheless, its promising capability and commercial prosperity has already attracted a significant amount of industrial attention.

To expedite the gas dissolution and reduce processing time, PBA is usually prepared into supercritical fluid (SCF). SCF is the state when a PBA is subjected to critical temperature and critical pressure ($T_{cr}$ and $P_{cr}$). At critical state, illustrated in Figure 2-2, the SCF possesses the characteristics of liquid and gas. Behaving like a gas, SCF has a low viscosity; behaving like a liquid, SCF has a high density. Meriting from both advantageous properties, SCF can be dissolved in polymer melt in a timely manner to meet the stringent industrial criteria on cycle time; on the other hand, it can be measured precisely by weight percentage to control the consistency of gas concentration in the system.
2.2.2. Preparation of homogeneous polymer/gas solution

Regarding PBA, the homogeneous polymer/gas mixture is not simply achieved by dosing SCF into the polymer melt. While the gas is being dosed into the melt, the gas stream is disrupted by the flight of the rotating screw. Then gas exists in a form of large bubbles or pockets in the melt as a second phase. The size of these gas pockets depends on 1. the pressure difference between gas dosing pressure and barrel pressure (i.e. back pressure); 2. the design of the wiping and mixing section of the screw. For the gas to be able to flow into the barrel, the gas dosing pressure must be larger than barrel pressure, however, a larger pressure difference results in larger gas pockets. Therefore, it is necessary to keep the pressure difference small to form smaller gas bubbles to enhance the later mixing and gas dissolution. Regarding the design of the screw, a larger number of flights will help to further reduce the size of gas bubbles repeatedly until they become droplets and easy to dissolve. Moreover, the shear flow field induced by the screw rotation will also help to reduce the size of the bubbles by stretching and elongating the bubbles. Once a critical bubble length (or a critical aspect ratio of elongated bubbles) is reached, in another word, the Weber number reaches its critical value, these larger bubbles will break into smaller bubbles. All of above reduces the diffusion time ($t_d$) for SCF,
which speeds up the mixing and dissolution process [15]. Consequently, the homogeneous polymer/gas mixture is prepared for injection and foaming. The ideal resultant of this step is a homogeneous, single-phase polymer/gas system.

2.2.3. Introduction of thermodynamic instability

Once the polymer/gas solution is injected into the mold cavity, foaming can be induced at different stages of the process via different techniques. From PVT point of view, foaming is effectively a change in volume which can be caused by change in either pressure [12, 13] or temperature [14] that leads to decrease of solubility of the polymer melt. However, temperature change is inapplicable in most of the FIM technologies due to the poor thermal conductivity of polymers. Therefore, pressure drop is the predominant method. When system pressure is dropped, the solution becomes supersaturated, consequently foaming is induced.

2.2.4. Molding technologies

When polymer/gas solution enters the cavity, due to the pressure drop at the gate, foaming (nucleation and growth) starts at the flow front during mold filling. Low-pressure foam injection molding (LP-FIM) is the practice when the cavity is only filled to a predetermined volume and the rest of the cavity is filled by foam expansion. LP-FIM features short processing cycle and low-tonnage clamping unit. However, the foam morphology is usually characterized by non-uniformed, sheared and elongated bubbles.

Though foaming starts upon entering the gate, these so-called gate nucleated cells (GNCs) can then be suppressed by applying packing pressure ($P_{\text{pack}}$). The amount of pressure required
to fully re-dissolve GNCs back to the melt depends on solubility pressure ($P_{sol}$). This ‘new’ solution can be slowly cooled until thermal contraction occurs that leads to a pressure drop in the cavity and consequently foaming. This process is termed high-pressure foam injection molding (HP-FIM) [16, 17]. Circular bubbles and a low cell density are the evidence of HP-FIM. On the other hand, it has a low expansion ratio and the foam density is high.

When the temperature is maintained high enough, right after the dissolution of GNCs via $P_{pack}$, a controlled opening of the mold before demolding of the part can be applied to induce pressure drop. Through this method expansion ratio can be dramatically increased, meanwhile accurately controlled. In this work, this method is coined high-pressure foam injection molding with mold opening (HP-FIM+MO). When mold opening (MO) is applied, the cavity is exposed to atmospheric pressure instantly. Thanks to the high-pressure drop rate, MO parts can achieve high cell density and uniform structure.

There are other innovative molding technologies developed to improve the foam morphology and cell density, for example gas-counter pressure (GCP) with LP-FIM, GCP with HP-FIM and MO, cavity compression followed by MO, microcellular co-injection molding and etc. [10].

2.3. Nucleation theories

Foaming is the result when a second phase (i.e. gas) separates from a metastable parent phase (i.e. polymer/gas solution) upon an introduction of a thermodynamic instability in order to restore thermodynamic stability. Nucleation occurs at the beginning stage of the phase separation, and nuclei (i.e. small clusters of molecules of second phase) is precipitated from
2.3.1. Classification of nucleation theories

Conventionally, existing theoretical approaches to nucleation can be categorized into four distinguished groups [11]:

i. Classical Nucleation Theory and its modifications (phenomenological approaches)

ii. Density functional theory

iii. Semi-phenomenological models

iv. Direct computer simulations (virtual experiment)

In this work, the focus will be on the phenomenological methods which is Classical Nucleation Theory and its modifications.

2.3.2. Classical Nucleation Theory (CNT)

Figure 2-3 illustrates the free energy change during a first-order phase change. In the context of foaming, the metastable state A (local minimum) represents the single-phase polymer/gas system, whereas stable state B (global minimum) represents the final polymer foam where both the polymer and gas are in their respective stable state [11]. The transition between state A and B involves overcoming the free energy barrier (ΔG). The polymer/gas mixture which is in metastable state is very sensitive to small fluctuations of the thermodynamic variables. When a large enough thermodynamic instability is introduced to the system in state A, the system will overcome the free energy barrier can nucleation will occur.
The nucleation process is **homogeneous nucleation** when it only depends on thermodynamic fluctuations. **Heterogeneous nucleation** on the other hand is the process during which the second-phase nucleate (or condensate) onto a pre-existing foreign particle or a surface. In the presence of a nucleating site, the free energy barrier is lowered, so that activation of nucleation requires less energy. **Figure 2-4** qualitatively illustrates the difference between the free energy barrier for nucleation to occur for homogeneous and heterogeneous nucleation.

![Figure 2-3 Sketch of the free energy as a function of the order parameter](image)

**Figure 2-3** Sketch of the free energy as a function of the order parameter [11]

According to CNT, depending on the relation between critical radius ($R_{cr}$) and nuclei size ($R_{bub}$), 3 distinct situations may occur, they are tabulated in **Table 2-1.**
Table 2-1  \( R_{bub} \) and \( R_{cr} \) on system stability and survival of bubbles

<table>
<thead>
<tr>
<th>( R_{bub} ) vs ( R_{cr} )</th>
<th>System stability</th>
<th>Survival of nuclei</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_{bub} &lt; R_{cr} )</td>
<td>Unstable, restore to state A</td>
<td>Collapse</td>
</tr>
<tr>
<td>( R_{bub} = R_{cr} )</td>
<td>Unstable, equilibrium</td>
<td>Remain</td>
</tr>
<tr>
<td>( R_{bub} &gt; R_{cr} )</td>
<td>Unstable, transform to state B</td>
<td>Grow</td>
</tr>
</tbody>
</table>

2.3.4.  Issues and modifications of CNT in foaming processes

It is important to realize that nucleation do not occur in just one way. In another word, homogeneous and heterogeneous nucleation could occur at the same time and competing with each other, along with other unidentified mechanisms.

In foaming, homogeneous nucleation is a theoretical situation to approximate foaming with no additives or fillers in the system. The stringent conditional requirements limit its applicability in foaming practice. Han et al. [18], and Leung et al. [19] indicated that nucleation rate in typical plastic foaming processes that were much higher than those calculated using homogenous CNT. Consequently, heterogeneous nucleation seems more predominant in foaming, as most of the commercial raw polymers do have various kind of additives, such as colorant, clarifying agents, crystal nucleating agents, functional fillers and etc. Depending on the size and surface treatment of the additives, these ‘impurities’ can work as sites of bubble nucleation.

Numerous studies have demonstrated the qualitatively consensus of the heterogeneous
CNT with experimental results; nonetheless theoretical predictions could not qualitatively agree with experimental findings without the use of fitting parameters (e.g. pre-exponential factors, energy barrier reduction factor, contact angle, filler geometry and etc.) [19-21].

Leung et al. demonstrated the impact of fitted parameter (i.e. contact angle, $\theta_c$) [19]. Shown in Figure 2-5(a), acceptable qualitative and quantitative agreement can be observed between the two results. However, it is important to realize that the simulation results was achieve at a particular contact angle ($\theta_c = 86.42^\circ$) obtained by iterative approach [19]. Figure 2-5(b) demonstrates the difference in simulation results caused by slight changes in $\theta_c$ [19].

**Figure 2-5** (a) Simulation and experimental results in batch foaming, $\theta_c = 86.42^\circ$,

(b) Effect of $\theta_c$ on simulation results

Therefore, it is of critical importance to input the correct $\theta_c$ to the simulation program. However, the real contact angle that is involved in the nucleation of a particular cell is unobtainable experimentally and its value is different for different cells.
2.4. Cell growth models

Once the Gibbs free energy barrier is breached, growth of nucleated bubbles starts. Growth of bubbles is a diffusion-induced process governed by the conservation laws of mass, energy and momentum. Compared by with nucleation, cell growth is comparably well studied [22-44]. Nearly all of the growth models can be categorized into 2 types:

i. The single bubble growth model [22-27]

ii. The cell model [28-29, 31-44]

2.4.1. The single bubble growth model

The single bubble growth model, shown schematically in Figure 2-6 [27], studies the growth one bubble in an infinite sea of liquid. Barlow and Langois were among the first researchers in modelling of the bubble growth phenomena in viscos liquid, in which they incorporated the both mass and momentum transfer equations into the model [22]. To further simplify the model, they assumed a thin boundary layer approximation, which assumes that the dissolve gas concentration gradient vanishes within a thin layer around the cell. Moreover, they

![Figure 2-6 Schematic diagram of a single bubble growth in a large pool of polymeric liquid](image)

[27]
also used the boundary assumption (for mass balance) that the gas concentration far from the bubble remains constant at its initial value which implies the infinite supply of gas for diffusion. Although their model was not quite applicable in foam processing due to the limited gas, and the viscoelastic nature of polymer melt, it led the direction of a number of researches.

Street studied the bubble growth study in elastic liquid by considering the momentum transfer, in which the Oldroyd three-constant model was employed to describe the viscoelastic behavior of the solution [23]. Because diffusion aspect of the growth process was neglected, they assumed a constant cavity pressure (i.e. system pressure), he concluded that the driving force for expansion of the spherical cavity (i.e. bubble) was the difference between the actual and equilibrium internal pressures. Later, Street et al. furthered his previous model to account for the energy, mass, and momentum balance [24]. The new model described a bubble growth in an infinite viscus solution under isothermal conditions. They then concluded the governing parameters of the bubble growth process is the diffusivity, and concentration of blowing agent and the viscosity of the solution.

Han et al. studied the bubble growth during mold filling that incorporated both the hydrodynamic and diffusion effects [25]. They approximated the concentration profile with the envelope surrounding the bubble with a third-order polynomial and simulated the rheology property of the solution with the Zaremba-DeWitt model. They showed that the growth rate is greatly influenced by the diffusion coefficient, but in the earlier stage of the growth, it is more affected by the hydrodynamic effect.

Papanastasiou et al. [30] studied the growth and collapse of a spherical bubble in an
infinite viscoelastic solution. The rheology of the solution was represented by a BKZ integral-type constitutive equation. They considered the growth of a bubble under a constant pressure difference which implies the negligence of the effect of the mass transfer. They concluded that increasing the Deborah number enhanced the growth and collapse rate.

Although the aforementioned studies had limited applications in actual foaming [26], they offered invaluable insight in bubble growth and built the foundation of later success in growth modelling.

2.4.2. The cell model

In industrial foaming processes, bubbles nucleated in proximity of each in a large quantity. During their growth, the swarm of bubbles grows simultaneously and competes the limited gas supply among each.

In attempt to more realistically describe the growth phenomenon, Amon and Denson [28] proposed the cell model which was well-accepted by fellow researchers [28-29, 31-44]. The cell model suggested by Amon and Denson describes the growth of closely spaced bubbles with limited gas concentration [28]. It assumes polymer solution is divided into a large number of spherical unit cells in which the bubble will only nucleate and grow. More significantly, each spherical unit cell is composed of a concentric gas bubble and a thin shell of polymer/gas solution with limited gas concentration surrounding the bubble. Figure 2-7 illustrates the unit cell which contains a shell (or envelope) of polymer/gas mixture and a gas bubble, wherein $C$, $R$, $S$, $P_{gb}$, and $H$ represents respectively gas concentration, bubble radius, shell radius, bubble pressure, and Henry’s law constant. The limited gas concentration is reflected by the zero-
concentration flux \( \left( \frac{\partial C}{\partial r} \right)_{r=R_{\text{shell}}}=0 \) at the outer layer of the shell. They simulated the bubble growth in Newtonian fluid and obtained qualitative agreement and reasonably quantitative agreement with experimental findings from other literatures.

Afremanesh and Advani adopted the cell model and more significantly took the viscoelasticity of the melt into account [36]. The viscoelastic fluid was represented by the quasi-linear, upper-convected Maxwell model. Despite the lack of experimental verification, they compared the growth profile obtained with a polynomial concentration profile and that obtained by solving the full diffusion equation under isothermal conditions; furthermore, they concluded it is necessary to solve the diffusion equation with proper boundary conditions. Later they mathematically re-formulated the equations based on potential theory and conducted stability analysis [37].

Ramesh et al. applied the cell model in the simulation of batch foaming [31]. They compared the difference in predicted growth profile between Power law based model (Newtonian fluid) and Maxwell based model (viscoelastic fluid). Without an in-situ visualization batch foaming chamber, they quenched their sample in liquid nitrogen at different times and performed SEM on the fractured surface. Later, they attempted to simulate foam

Figure 2-7 Schematic diagram of a unit cell of the cell model [28]
extrusion with transient cooling and modified boundary conditions to account for gas loss in extrusion [32]. Along with transient material properties (i.e. diffusivity and zero-shear viscosity), they were able to obtain accurate growth profile prediction compared with experimental results.

Leung and et al. simulated the bubble growth in batch foaming process [33]. Using the Maxwell viscoelastic solution and completely solving the diffusion equation, they were able to accurately predict the growth profile of bubbles nucleated at different times. Moreover, a thorough sensitivity study was conducted which showed that (a) surface tension affected only the onset of bubble growth; (b) relaxation time influenced the later stage; (c) Diffusivity greatly impacted the growth rate; whereas (d) zero-shear viscosity showed its influence on more elastic materials.

### 2.4.3. Bubble growth and FIM

As can be seen from previous Section 2.4.2. The cell model, despite its application in batching foaming process which is fairly close to assumed conditions, the cell model has been employed in extrusion foaming as well [32] and showed its applicability. However, considering the vast variety of molding technologies (see Section 2.2.4. Molding technologies), limited works has been conducted to simulate the bubble growth phenomena in FIM. In addition, the lack of access to in-situ visualization mold rendered some valuable simulation efforts long for experimental verification [34].

Amon and Denson attempted to simulate the bubble growth in low-pressure FIM [29] with the help of a visualized cavity. They obtained good qualitative agreement between experimental
and model-predicted results, but quantitative discrepancies were shown between them. They believed that the negligence of melt elasticity and bubble coalescence in low-pressure FIM were the main contribution to the quantitative discrepancy.

Afremanesh et al. also simulated bubble growth in a highly viscos solution in LP-FIM, furthermore they considered the pressure variations at the different thickness of the mold cavity [35]. They reported growth profile and foam density in normalized dimensionless form. They reported larger bubble size in the melt front and smaller bubbles near the gate which is consistent with experimental findings in other literature. Later Afremanesh and Advani designed and built a simplified foam injection setup with equipped with a visualized mold to simulated LP-FIM [38]. Again, they conducted simulation on the bubble growth in highly viscous medium in LP-FIM with both pressure and temperature gradient in the mold thickness direction. They reported only the normalized foam density as a function of time rather than cell size, and reasonable agreement between simulation and experimental results considering the different sources of error [38].

Han et al. employed the cell model and described the viscosity of the solution with modified Cross-WLF equation (i.e. viscous fluid) [39]. Even though they assume second-order polynomial concentration profile, they were able to predict the cell size distribution along the thickness of the cavity.

All these works, despite their applicability and accuracy, have significantly contributed to the understanding of bubble growth phenomena. Including some other undescribed works, Table 2-2 Literatures on bubble growth simulation (non-exhaustive) tabulates some of the most
significant works in this field along with their major features (i.e. constitutive model, diffusion equation, experimental verification and etc.). The simulation model proposed in this work is greatly affected by these efforts.
<table>
<thead>
<tr>
<th>Authors</th>
<th>Model</th>
<th>Solution methodology</th>
<th>Concentration profile</th>
<th>Temperature</th>
<th>Simulated process</th>
<th>Extrapolation adequacy</th>
<th>Reference</th>
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<td>LP-FIM</td>
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<td>No</td>
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<td>Single bubble growth</td>
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<td>LP-FIM</td>
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<td>Amin et al.</td>
<td>Single bubble growth</td>
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<td>LP-FIM</td>
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<td>Wang et al.</td>
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<td>No</td>
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3.1. Introduction

In this chapter, experimental studies focus on HP-FIM and HP-FIM followed with MO. The MO step is commonly practiced to increase expansion ratio of the product; however, if improperly executed, products with sheared cell structure and lowered cell density could be easily resulted due to the presence of gate nucleated cells (GNCs), the grow-while-travel nature of FIM and the non-uniform stress field [16-17]. Hence, it is of important industrial value to study the fundamental aspects of these common FIM process to enhance product quality.
Thanks to an in-house visualization mold developed by Dr. Shaayegan [34], on-line visualization can be performed to characterize the foaming behavior during the processes. Serving as an important characterization technique, visualization offer in-situ, and real-time access to the mold cavity during mold filling, melt packing/holding. It has been employed in a number of works to study filling patterns [45, 47], weldline [48], in-mold shrinkage [46], crystallization behavior [49] and filler orientation. More significantly, its capability in capturing real-time bubble nucleation and growth makes it suitable for fundamental studies in foaming.

Last but not least, the author wish to acknowledge that the experimental work listed in this chapter was extracted from a series of experiments that were conducted along with Dr. Shaayegan. Only discussion on phenomenal aspects of nucleation and growth will be presented in this chapter and will be used to verified later simulation results; whereas the further characterization of mechanical and insulation properties will not be displayed in this work.

3.2. Experimental

3.2.1. Equipment and materials

A 50-ton Arburg ALLROUNDER 270/320C injection molding machine, equipped with Trexel Mucell technology, was used to carry out high-pressure FIM experiments as shown in Figure 3-1 Foam injection molding machine with visualization setup. The nominal dimensions of the rectangular mold cavity, fed by a fan gate, were 135 mm × 111 mm × 3.2 mm. The injection molding machine is also capable of performing mold opening (MO). During MO, the moving platen of the mold can open up to a desired distance in thickness direction at a
predetermined mold opening speed.

The fix platen is a visualization mold that was used to observe the real-time foaming phenomena occurring inside the mold cavity [34]. Briefly, the visualization mold consists of a prism, incorporated into the stationary plate of the mold, which acts like a mirror to reflect cavity images to a camera. Three cavity pressure sensors were mounted in front of each visualization window on the moving platen; hence, we could measure the cavity pressure at the visualized location. Other imaging equipment includes a CV M10 camera from JAI, equipped with a magnifying lens from Navitar. Detailed description of the visualization setup was published in [34]. **Figure 3-2** Schematic diagrams of (a) top-view visualization mold [34], (b) injected part.

In addition, Scanning Electron Microscopy (SEM, JEOL JSM - 6060) was used to characterize the cellular structure of the sample, brittle-fractured under liquid nitrogen (LN). ImageJ software was used to analyze the visualization snapshots.

Polystyrene (PS 675) from Americas Styrenics, with an MFI of 7.0 gr/10min and a density
of 1.04 g/cm³ was used as the resin, and carbon dioxide (CO₂, 99% purity) from Linde Gas Canada was used as the blowing agent.

![Figure 3-2 Schematic diagrams of (a) top-view visualization mold [34], (b) injected part](image)

3.2.2. Processing parameters

To perform the HP-FIM experiments, a full-shot melt/gas mixture was first injected into the mold cavity. The injection was immediately followed by a melt-packing step. Nucleation was induced due to the pressure drop caused by in-mold melt shrinkage. Whereas in the HP-FIM with MO. After the packing phase, the mold was then rapidly opened up, nucleation started as the results of MO. The both processes were visualized and recorded. In the meantime, cavity pressure was also recorded for later simulation. The last column shows the processing parameters used to record pressure profiles of HP-FIM + MO. These trials are used only for investigation of the effect of packing pressure on cell nucleation rather than visual studies. Processing parameters used in the experiments are listed in Table 3-1.

### Table 3-1 Processing parameters

<table>
<thead>
<tr>
<th>Processing parameters</th>
<th>HP-FIM</th>
<th>HP-FIM + MO</th>
<th>HP-FIM + MO</th>
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</thead>
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<td>Gas content (wt%)</td>
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<td>5</td>
<td>5</td>
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<tr>
<td>Melt temperature (°C)</td>
<td>220</td>
<td>220</td>
<td>220</td>
</tr>
</tbody>
</table>

Pressure profiles only
### Mold Table

<table>
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<th>Value 1</th>
<th>Value 2</th>
<th>Value 3</th>
</tr>
</thead>
<tbody>
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<td>Mold temperature (°C)</td>
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<td>25</td>
<td>25</td>
</tr>
<tr>
<td>Injection speed (cm(^3)/s)</td>
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<td>80</td>
<td>80</td>
</tr>
<tr>
<td>Packing pressure (MPa)</td>
<td>6, 14, 20</td>
<td>6, 14, 24</td>
<td>20, 22, 24</td>
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<tr>
<td>Packing time (s)</td>
<td>8s</td>
<td>8s</td>
<td>8s</td>
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<td>Mold opening distance (mm)</td>
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<tr>
<td>Mold opening speed (mm/s)</td>
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<tr>
<td>Cooling time (s)</td>
<td>30</td>
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</tbody>
</table>

### 3.3. Results and discussion

The following set of figures (i.e. **Figure 3-3** and **Figure 3-4**) are snapshots of videos recorded during FIM experiments via the visualization setup described above. Row-wise, the figures show the different trials that were conducted; and column-wise, they depict the melt inside the cavity. For **Figure 3-3**, the reference time is injection stage (t=0s), during packing phase (t=5s), during cooling (t=first visual on a shrinkage induced cell), and at the end of cooling (t=27s). For **Figure 3-4**, the reference time is also injection stage (t=0s), during packing phase (t=7.5s, before MO), after mold opening (t=10.5s) and at the end of cooling (t=25s).

#### 3.3.1. Effect of packing pressure on foam structure

- **In high-pressure foam injection molding**

In HP-FIM with 6 MPa and 14 MPa packing pressures (**Figure 3-3 a and b**), elongated bubbles can be observed. These bubbles are nucleated as the solution were passing through the gate when a rapid pressure drop occurred. These gate nucleated bubbles (GNCs) started to grow while they were travelling with the melt to fill the cavity [16]. The stress field that were experienced by the growing bubbles deformed the bubble. Hence, GNCs are characterized by
elongated shapes. They remained in the system throughout the cooling stage during which shrinkage induced cells (SICs) started to nucleate and grow. As a result, the final structure contains both elongated cells and spherical cells as indicated by the white arrows in Figure 3-3 a) and b).

On the other hand, when packing pressure is sufficiently high, GNCs can be dissolved. This is evidenced by Figure 3-3c. No visually observable cells could be found during packing; more significantly, no elongated bubbles were in presence during cooling. Hence, the final structure contains only spherical cells.

Low expansion ratio, with relatively low cell density and spherical bubbles makes HP-FIM products desirable for products that requires a small amount of weight reduction without scarifying even a little bit of the mechanical properties of the bare-bone plastics. The bubbles loosely spaced in the foam can potentially act as crack arrestors [4] which improves both fatigue and impact performance of the product.

- **In high-pressure foam injection molding with mold opening**

Similar trends were observed for HP-FIM + MO. GNCs remained in the system for 6 MPa and 14 MPa packing pressure, as shown in Figure 3-4a and b. Whereas under higher packing pressure, shown in Figure 3-4c, GNCs re-dissolved under 24 MPa.

However, in addition to GNCs and SICs, a class of cells were nucleated due to the pressure drop upon the execution of MO. The MO induced cells (MICs) are characterized by large number density and consistent shapes (i.e. all spherical for small MO distance; all elongated with uniform aspect ratio for large MO distance).
Such structure is favorable when high expansion ratio is desired for applications such as thermal and acoustic insulations, material filtering and transports and etc.

3.3.2. Effect of packing pressure on cell nucleation

- In high-pressure foam injection molding

In HP-FIM, the effect of packing pressure on cell nucleation deteriorates final cell density. Despite the concentration used for these trials were at 3% which lower than 5% used for MO trials, the obvious reduction in cell density as packing pressure increases is due to dissolution of GNCs. As discussed above, in HP-FIM, the main source of cell nucleation is through pressure drop at gate and during thermal contraction. When packing pressure is applied, depending on the level of pressure, GNCs decreases in the system. When the packing pressure reaches above solubility pressure, a plummet in cell density can be observed in a) due to diminished GNCs. At 20 MPa packing, the main source of nucleation after packing is shrinkage induced. Hence, although uniformly sparsely spaced spherical bubble are desirable, the low cell density substantially reduces the expansion ratio.

- In high-pressure foam injection molding with mold opening

However, for the MO trials, the cell density increased as packing pressure were tuned up. Shown in b), cell density increased almost 5,000,000 cells/cm³ from an increase of packing pressure from 6 to 24 MPa. This is due to due to the volatile concentration that is available for nucleation upon mold opening is much larger at 24 MPa packing pressure that 6 MPa, thanks to dissolution of GNCs. At both 6 and 14 MPa, the modes of nucleation are a mixture of GNCs, MICs, and SICs; at 24 MPa, the mode of nucleation are primarily MO induced (combined with
a minor fraction of SICs).

- The effect of packing pressure on pressure drop rate.

Despite the observable increase in cell density, there has been no quantitative evidence that increase in packing pressure will induce more nucleation. Moreover, in this work, an attempt is made to justify such phenomenon by investigating the pressure profiles associated with those trials.

depicts the pressure profile recorded during HP-FIM + MP trials. The packing pressure of these trials are all well above packing solubility pressure of 12 MPa estimated at 180°C with 5% gas concentration based on measurements by Sato et al., 1996 [59]. Such pressure ensure that most of GNCs are dissolved, visual evidence can be found in Appendix A. As can be seen in Figure 3-7, increased packing pressure led to increased pressure drop rate. Hence, the increase in nucleation with increasing cell density can be attributed to increased pressure drop rate. However, the reason behind the increasing pressure drop rate due to increasing packing pressure remains un-explained. It is suspected that the increase in pressure leads to increase in compressibility, which in turn leads to faster response to depressurization when the system is homogeneous (i.e. single phase solution). Further experimental verification is required to provide more concrete evidence to such hypothesis.

3.3.3. Effect of packing pressure on cell growth

- In high-pressure foam injection molding

In the presence of GNCs, it is important to study the growth behavior of SICs, as the
GNCs compete with the desired SIC (in HP-FIM). **Figure 3-8** demonstrates the growth of SICs under various packing pressures. The origin in horizontal axis represents the end of cavity filling (or injection). It can be seen that for lower packing pressure cases, SIC appeared earlier compared with those under higher packing pressure. This is due to the time need to reach solubility pressure is short when the system pressure is low. Moreover, the growth rate of 20 MPa bubbles are larger than that of lower pressures. This can be caused by the lowered concentration in the system that is available for mass transfer in the presence of GNCs. The competition with GNCs for limited gas molecules not only reduces the growth rate but also leads to reduced final bubble size.
**Figure 3-3** Snapshots of HP-FIM trials with different packing pressure at different times
a) 6 MPa; b) 14 MPa; c) 20 MPa
(3%wt CO₂, 8s packing time, no mold opening)

**Figure 3-4** Snapshots of HP-FIM+MO trials with different packing pressure at different times
a) 6 MPa; b) 14 MPa; c) 24 MPa
(5%wt CO₂, 8s packing time, mold opened)
Figure 3-5 Effect of packing pressure on cell nucleation of a) NMO trials, b) MO trials

Figure 3-6 Pressure profile of HP-FIM + MO at different packing pressure
**Figure 3-7** Effect of packing pressure on pressure drop rate for HP-FIM+MO

**Figure 3-8** Effect of packing pressure on shrinkage induced cells in HP-FIM
Chapter 4

SIMULATION OF CELL GROWTH IN FOAM INJECTION MOLDING

4.1. Introduction

This chapter presents the research conducted in simulating the bubble growth phenomena in FIM. The cell model was adopted to simulate the bubble growth phenomena in viscoelastic, non-Newtonian fluid. Mathematical formulations of the governing equations of the bubble growth process are presented along with simplification and corresponding assumptions in the context of FIM. In addition, numerical methods that were chosen to solve each equation were
discussed. Moreover, the material and transport parameters involved in the model are outlined. The growth simulation is then verified with both HP-FIM and HP-FIM+MO experimental results that were obtained with a visualization mold thoroughly described in [9]. Last but not the least, a parametric study is presented to systematically investigate the behavior of the model against the changing of different parameters.

4.2. Modelling and simulation of bubble growth

To simulated the non-isothermal bubble growth phenomena, the mass conservation (or continuity equation), energy conservation (or energy equation) and momentum conservation (or momentum equation) are required to be solved along with the mass balance equation of the blowing agent and advection-diffusion equation. Moreover, to accurately describe the viscoelastic behavior of the foam-able mixture, a constitutive equation is required to correlate the stress field with shear rate associated with both viscous and elastic characteristics of the polymer/gas mixture. It is worth to note that the energy balance and thermal conduction are simulated with Autodesk Moldflow software using finite volume method. Hence, the number of governing equations reduced to 5 and required to be solved simultaneously with appropriate initial and boundary conditions.

Figure 4-1 Overview of FIM cell growth model
4.2.1. Cell model and assumptions

The cell model suggested by Amon and Denson describes the growth of closely spaced bubbles with limited gas concentration [2]. It assumes polymer solution is divided into a large number of spherical unit cells in which the bubble will only nucleate and grow. More significantly, each spherical unit cell is composed of a concentric gas bubble and a thin shell of polymer/gas solution with limited gas concentration surrounding the bubble. Figure 4-1 illustrates the unit cell which contains a shell (or envelope) of polymer/gas mixture and a gas bubble. Unlike previous works, this cell model could realistically describe the diffusion driven nature of bubble growth among a large quantity of bubbles in proximity to one another. This cell model was later recognized and adopted by various researchers as discussed in Chapter 2.

![Cell model with concentration profile](image)

**Figure 4-2** Cell model with concentration profile

To further reduce the complexity of mathematics involved in the actual foaming phenomenon, the following assumptions are made:

1) The bubble remains spherically symmetric throughout the growth process;

2) The polymer/gas solution is single-phase, homogeneous, incompressible and non-rotational;
3) Each unit cell represents a closed system (i.e. no mass transfer is allowed at the boundary \( \frac{\partial C}{\partial t} \bigg|_{r=R_{\text{shell}}} = 0 \));

4) Transient cooling for the unit cell is accounted, however, the temperature is independent of space vectors in the unit cell;

5) Material and transport properties are function of time but independent of space vectors in the unit cell;

6) Surface tension is assumed to be constant;

7) There are no interactions between neighboring bubbles during growth;

8) The pressure at the boundary of the shell is equal to system pressure at time \( t (P_{\text{sys}}(t)) \);

9) The gas inside the bubble is ideal gas and obeys ideal gas law;

10) The gas molecules distribute uniformly in the bubble;

11) The initial bubble pressure can be determined by the thermodynamic equilibrium condition, where the chemical potential of the gas in the gas bubble equals to that of the gas in the polymer/gas mixture and need to be determined by Simha-Somcynsky equation of state (SS-EOS) (i.e. \( \mu_{g,bub}(P_{\text{bub}}, T_{\text{sys}}) = \mu_{g,\text{sol}}(P_{\text{sys}}, T_{\text{sys}}, C_{\text{Rbub}}) \)), rather than simply assuming that it is equal to solubility pressure [33];

12) The initial stress in the polymer/gas solution around the bubble is zero;

13) The inertial forces and the effect of gravity on bubble growth are negligible;

14) The bubble pressure is related to the gas concentration at bubble-shell interface through
Henry’s law \( C_{R_{bub}}(t) = K_hP_{bub}(t) \);

With these assumptions, the governing equations can be analytically reduced to an implementable, stably solvable, and yet accurate form. Please refer to Appendix C for equations and basic theories involved in SS-EOS.

### 4.2.2. Development of bubble growth model

The governing equations of bubble growth is composed of conservation of mass and momentum. The exclusion of conservation of energy is because that the unit cell is in the magnitude of millimeters, and thermal conductivity of polymer is low, therefore the spatial dependence of temperature within the unit cell is negligible. In addition, it is worth to note that all the parameters involved in the following equations are function of time which reflects the transient nature of the model. Please refer to Appendix B for the detailed derivation of the governing equations.

- **Conservation of mass**

  Equation 4.1 describes the mass conservation of the unit cell during bubble expansion in spherical coordinates,

  \[
  \frac{\partial \rho}{\partial t} + \frac{1}{r^2} \frac{\partial (\rho r^2 v_r)}{\partial r} + \frac{1}{r \sin \theta} \frac{\partial (\rho \nu_\theta \sin \theta)}{\partial \theta} + \frac{1}{r \sin \theta} \frac{\partial (\rho \nu_\phi)}{\partial \phi} = 0
  \]

  where \( \rho \) is the density of the fluid or in this case the polymer/gas solution in the shell, \( t \) is time and \( \mathbf{V} \) is the velocity vector of solution in the shell which is composed of \([v_r, \nu_\theta, \nu_\phi]\) in spherical coordinate. Thanks to Assumption 1 and 2 Equation 4.1 reduces to Equation 4.2
\[ V_r = \frac{V_{RBub} R_{RBub}^2}{r^2} \]  

where \( V_r \) is the radial velocity of the solution, \( r \) is the space vector, \( R_{RBub} \) is the radius of the gas bubble and \( V_{RBub} \) is the radial velocity of solution at bubble-shell interface and is equal to bubble growth rate, \( \dot{R}_{RBub} \). It should be noted that even though density is changing with respect to time but due to the rate of bubble growth is far below Mach number of 0.3, the incompressible assumption stands [58].

- **Conservation of momentum**

Equation 4.3 is the transformed form of momentum equation in spherical coordinates,

\[
\rho \left( \frac{\partial V_r}{\partial t} + V_r \frac{\partial V_r}{\partial r} \right) = - \frac{\partial P}{\partial r} + \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \tau_{rr} \right) - \frac{\tau_{\theta \theta} + \tau_{\phi \phi}}{r} + \rho g_r 
\]

4.3

where \( P \) is pressure in the shell in radial direction, \( \tau_{rr}, \tau_{\theta \theta}, \) and \( \tau_{\phi \phi} \) are stresses in their respective direction.

With Assumption 1 spherical symmetry and Assumption 13 negligible gravity, Equation 4.3 can be transformed to

\[
\rho \left( \frac{\partial V_r}{\partial t} + V_r \frac{\partial V_r}{\partial r} \right) = - \frac{\partial P}{\partial r} + \frac{\partial \tau_{rr}}{\partial r} + 2 \left( \frac{\tau_{rr} - \tau_{\theta \theta}}{r} \right) 
\]

4.4

As the system is viscoelastic, the inertial and advective terms on the left-hand side of Equation 4.4 equates to 0, as stated in Assumption 12, it can now be reduced to

\[
P(R_{RBub}) - P_{sys} = \frac{2 \gamma}{R_{RBub}} + 2 \int_{R_{RBub}}^{R_{shell}} \frac{\tau_{rr} - \tau_{\theta \theta}}{r} \, dr = 0
\]

4.5

in which \( \gamma \) is surface tension.
As the solution is viscoelastic in nature, therefore it is necessary to choose an appropriate constitutive model to represent the time dependence of the strain response. The upper-convected Maxwell model is chosen in accordance with previous studies [10]. This model is capable of describing some of the most important viscoelastic behaviors of the solution, such as shear-dependent viscosity, normal stress effects, and stress relaxation. The general equation is transformed and simplified into

\[
\frac{d\tau_{rr}}{dt} = -\left(\frac{1}{\lambda} + \frac{4V_r}{r}\right)\tau_{rr} - \frac{4\eta_0 V_r}{\lambda}\frac{\tau_{rr}}{r} \quad 4.6a
\]

\[
\frac{d\tau_{\theta\theta}}{dt} = -\left(\frac{1}{\lambda} - \frac{2V_r}{r}\right)\tau_{\theta\theta} - \frac{2\eta_0 V_r}{\lambda}\frac{\tau_{\theta\theta}}{r} \quad 4.6b
\]

wherein, \(\lambda\) and \(\eta_0\) are relaxation time and zero-shear viscosity, and \(V_r\) can be identified by Equation 4.2.

Once the constitutive equations are substituted into equation 4.5, a physically sound bubble growth model can already be presented which satisfies both conservation of mass and momentum laws. It describes the hydrodynamic aspects of the growth process, namely, the stresses associated with bubble growth process. However, to more accurately describe the contribution of diffusion in the growth process and to more realistically simulate the growth of bubbles in proximity to one another, the cell model needs to be implemented.

- **Mass balance**

According the cell model, diffusion induced bubble growth is assumed. Therefore, mass balance of gas across the bubble-shell interface follows
\[
\frac{d}{dt}(m_g) = A_{\text{bub}} D \frac{\partial C}{\partial r} \bigg|_{r = R_{\text{bub}}}
\]  

4.7

the left-hand side of Equation 4.9 represents the rate of accumulation mass inside the bubble, whereas, the right-hand side of Equation 4.7 is the diffusive flux of the volatile according to Fick’s law, wherein D is the diffusivity, \( m_g \) is the mass of gas inside the bubble, and equals to

\[
m_g = V_{\text{bub}} \rho_g = \frac{4\pi}{3} R_{\text{bub}}^3 \rho_g
\]

4.8

where \( \rho_g \) is the density of gas. Substitute Equation 4.18 into 4.7 yields

\[
\frac{d}{dt} \left( \frac{4\pi}{3} R_{\text{bub}}^3 \rho_g \right) = 4\pi R_{\text{bub}}^2 D \frac{\partial C}{\partial r} \bigg|_{r = R_{\text{bub}}}
\]

4.9

• Mass Diffusion

To solve for the concentration flux at bubble-shell interface, Equation 4.10 which defines the diffusion of volatiles to be solved

\[
\frac{DC}{Dt} = -\nabla \cdot (D \nabla C)
\]

4.10

in which \( \frac{DC}{Dt} \) represents the substantial derivative (or material derivative) of concentration and not to be confused with diffusivity constant.

In spherical coordinates, along with Assumption 5, Equation 4.10 simplifies to

\[
\frac{\partial C}{\partial t} + V_r \frac{\partial C}{\partial r} = D \frac{\partial}{\partial r} \left( r^2 \frac{\partial C}{\partial r} \right)
\]

4.11

In accordance with the cell model and Assumption 13, initial and boundary conditions
for diffusion equation are

\[ C(r, t) = C_0, \quad \text{for } R_{\text{bub}} \leq r \leq R_{\text{shell}} \text{ and } t = 0 \]  \hspace{1cm} 4.12a

\[ \frac{\partial c(r,t)}{\partial r} = 0, \quad \text{for } r = R_{\text{shell}} \text{ and } t \geq 0 \]  \hspace{1cm} 4.12b

\[ C(r, t) = K_h P_{\text{bub}}, \quad \text{for } r = R_{\text{bub}} \text{ and } t > 0 \]  \hspace{1cm} 4.12c

Solving Equation 4.11 yields the concentration gradient at the bubble interface which can then be used to compute bubble radius \( R_{\text{bub}} \) from Equation 4.9.

The coupling of hydrodynamic and mass balance equations presents the complete mathematical formulation of the cell growth.

**4.2.3. Material and transport properties**

Most of existing works on simulation of bubble growth [33] are only capable of simulation a very short bubble growth period which was referred to the beginning stage of bubble growth. One of the main reason of the short simulation time domain is attributed to the use of constant material properties which mimics the growth under steady-state temperature condition at which temperature is not a function of time. Although, such simulation provides us some insights during the beginning stage of foaming, the results generated are not applicable for prediction of the final foam morphology that has undergone a relatively longer cooling process or a more complex temperature history. During such process, material and transport properties has undergone a substantial change. Therefore it is necessary to use more realistic material properties which could accurately describe each properties under a certain combination of temperature, gas concentration and pressure. To

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assure the accuracy of the models of material and transport properties, the models and values used in this work have been verified with experimental results in their respective source literature [50-52]. Moreover, it is important to note that the “foamable” solution in this work is PS/CO₂ system.

- **Zero-shear viscosity (η₀)**

Lee et al. from our group proposed a model of η₀ along with experimental verification in their work [50]. Their model is in a generalized form of Arrhenius equation and is capable of predicting the effects of temperature (T), pressure (P) and gas concentration in weight percent (X) in a PS/CO₂ system.

\[
\eta_0(T, P, C) = A \exp\left(\frac{\alpha}{T - T_{ref}} + \beta P + \psi X\right)
\]

\[A = 0.8298; \ T_{ref} = 341.1; \ \alpha = 1272.0; \ \beta = 6.032 \times 10^{-8}; \ \psi = -66.51\]

- **Relaxation time (λ)**

Due to the lack of literature on modelling of PS/CO₂, the λ model for PS proposed by Venerous et al. was adopted [51]. The model was experimentally verified [51].

\[
\log \left( \frac{\lambda(T)}{\lambda(T_{ref})} \right) = \frac{T_{ref} - 100}{T_{ref} - 50} - A \frac{T - 100}{T - 50}
\]

\[T_{ref} = 170; \ \lambda(170) = 75; \ A = 14\]

- **Diffusivity (D)**

The model of diffusivity of CO₂ in PS was proposed by Areerat et al. in the form of Arrhenius equation [52]. The model was obtained from fitting of the experimental results [52].
\[ D = D_0 \exp\left(-\frac{Ea}{R_g T}\right) \]

\[ D_0 = 1.58 \times 10^{-6}; \quad Ea = 2.51 \times 10^4; \quad R_g = 8.31441 \]

- **Surface tension (γ)**

Interpolated from surface tension data measured by Park et al. [56], 0.018 N/m was adopted as the surface tension in this work. Their measurements were conducted by using axisymmetric drop shape analysis-profile (ADSD-P) technique.

### 4.2.4. Numerical implementation

Equation 4.2, 4.5, 4.6, 4.9, 4.11 constitute the mathematical description of the bubble growth based on cell model. To obtain the bubble growth profile, these equations are to be solved simultaneously. The system of the governing equations is nonlinear and highly coupled, hence there does not exist a known closed-form or analytical solution [10, 11]. Therefore numerical methods are applied to obtain an approximate solution of the given problem.

**Table 4-1** tabulates the governing equations and the corresponding numerical methods used to obtain solution. The equations are solved by explicit finite difference and 4\(^{th}\) order Runge-Kutta method in accordance with literature [33]. As for stability issue associated with solving the diffusion partial differential equation (PDE) explicitly, von Neumann stability criteria is employed.

<table>
<thead>
<tr>
<th>Conservation of mass</th>
<th>Explicit finite difference (backward)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conservation of momentum</td>
<td>Explicit finite difference (backward) and trapezoidal integration</td>
</tr>
<tr>
<td>Maxwell constitutive equations</td>
<td>4&lt;sup&gt;th&lt;/sup&gt; order Runge-Kutta method</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>----------------------------------------</td>
</tr>
<tr>
<td>Mass balance</td>
<td>Explicit (backward) finite difference</td>
</tr>
<tr>
<td>Advection-diffusion equation</td>
<td>Explicit finite difference (backward and central, 1&lt;sup&gt;st&lt;/sup&gt; and 2&lt;sup&gt;nd&lt;/sup&gt; order)</td>
</tr>
<tr>
<td>Stability criteria for diffusion</td>
<td>von Neumann stability criteria</td>
</tr>
<tr>
<td></td>
<td>[ \Delta r = \frac{V_r + \sqrt{V_r^2 + 8DF}}{2\Delta t}, \quad F = 0.9 ]</td>
</tr>
<tr>
<td>Boundary immobilization</td>
<td></td>
</tr>
<tr>
<td>(Normalization)</td>
<td>[ y = \frac{r^3 - R_{bub}^3}{R_{shell}^3 - R_{bub}^3} ]</td>
</tr>
<tr>
<td>Initial bubble size [33]</td>
<td>[ R_{bub}(0) = \frac{2y}{P_{bub,cr} - P_{sys}} \times 1.01 ]</td>
</tr>
<tr>
<td>Initial shell size [33]</td>
<td>[ R_{shell}(0) = \left( \frac{3}{4\pi} \ast (V_{shell} + V_{bub}(t)) \right)^{\frac{1}{3}} ]</td>
</tr>
</tbody>
</table>

4.2.5. Simulation strategy

**Figure 4-3** and **Figure 4-4** Detailed simulation strategy illustrates the simulation strategy that is used to implement the numerical model for bubble growth. It can be clearly seen that the growth solver which consists of the 5 equations are iterative in nature.

![Figure 4-3 Overall simulation strategy](image_url)
Figure 4-4 Detailed simulation strategy
4.3. Experimental verification

To validate the proposed model and numerical implementation, the predicted cell growth profiles was compared with 2 distinct trials of FIM experiments.

4.3.1. Experimental results

The experimental setup and materials are thoroughly described in Chapter 3. To demonstrate the validity of the model, 2 distinct trials were used. Table 4-2 illustrates the processing parameters and simulation input used to verify the growth model. It needs to be noted that the pressure profiles were measured by pressure transducers during the experiments, whereas the temperature were simulated with Moldflow, Autodesk using the same processing parameters as experimental trials.

<table>
<thead>
<tr>
<th>Table 4-2 Processing parameters and simulation input</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Processing parameters</strong></td>
</tr>
<tr>
<td>HP-FIM 3-20-8-NMO</td>
</tr>
<tr>
<td>HP-FIM+MO 5-24-8-MO</td>
</tr>
</tbody>
</table>
4.3.2. Comparison between simulation and experimental results

Figure 4-7 shows cell growth profiles obtained both by simulation and experimental visualization for the two conditions shown above. Predicted growth profiles match reasonably well with experimental results.
For the HP-FIM, the bubble growth starts to growth with an increasing growth rate at the beginning stage, and then growth rate reduced as time proceed. Leung et al. also reported similar trend and attributed this to the contribution of surface tension to the bubble [33]. When the bubble is small surface tension players a larger role in retarding growth, while its effect continuously reduces as the bubble grows. Such effect can also be found in HP-FIM+MO but in a much short time due to the large growth rate.
Then, the cell grew faster. This because in addition to the reduced effect of surface tension on retarding cell growth, the concentration gradient at bubble-shell interface \( \frac{\partial c}{\partial r} \bigg|_{r = R_{\text{pub}}} \) increased as the same time.

At the end, the growth rate decreased to zero, as the concentration gradient started to reduce due to decreasing gas supply in the shell and decreasing diffusivity of CO₂.

4.3.3. Driving forces for bubble growth

Based on the governing equations, bubble growth is driven by two main factors [28].

1. Hydrodynamic driven growth

Equation 4.5 describes the stress balance across the bubble, it is shown here for convenience.

\[
P(R_{\text{pub}}) - P_{\text{sys}} - \frac{2\gamma}{R_{\text{pub}}} + 2 \int_{R_{\text{bub}}}^{R_{\text{shell}}} \tau_{rr} - \tau_{\theta\theta} \frac{dr}{r} = 0
\]

Equation 4.5

As shown in Figure 4-8 Pressure balance across the cell model, the first term can be interpreted as gas pressure within the bubble, the second term is the system pressure exerted by the neighboring melt, the third term represents the surface tension, and the last term is the viscoelastic stress caused by growing bubble. Surface tension \( \gamma \), zero-shear viscosity \( \eta_0 \), and relaxation time \( \lambda \) are the main governing material properties in this equation.

As mentioned before, Equation 4.5 along was used to model bubble growth that is controlled mainly by the pressure difference across the bubble surface (i.e. the shell in this case). Its applications are mainly found in bubble blowing areas for example blow molding
technologies. However, in order to accurately describe the bubble growth during a phase separation process in foaming, such hydrodynamic model along is not competent enough to fully elucidate the entire phenomena.

![Figure 4-8](image)

Figure 4-8 Pressure balance across the cell model

2. Diffusion driven growth

The basics of the cell model is to accurate simulate the complex mass diffusion phenomena in a multi-body system in which each of the bubbles absorbs gas from the surroundings. The cell model defines a fictional shell surrounding each bubble, only from the shell, the bubble can withdraw gas molecules. Thus, the mass balance can be established.

\[
\frac{d}{dt} \left( \frac{4\pi}{3} R_{bub}^3 \rho_g \right) = 4\pi R_{bub}^2 D \frac{\partial C}{\partial r} \bigg|_{r = R_{bub}}
\]

As Equation 4.9 described, the rate of change of the mass of gas inside the bubble must be equal to the diffusive flux over the entire surface of the bubble. The governing transport property is the diffusion coefficient \((D)\).
4.4. Parametric analysis

With an accurate model of cell growth, it is necessary to investigate the sensitivity of the model to the variation of different parameters. Hence, parametric study was conducted to demonstrate the effect of various parameters on the behavior of the model. Moreover, the results from the parametric analysis will be discuss in the context of FIM to provide instructive advices in achieving uniform cell structure or small cell size. In the following study, the HP-FIM conditions were used demonstrate the model behavior.

- Effect of temperature history

As one of the main goal of the proposed model is to predict the cell size distribution along the thickness direction of the part. At different thickness location, the melt experiences different temperature history. Referencing the core as t=0, Figure 4-9a shows the simulated temperature history by Moldflow, Autodesk at varying distance from the core using the same processing conditions. Figure 4-9b demonstrates the effect of temperature history on cell growth. By comparing t=0mm and t=0.53mm, it can be concluded the growth is not sensitive to slight change in temperature while other parameters are maintained. Whereas when initial temperature decrease is large, the bubble experiences a slower growth rate and stop growing earlier due to solidification of the structure. Plotting the final cell size against distance from the core, Figure 4-10 shows the cell size distribution along the thickness direction. As can be seen, when temperature was relatively more uniform, the final cell sizes were almost the same at t=0mm and t=0.53mm, however, when the temperature non-uniformity is large, the cell size varies largely along the thickness direction.
Plotting the cell size distribution over the entire growth profile, Figure 4-11 demonstrates change of the cell size distribution over the entire molding period. Hence, instructive advice can be made that a uniform cell structure can be obtained by keeping a uniform temperature history throughout the mold cavity. One the other hand, a rapid temperature drop can be used to ‘freeze’ the cell structure and obtain parts with much smaller cell size. Such ‘freezing’ can be achieved by rapid mold temperature control technologies. Moreover, final cell morphology of HP-FIM as discussed in Chapter 3 was composed of large cells and low cell density. With the aid of the simulation, it can be further concluded that when HP-FIM was properly executed, the resulting cell size distribution should be similar to Figure 4-10. Therefore, in industrial application where visualized experiments were not available, obtaining a morphology similar to the description above indicates that all GNCs were dissolved and MO or other molding technologies can be properly induced to have better control over the final foam morphology.

**Figure 4-9** a) Temperature history at different thickness locations from the core (t); b) Effect of temperature history on cell growth
Figure 4-10 Cell size (radius) distribution along thickness direction

Figure 4-11 Cell size (radius) distribution over the entire growth history

- **Effect of diffusivity (D)**

Diffusivity is the main parameter in the diffusion driven bubble growth. Figure 4-12 shows the effect of diffusivity on cell growth. As can be seen from the figure, firstly, constant diffusivity settings lead to similar final cell size. This is analogous to steady-state temperature situation ($\frac{dT}{dt} = 0$) during which the effect of mass diffusion driven growth predominates the effects of increased elasticity and viscosity on the hydrodynamic aspects of the growth. In such scenarios, the end of bubble growth is equivalent to the end of mass diffusion when
concentration gradient is \( \frac{\partial C}{\partial r} \) throughout the shell. Thus, despite the growth rate, with all the other parameters kept the same, different values of steady-state diffusivity will always lead to the same final cell size. [36]. On the other hand, when transient temperature history is applied along with transient material properties, the contribution of rheological properties takes over in the meantime the contribution of mass diffusion fades due to decreasing of diffusivity.

Secondly, the larger the diffusion coefficient is, the larger the growth rate is at the beginning stage; thus, leading to slower growth rate due to lowered gas concentration with in the shell.

Based on the discussion above, the use of gas with lower diffusivity can theoretically reduce the final cell size at a short cooling time which is standard in industry. Such gas could be nitrogen (N\textsubscript{2}) whose diffusivity is slightly less than that of CO\textsubscript{2} in PS. Numerous researchers have confirmed that under similar processing conditions, N\textsubscript{2} produces smaller cells at higher cell density than CO\textsubscript{2} [44, 53-55]. However, it needs to be noted that reducing diffusivity will increase the diffusion time to some extent and extent the duration of preparation of the single-phase homogeneous solution inside the barrel.

![Effect of diffusivity on cell growth](image-url)

**Figure 4-12** Effect of diffusivity on cell growth
• **Effect of surface tension (γ)**

**Figure 4-13** illustrates the effect of surface tension on cell growth. It can be seen that compared to other parameters, surface tension has less profound effect on the growth profile and final cell size even when increased by 10 times. The largest variation is shown when surface tension is increased to 1.8 \( N/m \). The difference is started to show at the beginning stage of the growth. This can be attributed to Young-Laplace equation, according to which increase in surface tension leads to increase in initial cell size which in turn leads to a larger bubble surface area and an increased mass diffusion flux. Nonetheless, the fact that 1.8 \( N/m \) is rarely the case for polymer foaming draws the conclusion that surface tension plays a less critical role in cell growth. Similar conclusion was made by Leung et al. [33]. However, it does show impact on cell nucleation.

![Effect of surface tension](image)

**Figure 4-13** Effect of surface tension on cell growth

• **Effect of zero-shear viscosity (η₀)**

Zero-shear viscosity describes the viscous behavior of a polymer. As shown in **Figure 4-14**, zero-shear viscosity acts as a retarding force to cell growth, increase in viscosity leads to
smaller cell size and slower cell growth. At low $\eta_0$, the bubble growth is dominated by diffusion, whereas at high $\eta_0$ value, bubble grow at a much slower rate and stop growing a much smaller size due to the high retarding force. Moreover, as discussed by Leung et al. [33], the sensitivity of growth to $\eta_0$, increases as melt elasticity decreases. In real FIM processing, it is almost impossible to decouple $\eta_0$ from relaxation time, as they are together form the viscoelastic nature of polymer melt. Hence, it is possible to achieve desired cell structure by fine tuning the rheological properties of polymer/gas solution, which in turns demands more intensive fundamental studies on rheology of melt/gas mixture and improved technology in rheometer to be able to accommodate the high pressure associated with gas–charged melt.

![Effect of zero-shear viscosity on cell growth](image)

**Figure 4-14** Effect of zero-shear viscosity on cell growth

- **Effect of relaxation time ($\lambda$)**

  Relaxation time as another important part of rheological property of a polymer/gas solution represents the elasticity of the melt. A larger $\lambda$ also indicates that the polymer is more elastic. The larger $\lambda$ value is, the longer it takes for the polymer to relax from a pre-exerted stress and to accumulate stress [57]. In this work, the effect of melt elasticity is predicted as
increases in relaxation time lead to increases in growth rate. Similar prediction has been reported by Afremanesh and Advani [36]. They hypothesized that this increase in growth rate is since the total stress in the shell exerted on the bubble (5th term in Equation 4.6) in viscoelastic solution is much smaller than that in a Newtonian fluid. Despite the relaxation model adopted was developed to describe PS [51], it still delivers the concept that increasing melt elasticity enhances bubble growth.

Image: Figure 4-15 Effect of relaxation time on cell growth

4.5. Conclusion

A mathematically accurate model was adopted to describe the bubble growth phenomenon in HP-FIM. By incorporating realistic material properties and PVT equations, the complete growth profile of bubble growth under two distinct FIM processing path were compared. Using a visualized mold, the bubble growth prediction was successfully verified. Compared with existing works, this simulation can simulate a user specified during of bubble growth. The validity of this work is also verified by conducting a series of parametric analysis, in which the trends agree with most of literature.
CONCLUSION AND FUTURE RECOMMENDATION

5.1. Conclusion

A thorough literature review on fundamental studies and simulation of bubble growth was conducted. Systematic comparison between existing simulations of bubble growth in gas-charged polymer melt was summarized.

Visualization foam injection molding experiments were performed in the context of HP-FIM and HP-FIM with MO. The nucleation, growth and final morphology associated with
different packing pressures were studied. Results indicated that increase in packing pressure leads to higher cell density in MO trials, which suggests that cell density can be individually tuned by controlling packing pressure without sacrificing expansion ratio.

The cell model proposed by Amon and Denson was employed and modified to simulate bubble growth in foam injection molding. Transient, semi-nonisothermal bubble growth simulation was conducted for the entire cooling process. The simulation is based on realistic material and transport properties, revised SS-EOS [60], and experimentally measured pressure profiles. Quantitative agreement was observed when compared with experimental results for both MO trials and non-MO samples. Parametric study was also conducted which reviewed qualitative agreement with most literature reviews. Superior to existing works, the proposed simulation strategy is capable of predicting the contribution of both hydrodynamic and diffusion-driven aspects of the growth phenomenon for the entire life span of a bubble.

5.2. Future recommendation

There are many area left to extend in order to accurate model the complete bubble growth behavior in foam injection molding process. The following are some suggestions on which effort could be devoted to improve the proposed model.

i. Full integration of conservation of energy into the existing model;

ii. Bubble deformation in drag and extensional flows;

iii. Bubble growth of semi-crystalline materials which requires a module that describes gas expulsion from the crystal upon cooling;
iv. Theoretical development of modified Tait’s equation which incorporates volatile concentration, temperature and pressure to replace SS-EOS for faster computation;

v. Growth simulation with bubble deformation;
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Appendix A

Visual observation from high packing pressure trials in HP-FIM + MO

This section presents the visual observation for the trials used in Chapter 3 for pressure drop rate analysis. The following figures demonstrate the cavity image after injection, end of packing (i.e. right before MO), and end of cool under different packing pressures. It can be seen that most of the GNCs are dissolved back into the system, so that it is reasonable to assume the solution prior to MO is homogeneous in nature.

Figure A-1 Snapshots of videos recorded at different packing pressures i.e. 20, 22, 24 MPa
Appendix B

Derivation of governing equations for bubble growth

This section entails the derivation of the conservation equations.

![Schematic of spherical coordinates](image)

**Figure B-1** Schematic of spherical coordinates

- **Conservation of mass**

\[
\frac{\partial \rho}{\partial t} + \frac{1}{r^2} \frac{\partial (\rho r^2 V_r)}{\partial r} + \frac{1}{r \sin \theta} \frac{\partial (\rho v_{\theta} \sin \theta)}{\partial \theta} + \frac{1}{r \sin \theta} \frac{\partial (\rho v_{\phi})}{\partial \phi} = 0 \quad \text{B-1}
\]

\[
\frac{1}{r^2} \frac{\partial (\rho r^2 V_r)}{\partial r} = 0 \quad \text{B-2}
\]

\[
\frac{\partial (r^2 V_r)}{\partial r} = 0 \quad \text{B-3}
\]

\[
2r v_r + \frac{\partial V_r}{\partial r} r^2 = 0 \quad \text{B-4}
\]

\[
2r V_r + \frac{\partial V_r}{\partial r} r^2 = 0 \quad \text{B-5}
\]

\[
\frac{1}{V_r} \frac{\partial V_r}{\partial r} = -\frac{2}{r} \quad \text{B-6}
\]

\[
\int_{V_r}^{V_r} \frac{1}{V_r} \frac{\partial V_r}{\partial r} = \int_{R_{\text{sub}}}^{r} -\frac{2}{r} \, dr \quad \text{B-7}
\]
\[ \ln V_r - \ln V_R = -2(\ln r - \ln R_{bub}) \] B-8

\[ \ln \left( \frac{V_r}{V_R} \right) = \ln \left( \frac{R_{bub}^2}{r^2} \right) \] B-9

\[ V_r = \frac{V_R R_{bub}^2}{r^2} \text{, where } V_R = \dot{R} \] B-10

\[ V_r = \frac{\dot{R} R_{bub}^2}{r^2} \] B-11

- **Conservation of momentum**

The following equations comprise the momentum equations in spherical coordinates.

\[ \rho \left( \frac{\partial \dot{r}_r}{\partial t} + v_r \frac{\partial \dot{r}_r}{\partial r} + \frac{v_\theta}{r \sin \theta} \frac{\partial \dot{r}_r}{\partial \theta} + \frac{v_\phi}{r} \frac{\partial \dot{r}_r}{\partial \phi} - \frac{v_\theta^2 + v_\phi^2}{r} \right) \]

\[ = - \frac{\partial P}{\partial r} + \left( \frac{1}{r^2} \frac{\partial (r^2 \dot{\tau}_{rr})}{\partial r} + \frac{1}{r \sin \theta} \frac{\partial (\dot{\tau}_{r\theta} \sin \theta)}{\partial \theta} \right) + \left( \frac{1}{r \sin \theta} \frac{\partial (\dot{\tau}_{r\phi} \cot \theta)}{\partial \phi} \right) + \rho g_r \] B-12

\[ \rho \left( \frac{\partial v_\theta}{\partial t} + v_r \frac{\partial v_\theta}{\partial r} + \frac{v_\theta}{r \sin \theta} \frac{\partial v_\theta}{\partial \theta} + \frac{v_\phi}{r} \frac{\partial v_\theta}{\partial \phi} - \frac{v_\phi}{r} \frac{v_\theta^2 \cot \theta}{r} \right) \]

\[ = - \frac{1}{r \sin \theta} \frac{\partial P}{\partial \theta} + \left( \frac{1}{r \sin \theta} \frac{\partial (r^2 \dot{\tau}_{\theta\theta})}{\partial r} + \frac{1}{r \sin \theta} \frac{\partial (\dot{\tau}_{\theta\phi} \cot \theta)}{\partial \phi} \right) + \left( \frac{1}{r \sin \theta} \frac{\partial (\dot{\tau}_{\theta\phi})}{\partial \phi} \right) + \rho g_\theta \] B-13

\[ \rho \left( \frac{\partial v_\phi}{\partial t} + v_r \frac{\partial v_\phi}{\partial r} + \frac{v_\theta}{r \sin \theta} \frac{\partial v_\phi}{\partial \theta} + \frac{v_\phi}{r} \frac{\partial v_\phi}{\partial \phi} - \frac{v_\phi}{r} \frac{v_\phi^2 \cot \theta}{r} \right) \]

\[ = - \frac{1}{r \sin \theta} \frac{\partial P}{\partial \phi} + \left( \frac{1}{r \sin \theta} \frac{\partial (r^2 \dot{\tau}_{\phi\phi})}{\partial r} + \frac{1}{r \sin \theta} \frac{\partial (\dot{\tau}_{\phi\theta} \cot \theta)}{\partial \theta} \right) + \left( \frac{1}{r \sin \theta} \frac{\partial (\dot{\tau}_{\theta\phi})}{\partial \phi} \right) + \rho g_\phi \] B-14

With the assumptions stated in Chapter 4, it can be easily reduced to

\[ 0 = - \frac{\partial P}{\partial r} + \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \tau_{rr}) - \frac{\tau_{\theta\theta} + \tau_{\phi\phi}}{r} \] B-15

\[ \frac{\partial P}{\partial \theta} = 0 \] B-16

\[ \frac{\partial P}{\partial \phi} = 0 \] B-17

So the only equation requires solving is B-15. And \( P \) is now only a function of \( r \).
\[
\frac{dP}{dr} = \frac{d\tau_{rr}}{dr} + \frac{2\tau_{rr}}{r} - \frac{2\tau_{\theta\theta}}{r} \quad \text{B-18}
\]
\[
\frac{dP}{dr} = \frac{d\tau_{rr}}{dr} + 2\frac{\tau_{rr} - \tau_{\theta\theta}}{r} \quad \text{B-19}
\]
\[
\int_{P_{bub}}^{P_{shell}} dP = \int_{\tau_R}^{\tau_{shell}} d\tau_{rr} - 2\int_{R_{bub}}^{R_{shell}} \frac{\tau_{rr} - \tau_{\theta\theta}}{r} \, dr \quad \text{B-20}
\]

With the following boundary conditions, bubble pressure in B-20 can be solved.

\[
P_{shell} - \tau_{shell} = P_{sys}, \quad \tau_R = \frac{2\gamma}{R_{bub}} \quad \text{B-21}
\]
\[
P_{bub} - P_{sys} = \frac{2\gamma}{R_{bub}} + 2\int_{R_{bub}}^{R_{shell}} \frac{\tau_{rr} - \tau_{\theta\theta}}{r} \, dr = 0 \quad \text{B-22}
\]
Appendix C

Simha-Somcynsky equation of state (SS-EOS)

This section briefly introduces the concept of SS. For detailed explanation and derivation and revision of equations and optimization for fitting parameters, please refer to G. Li , 2007 [60]. For original assumptions and derivation refer to literature [61] and [62].

- **Introduction**

SS-EOS also known as hole theory describes a square lattice of sites which can be occupied by small molecules, a chain segment, or empty. In a saturated polymer/gas solution, the small molecules are gas molecules, chain segments are mers, and empty site represents free volume as shown in Figure C-1.

![Figure C-4-16 Schematic of SS-EOS lattice configuration [60]](image)

- **Mathematical formulation**

Here, a list of necessary equations involved in formulating and solving the SS lattice configuration is outlined.
1. Configurational factor for SS hole configuration

\[ Z = g(N, y)\left[v_f(V_{total}, y)\right]^{CN} \exp\left[-\frac{E_0(V_{total}, y)}{KT}\right] \tag{C-1} \]

\[ g(N, y) = y^{-N}(1 - y)^{-Ns\frac{1-y}{y}} \tag{C-2} \]

\[ v_f = \tilde{v}_f v^* = v^* \left[y \left((y\tilde{V})^{1/3} - 2^{-1/6}\right) + (1 - y)(y\tilde{V})^{1/3}\right]^3 \tag{C-3} \]

\[ E_0 = \frac{1}{2} yNqz\varepsilon^*[1.011(y\bar{v})^{-4} - 2.409(y\bar{v})^{-2}] \tag{C-4} \]

\[ \tilde{v} = \frac{V}{V^*}, \quad V^* = Nsv^* \tag{C-5} \]

\[ T = \frac{T^*}{T}, \quad T^* = \frac{qz\varepsilon^*}{cK} \tag{C-6} \]

\[ \bar{p} = \frac{p}{p^*}, \quad p^* = \frac{qz\varepsilon^*}{sv^*} \tag{C-7} \]

\[ qz = s(z - 2) + 2 \tag{C-8} \]

2. Chemical potential of gas in binary system

\[ \mu_{g, mixture} = G_m + x_2 \frac{\partial G_m}{\partial x_1} \tag{C-9} \]

\[ G_m = A + PV_{total} \tag{C-10} \]

\[ A = -KT\ln Z \tag{C-11} \]

\[ \frac{\partial A}{\partial y} \bigg|_{V,T} = \frac{\partial (-KT\ln Z)}{\partial y} \bigg|_{V,T} = -\frac{KT}{Z} \frac{\partial Z}{\partial y} \bigg|_{V,T} = 0 \tag{C-12} \]