RHEOLOGICAL SCALING AND BUBBLE NUCLEATION OF A POLYMER-DILUENT SOLUTION IN EXTRUSION FOAMING

DISSERTATION

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ABSTRACT

In this work, a new methodology is developed that describes the viscoelastic scaling of a polymer – physical foaming agent (PFA) solution in a detailed and internally consistent manner. The approach is new in that while previous researchers have largely focused on scaling down experimentally obtained high pressure polymer-PFA solution viscosity data onto a master curve for the viscosity of the undiluted polymer melt at a reference temperature and atmospheric pressure, we have generated the shear viscosity data required for our simulations by systematically scaling up the viscosity values obtained through a single set of experiments on the undiluted pure polymer melt at atmospheric pressure. The power and the utility of the methodology developed lies in the fact that in principle, from a single accurate viscosity-shear rate measurement conducted at a reference temperature and atmospheric pressure, and from only a basic knowledge of the type of polymer and PFA involved, it is possible to obtain the shear viscosity of the polymer – PFA solution for any arbitrary temperature, pressure and diluent concentration in the processing window.

Briefly, small amplitude oscillatory shear measurements of complex viscosity of pure polystyrene melt were made on a parallel plate rheometer in our laboratory for
a temperature range of 140°C to 240°C. Concentration shifting of the shear viscosity data was performed using the WLF-Chow correlation. The shear-rate dependence of viscosity of the polymer – gas system could be adequately represented using the three-parameter Cross model and reasonable predictions of the viscosities at the higher shear-rates characteristic of extrusion flows could be made by extending the model to the shear rates of interest. The pressure and temperature corrections of the viscosity were implemented using a WLF-type correlation and were incorporated into the simulation in a dynamic way by writing appropriate user defined functions and linking them to the solver while it computed the profiles of the basic field variables – temperature, pressure and shear rate.

The simulations were run for the flow of a polymer – PFA solution through an extrusion foaming die with an abrupt axisymmetric contraction. Values of pressure drops across the die obtained through the simulations showed good qualitative agreement with experimental pressure drop measurements on the foaming extrusion die obtained previously in our laboratory under nearly identical processing conditions. Non-isothermal effects were localized but significant – the bulk “mixing-cup” temperature of the fluid did not increase significantly but the simulations predicted a temperature rise of up to 24°C in the polymer – gas solution exiting the capillary in the region near the wall for the higher shear rates used. The field values of temperature and pressure were extracted from the simulations and fed into a separate program, which computed the saturation curves in the die using the Sanchez-Lacombe Equation of State. The critical pressure for bubble inflation is not appreciably different from the
saturation pressure, and hence, to a first approximation, the saturation curves are interchangeably referred to as nucleation onset or incipient nucleation curves. The pressure drop rates and temperature rise rates were estimated at the surface of incipient nucleation – quantities which have been reported previously to be having significant impact on the number of bubbles nucleated in a supersaturated polymer – gas mixture. Since the mean residence time of the fluid in our die is small enough so as not to allow significant bubble growth in the die, and since little is known about the time lag for nucleation for polymer–diluent systems, we believe that the assumption of approximating the flow as a single phase flow in our simulations is still expected to give useful insights on the dynamics of flow in a non-isothermal foaming die.

Once the values of pressure and temperature were obtained along each point in the foaming die, classical nucleation theory for bubble nucleation, in the form developed originally by Zeldovich, was invoked to predict the local bubble nucleation rate downstream of the saturation surface. The hydrodynamic constraints to the nucleation rate were calculated using Kagan’s extension of the Zeldovich theory. Diffusional constraints were incorporated into the theory using the method suggested by Katz and his coworkers. The capillarity approximation was found not to be valid for bubble nucleation of CO$_2$ in polymers; a correction on the lines suggested by Tolman was applied to get non-zero nucleation rates for the system.
Dedicated to my family for their unwavering support
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CHAPTER 1

INTRODUCTION

US consumption of plastic foams was projected to exceed 7.8 billion pounds in 2005 (Spitael, Macosko et al. 2004). Thermoset polyurethane, polystyrene and polyethylene foams dominate the plastics foam market with polystyrene foams accounting for 25% of the total market share (Throne 2004). Polystyrene (PS) foams produced by continuous processes like extrusion or semi-batch processes like injection molding represent 90% of the total PS foam production in the US.

Low-density thermoplastic foams have been produced in the plastics industry for over four decades now. Blowing agents used for foaming polymers can be generally classified as either Chemical Blowing Agents (CBAs) or Physical Foaming Agents (PFAs). Chemical blowing agents are chemical compounds that release gas when they are activated (decomposed) at higher temperatures (e.g. azodicarbonamide and sodium bicarbonate). Since chemical blowing agents are activated (decomposed) at higher temperatures, the foaming die block and extruder barrel nozzle can be
selectively maintained at higher temperatures to initiate the decomposition of the blowing agent. The use of chemical blowing agents does not require very high pressures or pressure drops across the foaming die and hence running experiments using chemical blowing agents does not necessitate the use of elaborate and expensive high-pressure equipment.

Physical blowing agents are substances like simple gases (e.g. Chlorofluorocarbons (CFCs), Hydro Chlorofluorocarbons (HCFCs), Carbon Dioxide ($CO_2$), Nitrogen ($N_2$), and some hydrocarbons (e.g. Pentane, Hexane), which are soluble in the matrix material at a certain pressure and temperature but become insoluble either when the pressure of the system is lowered or when the temperature of the system is changed. The bulk of the foaming in the polymer foam industry today is carried out using physical foaming agents since physical foaming agents give higher volume expansion ratios and the phase separation times for physical foaming agents are of the order of microseconds or milliseconds as against the decomposition half life of the order of minutes for chemical blowing agents. Another advantage of physical foaming agents is that they leave no solid residue in the final foam unlike chemical blowing agents, which leave more than 50% of their weight as residue.

1.1. Motivation for using $CO_2$ as a blowing agent and its role in the production of microcellular foams

Conventionally, the polymer foaming industry has been using CFCs and HCFCs for foaming since these compounds have the highest solubility in most
commodity plastics and yield foams with the highest volume expansion ratios. The foams using CFCs and HCFCs have cell sizes typically exceeding 100 μm and cell densities ~ $10^6$ cells/cm$^3$ and are known as structural foam. Typical densities of extruded foam sheets are on the order of 5% to 50% of the base material. The primary application of polystyrene structural foam is for building insulation and for producing styrofoam cups and take-away food containers. However, due to the continuous pressure on the industry to move away from hazardous volatile organic carbons (VOCs) and ozone depleting substances, there is great interest in exploring alternative, environmentally benign blowing agents like CO$_2$ and N$_2$. CO$_2$ is a reasonably good physical foaming agent for commodity plastics and there is interest in understanding the foaming process for polymer-CO$_2$ systems especially since the Kyoto protocol calls for banning CFCs and HCFCs as foaming agents by the year 2010 – CFCs and HCFCs being detrimental to the ozone layer in the Earth’s atmosphere.

Another reason for studying the foaming of polymers with inert gases like N$_2$ and CO$_2$ is the possibility of producing microcellular foams using them. Microcellular foams are typically defined as having cell sizes less than ~ 10 μm and cell densities > $10^9$ cells/cm$^3$. Microcellular polymers have shown improved fatigue life and energy absorption, higher mechanical strength-to-weight ratio, higher impact strength and toughness, and higher thermal and dimensional stability as compared to structural foamed parts. Moreover, since the cells are so small, the foam possesses an excellent texture – so to the casual observer the foamed plastic part retains the appearance of a solid plastic. Typical extruded foam densities for microcellular polymers are between
30% to 60% of the base material – thus there is lesser material savings while using microcellular foams as compared to structural foams. So far, microcellular foams have been of greater interest to academia and to specialty foam producers but due to the safety hazards associated with potentially explosive alternative blowing agents like hydrocarbons and with the phase out of CFCs and HCFCs, there is increasing commercial interest in producing microcellular polymers.

Experimental studies on foaming of polymers using CO$_2$ as the physical foaming agent has been an area of very active research in the last decade. Tomasko et. al. (Tomasko, Li et al. 2003) have provided an excellent review on the CO$_2$ applications in the processing of polymers.

1.2. Overview of the Extrusion Foaming Process

Extrusion foaming of thermoplastics essentially comprises of three main steps. The first step is the generation of a homogenous polymer-PFA solution in the extruder. Typically, polymer pellets are melted in an extruder and a metered amount of the PFA is injected at high pressure into the molten polymer through a gas injection port. Mixing of the polymer-PFA solution takes place via the process of convective diffusion (Park and Suh 1996). In this process, the matrix material is stretched and folded by the action of flow in the screw channels while blobs of the injected gas in contact with the convecting polymer melt break up due to interfacial tension forces (Ottino 1989). The boundaries between the polymer and the gas become diffuse and the extent of mixing is given by level curves of concentration. The surface area of the
polymer melt gets rapidly renewed under the influence of the combined shearing, elongational and kneading action in the screw channels, facilitating rapid diffusion of the gas into the polymer melt (Tadmor and Gogos 1979). The homogenization of the polymer-PFA solution is aided by the provision of mixing elements on the extruder screw downstream of the gas injection port or by provision of a static mixer following the extruder barrel or both.

The second step is nucleation and growth of gas bubbles in a predominantly shear flow field. The pressure of a fluid element monotonically decreases as it moves along the die. Phase separation of the PFA from the thermoplastic matrix occurs following a small time period called the induction time or time lag of nucleation once the pressure of the polymer-PFA solution falls below the solubility limit of the PFA in the polymer. The nucleated bubbles continue to grow in the closed channel either under a shear flow field (if die diameter stays constant downstream of the surface of incipient nucleation), or under a flow field where the elongational flow is superposed on the shear (if the shaping die has a different geometry than the foaming die).

The third step is the growth of the PFA bubbles in the cooling polymer foam exiting the die followed by freezing of the morphology once the temperature of the matrix material falls below its glass transition temperature. Most of the bubble growth in conventional foaming processes occurs during the extensional free surface flow of the extrudate exiting the die channel. The bubble growth, at least at lower temperatures (close enough to the glass transition temperature) is diffusion – driven, although at higher temperatures bubble coalescence and/or bubble collapse following an
accelerated loss of gas to the surroundings may dominate the final foam morphology (Park, Behravesh et al. 1998; Xu, Park et al. 2003; Naguib, Park et al. 2004).

1.3. Overview of past studies on the thermoplastic foaming of polymers

Because of the commercial importance and complexity of the polymer foaming process, numerous studies have been carried out to understand the effect of the processing variables on the final foam morphology. Initial studies focused more on thermoplastic foam extrusion using chemical blowing agents since foam production using chemical blowing agents is easier than foam production using physical blowing agents. Notable among the studies on continuous foaming of polymers using chemical blowing agents are the studies conducted by Hansen (Hansen 1962), Han et. al. (Han, Kim et al. 1976), Blyler et. al. (Blyler and Kwei 1971) and Oyanagi et. al. (Oyanagi and White 1979) on the extrusion foaming of low density polyethylene using azodicarbonamide as the blowing agent, and the studies conducted by Oyanagi et. al. (Oyanagi and White 1979) and Han et. al. (Han and Villamizar 1978) on the extrusion foaming of PS using azodicarbonamide or sodium bicarbonate as the blowing agent. An excellent overview of foaming using CBAs and chlorofluorocarbon type PFAs is available in Han (Han 1984).

Starting with the pioneering work of Prof Suh’s group at MIT (Martini 1981) on the foaming of polymers with PFAs (basically, N₂), a number of studies have been conducted in recent years with physical foaming agents for both batch (Colton and Suh 1987; Colton and Suh 1987; Kumar and Suh 1990; Ramesh, Rasmussen et al. 1994;
Ramesh, Rasmussen et al. 1994; Goel and Beckman 1995; Arora, Lesser et al. 1998; Rodeheaver and Colton 2001; Taki, Nakayama et al. 2003) and continuous foaming (Han and Ma 1983; Han and Ma 1983; Han 1984; Han and Han 1988; Park, Baldwin et al. 1995; Park and Suh 1996; Park, Behravesh et al. 1998; Lee 2000; Shimoda, Tsujimura et al. 2001; Chen, Wang et al. 2002; Gendron, Huneault et al. 2002; Han, Koelling et al. 2002; Tsujimura, Toru et al. 2002; Han, Koelling et al. 2003; Taki, Nakayama et al. 2003; Vachon and Gendron 2003; Xu, Park et al. 2003; Naguib, Park et al. 2004; Tatibouet and Gendron 2004) for structural as well as microcellular foams. Since this work primarily deals with continuous microcellular foaming of a thermoplastic (polystyrene (PS)) using a physical foaming agent (carbon dioxide (CO₂)) as the blowing agent through an extrusion capillary die, the relevant literature is discussed in some detail below.

Han et. al. (Han and Ma 1983; Han and Ma 1983) performed experiments to determine viscosities of low-density polyethylene and polystyrene charged with fluorocarbon blowing agents using a capillary foaming die. They correlated their experimental data in terms of a viscosity reduction factor defined as the ratio of the viscosity of polymer-blowing agent mixture to that of the pure polymer melts. They demonstrated how their correlation could predict the viscosities of mixtures of low-density polyethylene and polystyrene charged with fluorocarbon blowing agents from data for the viscosity of the pure polymer melts alone.

In a later work, Han et. al. (Han and Han 1988) made visual observations of nucleated bubbles in a slit die for the polystyrene (PS) – trichlorofluoromethane (FC-
11) system. They concluded, based on their observations, that flow-induced bubble nucleation was the dominant mechanism at locations near the center line of the slit die while shear induced bubble nucleation was the dominant mechanism at positions close to the die wall. Their study also appeared to indicate that bubble nucleation could occur in an unsaturated condition in a shear flow field. Their work is discussed in greater detail in Chapter 3 of this dissertation.

Gendron and his coworkers (Sahnoune, Tatibouet et al. 2001; Gendron, Huneault et al. 2002; Tatibouet and Gendron 2004) at National Research Council (NRC), Canada, utilized the ultrasonic technique to study the onset of bubble nucleation in polystyrene – PFA (HFC-134a and CO$_2$) mixtures flowing through extrusion foaming dies. The ultrasonic technique depends on measuring the propagation characteristics of small amplitude mechanical waves having frequency between 2.25 and 10.0 MHz. The ultrasonic parameters (attenuation and sound velocity) are very sensitive to the degree of the plasticization of the melt. The homogeneous PS-PFA mixture was initially maintained at a fixed temperature and high pressure to prevent premature bubble nucleation in the extrusion foaming die. Then the pressure was lowered at a pre-specified constant rate. As soon as phase separation occurred, the viscosity of the PS-PFA mixture increased suddenly, and the ultrasonic velocity through the PS-PFA mixture also increased in proportion. The formation of gas bubbles caused scattering of the ultrasonic waves, which caused an abrupt increase in attenuation. Thus, the onset of bubble nucleation could be measured in a non-intrusive manner using ultrasonic techniques. Recently, Tatibouet and Gendron (Tatibouet and Gendron 2004)
investigated the influence of flow on the foaming conditions of PS-HFC134a mixtures and concluded that the degassing pressure (defined as the pressure at which phase separation occurred between PS and PFA) were much higher under dynamic extrusion foaming conditions than under static (no flow) conditions. Their work is also discussed in greater detail in Chapter 3 of this thesis.

1.4. Past studies on microcellular foaming of thermoplastic polymers using PFAs

Park et. al. (Park, Baldwin et al. 1995) investigated the effect of the pressure drop rate on cell nucleation in microcellular extrusion foaming of high impact polystyrene with CO$_2$ as the blowing agent. Foaming was carried out in nozzles of different geometries (different radii and lengths) chosen such that for identical processing conditions and for the same amount of gas dissolved, the total pressure drop remained constant across each nozzle. The total number of cells nucleated was found to be a strong function of the pressure drop rate. The nucleation of a larger number of cells at higher pressure drop rates was attributed to the greater thermodynamic instability (higher solubility-drop rate) induced in polymer-gas solutions flowing through nozzles of smaller radii.

In a separate publication, Park et. al. (Xu, Park et al. 2003) employed a set of dies with differing geometries (capillaries with different lengths and radii) in a foaming extruder while systematically varying the contents of blowing agent (CO$_2$) and nucleating agent (Talc) with Polystyrene (PS 101, Nova Chemicals) as the matrix material. They also varied the die temperature from 170°C to 120°C with a decrement
of 5°C and also conducted experiments in which they varied the net pressure drop across the dies (while keeping the pressure drop rate constant). The authors observed that processing temperature had only a marginal effect on the cell density. They found that for all nucleating agent and blowing agent concentrations that they used, cell density increased significantly as pressure drop rate increased. However, changing the total die pressure across the foaming die (by altering either the die temperature or the die geometry) appeared to have no effect on the cell density, though it appeared to have a significant effect on the cell morphology of the obtained foams especially at low pressures (corresponding to higher CO$_2$ concentrations). The authors also found that the cell density increased with an increase of CO$_2$ concentration, regardless of the talc content, for all dies studied. Increasing the talc content was found to improve the cell density although the increase of the cell density with respect to the talc content was not high. The authors also observed that though the melt flowing near the wall of the die did not have a high pressure drop rate due to the retarded motion of the fluid close to the wall, the cell densities were observed to be slightly higher (up to 30% higher) than those of the core area in most cases. The higher cell density in the slowly flowing surface region was attributed to nucleation induced by the shear action.

Han. et. al. (Han, Koelling et al. 2002; Han, Koelling et al. 2003) carried out experiments in which they carried out microcellular foaming of polystyrene (PS 685D) supplied by the Dow Chemical Company with CO$_2$ as the physical foaming agent. Experiments were carried out on an extruder equipped with a simple capillary foaming die to study the effects of the following key variables – foaming temperature, total
pressure drop, pressure drop rate, and CO₂ concentration, on the final foam morphology in the PS-CO₂ system. Preliminary simulations were run using the Computational Fluid Dynamics (CFD) package FLUENT to analyze the flow field in the foaming die. Since detailed viscoelastic scaling of the shear rheology data was not carried out for this work, the simulated results showed some discrepancies from experimental measurements.

1.5. Complexity of the microcellular foaming process for thermoplastics

The foaming of polymers is a complex process since it is controlled by a large number of process variables many of which are interdependent. Figure 1.1 depicts the dependence of the foam morphology on the material properties, operating variables and field variables. The operator can choose the type of resin and the type of physical foaming agent to run on the process line and also the die geometry. The operator can also control the rate of heat exchange in various parts of the process line and the back pressure in the extruder (by provision of a gear pump, etc.) and set the throughput rates for the resin and the gas for the process.

Choice of a resin and physical foaming agent and setting the throughput rate together sets the material properties. The material properties and the basic field variables are interdependent as shown in Figure 1.1. Material properties show intricate dependencies on the amount of physical foaming agent dissolved and on the basic field variables. For example, the shear viscosity is a complex function of temperature, pressure, shear rate and CO₂ weight fraction but these dependencies are known.
However, the dependency of some material properties on the amount of gas dissolved in the polymer and on the basic field variables is not precisely known. The question mark “?” in front of a material parameter indicates such an unknown or un-quantified dependency.

For example, little is known about the dependence of thermal conductivity on the shear rate. Experimental measurements of anisotropic thermal conductivity in a flowing polymer melt are scarce in the open literature and somewhat ambiguous. Picot and his coworkers measured the effective thermal conductivity of a polymer liquid as a function of a strain rate in a modified Couette flow cell that utilized a hot wire probe technique. The authors found that the effective thermal conductivity of the commercial PDMS samples that they tested increased with increasing strain rate in the flow direction (Cocci and Picot 1973). However, for a Polyethylene melt of unspecified molecular weight that they tested subsequently, they found that at low shear rates a slight increase in thermal conductivity occurred followed by a gradual decrease at higher shear rates (Picot, Goobie et al. 1982). In yet another publication, carried out on low as well as high molecular weight PE samples, the authors reported that for the low molecular weight PE samples the thermal conductivity actually decreased for all shear rates tested while for the higher molecular weight PE samples tested, the effective thermal conductivity decreased at low shear rates and increased at higher shear rates relative to the equilibrium value (Wallace, Moreland et al. 1985). Very recently, Venerus et. al. (Venerus, Schieber et al. 1999; Venerus, Schieber et al. 2004) studied anisotropic thermal conduction in an entangled polymer melt undergoing uniform shear
deformation using a technique called Forced Rayleigh Scattering. They measured the complete thermal diffusivity tensor including three diagonal and one off-diagonal component. Based on the thermal diffusivity data and the stress measurements they took, they concluded that the thermal conductivity tensor $\kappa$ and the extra stress tensor $\tau$ are linearly related in a deformed polymer liquid as per the “stress-thermal rule” suggested by van den Brule (Brule 1989):

$$k = \frac{1}{3} \text{tr}(k) = \kappa_{eq} C_t \left[ \frac{1}{3} \text{tr}(\tau) \right]$$

(1.1)

where $\kappa_{eq}$ is the equilibrium thermal conductivity and $C_t$ is the stress-thermal coefficient. Their measurements of anisotropic thermal conduction in a polyisobutylene melt following a step shear deformation showed that thermal conduction was enhanced in the flow direction and reduced in the neutral (or vorticity) direction, relative to the equilibrium level. The authors assert that their data is more reliable than the earlier measurements of Picot et. al. since they used the non-invasive Forced Rayleigh Scattering technique as opposed to the invasive hot wire probe method used by Picot et. al. earlier. The anisotropy of the thermal conductivity tensor might have important implications on the heat transfer mechanism, but no experimental data for PS melt is available in the literature. Furthermore, no data on even the equilibrium thermal conductivity value for the PS-CO$_2$ system is available in the open literature. In view of the paucity of data, the only recourse is to resort to relevant values for the pure polymer to get the closest approximation to the true value of the relevant material property for the PS-CO$_2$ solution.
1.6. Objectives of this work

This work focuses primarily on the microcellular extrusion foaming of the PS-CO$_2$ system. The PS is PS685D supplied by the Dow Chemical Company. The CO$_2$ is 99.9% pure supplied by Praxair. The primary objective of this work is to develop a detailed methodology to simulate the contraction flow of PS-CO$_2$ solution through an extrusion foaming die using the CFD package FLUENT. The effects of die temperature and screw rotation rate (processing rate) on the temperature, pressure and velocity profiles for an adiabatic foaming die have been investigated for CO$_2$ concentrations of 1.0 wt % and 2.5 wt% in PS. The influence of varying the CO$_2$ concentration and of operating with an isothermal die wall instead of an adiabatic die wall form the focus of the next step of our investigation.

Another objective of this work is to develop a better understanding of the bubble nucleation and growth processes in the extrusion foaming of polymer-PFA systems systems, with an emphasis on understanding the hydrodynamic and diffusional constraints in nucleating PS-CO$_2$ mixtures. The hydrodynamic constraints are evaluated based on the theory of Zeldovich and Kagan, the diffusional constraints are calculated based on the extension of the Zeldovich-Kagan theory by Blander et. al. Both the above mentioned constraints can reduce the nucleation rate of CO$_2$ in PS by orders of magnitude – since the diffusion of low molecular weights solutes in polymer matrices is low and the viscosity of the polymer-blowing agent solutions is very high. For want of an appropriate value of surface tension that could account for the radius of curvature dependence of this quantity for the small nucleating bubbles, a quantitative
prediction of nucleation rates using classical nucleation theory was not possible in this work. However, some qualitative results for nucleation rates that could account for some experimentally observed trends in bubble size distributions in foams are included in this work.

1.7. Organization of this thesis

This thesis is organized as follows. The modeling of thermophysical properties—shear viscosity, density, specific heat capacity and density—for the PS-CO₂ solution is discussed in Chapter 2. Since the shear viscosity of the PS-CO₂ solution is, by far, the most important property affecting the flow behavior within the extrusion foaming die, particular emphasis is laid on the viscoelastic scaling of the PS-CO₂ solution. A detailed methodology that describes the shear dependence of viscosity of PS-CO₂ solution on temperature, pressure, CO₂ concentration and rate of shear is discussed elaborately in this chapter.

Once appropriate estimates of thermophysical properties necessary to model the flow of the PS-CO₂ solution through the extrusion foaming die are obtained as described in Chapter 2, the simulations are run as described in detail in Chapter 3. The model system studied as well as the conditions used for the simulation are described in the initial part of Chapter 3. Thereafter, the pressure, temperature and velocity profiles in the extrusion foaming die for a typical flow rate are discussed thoroughly. Possible reasons for discrepancies of the pressure drop predicted from simulations with values obtained from experiments are discussed. Finally field gradients for the pressure and
temperature fields in the foaming die are computed at the saturation surface and these values are used to derive pressure drop rates and temperature rise rates downstream of the saturation surface.

Bubble nucleation in extrusion foaming of polymer-PFA solutions is discussed in Chapter 4 using classical nucleation theory. The theory of phase separation developed by Zeldovich and modified subsequently by Kagan to account for hydrodynamic and inertial constraints to the nucleation rate and later by Blander and Katz to incorporate diffusional constraints on the nucleation rate is described and used to estimate nucleation rates for a typical processing condition of the PS-CO$_2$ mixture through the foaming die.

The main conclusions of this work are outlined in Chapter 5. Future directions pertaining to the coupling of the nucleation rate with the bubble growth rate are discussed.
Operating Variables
- Material: Resin, PFA, Nucleating agent, Additives
- Die Geometry
- Throughput Rate (Screw r.p.m.)
- External Heating/Cooling through Heater/Heat Exchanger
- Gas Injection Rate, Gas Temperature, Gas Pressure
- Back Pressure in the screw channel

Basic Field Variables
- Pressure, $P$
- Temperature, $T$
- Strain Rate, $\dot{\gamma}$

Material properties
- Shear Viscosity ($P,T, \dot{\gamma}, \phi$)
- Extensional Viscosity ($P,T, \dot{\gamma}, \phi$?)
- Thermal Conductivity ($P?, \dot{\gamma}?, \phi?$)
- Specific Heat Capacity ($P,T, \dot{\gamma}?, \phi?$)
- Density ($P,T, \phi$)
- Surface Tension ($P,T, \dot{\gamma}?, \phi$)
- CO$_2$ Solubility ($P,T, \dot{\gamma}$)
- CO$_2$ Diffusivity ($P,T, \dot{\gamma}?, \phi$)
- Glass Transition Temp, $T_g$ ($\phi,P,dT/dt$)

Foam Morphology
- Number of bubbles/(volume.time)
- Size of Bubbles
- Distribution of Bubbles across the foam sample
- Open-cell/Close cell foams

Figure 1.1: Summary of variables affecting final foam morphology in the foam extrusion process. Operating variables are ones that the experimenter/operator has control over. Material properties – both thermo-physical and rheological, exhibit a strong dependence on the basic field variables – pressure, temperature and shear rate as also on the diluent concentration in the melt. The question mark in the argument of a material property denotes an undetermined or unquantified dependency.
CHAPTER 2

MODELING OF THERMOPHYSICAL PROPERTIES

Simulation of the extrusion foaming process requires the estimation of various thermophysical properties – viz. viscosity, thermal conductivity, density and specific heat capacity for the polymer-blowing agent system under consideration. Of these, viscosity estimation is the most important since viscosity can change by orders of magnitude with changes in shear rate, diluent concentration and temperature and can also change significantly with pressure. In this work, a detailed methodology has been developed that integrates the concentration, temperature and pressure shift of the viscosity with the shear rate dependence of the viscosity in an internally consistent manner. The approach is novel in that while previous researchers have largely focused on scaling down experimentally obtained high pressure polymer-blowing agent solution viscosity data onto a base curve for the viscosity of the undiluted polymer melt at a reference temperature and atmospheric pressure, we have succeeded in generating the shear viscosity data for our needs by scaling up the viscosity values obtained.
through a single set of experiments on the undiluted pure polymer melt at atmospheric pressure. The power and the utility of the methodology lies in the fact that in principle, from a single accurate viscosity-shear rate measurement conducted at a reference temperature and atmospheric pressure, it is possible to obtain the shear viscosity of the polymer – diluent solution for any arbitrary temperature, pressure and diluent concentration in the processing window. Estimation of other thermophysical properties like thermal conductivity, specific heat capacity and density is also discussed below.

2.1. Viscoelastic scaling of PS-CO$_2$ solution

The viscosity of a polymer melt reduces appreciably when a suitable physical foaming agent is added to it. Data for polymer-physical foaming agent solution viscosities are difficult to obtain experimentally since the measurements have to be performed on elaborate high pressure systems wherein the system pressure has to be maintained in excess of the degassing pressure of the physical foaming agent at all times to avoid the problems pertaining to phase separation in the system. As a result only a handful of data on PS-CO$_2$ systems are available in the open literature. Free-volume based arguments can be invoked to explain viscosity reduction of a polymer on addition of a physical foaming agent (Gerhardt, Manke et al. 1997; Bae and Gulari 1998; Gerhardt, Garg et al. 1998; Kwag, Manke et al. 1999; Lee, Park et al. 1999; Royer, Gay et al. 2000; Kwag, Manke et al. 2001; Royer, DeSimone et al. 2001; Areerat, Nagata et al. 2002), the paucity of data need not be a deterrent in carrying out
simulations that can foster at-least a qualitative (or even a semi-quantitative) understanding of the mechanism of foaming in the extrusion die.

Gerhardt et. al. (Gerhardt, Manke et al. 1997; Gerhardt, Garg et al. 1998) in their work with the Poly(dimethyl siloxane) PDMS-CO$_2$ system demonstrated that classical viscoelastic scaling methods could be applied to reduce the PDMS-CO$_2$ solution viscosity curve to a master curve of pure PDMS. Kwag et. al. (Kwag, Manke et al. 1999; Kwag, Manke et al. 2001) and later, Royer et. al. (Royer, Gay et al. 2000) applied their viscoelastic scaling approach to PS-CO$_2$ systems to reduce their experimental viscosity data to a master curve of scaled viscosity $\eta(a_c^* \dot{\gamma})/a_c$ identical to the viscosity curve $\eta(\dot{\gamma})$ of pure PS at the same temperature and pressure. The authors reasoned that the physical foaming agent concentration scaling factor $a_c$ “corrects” the viscosity of the polymer-CO$_2$ solution for the amount of CO$_2$ dissolved in the melt in the same way as the well-known temperature scaling factor “corrects” the viscosity for temperature or the pressure shift factor “corrects” the viscosity for the hydrostatic pressure imposed on the melt. Thus, in order to reduce their experimental viscosity curve for PS-CO$_2$ solution flowing through a capillary die, the authors first converted their apparent viscosity vs. apparent shear rate data into a true viscosity vs. true shear rate data through either a Rabinowitsch or Schuemmer (Schummer and Worthoff 1978) type correction and then computed pressure, temperature and concentration shift factors such that when true viscosity/(a$_T$a$_P$a$_C$) was plotted vs. true shear rate*(a$_T$a$_P$a$_C$), the data collapsed perfectly onto the $\eta(\dot{\gamma})$ vs. $\dot{\gamma}$ curve for the pure melt at the reference temperature (base temperature) and atmospheric pressure. Since in this
study, “scaling-up” of the data from $\eta (T=T_{ref}, P=1\text{ atm}, C=0\% \text{ CO}_2)$ to an $\eta$ at an arbitrary $T$, $P$, and $C$ within the foaming die was carried out, as opposed to the “scaling-down” done by the afore-mentioned authors to collapse their actual experimental data on PS-CO$_2$ solution flowing through a capillary die, an approach opposite to that prescribed by the above authors in their publications was followed. The approach adopted is described in detail below.

Viscosity-shear rate data for pure PS melt was obtained on a parallel plate rheometer supplied by Rheometrics Inc (RMS-800) and is shown in Figure 2.1. The data covered a broad temperature range (140 °C to 240° C, at 10°C intervals) encompassing the processing window on the foaming extruder and was measured as complex viscosity over three decades of frequency (0.1 s$^{-1}$ to 100 s$^{-1}$, with 10 points per decade). According to the empirical Cox-Merz relationship, the shear rate dependence of the steady state viscosity is equal to the frequency dependence of the complex viscosity. Thus 11 sets of data, from 140° C to 240 °C, with 30 points in each set viz. 330 points in all, were obtained via measurements conducted on the parallel plate viscometer and served as “raw data”.

Once the raw data had been obtained, the first step in the formulation of a viscosity model for the PS-CO$_2$ system was to ascertain whether the kinetic bottleneck for molecular motions was the free-volume availability (in which case the data would fit a WLF type equation better) or whether the rate-limiting step for molecular mobility was an apparent activation energy for flow (wherein the Arrhenius relation would better fit the data). Williams et. al. (Williams, Landel et al. 1955) in their original paper
on the WLF equation had cautioned that outside the range of 100°C above the T\textsubscript{g}, the WLF equation could not be expected to hold for most glass-forming liquids. Their reasoning was that for ordinary glass-forming liquids far above their glass transition temperatures, specific details of molecular structure, through an apparent activation energy of flow, would dominate the flow behavior of the liquid, whereas in supercooled liquids, in the range of about 100°C above their T\textsubscript{g}, a “universal” temperature dependence, prescribed by the WLF equation, would overwhelm the specific structure-dependent differences and would control the flow behavior.

PS melt is an amorphous glass forming-liquid but since the experimental data had been obtained over a temperature range extending beyond T\textsubscript{g}+100°C (the T\textsubscript{g} for pure PS at 1 atmospheric pressure is 100°C), the experimental data was fit to both the Arrhenius relation (Rohn 1995) as well as to the WLF equation (Williams, Landel et al. 1955). A far better fit was obtained when the WLF equation was used to fit the data over the entire temperature range. Next, a “hybrid” fit was attempted in which the WLF equation was used to fit the data in the temperature range of 140-180°C and the Arrhenius equation was used to fit the data over the temperature range of 200-240°C. The fit (in the normalized least-squares sense) was now found to be comparable with the case when the WLF fit was applied over the entire temperature range.

Reports of PS melt viscosities at higher temperatures in the literature are somewhat ambiguous (Mendelson 1976; Lomellini 1992) and there is no universal agreement about when the transition from the WLF temperature dependence to the Arrhenius temperature dependence of viscosity occurs. However, in a recent
publication, Lomellini (Lomellini 1992) argues that since PS has a bulky jumping unit, free volume is most likely the rate-limiting factor for molecular interactions over a wider temperature range than for ordinary glass-forming liquids. In fact, the author asserts that over the whole temperature range that he investigated (up to 290°C), the WLF free-volume description was uniformly obeyed for PS melt.

Guita et. al. (Guaita, Chiantore et al. 1985), while studying the thermal degradation of polystyrene found that PS undergoes a slight decrease in the number average molecular weight ($M_n$) between 180 and 220°C. The authors attributed this drop in molecular weight of PS to random scissions of weak links in the chain. After the initial chain cleavages, no further reduction in $M_n$ was observed for temperatures below 250°C. Clay (Clay 1997) in our group at the Ohio State University corroborated the findings of Guita et. al. through his GPC (Gel Permeation Chromatography) and melt viscosity measurements. Zero shear melt viscosity measurements of Wingert et. al. (Wingert and Tomasko 2005) that have been recently carried out here have provided further evidence of the thermal degradation of PS melt in the vicinity of 200°C temperature.

Given the complexity induced by the thermal degradation of PS melt at temperatures approaching 200°C, a detailed investigation involving further data-procurement and analysis of pure PS melt viscosity is required to help clarify the issue of what model to choose for pure PS melt viscosity at higher temperatures. However, for now, since the WLF fit is as good as the “hybrid” fit and since it would be more convenient to use a uniform temperature-dependence-of-viscosity-descriptor over the
entire temperature range, we presume that the WLF equation adequately describes the temperature dependence of PS melt over the entire processing window.

2.1.1. Temperature correction of viscosity

The WLF equation was used to implement the temperature correction of viscosity. The WLF equation can be written as:

$$\log(a) = \frac{-C_1(T - T_s)}{C_2 + T - T_s}$$  \hspace{1cm} (2.1)

where $T_s$ is a reference temperature and $C_{1s}$ and $C_{2s}$ are the WLF constants. Williams et. al. (Williams, Landel et al. 1955) recommend that $T_s$ should be chosen around 50°C higher than the $T_g$ of the liquid (i.e. about the middle of the range over which the WLF equation is valid) to get the most appropriate values of $C_1$ and $C_2$ for shifting.

Figure 2.2 shows the time temperature superposition of the small angle oscillatory shear data of Figure 2.1. The reference temperature, $T_s$ is chosen to be 150°C for the pure PS viscosity data shift, since it provides the best $C_1$ and $C_2$ values to shift the viscosity to other temperatures – larger deviations are observed between the shifted viscosity and the measured viscosity for all other choices of reference temperature $T_s$.

Starting with the reference curve, the shear viscosity curves in Fig 2.2 for different temperatures are made to align with each other by approximating the shifted curves with polynomial expressions of suitable order and shifting the data points for the nearest temperature for which shear viscosity measurements have been made using
that value of $a_T$ which minimizes the sum of the square of the deviation between the originally shifted data points and the data points currently undergoing shifting. Once the values of $a_T$ corresponding to each temperature are obtained in the manner described above, a plot of $T-T_s/(\log a_T)$ vs. $(T-T_s)$ gives a straight line with slope $s$ and intercept $i$ such that the WLF constants in Equation 2.1 can be evaluated using (Ferry 1980):

$$C_{1s} = -1/s \quad (2.2.a)$$

$$C_{2s} = i/s \quad (2.2.b)$$

Once $C_{1s}$ and $C_{2s}$ corresponding to the reference temperature $T_s$ are obtained, $C_{10}$ and $C_{20}$, corresponding to any arbitrary reference temperature $T_0$ can be obtained simply by using the relations (Williams, Landel et al. 1955; Tanner 2000):

$$C_{20} = C_{2s}+T_0-T_s \quad (2.3.a)$$

$$C_{10} = (C_{1s}C_{2s})/C_{20} \quad (2.3.b)$$

In this manner, the values of $C_{1g}$ and $C_{2g}$, corresponding to the glass transition temperature, $T_g$, are obtained. The values of $C_{1g}$ and $C_{2g}$ so obtained over the usual range of validity of the WLF equation (i.e. $T_g$ to $T_g+100^\circ$C) are 13.28 and 48.53 respectively, which compare favorably with the values cited in the literature (Ferry 1980). For the range $T_g+100^\circ$C to $T_g+140^\circ$C, $C_{1g}$ and $C_{2g}$ are obtained as 13.45 and 37.21 respectively. Use of these values for the concentration shifting of the viscosity data is described in the next section.
2.1.2. Concentration correction of viscosity

Following Royer et. al. (Royer, Gay et al. 2000) and Kwag et. al. (Kwag, Manke et al. 1999), the concentration shift factor was computed using the basic notion that the combined shift factor “a” can be written down as a product of the individual scaling shift factors for temperature \( a_T \), pressure \( a_P \) and concentration \( a_C \). Thus,

\[
a = a_T \cdot a_C \cdot a_P
\]

Therefore,

\[
\log(a) = \log(a_T \cdot a_C \cdot a_P) = \log(a_T) + \log(a_C) + \log(a_P)
\]

Since concentration scaling is carried out first on the raw data at atmospheric pressure, \( a_P = 1 \) and the above equation becomes:

\[
\log(a_C) = \log(a_T \cdot a_C) - \log(a_T)
\]

Therefore,

\[
\log(a_C) = \frac{-C_{1g,\text{mix}}(T - T_{g,\text{mix}})}{C_{2g,\text{mix}} + T - T_{g,\text{mix}}} + \frac{C_{1g}(T - T_g)}{C_{2g} + T - T_g}
\]

where, \( a_C = \) concentration shift factor, \( C_{1g} \) and \( C_{2g} \) are the WLF constants for the pure polymer and \( C_{1g,\text{mix}} \) and \( C_{2g,\text{mix}} \) are the WLF constants for the PS-CO\(_2\) solution which may or may not be equal to \( C_{1g} \) and \( C_{2g} \). \( T_{g,\text{mix}} \) refers to the glass transition temperature of the PS-CO\(_2\) mixture were it possible to dissolve the prescribed amount of CO\(_2\) into the PS melt at atmospheric pressure.

Only a few models are available in the literature to predict \( T_g \) depression on addition of a diluent for different polymer-diluent systems. For the PS-CO\(_2\) system, two models are in popular use – the robust but slightly complex model of Condo et. al. (Condo, Sanchez et al. 1992) and the simple but approximate model of Chow. For the purpose of this work, \( T_{g,\text{mix}} \) is computed using the Chow model (Chow 1980), which
gives reasonably valid estimates of $T_g$ depression for PS-diluent systems, at least at low concentrations of $CO_2$ in the melt. The Chow model is based on the mean-field (Braggs-Williams) approximation for lattice fluid mixtures. In the Braggs-Williams approximation, originally derived for a lattice gas (Hill 1960), the configurational degeneracy and average nearest neighbor interaction energy are both handled assuming a random distribution of molecules among sites (implying a nearest neighbor energy of 0). The Chow model can be expressed as:

$$\ln \left( \frac{T_g}{T_{g,\text{mix}}} \right) = \beta [(1-\theta)\ln(1-\theta)+\theta\ln\theta]$$

(2.5)

In the above equation, $\beta$ and $\theta$ are dimensionless parameters defined as:

$$\beta = \frac{zR}{M_p \cdot \Delta C_{pp}}, \quad \theta = \frac{M_p \cdot w}{zM_d \cdot (1-w)}$$

Here, $M_p$ and $M_d$ refer to the molecular weight of the monomer and the diluent respectively, $\Delta C_{pp}$ is the excess transition isobaric specific heat of the polymer, $w$ is the mass (or weight) fraction of the diluent, $z$ is the lattice coordination number and $R$ is the gas constant. Addition of a small amount of diluent in a polymer mainly affects $\theta$, $\beta$ being usually fixed for a given polymer. Chow used a value of 2 for $z$ to compare his theory with experimental data for various PS-diluent systems and found that his model predicted $T_g$ depressions reasonably well for the diluents considered. Chiou et. al. (Chiou, Barlow et al. 1985) used Differential Scanning Calorimetry to estimate the glass transition temperature of many polymer-diluent systems (including PS-CO$_2$)
solution). They found that the Chow model with a value of $z = 1$ could fit their PS-CO$_2$ $T_{g,mix}$ data better than the $z=2$ case.

Figure 2.3 shows the difference in $T_g$ depression for different weight percent of CO$_2$ dissolved in PS, when $z$ is taken as 1 instead of 2 in the Chow model. As can be seen from the figure, at low concentrations of CO$_2$ in PS, the difference in the Chow model predictions on using $z=1$ instead of $z=2$ is inconsequential, however, at higher CO$_2$ concentrations, the difference in the predicted $T_{g,mix}$ values becomes significant. Although, the Chow model has been extensively used for predicting $T_g$ depression in polymer-PFA mixtures, there is still no universal consensus among researchers whether a value of $z=1$ or $z=2$ (or a different value of $z$) is the appropriate value to be used in the Chow model.

Although, the Chow-WLF type correlation can be used at very low concentrations of CO$_2$ in the melt to scale the viscosity of PS-CO$_2$ solution, the following limitations of the correlation should be borne in mind when applying the correction:

- Since $T_g$ of the polymer is depressed on addition of the diluent to a new value $T_{g,mix}$, it can reasonably be expected that the upper limit of the validity of the WLF equation would be reduced from $T_g + 100$ °C to $T_{g,mix} + 100$ °C.
- Neither Chow (Chow 1980) nor Chiou et. al. (Chiou, Barlow et al. 1985) offer a rigorous explanation on statistical mechanical grounds as to why they chose the values of the lattice coordination numbers to be $z=2$ and $z=1$ respectively. Chiou et. al. (Chiou, Barlow et al. 1985), in particular, appear to be using $z$ as a fitting parameter. This lends a certain degree of arbitrariness to the model.
The Chow model doesn’t seem to account for the interaction between the solvent and the polymer in any way. In other words, the interaction parameter in the Sanchez-Lacombe Equation of State (SLEOS) for the PS-CO₂ solution is assumed to be zero. Ferry and Stratton (Ferry and Stratton 1960) note that the concept of using the fractional free volume, f, to scale the temperature, pressure and concentration dependence of relaxation times of polymers can be reasonably supposed to hold if the value of f lies between 0.025 and 0.08. Addition of a diluent increases the value of f. Since the WLF equation is based on the free volume concept and since the range of applicability of the WLF equation (T₉+100°C for a pure melt) is, in turn, based on the fractional free volume limit roughly corresponding to f ≤ 0.08, it can inferred that addition of a diluent would shrink the range of applicability of WLF for the PS-CO₂ solution. In other words, since a primary effect of the diluent is to enhance the free volume of the polymer, if the WLF equation is valid for the range of T₉ to T₉+100 for a pure polymer melt, it would be valid for the range of T₉,mix to a value less than T₉,mix+100°C for a gas-charged polymer solution.

The free volume concept itself is not rigorously defined – an informal definition of free volume agreed upon by many authors is: the excess volume beyond the “occupied volume” extrapolated to the absolute value of temperature. Bondi (Bondi 1954; Bondi 1964) has postulated at least two types of free volume, an “Empty volume” defined as the total volume minus the van der Waals volume of the molecules and an “Expansion volume” defined as total volume minus
volume of closest molecular packing. Assuming that the volume of closest packing is the same as that of the crystal at 0 K, Bondi and later, Haward et. al. (Haward, Breuer et al. 1966) have arrived at values of the expansion free volume. However, the values of the expansion free volume obtained in the manner described above were always found to be different from the value derived from viscosity measurements of polystyrene melt (see, for example, Williams (Williams 1958)). To the best of our knowledge, the question about the essential difference between the expansion free volume and the rheological free volume has still not been convincingly resolved, and we believe that any fuzziness in the definition of the free volume could be carried over to any results that a theory involving free volume could be called upon to predict.

2.1.3. Approach followed to apply Concentration and Temperature correction of viscosity in this work

Following Chiou et. al. (Chiou, Barlow et al. 1985), a value of \( z = 1 \) was adopted to calculate the \( T_g \) depression of PS on addition of \( \text{CO}_2 \) along with the following values for the other model parameters : \( T_g = 100^\circ\text{C}, \ M_p = 104 \text{ g/mol}, \Delta C_{pp} = 0.0767 \text{ cal/(g.}^\circ\text{C)}, \ w = 0.01, \ M_d = 44.06 \text{ g/mol}, \ R = 1.987 \text{ cal/(mol.}^\circ\text{C}). \) The value of \( T_{g,\text{mix}}, \) corresponding to 1.0 wt% \( \text{CO}_2 \) in PS was found to be 89.67°C. Using this value of \( T_{g,\text{mix}}, \) \( a_C \) was computed using Equations 4 and 5. This value of \( a_C \) was used to reduce all pure PS viscosity data in Figure 1 to 1.0 wt% \( \text{CO}_2 \) in PS data. Time-temperature
superposition of the concentration shifted data then yielded the lower curve in Figure 2.2.

The WLF constants, $C_1$ and $C_2$, corresponding to the reduced (or concentration shifted) data were calculated using the procedure described in section 2.1.1. These values are listed in Table 2.1. Two approaches were followed to generate $C_1$ and $C_2$ values in Table 1. In the first approach, 150°C was chosen as the reference temperature and Equation 2.3 was used to obtain $C_1$ and $C_2$ at other temperatures. In the second approach, $a_T$ was still obtained using 150°C as the reference temperature but then the $a_T$ was rescaled based on the temperature of interest. For example, when $T_s$ was chosen as 180°C, $a_T$ at 180°C was assigned as 1 and the other $a_T$ values were scaled relative to the value of 1 for $a_T$ at 180°C. As can be seen from Table 2.1, the WLF constants obtained via the two approaches were found to differ more and more as the reference temperature $T_s$ was chosen further and further away from the reference temperature for calculating $a_T$ in the first place viz. 150°C.

Figure 2.4 highlights the difference in the temperature shift of the concentration-corrected viscosity data when the reference temperature was chosen as 150°C as against when it was chosen to be the temperature of interest. It is found that the temperature shift is more accurate when the temperature of interest is chosen to be the reference temperature – however, the difference is not very significant and for this work, approach 1 has been used to get $C_1$ and $C_2$ data throughout.
2.1.4. Pressure correction of viscosity

The effect of pressure on the capillary flow of Polystyrene melt has been investigated by many researchers (Penwell and Porter 1969; Penwell and Porter 1971; Penwell, Porter et al. 1971; Kadijk and vandenBrule 1994; Liang 2001). Penwell and Porter (Penwell and Porter 1971) carried out experiments on nearly monodisperse ($M_w/M_n<1.10$) low molecular weight (20,400) and high molecular weight (670,000) polystyrene fractions flowing through a capillary. The low molecular weight PS fraction was chosen since viscous dissipation could be assumed to be negligible for it and since it gave no indication of elastic energy storage (as evidenced by insignificant die swell and small entrance losses) at low enough rates of flow through the capillary dies. Thus the pressure effect could be more readily segregated once the flow rates were increased. The high molecular weight PS fraction was chosen since it resembles better the real PS melt flowing through most commercially relevant geometries.

The authors found that for the low molecular weight material, the Pressure vs. L/D curves for different values of the shear-rate became progressively non-linear for higher shear-rates at both temperatures (160 °C and 140 °C) studied. More importantly, they showed that the application of a WLF type correction (through an accounting of the $T_g$ elevation due to pressure, evaluated at the mean pressure of the flow) could make the non-linear curves at higher pressures linear. They thus demonstrated that for the low molecular weight material, the application of a WLF type correction sufficed to explain the pressure effect on viscosity.
For the higher MW material, though, application of a WLF type correction after correcting for entrance and die-swell effects greatly over-predicted the viscosity. The authors rightly attributed the over-prediction to ignoring the shear-thinning of the polymer due to viscous heat generation for the higher molecular weight PS fraction. Accounting for the shear-dependence of viscosity separately would enable a WLF type correlation to correct for the PS melt viscosity at high pressures. As in the case of concentration correction of the viscosity, the pressure correction, for this work, was also implemented through accounting for a change in \( T_g \) of the polymer melt with the affecting variable (here pressure).

Thus, for a specified \( \text{CO}_2 \) concentration in PS, one can write, following Penwell et. al. (Penwell, Porter et al. 1971) and Royer et. al. (Royer, Gay et al. 2000):

\[
\log(a_p) = \log(a_p \cdot a_T) - \log(a_p)
\]

Therefore,

\[
\log(a_p) = \frac{-C_{1g,\text{mix}} (T - T_{g,\text{mix},p})}{C_{2g,\text{mix}} + T - T_{g,\text{mix},p}} + \frac{C_{1g,\text{mix}} (T - T_{g,\text{mix}})}{C_{2g,\text{mix}} + T - T_{g,\text{mix}}} \quad (2.6)
\]

Many researchers have investigated the effect of pressure on the \( T_g \) of polymer melts. There is pretty good agreement between the various bodies of research that for pressures routinely encountered in polymer processing operations like extrusion and injection molding, \( T_g \) increases linearly with pressure. Following Penwell et. al. (Penwell, Porter et al. 1971):

\[
T_{g,p} = T_{g,p_0} + A_1 \cdot P \quad (2.7)
\]

where \( A_1 = \frac{\partial T_g}{\partial P} \) is the pressure coefficient of viscosity.
Several researchers have determined the value of the coefficient $A_1$ (Schouten, Scholten et al. 1991) and these values typically fall in a pretty narrow range (0.28 to 0.31 K/MPa). The value of 0.29 K/MPa determined by Quach and Simha (Quach and Simha 1971) was used for our calculations.

Figure 2.5 depicts the relative importance of pressure and concentration shifting of viscosity at an arbitrarily chosen temperature and pressure in the processing window for the PS-CO$_2$ solution. It can be clearly seen that the concentration shift of viscosity is much more pronounced than the pressure shift, even for a CO$_2$ concentration of as little as 1.0 wt% in PS. However, as our simulation results reveal later in this work, at a fixed diluent concentration in the melt, the pressure dependence of viscosity can play a significant role in determining the flow behavior, and should not be ignored in flow simulations within extrusion dies and injection-molding gates and runners.

2.1.5. Shear-rate dependence model for the viscosity of PS-CO$_2$ solutions

The Cross model (Cross 1965; Cross 1966; Cross 1969; Cross 1979) is chosen to represent the shear-viscosity dependence of the PS-CO$_2$ system. The reasons behind choosing the Cross model in its particular form and the physical significance of the model parameters are discussed below in detail.

Cross originally derived his model at a time when the entanglement concept in polymer rheology was not yet known (Cross 1965). He developed his model to account for the viscosity-shear-rate dependence in dispersed systems exhibiting flocculation behavior. He assumed that flocculation involves groups of linked particles and
conjectured that the average group size depended on the magnitude of the applied shear. He then used kinetic arguments to derive the basic expression:

\[ \eta = \eta_0 + \left( \eta_0 - \eta_\infty \right) \left( \frac{1}{1 + \alpha \gamma^{2/3}} \right) \]

where \( \eta_0 \) represents the zero-shear-rate Newtonian viscosity, \( \eta_\infty \) represents the infinite-shear-rate Newtonian viscosity and \( \alpha \) is a constant. The relation was found to fit experimental data in a number of pseudoplastic systems, ranging from suspensions to optically clear solutions, very well (Cross 1965). In a later publication (Cross 1966), Cross generalized his model by replacing the shear-rate exponent 2/3 by \( m \). The generalization required merely that (1) At any finite rate of shear, \( \eta \) must assume a value between \( \eta_0 \) and \( \eta_\infty \) and (2) Except for very high and very low values of shear rate, wherein \( \eta \) assumes limiting values of \( \eta_0 \) and \( \eta_\infty \) respectively, there should be a monotonic, one-to-one correspondence between \( \eta \) and \( \dot{\gamma} \). It is this generalized model, which we know as the Cross model today:

\[ \eta = \eta_0 + \left( \frac{\eta_0 - \eta_\infty}{1 + \alpha \gamma^{m}} \right) \]

The above model was applied to a number of Non-Newtonian fluid systems (including undiluted polymer melts) (Cross 1966) and gave good fits of experimental data.

The entanglement and reptation concepts in polymer rheology were firmly established by the late seventies. Soong and his coworkers (Hong, Soong et al. 1977; Soong and Shen 1980; Soong and Shen 1981) derived a kinetic network model to describe the nonlinear viscoelastic properties of entangled polymer melts. Ignoring the
segmental friction contribution, and considering the bulk polymer to be composed of flexible, randomly coiled chains, entangling with and disengaging from each other under the competing influences of Brownian motion and applied shear respectively, the authors derived the following equivalent expression to the Cross model, in which each parameter now has a molecular interpretation (Soong and Shen 1981).

\[
\frac{\eta(\dot{\gamma})}{\eta_0} = \frac{1}{1 + b(\lambda \dot{\gamma})^a}
\]

The authors assumed that the rate of disengagement of polymer chains is governed by the shear rate while the regeneration of lost entanglements occurs solely through thermal diffusion of the polymer chains. The parameter \(b\) in their equation is the ratio of the loss constant (characterizing shear-induced disengagement of coils) to the regeneration constant (characterizing reformation of entanglements due to thermal diffusion of the chains). The parameter \(\lambda\) denotes a characteristic time, defined as the time required for the polymer coils to diffuse enough distance to form a new entanglement, and is thus equivalent to the “renewal time” in the reptation model of De Gennes. The parameter \(a\) varies between 0 and 1 and accounts for the stretchability of the polymer molecules, and the orientational and rotational freedom of the long chain polymer backbone. The parameter \(a\) approaches the value of unity for very heavily entangled melts and assumes the limiting value of unity only for undeformable rigid polymer networks. The segmental distribution configuration between pairs of entanglements in moderately entangled polymer networks tends to undergo partial deformation, thereby reducing the effective dislocation of the entangled points and
decreasing the rate of their disappearance, so that \(0 < a < 1\) for moderately entangled polymer melts.

Even though Equations (a) and (b) are equivalent, it is necessary to realize that the shear rate exponents in the two cases are different. Cross (Cross 1969) showed that for linear polymers in absence of branching he could correlate his data using:

\[
m = \left( \frac{M_n}{M_w} \right)^{1/5}
\]

Thus the exponent \(m\) in the original Cross model accounts only for the polydispersity, assuming an upper limit of unity for monodisperse systems. However, in the model of Soong and Shen, the exponent \(a\) accounts for the polydispersity as well as the degree of entanglement.

Investigation into the effect of adding a supercritical diluent like \(\text{CO}_2\) on the entanglement density of the polymer has not received much attention. But it should become apparent from the above discussion that beyond a critical concentration of \(\text{CO}_2\) in the PS melt beyond which the degree of entanglement of the polymer chains becomes noticeably affected, the shear-rate exponent \(a\), can, in fact, change.

Vinogradov and Malkin (Vinogradov and Malkin 1964; Vinogradov and Malkin 1966) investigated the temperature-independent viscosity characteristics of polymer systems in their seminal paper. They began with the very general assumption that the shear viscosity of a polymer could be expressed in the following form:

\[
\eta = \eta_0 \cdot f(\theta, \dot{\gamma})
\]
where $\theta$ is the apparent relaxation time (expressed in units of time) and depends on the entire relaxation spectrum of the polymer, i.e.,

$$\theta = \varphi(\theta_1, \theta_2, \ldots, \theta_n)$$

On the basis of molecular theories concerning the temperature dependence of the viscoelastic properties of polymers (Rouse 1953), the authors could express the $i^{th}$ relaxation time in the relaxation spectrum as:

$$\theta_i = a_i \frac{\eta_0(T)}{\rho(T)T}$$

Since $a_i$ is independent of temperature (Rouse 1953), they could write for a given temperature $T$ and for any arbitrary reference temperature $T'$:

$$\frac{\theta_i}{\theta_i'} = \left[ \frac{\eta_0(T)}{\eta_0'(T')} \right] \left[ \frac{\rho'T'}{\rho'T} \right]$$

Plugging the above expression into the general viscosity expression given above, they finally obtained:

$$\frac{\eta}{\eta_0} = f\left(\dot{\gamma}\eta_0\rho'T'/\rho'T\right)$$

Since $\frac{\rho'T'}{\rho'T} \approx 1$,

the authors could finally write

$$\frac{\eta}{\eta_0} = f\left(\dot{\gamma}\cdot\eta_0(T)\right)$$

The temperature dependence of the shear viscosity of polymers is thus accounted for solely through its effect on the zero shear viscosity.
The temperature independent viscosity characteristics of polymer melts can now be accommodated in the Cross model by writing it in the following form:

\[
\eta = \frac{\eta_0}{1 + \left( \frac{\eta_0 \dot{\gamma}}{\tau^*} \right)^{1-n}}
\]

where \( \tau^* \) is a constant. Note that for high enough shear rates, the above equation can be reduced to the power-law model with \( n \) representing the flow behavior index.

As originally pointed out by Vinogradov et. al. and substantiated later by other researchers, a plot of \( \frac{\eta}{\eta_0} \) vs. \( \dot{\gamma} \cdot \eta_0(T) \) allows one to scale out the temperature (and pressure) dependence of \( \eta \) and thereby to isolate the shear-rate dependence alone. Fig 2.6 shows the result of applying such a scaling on master-plot coordinates for 1.0 wt% CO\(_2\) in PS. The data points show good superposition on the master-coordinates and the Cross model fits the superposed data remarkably well. Figure 2.7 represents the extension of the Cross model to higher (and lower) shear rates than the ones on which viscosity-shear rate data could be obtained on the parallel plate rheometer. Determination of the Cross Model parameters through the approach mentioned above ensures that no cross-over of the viscosity – shear rate curves occurs at the high shear rates typically encountered in extrusion and injection molding and also maintains consistency in the zero-shear viscosity values between the Cross model and the WLF equation.

In order to represent the shear-rate dependence of the shear viscosity of polymer melts, Hieber and Chiang employed the following functional form, which is a
generalization of the popular models of Cross and Carreau (Hieber and Chiang 1989; Hieber and Chiang 1992):

$$\eta = \frac{\eta_0}{1 + \left(\frac{\eta_0 \dot{\gamma}}{\tau^*}\right)^c} \left[1 + \left(\frac{\eta_0 \dot{\gamma}}{\tau^*}\right)^c\right]^{(1-n)/c}$$

In this model, $\eta_0$ represents the zero-shear-rate Newtonian viscosity and $n$, $\tau^*$ and $c$ are model constants. Equation (1) reduces to the Cross Model for $c = 1-n$, to the Carreau model if $c=2$ and to the “modified Carreau model” if $c = 1$. The parameter $c$ characterizes the breadth of the transition between the Newtonian and power law regimes of the viscosity dependence on shear, being broadest for the Cross model ($c = 1-n <1$), less broad for the modified Carreau model ($c=1$) and narrowest for the Carreau model ($c=2$). Since the breadth of the transition between the Newtonian and power law regimes is narrower for Narrow Molecular Weight Distribution and broad for broader molecular weight distributions, we can expect that the Carreau model will better fit the Narrow Molecular Weight Distribution case while the Cross model will be more appropriate for the Broad Molecular Weight Distribution case. Hieber and Chiang have shown, based upon extensive data from literature as well as in-house measurements, that the Cross model is more suitable for commercial grade PS melts, which tend to be of Broad Molecular Weight Distribution whereas the modified Carreau model is more appropriate for PS of Narrow Molecular Weight Distribution. Since we are working with a commercial PS grade (PS 685D, supplied by Dow chemical company), having a Broad Molecular Weight Distribution, we expect the Cross model to fit our data better.
Indeed, when we try out actual fits for the Cross, modified Cross, and Carreau models, the Cross model gives the best fit to our data.

Although the generalized Cross-Carreau model with an additional parameter, c, gives slightly better fits of our data, we use the Cross model to fit our data, since it does meet the necessary requirements that a good model should posses in order to fit a given set of data:

- It gives a good fit of experimental data over a wide shear rate range.
- A minimum number of independent constants are involved in the model.
- Each constant possesses a physical significance and is amenable to easy evaluation.

Increasing the number of independent constants makes it increasingly difficult to evaluate them through non-linear least-squares sub-routines while still retaining their physical significance. That is the reason why the Cross and Carreau models enjoy such wide popularity in fitting viscosity-shear-rate data of polymers (Bird, Armstrong et al. 1987).

2.2. Thermal Conductivity

Since no thermal property estimates were available for PS-CO$_2$ solutions in the literature, corresponding values under the prescribed processing conditions for pure PS were used for our simulations. Sakakibara et. al. (Sakakibara, Yamada et al. 1990) estimated the thermal conductivity of pure PS above and below the glass transition temperature. For a temperature range between 416 K and 513 K for a PS sample with a
viscosity average molecular weight in the range of 141,000 to 148,000, they estimated the thermal conductivity to be 0.1659 W/(m.K) to a maximum deviation of 1.2% in the measured values. This value was obtained under static conditions and was the one chosen for our simulations.

2.3. Density

The Sanchez-Lacombe Equation of State (SLEOS) which is based on the lattice fluid theory of polymer solutions gives reasonable approximations of the density of many polymer-diluent mixtures (Sanchez and Lacombe 1978) and gives very good estimates of the density of PS-CO$_2$ solutions under normal processing conditions for the mixture (Tomasko, Li et al. 2003). The SLEOS is the most widely used model to correlate the solubility of CO$_2$ in PS (Tomasko, Li et al. 2003). The SLEOS is based on the Ising or lattice fluid model, is capable of semi-quantitatively describing the thermodynamics properties of a wide variety of molecular fluids of arbitrary size and geometry, and is simple to apply (Sanchez and Lacombe 1976). Unlike the well-known lattice theory of polymer solutions developed by Flory and Huggins, the SLEOS theory allows for empty lattice sites or free volume. This allows the SLEOS theory to calculate the volume change on mixing, which had not been possible with the earlier Flory-Huggins theory (Lacombe and Sanchez 1976). In the SLEOS theory, pure fluids are completely characterized by three molecular parameters, which are known for many fluids (including PS and CO$_2$). The SLEOS can be expressed as:

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T} \ln(1-\tilde{\rho}) + \tilde{\rho} = 0 \quad (2.9)$$

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where $\bar{\rho}$ is the reduced density ($\bar{\rho} = \rho / \rho^*$), $\bar{P}$ is the reduced pressure ($\bar{P} = P / P^*$), $\bar{T}$ is the reduced temperature ($\bar{T} = T / T^*$). The equation-of-state parameters for the mixture $\rho^*, P^*$ and $T^*$ are computed from the corresponding pure-component values using conventional (though somewhat arbitrary) mixing rules. The mixing rules are discussed in detail in Chapter 3 under the heading “Location of Saturation Surface”.

2.4. Specific Heat Capacity

No data on specific heat capacity of PS-CO$_2$ mixtures is available in the open literature. Also, little is known about the change in heat capacity on application of a shear field. It is known that heat capacity depends on the internal degrees of freedom of a polymer fluid (Sanchez and Lacombe 1976) but since this configurational dependence has not been quantified, $C_p$ data on pure PS under static conditions from Karasz et. al. (Karasz, Bair et al. 1965) was fitted to obtain the $C_p$ values that we used in our simulations. The specific heat capacity was found to vary linearly with temperature according to the following equation under prescribed processing conditions:

$$C_p = 3.2723T + 612.53$$

(2.10)

where $C_p$ is the specific heat capacity in J/(kg.K) and T is the temperature in K.
<table>
<thead>
<tr>
<th>Reference Temperature, Ts</th>
<th>$C_{1,140}$ (Ts=140°C)</th>
<th>$C_{2,140}$ (Ts=140°C)</th>
<th>$C_{1,Ts}$ (Ts=Ts)</th>
<th>$C_{2,Ts}$ (Ts=Ts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>140°C</td>
<td>5.58</td>
<td>88.24</td>
<td>5.58</td>
<td>88.24</td>
</tr>
<tr>
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<td>98.24</td>
<td>5.02</td>
<td>98.55</td>
</tr>
<tr>
<td>160°C</td>
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<td>108.24</td>
<td>4.57</td>
<td>108.19</td>
</tr>
<tr>
<td>170°C</td>
<td>4.17</td>
<td>118.24</td>
<td>4.06</td>
<td>114.32</td>
</tr>
<tr>
<td>180°C</td>
<td>3.84</td>
<td>128.24</td>
<td>3.57</td>
<td>119.88</td>
</tr>
<tr>
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<td>3.56</td>
<td>138.24</td>
<td>2.31</td>
<td>100.44</td>
</tr>
<tr>
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<td>148.24</td>
<td>3.47</td>
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</tr>
<tr>
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<td>3.52</td>
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</tr>
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</tr>
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<td>240°C</td>
<td>2.62</td>
<td>188.24</td>
<td>3.39</td>
<td>218.92</td>
</tr>
</tbody>
</table>

Table 2.1: Listing of $C_1$ and $C_2$ values obtained through time-temperature superposition of data in the bottom curve of Figure 2 for Ts=140°C and Ts=Ts. The $C_1$ and $C_2$ values obtained via the two different approaches diverge as T becomes increasingly different from Ts.
Figure 2.1: Measurement of complex viscosity of pure PS melt on the parallel plate rheometer (RMS 800) using small angle oscillatory shear at temperatures ranging from 140°C to 240°C. The temperature range chosen is such as to encompass the extrusion temperature window over which foaming experiments had been previously conducted in our lab.
Figure 2.2: The upper curve shows time-temperature superposition of the complex viscosity data of Figure 2 with a view to obtain the shift factor for each temperature with the 150°C curve serving as a reference. The lower curve depicts the concentration shift of the data of the upper curve were it possible to dissolve 1.0 wt% CO$_2$ into the pure PS melt at atmospheric pressure and at 150°C temperature.
**Figure 2.3:** The Chow model is used to estimate Tg depression in this study. The figure shows the effect of choice of value of $z$ in the Chow model on Tg depression. $z=2$ was suggested in the original paper by Chow. $z=1$ was suggested by Chiou, Barlow and Paul.
Figure 2.4: Effect of choosing the reference temperature, Ts=150°C instead of choosing Ts = the temperature from which the shift of the viscosity data is desired. If the temperature from which the shift is to be performed is closer to the temperature being shifted to (than 150°C is to the temperature being shifted to), using the later Ts gives better shift of the viscosity data.
**Figure 2.5:** Relative importance of concentration and pressure shifting of viscosity at a temperature of 240°C and a mean pressure of 5.65 MPa. Pure PS data is at T=240°C and P = 1 atm. Concentration shifted data is the reduced viscosity data that would be obtained were it possible to dissolve 1.0 wt% CO\textsubscript{2} in PS at T = 240°C and P = 1 atm. Concentration and pressure shifted data is at T = 240°C and P = 5.65 MPa. The plot shows that even for as low as 1.0 wt% CO\textsubscript{2} dissolved in PS, the viscosity change induced by CO\textsubscript{2} dissolution is much more significant than that brought about by pressure imposed in the die under typical extrusion foaming conditions.
Figure 2.6: Concentration shifted viscosity data plotted on Master Coordinates (reduced viscosity vs. reduced shear rate). The plot enables the determination of the Cross model parameters $n$ and $\tau^*$ in such a manner that the zero shear viscosity can acquire values which are consistent with both the WLF equation and the Cross model simultaneously.
Figure 2.7: Comparison of the concentration shifted viscosity data with the Cross model predictions and extension of the Cross model prediction to higher shear rates value typically encountered in commercial extrusion dies.
3.1. CFD Modeling Technique

The die geometry consists of a die insert which has a length of 56.12 mm and an internal diameter of 7.8 mm followed by the foaming capillary die which has a length of 10 mm and an internal diameter of 0.5 mm. However, since most of the important flow physics occurs in the capillary die and since the flow in the die insert far upstream of the contraction does not significantly affect the flow in the capillary die, only 23.4 mm of the guiding hollow tube and 10 mm of the foaming die were simulated. Such a selective elimination of volume is very desirable from the point of view of computational economy and significantly aids mesh refinement and data analysis in FLUENT. The geometry of interest is displayed in Figure 3.1(a).

The mesh is created on the preprocessor GAMBIT (version 2.0.4). Figure 3.1(b) displays the mesh. The mesh as created in GAMBIT contains ~ 61,000
triangular cells. Further refinement of the mesh is carried out in regions of high
temperature gradients near the entrance corner and the walls of the foaming die – a
process called grid adaption. An enlarged view of the adapted mesh near the entrance
corner is shown in Figure 3.1(c).

The steady, two-dimensional, axi-symmetric, segregated solver formulation
incorporating an implicit discretization scheme was used to solve the flow problem in
FLUENT. The two dimensional double-precision solver was chosen in FLUENT to
model the die geometry. The double-precision feature of the solver enhances the
numerical accuracy of the solution. Since the liquid flows from a capillary of relatively
large diameter, through an abrupt contraction, and into a capillary of smaller diameter,
the axisymmetric \((x,r)\) formulation of the equations of change is used. The advantage
of using this formulation is that the 3-dimensional \((x,y,z)\) problem in Cartesian
coordinates is reduced to a 2d \((x,r)\) problem in cylindrical coordinates while still
retaining most of the essential physics of the 3d \((x,y,z)\) problem. This simplifies the
meshing of the geometry considerably, makes it much easier to extract and interpret the
simulation data, and substantially speeds up the iteration process (so that the solution
converges in a matter of hours instead of converging in days).

The conservation equations were cast in the following form given in tensor
notation:
Mass Conservation Equation (Continuity Equation):
\[ \nabla \cdot (\rho \mathbf{v}) = 0 \]  
(3.1)
where \( \rho \) is the mass density, and \( \mathbf{v} \) is the velocity vector.

Momentum Conservation Equation:
\[ \nabla \cdot (\rho \mathbf{v} \mathbf{v}) = -\nabla p + \nabla \cdot \tau \]  
(3.2)
where \( p \) is the pressure and \( \tau \) is the stress tensor.

Energy Conservation Equation:
\[ \nabla \cdot (\rho \mathbf{v} E + p) = \nabla \cdot (k \nabla T + \tau) \]  
(3.3)
where \( k \) is the thermal conductivity and \( E \) is the internal energy given as:
\[ E = h - \frac{p}{\rho} \frac{v^2}{2} \]
h is the sensible enthalpy which for incompressible flows is defined by:
\[ h = \int_{T_{ref}}^{T} C_p dT + \frac{p}{\rho} \]
where \( T_{ref} \) is a reference temperature.

In the finite volume method, the numerical algorithm is implemented through three steps (Versteeg and Malalasekera 1995). The first step is formal integration of the governing equations of fluid flow and heat transfer over all the (finite) control volumes or cells of the solution domain. The second step is the substitution of a variety of finite-difference-type approximations for the terms in the integrated equation representing flow processes. And the third step is the solution of the algebraic equations by an
iterative scheme. The efficiency of the solution for the segregated solver in FLUENT is enhanced by using the Algebraic Multi-Grid (AMG) scheme in conjunction with the Gauss-Siedel Method.

The materials panel in FLUENT was used to feed in the thermo-physical properties, $k$ and $C_p$ and the bulk density, $\rho$ for the fluid into the simulation. The density of the fluid varies only by a very small extent over the flow length in the die for the pressure conditions used (only around 1% variation in density for the maximum pressure drop under the simulation conditions studied). Therefore, for the purpose of this simulation, variations in density were ignored and the fluid was assumed to be incompressible. The Tait equation was used to correct for the density at the entrance of the die geometry and it was this density, which was used to compute the inlet velocity of the fluid for the simulation. The pressure and temperature corrections of the concentration-shifted viscosity were incorporated into the simulation in a dynamic way by writing appropriate user defined functions and linking them to the FLUENT solver.

Convergence of the solutions was tested using two approaches. The first approach was to decrease the grid spacing in regions of high gradients (like corners and walls) viz. selective mesh refinement via grid adaption. The second approach was to place more stringent criteria on the mass, momentum and energy residuals than the default criteria in FLUENT. In all cases, the default criteria for residuals in FLUENT were found to be inadequate for convergence. Also, decreasing the grid spacing caused no change in the solution properties at lower flow rates and/or higher temperatures but mesh refinement through grid adaption based on temperature gradients caused
significant change in the solution properties at lower temperatures and/or higher flow rates.

The SIMPLEC (SIMPLE Consistent) Algorithm was used for the pressure-velocity coupling. The acronym SIMPLE stands for Semi-Implicit Method for Pressure-Linked Equations and is essentially a guess-and-correct procedure for the calculation of pressure on the staggered grid arrangement in FLUENT. The SIMPLEC method is a refinement of the SIMPLE method that enhances the economy and stability of the simulation. The Second Order Upwind differencing scheme, which fulfils the requirements of conservativeness, boundedness and transportiveness, was used for discretization of the governing equations. Since the flow is not aligned with the grid lines for our geometry, the distributions of transported properties tend to become smeared – a process referred to as false diffusion. Selective mesh refinement and use of a higher order differencing scheme minimizes, but does not completely eliminate smearing. The resulting error due to false diffusion is expected to be small, but an exact assessment of the error still needs to be made. Finally, a judicious choice of under-relaxation factors for the continuity, momentum as well as energy equations had to be made for all our simulations. The under-relaxation factors for momentum and energy, especially, had to be assigned very low values initially but could be gradually incremented, as the solution proceeded, to speed up the convergence of the solution.
3.2. Assumptions inherent in the mathematical model

An important assumption that has been made in order to simplify our computations was that the formation of a two-phase mixture beyond the line of incipient nucleation in the die, does not significantly affect the profiles of the field variables (temperature, pressure and shear-rate) in the die. This assumption was made in order to simplify the physics of the problem and avoid the problems arising from phase separation on the flow physics. Although this might appear as a severely limiting assumption at first glance, two points must be mentioned which go in its favor. (1) The average time that a fluid element spends in the die downstream of the point of incipient nucleation is only \( \sim 0.015 \) s at low processing rates (corresponding to 10 rpm screw rotation rate) and lesser still at higher processing rates. Such a short time comprises a very small fraction of the total bubble growth time of 2-10 seconds documented in numerous studies on bubble growth. Such short residence times are typical of continuous microcellular foaming processes, which require very high pressure drop rates for bubble nucleation densities to approach the microcellular regime. (2) In many studies of bubble nucleation, a time period of the order of microseconds or milliseconds (depending on the system being studied) has been observed from the time when the nucleation is thermodynamically favored to the time when critical nuclei actually appear. This time period is called the time lag of nucleation, and so far as we know, experimental data on the time lag of nucleation in polymer – supercritical diluent systems is not available. Moreover, it has been noted that the phase separation kinetics in the case of polymer foaming are often slow enough to differentiate between the formation of a single phase
metastable state from the subsequent nucleation and growth stages so that the pressure drop step can be modeled as a single phase, multi-component adiabatic pressure drop (McClurg 2004). Thus, the assumption of approximating the flow as a single phase flow throughout the capillary die length might not be very unreasonable for microcellular foaming through extrusion dies and can give useful insights into the dynamics of flow in a non-isothermal foaming die.

A second assumption that has been made is that the fluid flow is laminar and steady state at all times. The laminar flow assumption is justified on the basis of the very low Reynolds numbers (<1) prevailing in the flow system at any point in the capillary die.

It is widely accepted in the polymer-processing community that polymer melts, unlike Newtonian fluids, may violate the classic no-slip boundary condition when the shear stress exceeds a critical value (usually about 0.1 MPa). Shidara et. al. (Shidara and Denn 1993) studied the slip behavior of Polyethylene (PE) and PS through very thin slit dies (gaps ranging between 34 and 765 μm). They reported that while slip was exhibited at the wall for the PE melt, no slip was observed for the PS melt under similar processing conditions. Later on, Rosenbaum et. al. (Rosenbaum and Hatzikiriakos 1997) carried out a numerical analysis for a hypothetical PS fluid and suggested, based on their numerical results, that slip could be occurring in the experiments conducted by Shidara et. al. (Shidara and Denn 1993) on PS, but since viscous heating in the case of PS is significant, it could be dominating the wall-slip effect for the polymer. However, although Rosenbaum et. al. (Rosenbaum and
Hatzikiriakos 1997) procured experimental data for LDPE, HDPE and Polypropylene (PP) to demonstrate the agreement of their model predictions with experimental data, they have not carried out experiments to corroborate the wall slip effect for PS. For simplicity, and in want of more conclusive data, the no slip condition has been imposed at the wall for all our simulations.

Although normal stresses could be important in contraction flows and especially through capillaries of small length (where the flow time could well be comparable to the characteristic polymer segment relaxation time), this paper considers only shear stresses. Also, the effect of gravity on flow has been assumed to be negligible.

3.3. Choice of Processing Conditions for the Simulation

Continuous microcellular foaming of PS-CO$_2$ mixtures at 1.0 wt% blowing agent concentration had been carried out earlier in our laboratory at two different screw rotation rates, 10 rpm and 30 rpm. For the lower screw rotation rate of 10 rpm, foams had been produced for inlet melt temperatures (into the die insert) corresponding to 140°C, 160°C, 180°C, 200°C, 220°C and 240°C. For the higher screw rotation rate of 30 rpm, foams had been produced for inlet melt temperatures corresponding to 160°C, 180°C, 200°C, 220°C and 240°C. Processing at 140°C for the higher screw rotation rate of 30 rpm was not carried out due to the pressure limitations of the die. Table 3.1 summarizes the process conditions for extrusion foaming of PS-CO$_2$ solution carried out in our lab. The experimental set-up and results have been discussed earlier in detail.
by Han et. al. (Han, Koelling et al. 2003). The velocities and temperatures listed are the inlet velocities and temperatures of the homogenous fluid stream entering the die insert. In the discussion that follows, the focus is on the simulation results and on the comparison of the experimental findings and the model predictions. Note that in the discussion below, the low processing rate always corresponds to 10 rpm screw rotation rate and the high processing rate always corresponds to 30 rpm screw rotation rate. Also, the temperatures correspond to the inlet melt temperature of the polymer entering the die insert, unless otherwise specified.

3.4. Pressure, Temperature and Velocity Profiles in the Extrusion Foaming Die

The pressure drop profiles along the die for the low flow rates (corresponding to 10 rpm screw rotation rate) for all the different inlet temperatures studied are shown in Figure 3.2. Several features of interest can be observed from the figure. Most of the pressure drop occurs in the thin capillary region of the foaming die. The pressure in the die insert stays almost constant for all inlet melt temperatures studied – even for the case of the lowest temperature, 140°C, (corresponding to the highest viscosity), only a very small fraction of the total pressure drop occurs in the die insert. The pressure profile along the capillary is highly non-linear. Pressure drops appreciably in the initial entrance section of the capillary and falls less steeply in the region of the capillary away from the contraction. The total pressure drop in the die is a sensitive function of the inlet melt temperature and the sensitivity increases as temperature decreases. Pressure contours were also obtained to analyze the radial variation in pressure at a
given axial location— the pressure contours were found to become flat after a small entrance length in the capillary die implying that variation in pressure in the radial direction is negligible for all processing conditions studies. The pressure drop profiles along the die for the high flow rates (corresponding to 30 rpm screw rotation rate) for all the different inlet temperatures studied are qualitatively similar to the ones at low flow rates and are shown in Figure 3.3.

The nonlinearity of the pressure drop profiles in the capillary could be attributed to a number of factors, particularly, non-isothermal nature of the flow due to viscous dissipation, viscosity dependence of the PS-CO₂ mixture on pressure and temperature, and hydrodynamic entrance effects. An important implication of the pressure dropping more steeply in the entrance region of the capillary would be that the surface of incipient nucleation is shifted towards the die entrance, as compared to the case in which a linear pressure profile along the entire length of the capillary is presumed. Consequently, a larger time would be available for the nucleation and bubble growth processes to occur inside the capillary die as compared to the linear pressure drop case. Simultaneously, a reduction in the absolute magnitude of the slope of the pressure profile at the point of incipient nucleation would result in a reduced rate of nucleation.

The axial profiles of temperature and velocity for a representative flow condition of 180°C solution temperature at inlet, 1.0 wt% CO₂ concentration, and 10 rpm screw rotation rate are shown in Figure 3.4. On examining the axial temperature profiles corresponding to different radial sections in the foaming die (see Figure
3.4(a)), we find that most of the temperature rise is concentrated in a region very close to the wall. The temperature rise (~ 15°C) is pretty significant and for the highest flow rates studied, the maximum temperature rise could be as much as ~24°C. The heated polymer has a lower viscosity and this exaggerates the concentration of shearing near the wall. This tends to localize the viscous heating near the wall, and since the low thermal conductivity limits the rate of heat transfer out of the high-shear-rate region, it can lead to unexpectedly large local temperature rises like the ones we observe (Dinh and Armstrong 1982). The role of the limited thermal conduction of heat in the melt can also be clearly observed in Figure 3.4(a). The greatest temperature rise for the adiabatic die is observed at the wall (~15°C), while at the centerline the rise in temperature is merely ~ 1°C. The most rapid temperature rise with respect to axial distance occurs in the entrance region of the capillary near the wall and can be attributed to the higher values of the pressure-dependent viscosity and the high shear rates prevailing in this region. The temperature rise per unit axial length decreases with increasing axial distances along the die as can be inferred from the concave-downward nature of the curves for the region near the wall (r/R>~0.72 in Figure 3.4(a)). This can be attributed to the monotonically decreasing pressure-dependent shear viscosity as also to the enhanced thermal conduction due to higher radial temperature gradients with increasing axial distances along the die. On the other hand, the temperature rise per unit axial length increases with increasing axial distances along the core of the capillary die (r/R<~0.72 in Figure 3.4(a)) as evident from the concave-upward nature
of the curves. This is due to enhanced thermal conduction with increasing distance from the entrance of the die.

The axial velocity profiles corresponding to different radial sections in the foaming die are shown in Figure 3.4(b). For an entrance velocity of 0.00135 m/s of the fluid into the guiding hollow tube, the maximum velocity observed in the capillary die is 0.438 m/s – which corresponds to an increase of ~ 325 times. Also, as can be observed from Figure 3.4(b), right at the entrance of the capillary die, a hump is observed in the velocity magnitude along the core of the flow (r/R<~0.72). This hump could possibly be attributed to the redistribution of the velocity components just downstream of the contraction. There is a significant radial component of the velocity as the fluid enters the contraction and the hump, very possibly, represents that region of the die in which radial flow is important enough to contribute significantly to the net velocity magnitude of the fluid flowing through the die. The velocity redistributes itself within the small capillary die once it has passed through the abrupt contraction. At ~5 mm downstream of the contraction (i.e. about half-way through the capillary), the velocity profile in the die assumes a fixed shape and hardly changes for greater axial distances along the capillary die.

3.5. Possible reasons for the discrepancy between measured and simulated values of the total pressure drops across the foaming die

A comparison between experimental and simulated pressure drops is depicted in Figure 3.5. It can be seen from Figure 3.5(a) that at the lower flow rates through the
die (corresponding to 10 rpm screw rotation rate), fairly good agreement is obtained between simulated and experimental pressure drops at the higher temperatures (>180°C) studied, but the simulations under predict the pressure drops somewhat at lower temperatures. Figure 3.5(b) shows that a similar trend is observed for the higher flow rates (corresponding to 30 rpm screw rotation rate) through the die too. Additionally, on comparing Figs 3.5(a) and 3.5(b), it appears that the agreement between the experimentally and computationally predicted pressure drops is better for the lower flow rates studied.

A primary reason behind the greater discrepancy in the measured and simulated values of the total pressure drop over the die at lower inlet melt temperatures or higher flow rates could be the non-inclusion of extensional effects in the simulation. As pointed by Han (Han 1984; Han and Han 1988), what a pressure transducer measures when flush-mounted on a capillary is not just the hydrostatic pressure, $p$, but in fact is the outward-acting total wall normal stress, $S_{rr}(R,x)$, which is defined as:

$$S_{rr}(R,x) = p(R,x) + \tau_{rr}(R,x)$$  \hspace{1cm} (3.4)$$

where $\tau_{rr}(R,x)$ is the extra (extensional) stress which is generated due to the deformation of the fluid. In practice, the normal stresses cannot be specified on an absolute basis because of the arbitrariness of the hydrostatic pressure, and data needs to be expressed in terms of the primary normal stress coefficient defined as:

$$\psi_1 = \frac{\tau_{11} - \tau_{22}}{\dot{\gamma}^2}$$

and secondary normal stress coefficient defined as:
\[ \psi_2 = \frac{\tau_{22} - \tau_{33}}{\dot{\gamma}^2} \]

in order to cancel the hydrostatic pressure effect (Schowalter 1978). Note that in the above equations, the “1”, “2” and “3” directions refer respectively to the direction of fluid velocity, the direction of velocity variation and the neutral direction respectively.

The second normal stress coefficient is negative for concentrated polymer solutions and is generally less than 20% of the magnitude of the first normal stress coefficient and so doesn’t play as dominant a role as \( \psi_1 \) does in dictating fluid rheology (Tanner 2000). Bird et. al. (Bird, Armstrong et al. 1987) have noted that \( \psi_1 \) is positive for most polymers and has a large power law region in which it could decrease by as much as a factor of \( 10^6 \). Furthermore, the authors have pointed out that for most polymer systems, the rate of decline of \( \psi_1 \) with increasing shear rate is greater than that of \( \eta \) with increasing shear rate. This could help explain why there is a greater discrepancy in the measured and simulated pressure drops at higher flow rates than at the lower flow rates.

Vinogradov and Malkin (Vinogradov and Malkin 1980) have discussed the temperature dependence of normal stresses and have concluded that the temperature dependence of the first normal stress coefficient \( \psi_1 \) must be stronger than the temperature dependence of the viscosity \( \eta \). This would imply that at lower temperatures, the extensional effects would begin playing an increasingly dominant role in the rheology of the fluid as compared to their effect at higher temperatures and
this could help explain the observation that the experimental and simulated pressure drop rates differ more at lower temperatures than they do at higher temperatures.

Other reasons that could possibly contribute to the slight under prediction of simulated pressure drops from experimental measurements could be the absence of an interaction term in the Chow model to estimate $T_g$ depression for the PS-CO$_2$ mixture, uncertainty in the value of key material properties like thermal conductivity and specific heat capacity for the flowing polymer solution, incompressibility assumption - the density variation of the PS-CO$_2$ solution over the flow length of the die is not accounted for, and non-accountability of the presence of a two-phase polymer-gas mixture in the die downstream of the point of incipient nucleation. Simulating the flow under adiabatic conditions while the experiments were conducted for a nearly isothermal die block could also contribute to a small extent in the difference observed between experimental measurements and simulated results. Real flow situations would neither be perfectly adiabatic, nor would they be perfectly isothermal, but would probably resemble an intermediate regime between these two situations (Cox and Macosko 1974).

It must be pointed out that Xue and Tzoganakis (Xue and Tzoganakis 2003) have measured the entrance pressure losses for PS-CO$_2$ solutions as a function of CO$_2$ concentration (0 to 4 wt % CO$_2$ in PS), upstream pressure (20 to 35 MPa) and wall shear stress (0.04 to 0.1 MPa). They have shown that dissolution of CO$_2$ into the PS melt reduces the entrance pressure drop for a given upstream (or entrance) pressure, and that for the conditions that they tested, the extra pressure losses account for only
about 5% of the total pressure drops encountered for the solution on flowing through the dies. However, their measurements have only been performed for temperatures above 200°C, where extensional effects are not as significant.

Yet another possible reason why the simulated pressure drops could be less than the experimentally observed pressure drops could be the observation made by Nigel et. al. (Nigen and Walters 2002) that under some conditions, as the liquid flow rate is increased across axisymmetric contractions, an unsteady three dimensional flow could set in near the entrance (contraction) region (Nguyen and Boger 1979; Boger, Hur et al. 1986; Evans and Walters 1986). This implies that beyond a certain velocity, a computational rheologist has to consider the steady two-dimensional axisymmetric problem to be a three-dimensional, unsteady one in order to capture all of the physics of the process.

3.6. Unresolved Issues at temperatures closer to the glass transition temperature

Although the viscoelastic scaling approach and the simulations described above give reasonably good pressure-drop predictions under the processing conditions considered, caution must be exercised in using the above procedure while predicting the process performance near the $T_g$ of the polymer-blowing agent solution. The glass transition temperature is approximately defined as (Tanner 2000): The characteristic temperature at which an amorphous polymer (composed of randomly packed chains) changes from brittle, glassy solids to rubbery liquids (or vice versa). In practice, in order to estimate the glass transition temperature, $T_g$, for a given polymer, an
experimentalist carefully monitors how a property of the polymer dependent on the thermal expansion - for example specific volume (Saito, Okano et al. 1963) or specific heat capacity (Ferry 1980) or refractive index (Bueche 1962) changes with temperature, and marks the glass transition temperature as that temperature at which the property when plotted vs. temperature undergoes a sharp change in its slope. However, it is now fairly well recognized that the glass transition temperature, \( T_g \), itself shows a marked dependence on the rate of heat application (heating or cooling) and thus is not a fixed quantity for a given polymer (Bueche 1962; Saito, Okano et al. 1963; Matsui and Bogue 1977; Carey, Wust et al. 1980; Ferry 1980; Gupta and Metzner 1982).

Carey et. al. (Carey, Wust et al. 1980) measured the apparent glass transition temperature as a function of the cooling rate for commercial polystyrene samples (Shell TC 3-30). They found that as the cooling rate of the samples was increased from 0.003 °C/s to 1°C/s, the apparent glass transition temperature that they measured increased from 93.5°C to 109.5°C – which amounts to an increase of 16°C!! Choice of an arbitrary reference temperature can help minimize the error in the temperature shift of viscosity (Ferry and Stratton 1960), but in the pressure shift and especially in the concentration shift of viscosity, where \( T_g \) enters explicitly into the formulation, the “moving” value of \( T_g \) is bound to introduce some degree of error.

Note that a more precise evaluation of the “equilibrium value” (value obtained at the slowest cooling rates) of the glass transition temperature for the particular polymer being studied would not resolve the issue, since the “equilibrium value” of the
glass transition temperature itself is arbitrary. Nor would a recasting of the viscoelastic scaling laws that are currently based on the kinetic glass transition temperature $T_g$ (derived from “quasistatic” experiments) to a form based on the equilibrium second-order transition temperature $T_2$ (derived from either statistical mechanical theory or extrapolations of experimental data) as expounded in the Gibbs-DiMarzio theory be capable of giving improved predictions (Gibbs and DiMarzio 1958; Adam and Gibbs 1965). The problem of $T_g$ being a “moving” value is closely intertwined with another one that pertains to the following observation made by several investigators working in the field of non-isothermal rheology (Matsumoto and Bogue 1977; Gupta and Metzner 1982; Wiest 1988; Wiest and Phan-Thien 1988; Dressler, Edwards et al. 1999) – that the use of shift factors derived from isothermal measurements on a given polymer could be questionable when applied in a non-isothermal situation to the same polymer. Wiest (Wiest 1988) has derived an equation, starting from the Diffusion equation for the Bead-Spring Chain with Hookean Springs (Bird, Armstrong et al. 1987), in which he shows that the thermal history of the material contributes to the state of stress of the material in a very complex way – by way of multiple integrals over the history of the shift factor. Wiest has stated that the error introduced in using a fluid-temperature-history-independent shift factor would depend on the specific non-isothermal flow situation under consideration, but experiments conducted by Wiest et. al. (Wiest and Phan-Thien 1988) and Matsumoto et. al. (Matsumoto and Bogue 1977) for the case of simple uniaxial extension on many polymers have shown that the error could be significant at temperatures close to the glass transition temperature of the polymer.
Dressler et. al. (Dressler, Edwards et al. 1999) have provided an excellent critical review dealing with the thermodynamics and mechanics of non-isothermal polymeric fluids and have derived a thermodynamically consistent set of evolution equations for the basic field variables necessary to describe a flowing polymer liquid using the GENERIC formalism proposed by Beris and Edwards earlier (Beris and Edwards 1994).

### 3.7. Location of Saturation Surface

The solubility of polymer-CO$_2$ systems has been widely studied for the glassy as well as the melt/rubbery state of polymers (Tomasko, Li et al. 2003). Sato et. al. have carried out solubility measurements on several polystyrene PS-physical foaming agent systems (Sato, Yurugi et al. 1996; Sato, Takikawa et al. 2001). They found that for CO$_2$ and for most conventional PFAs like HCFCs and HFCs, the solubility decreases with increasing temperature. However, for Nitrogen and other gases having low critical temperatures like Helium, Hydrogen and Oxygen, solubility increases with increasing temperature, a phenomenon called reverse solubility.

Sato et. al. (Sato, Yurugi et al. 1996) measured the solubility of carbon dioxide in PS using a pressure decay method for temperatures ranging from 373.2 K to 453.2 K and for pressures up to 20 MPa. They used the following values of characteristic parameters: $P^* = 720.3$ MPa, $\rho^* = 1580$ kg/m$^3$, $T^* = 269.5$ K for PS and $P^* = 1036$ MPa, $\rho^* = 803.4$ kg/m$^3$, $T^* = 159$ K for CO$_2$. The mixing rules that we used in this work can be expressed, following Sato et. al. (Sato, Yurugi et al. 1996), as:
\[ P^* = \Sigma \Sigma \phi_i \phi_j P^*_{ij} \]  
(3.5)

\[ P^*_{ij} = \left( 1 - k_{ij} \right) \left( P^*_i P^*_j \right)^{0.5} \]  
(3.6)

\[ T^* = P^* \Sigma \left( \phi_i^0 T^*_i / P^*_i \right) \]  
(3.7)

\[ 1/r = \Sigma \left( \phi_i^0 / r_i^0 \right) \]  
(3.8)

\[ \phi_i^0 = \phi_i P^*_i / \Sigma \left( \phi_j P^*_j / T^*_j \right) \]  
(3.9)

\[ \phi_r = \left( w_r / \rho_r^* \right) / \Sigma \left( w_j / \rho_j^* \right) \]  
(3.10)

where \( T_i^*, P_i^*, \rho^* \) and \( r_i^0 \) are the characteristic parameters of \( i^{th} \) component in the pure state. The temperature dependent binary interaction parameter \( k_{ij} \) in the mixing rules was determined by minimizing the relative deviations between experimentally measured and SLEOS predicted solubility measurements for the PS-CO\(_2\) system and can be expressed in the following form (Liu and Tomasko 2005):

\[ k_{ij} = -0.0005T + 0.1149 \]  
(3.11)

The chemical potential of the gas in the mixture is computed using the relation:

\[ \mu_i = RT \left\{ \ln \phi_i + \left( 1 - r_1 / r_2 \right) \phi_2 + r_1^0 \rho \left( P_1^* P_2^* - 2 P_{12}^* \right) \left( P_1^* T_1 \right) \phi_2 \right\} \]  
(3.12)

\[ + r_1^0 RT \left\{ - \rho / T + \rho \left( \rho / T \right) \left( 1 / \rho - 1 \right) \ln \left( 1 - \rho \right) + \left( 1 / r_1^0 \right) \ln \rho \right\} \]

where \( \mu_i \) is the chemical potential of component 1 (gas) in the binary mixture, \( R \) is the gas constant, and the other terms arise from the mixing rules discussed earlier.
\( k_{ij} \) is the only interaction parameter that is used in fitting SLEOS to laboratory measurements – it accounts for the “non-idealities” of the binary system (for example, the heat and volume changes of mixing) of the two components.

The equilibrium solubility of the PS-CO\(_2\) mixture was computed by equating the chemical potential of CO\(_2\) in the liquid and vapor phases and this information was used to determine the location of the saturation curves under the process conditions chosen. Tsujimura et. al. (Tsujimura, Toru et al. 2002) estimated the critical pressure for bubble inflation in foam extrusion for the polypropylene – isobutane system and their calculations revealed that the critical pressure was about 0.2 ~ 0.4 MPa lower than the equilibrium (saturation) pressure for the mixture. In the discussion that follows, as a first approximation, the terms “surface of incipient nucleation” and “position of nucleation onset” have been used interchangeably to denote that position along the foaming die, when the polymer solution first becomes supersaturated in its passage through the die, (which is, in principle, different from the position corresponding to the critical pressure for bubble inflation which is typically used to denote the formation of the second phase in nucleation literature). As shown in Figure 3.6(a), the position of nucleation onset was located between 27.5 mm and 30 mm for the different process conditions chosen. Since a large part of the pressure drop occurs in the entrance region of the capillary, the surface of incipient nucleation is located around the middle of the capillary instead of near the exit. Several observations can be made from Figs 3.6(b), 3.6(c) and 3.6(d) about the location of the surface of incipient nucleation in the adiabatic foaming die.
A rise in inlet melt temperature shifts the surface of incipient nucleation towards the entrance of the capillary. For low flow rates (corresponding to 10 rpm screw rotation rate) it appears that the shift is more sensitive to temperature at the lower temperatures used. However, no such sensitivity dependence is apparent at the higher flow rates used. It can be seen from Figure 3.6(d) that the location of the surface of incipient nucleation is very sensitive to the flow rate (screw rotation rate) at higher temperatures, but the sensitivity diminishes rapidly at lower temperatures. Thus for example, a rise in the screw rotation rate from 10 rpm to 30 rpm shifts the incipient nucleation surface by ~0.75 mm at 240°C while a similar rise in screw rotation rate hardly affects the position of nucleation onset at 180°C.

For all process conditions studied, nucleation appears to occur first at the wall and then at the centerline. This observation appears to be in contrast with the handful of visual observations of bubble nucleation made by researchers on extrusion dies (Han and Han 1988; Taki, Nakayama et al. 2003) and possible reasons for this discrepancy are discussed below in detail. For our capillary die, the earlier onset of nucleation at the wall (than at the centerline) can be attributed to the reduced solubility at the higher temperature due to viscous heat generation near the wall. Also, on comparing Figs 3.6(a) and 3.6(b), it can be clearly observed that the curvature of the surface of incipient nucleation is more pronounced at the higher flow rates than at the lower flow rates. This is as expected since the viscous dissipation (and hence the temperature rise) is greater at higher flow rates.
The effect of shear on bubble nucleation in polymer-gas systems is still not completely understood. Han et. al. (Han and Han 1988) investigated the phenomenon of bubble nucleation in a slit die for the PS-trichlorofluoromethane system. A He-Ne laser was used to illuminate the PS-gas mixture and visual observations of the nucleating and growing bubbles could be made through the provision of an optically clear glass window. The authors observed that the bubbles nucleated first at the center of the slit die (y = 0 position) for the PS-trichlorofluoromethane system. Furthermore, the position of nucleation onset was found to shift towards the die exit on moving away from the slit axis in the cross-channel (y) direction but then began shifting again towards the die entrance beyond a certain critical value of y (y = y_{nc}). To explain their observations, the authors suggested that bubble nucleation at positions between y = 0 and y = y_{nc} was induced by flow and bubble nucleation at positions between y = y_{nc} and y = h (die wall) was induced by shear stress. The authors also noted that cavitation brought about by the surface roughness of the wall and by thermal fluctuations due to the heat transfer between the die wall and the polymer solution could induce nucleation earlier near the wall, but such events would be sporadic and could be ignored so that shear-effects would be the dominant mechanism for triggering nucleation earlier near the die wall. Our results lend support to the interpretations of Han et. al. (Han and Han 1988) for the observed trend in the position of nucleation onset between y = y_{nc} and y = h and demonstrate how shear stress through viscous heat generation at the wall can bend the surface of incipient nucleation towards the die entrance and induce nucleation first near the wall. However, further analysis is required to explain the experimentally
observed trend in the position of nucleation onset between the cross-channel positions $y = 0$ and $y = y_{nc}$.

Another very interesting observation that Han and Han (Han and Han 1988) made was that while supersaturation seems to be a necessary condition in a homogeneous isotropic system for bubble nucleation to occur under static conditions, for a flowing polymer-gas mixture, bubble nucleation could occur even in an unsaturated condition. It is now well known that the orientation of polymer chains changes in a flow field – with the long polymer chains aligning themselves in the direction of the flow so that they assume a distinctly distinguishable (though difficult to quantify) configuration under flow from their configuration at rest. Han and Han used the Flory Huggins theory to compute their equilibrium solubility curve, which, as noted earlier, does not account for the vacant lattice sites. It will be of interest to compare the experimental results of Han and Han with the equilibrium solubility values for the PS-trichlorofluoromethane system obtained through the SLEOS.

Recently, researchers from the Industrial Materials Institute, NRC, Canada (Sahnoune, Tatibouet et al. 2001; Vachon and Gendron 2003; Tatibouet and Gendron 2004) used an inline detection method based on ultrasonic sensors to investigate the influence of the flow on the foaming behavior of various PS-gas mixtures in an extrusion slit die. The authors observed that under flow conditions, the degassing pressure was consistently higher than the solubility pressure. A tentative explanation was offered by Tatibouet et. al. (Tatibouet and Gendron 2004) to account for their experimental observations. The authors suggested that the extensional stresses do not
have sufficient time to relax at low processing temperatures or for polymers with low values of melt flow index or with large values of compliance and this could lead to premature degassing of the PS-PFA mixture along the die length. Additionally, the authors have quoted the observation of Kim et. al. (Kim and Dealy 2002) that the amount of stretching is at its maximum along the centerline, and have speculated based on this observation that the influence of tensile deformation on degassing could help explain the observation of Han and Han that bubbles nucleate first along the axis in their slit die. Kim et. al. (Kim and Dealy 2002) in their paper, do not appear to have made the observation of stretching being a maximum along the centerline explicitly, but do quote Ramamurthy et. al (Ramamurthy and McAdam 1980) as having demonstrated that the velocity on the center streamline has a large maximum just before the die entry and then falls further downstream – which implies that there is a strong stretching along the centerline and appears to validate the premise of Tatibouet et. al. (Tatibouet and Gendron 2004). Although Tatibouet et. al. (Tatibouet and Gendron 2004) have suggested a probable cause for the bubbles nucleating first along the centerline of the slit die of Han and Han (Han and Han 1988), considerable work still needs to be done in this area to understand the process within a combined framework of rheology and thermodynamics.
3.8. Effect of Field Gradients on Foam Morphology

Nucleation events depend on the pressure and temperature history of a fluid element in the foaming die. In this section, the foam morphology is related to the basic field variables - temperature, pressure and shear rate in the foaming die.

Park et. al. (Park, Baldwin et al. 1995) have demonstrated the importance of the pressure drop rate on the nucleation density of the polymer foam. Their results have been verified by the experimental work of Han et. al. (Han, Koelling et al. 2003) in our laboratory. The pressure drop rate and the temperature rise rate directly affect the solubility drop rate, thereby influencing the foam morphology. The pressure does not change much in the radial direction in the region of nucleation onset in the die. Thus dP/dx hardly changes across the die cross-section in the region of the die where the pressure in the capillary falls below the degassing pressure of the PS-CO$_2$ solution. The velocity is predominantly unidirectional in the region of nucleation onset in the capillary and the pressure drop rate can be simply computed as:

\[
\frac{dP}{dt} = \frac{dP}{dx} v_x
\]  

(3.13)

where $v_x$ is the local axial velocity. The pressure drop rate along the saturation surface for the different conditions studied for the 10 rpm and 30 rpm screw rotation rates is presented in Figures 3.7 and 3.8 respectively. Note that the pressure drop rate profile has exactly the same shape as the velocity profile along the surface of incipient nucleation since dP/dx is constant. Also, note that the dP/dt value for the same radial location in the die is about three times as much for the 30 rpm case than for the 10 rpm
case because the corresponding velocity is about three times higher for the former (as compared to the later) screw rotation rate.

Han et. al. (Han, Koelling et al. 2003) had observed earlier that while operating at the lowest temperature (140°C) of their processing window, the cell morphology was found to change appreciably from the one observed at higher temperatures – in that larger, conjugated, polyhedral cells were observed under this condition. Their observation is reproduced as Figure 3.9 here. The authors attributed this change in foam morphology to the increased viscosity and rigidity of the polymer matrix at the lower processing temperature and to the accelerated vitrification of the foam on exiting the extrusion die. Our simulation results indicate that the pressure drop rate is significantly lower for the 140°C case than for any other temperature studied (see Figure 3.7), which, following Park et. al.’s (Park, Baldwin et al. 1995) argument, implies that a lesser number of bubbles are able to nucleate under the given conditions which can eventually grow to larger sizes and impinge on each other forming the polyhedral, conjugated morphology observed by Han et. al. (Han, Koelling et al. 2003).

SEM micrographs of foam cross-sections obtained at two different processing rates (corresponding to 10 rpm and 30 rpm screw rotation rate) for 180°C inlet melt temperature and 1.0 wt% CO₂ are shown in Figure 3.10. Cell density was calculated at four different radial locations for each SEM micrograph using the following well-known expression (Kumar and Suh 1990).

\[ N_f = \left( \frac{nM^2}{A} \right)^{3/2} \quad (3.14) \]
where $N_f$ is the number of bubbles per cm$^3$ of the final foam, $n$ is the number of bubbles in the micrograph, $A$ is the area of the micrograph, cm$^2$ and $M$ is the magnification factor of the micrograph.

The cell density (expressed as # of cells/cm$^3$) is plotted against radial position (expressed as r/R) in Figure 3.10. For each throughput rate used, cell density was found to decrease by almost an order of magnitude in going from the center to the edge of the foam section. Also, for the same r/R, the cell density in the foam sample corresponding to the higher throughput rate was found to be higher by almost an order of magnitude as compared to the cell density in the foam sample corresponding to the lower throughput rate. These observations substantiate the observations of Park et. al. (Park, Baldwin et al. 1995) and Han et. al. (Han, Koelling et al. 2003) regarding the importance of the pressure drop rate in determining bubble nucleation density.

However, the morphology of our foam samples differs from the foam morphologies obtained by Chen et. al. (Chen, Wang et al. 2002) and Xu et. al. (Xu, Park et al. 2003) in one essential respect – in that they observed an increase in cell density (and a corresponding decrease in cell size) near the edge of their foam samples while we observed fewer and larger cells near the edge of all our foam samples. Complete details regarding how the process parameters were controlled for their foaming experiments are not available, and hence it is not clear what the above-mentioned differences in cell morphologies might be attributed to.

Thermal gradients across adjacent mesh volumes are appreciable in the capillary die due to significant viscous heat dissipation. The temperature rise rate $dT/dt$
of a given fluid element in the die is calculated based on the following procedure. The axial temperature distribution along a specified radial distance in the capillary is approximated using a polynomial expression of appropriate degree. The axial temperature gradient at the surface of incipient nucleation is then computed by taking the derivative of the polynomial expression at the point of interest. The temperature rise rate along the die can now be calculated using an expression equivalent to equation (3.13), i.e.:

$$\frac{dT}{dt} = \frac{dT}{dx} v_s$$  \hspace{1cm} (3.15)

Figure 3.11 represents the temperature rise rate along the surface of incipient nucleation for the different conditions studied for 10 rpm screw rotation rate. The temperature rise rate peaks at around four-fifth of the radial distance from the center, as can be seen from Figure 3.11. Unlike the pressure drop rate, the temperature rise rate doesn’t seem to have a significant effect on the cell size distribution under the prevailing flow conditions.

Figure 3.12 shows a comparison of the temperature rise rate along the surface of incipient nucleation for the 30 rpm versus 10 rpm screw rotation rate. The peak for the 30 rpm case for both temperatures studied is 4-5 times the peak for the 10 rpm case.
3.9. Comment on shear effects on bubble nucleation density in thermoplastic foams

Lee (Lee 1993; Lee 2000) conducted experiments on Polyethylene foam, with and without nucleating agent (talc), to study the shear effects on foam nucleation in an extrusion die. He has shown that for the case of no nucleating agent in the polymer matrix (Lee 1993; Lee 2000), the number of bubbles nucleated per unit volume increased strongly (exponentially) with increasing Capillary number. He concluded, based on this observation, that the Capillary number, which is a ratio of shear forces to surface tension forces, plays a dominant role in determining nucleation density in polymer foams and suggested that this dependence of bubble density on Capillary number implies that shear force rather than shear rate alone is the principal mechanism affecting bubble nucleation. In order to compute the Capillary number, Lee used an averaged shear rate from the throughput rate and the dimensions of his extrusion die end opening and used a mean critical radius value of 0.3 μm from the work of Han and Han (Han and Han 1990) for his bubble radius. Since bubble nucleation is a local phenomenon, we feel that it is more appropriate to compute Capillary numbers locally at different locations at and downstream of the surface of incipient nucleation rather than use global averaged values. The Capillary numbers as a function of axial distance for different radial sections for our extrusion die are plotted in Fig 16. It can be clearly observed that at the surface of nucleation onset (where the bubbles would assume their critical size if the nucleation were instantaneous), there is an order of magnitude difference in the Capillary number values across the die cross-section. However, the
cell density does not appear to increase in proportion with the Capillary number across the die cross-section.

Xu et. al. (Xu, Park et al. 2003) noted that most of their samples showed very little variations in the distribution of cells across their extrudates of circular cross-section. They suggested that in the slowly flowing polymer melt near the wall, where the pressure drop rates were the smallest, the higher shear rates enhanced the cell nucleation while in the core region, it was the significant pressure drop rates experienced by the fast-flowing fluid elements that resulted in bubble nucleation. This appears to validate the analysis and conclusions of Lee qualitatively. But a closer quantitative examination shows that the exponential dependence of bubble density that Lee correlated with the Capillary number is not borne out in our case. From Fig 12 (a) (pressure drop rate, 10 rpm), we can see that the pressure drop rate stays virtually at its centerline value at a radial distance of 0.15 mm from the die axis. However, the capillary number at r = 0.15 mm (line 9 in Fig 16) is ~ 7 times its value at r = 0 mm (centerline in Fig 16). The constancy of cell size is difficult to reconcile with the analysis of Lee. Moreover, Lee’s use of an average Capillary number for the die when it is widely accepted that bubble nucleation is a local phenomenon is questionable. Since bubble nucleation and growth in the extrusion foaming die is such a complex process, one cannot be too circumspect in one’s interpretations and conclusions.

Chen et. al. (Chen, Wang et al. 2002) developed a device called the Foaming Process Simulator to segregate the pressure drop rate effect and the shear effect on nucleation and to focus exclusively on the effect of shear stress on the foaming
process. The principal component of their device was a test chamber holding the polymer samples which could be pressurized up to 34.5 MPa and heated up to 250°C. Gas could be injected through an inlet port into the test chamber. Shear stress was applied on the samples by the aid of a rotor. The rotor was driven by an AC variable motor equipped with a break system and so could be stopped instantly when desired. In a typical experiment, PS samples were loaded onto the test chamber and heated to a desired temperature; CO$_2$ was then injected into the test chamber and the absorption of gas into the polymer was aided by rotating the rotor at 50 s$^{-1}$ for a time sufficient enough to ensure complete saturation of the polymer with the gas. The shear rate was then stepped up for a short time (100 s$^{-1}$ for 20 s, or 200 s$^{-1}$ for 10 s, or 400 s$^{-1}$ for 5 s) and once stable shear for the desired time had been applied, the rotor was stopped instantly using the break system. Once the rotor had stopped, the gas was released immediately to induce foaming and the test chamber was opened to expedite cooling of the sample. On observing the morphology of their foams through SEM, the authors reported that shear stress had a significant effect on the cell density; the higher the shear stress the more significant was the effect on cell density. The authors developed a cell stretch model to explain their observations.

Although the authors have expended a lot of effort in developing an innovative experiment and collecting their data, their interpretation of results is not entirely convincing. In their experiment, the authors had stopped the rotor just before foaming took place. This means that shear force (and hence shear stress) was no longer being applied at the actual time of foaming. Rather than experiencing a steady shear field, the
material was undergoing elastic recoil and stress relaxation after cessation of steady shear flow. Bird et. al. (Bird, Armstrong et al. 1987) have noted that after sudden cessation of a steady shear flow, both normal stresses and shear stresses decrease monotonically to zero and the stresses relax more rapidly as the shear rate in the preceding shear flow is increased. Furthermore, they have noted that shear stress relaxes more rapidly than normal stress following cessation of steady shear flow.

West (West 1969) has tabulated the maximum relaxation times that he observed for both monodisperse and polydisperse PS samples with molecular weights and distributions comparable to commercial PS. The relaxation times that he reported ranges from 0.011 s to 0.488 s for his different samples. Such short relaxation times further complicate the analysis of the results of Chen et. al. Thus, although Chen et. al. have made a good attempt at segregating the pressure drop effects and shear effects by devising the Foaming Process Simulator, the bubble nucleation is complicated by the fact that it is occurring in a regime wherein the polymer chains are undergoing complex transitional rearrangements to their equilibrium configuration and where extensional effects through elastic recoil may play as important a role as shear effects. Thus, further experiments are required to precisely understand the effects of the controlling variables (see Fig 1), particularly the pressure drop rate and the shear rate on bubble nucleation and growth in extrusion foaming dies.
<table>
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<th>Velocity at 30 rpm screw rotation rate (m/s)</th>
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<td>0.0016723</td>
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</tr>
</tbody>
</table>

**Table 3.1:** Summary of Process Conditions for Extrusion foaming of PS-CO₂ solution. The velocities and temperatures listed are the inlet velocities and temperatures of the homogenous fluid stream entering the die insert.
Figure 3.1 (a) Top: Geometry of the contraction. Since the die is axisymmetric, only the symmetric part of the 2D geometry needs to be meshed. (b) Middle: Diagram showing the mesh. The mesh has ~76000 triangular cells (~40000 nodes). Since the mesh is very fine, it is hard to observe individual cells. (c) Bottom: Enlarged view of the grid near the contraction. Grid adaption based on temperature gradients has been carried out in the region near the wall and near the entrance corner.
Figure 3.2: Pressure profiles along the die for different inlet PS-CO$_2$ solution temperatures (10 rpm screw rotation rate).
Figure 3.3: Pressure profiles along the die for different inlet PS-CO$_2$ solution temperatures (30 rpm screw rotation rate).
Figure 3.4 (a) Top: Temperature profiles along the die length (180°C, 1.0 wt% CO$_2$, 10 rpm screw rotation rate) (b) Bottom: Velocity Profiles along the die length (180°C, 1.0 wt% CO$_2$, 10 rpm screw rotation rate)
Figure 3.5 (a) Top: Comparison of Simulated and Experimental Pressure Drops across the die for different inlet PS-CO$_2$ solution temperatures (10 rpm screw rotation rate) (b) Bottom: Comparison of Simulated and Experimental Pressure Drops across the die for different inlet PS-CO$_2$ solution temperatures (30 rpm screw rotation rate)
Figure 3.6 (a) Top: Location of saturation surface in the die. (b) Top middle: Saturation surface curves, 10 rpm. (c) Bottom middle: Saturation surface curves, 30 rpm (d) Bottom: Effect of screw rotation rate on the location of the saturation surface
Figure 3.7: Pressure drop rate at different temperatures (10 rpm screw rotation rate) at the saturation surface. The straight lines are pressure drop rates computed for an average velocity and a linear pressure drop profile along the die length. Note that because of the very steep pressure drop near the entrance of the capillary die for the 140°C case, the pressure drop rate predicted from an average velocity and a linear pressure drop is far higher than the true pressure drop rate at the saturation surface.
Figure 3.8: Pressure drop rate at different temperatures (30 rpm screw rotation rate) at the saturation surface.
Figure 3.9: SEM micrographs depicting cell morphology at 160°C, 10 rpm (left) and 140°C, 10 rpm (right). Note the much larger, non-coalescing cell morphology at 40°C (right) compared to the smaller, coalescing cell morphology at 160°C (left).
**Figure 3.10 (a) Top:** Cell Morphology (180°C). The figs at the left and right represent the morphology at the lower processing rate (corresponding to 10 rpm screw rotation rate) and higher processing rate (corresponding to 30 rpm screw rotation rate) respectively. **(b) Bottom:** Cross sectional cell density distribution for the micrograph corresponding to Figure 14(a). There is a significant decrease in cell density as one goes from the center to the edge of each SEM micrograph in Figure 14(a). Also, there is about an order of magnitude increase in cell density for corresponding positions of the cell morphology for the higher processing rate micrograph (30 rpm) as compared to the lower processing rate micrograph (10 rpm).
Figure 3.11: Dependence of Temperature rise rate on inlet melt temperature (10 rpm screw rotation rate) at the saturation surface. Notice that for the slower moving melt (140°C) there is greater time available for the viscous heat generated to diffuse inwards and thus the 140°C curve has a broader radial spread than the others.
Figure 3.12: Comparison of Temperature rise rate at the saturation surface for 30 rpm screw rotation rate versus 10 rpm screw rotation rate for two different temperatures. The peak for the 30 rpm case is 4-5 times higher than the peak for the 10 rpm case.
A pure liquid can be cooled to a temperature below its normal freezing point – when this happens, the liquid is said to be supercooled. Also, a pure liquid can be heated to a temperature above its normal boiling point. Such a liquid is said to be superheated. Suspended particles, mechanical vibrations or roughness in the walls of the vessel containing the liquid can facilitate phase separation below the freezing point or above the normal boiling point of the liquid. In fact the greater is the degree of cooling of the liquid or its degree of heating above the normal boiling point, the more susceptible it is to phase separation. However, even without the addition of impurities to a liquid, it eventually reaches a condition in which freezing or boiling of the liquid (depending on whether it is being cooled or heated) can no longer be prevented and phase separation ensues. This is because spontaneous molecular motions in the liquid
become important enough to drive the system towards the condition of greater stability through the formation of a new phase.

4.1. Overview of Bubble Nucleation in Newtonian Liquids using Classical Nucleation Theory

A liquid or liquid mixture below its freezing point or above its normal boiling point is under a precarious condition thermodynamically, since minor external disturbances can trigger the sudden appearance of one or more new phases. Such a condition of precarious equilibrium is called metastable equilibrium and supercooled and superheated liquids are collectively referred to as metastable liquids (Debenedetti 1996).

A liquid under a pressure lower than its vapor pressure is thermodynamically unstable with respect to formation of bubbles filled with its vapors. If the fluid is a multi-component mixture, the more volatile component(s) would tend to phase separate as a result of this instability, provided that a large enough quantity of work (in excess of the work of “critical nucleus” formation) is available. Nucleation is the process in which a critical amount of a secondary component dissolved in a primary phase comes together to form a second stable phase, such as a gas bubble in a homogenous liquid.
4.2. Drawbacks of Previous Work on Bubble Nucleation in Polymeric Liquids

Various mechanisms of nucleation have been proposed in the literature for nucleation of gas bubbles in thermoplastics, including homogeneous, heterogeneous, mixed-mode, shear-induced and void nucleation theories (Ramesh 2004). However, none of these theories give quantitative predictions for even the simplest cases of bubble nucleation in polymeric liquids. The last two mechanisms especially – viz. shear-induced and void nucleation, lack a rigorous mathematical structure and are little more than qualitative conjectures by the authors who proposed and advocated them.

4.3. Chemical and Mechanical Equilibrium of a Critical Nucleus

A critical bubble is in a state of mechanical and chemical equilibrium with the liquid surrounding it. The condition of mechanical equilibrium is given by the Laplace equation, which relates the pressure of the critical bubble with the pressure of the surrounding liquid as:

\[ p_c = p_0 + \frac{2\sigma}{r_c} \]  

(4.1)

where \( p_c \) is the pressure of the critical bubble, \( p_0 \) is the pressure of the surrounding liquid, \( \sigma \) is the surface tension and \( r_c \) is the radius of the critical nucleus.

The condition of chemical equilibrium demands that the chemical potential of the volatile component in the liquid and the gas phases should be equal for the critical bubble.

\[ \mu'(p_c, T_0) = \mu''(p_0, T_0) \]  

(4.2)
where $\mu'$ is the chemical potential of the volatile component in the critical bubble and $\mu''$ is the chemical potential of the volatile component in the liquid phase.

4.4. The reversible work of Critical Nucleus Formation in a Homogeneous Liquid

For a new phase to appear in a homogeneous metastable liquid, an interface must be formed. This process occurs through the formation of small, localized embryos of the new phase within the bulk metastable phase. In the absence of any suspended impurities or solid surfaces, the embryos are formed as a result of spontaneous density or composition fluctuations. The formation of embryos of a critical size in a metastable liquid is an activated process – a free energy barrier needs to be overcome for nuclei of a critical size to form, beyond which they can grow spontaneously to macroscopic sizes.

Gibbs (Gibbs 1961), in his seminal work on the equilibrium of heterogeneous substances, has given a rigorous derivation for the expression of the reversible work of critical nucleus formation for a spherical nucleus. The interested reader may consult his treatise for details. We only present below a brief discussion based on physical grounds adapted from the work of Blander and Katz (Blander and Katz 1975).

It is desired to derive an expression for the minimum work of critical nucleus formation, $W$, from a homogeneous metastable liquid under isothermal conditions. Let the critical nucleus be a bubble of volume $V_G$ having a surface area $A$ and consisting of $n$ gas molecules. The total work of critical nucleus formation can be expressed in the following form:
\[ W = W_s - W_1 - W_2 \]  \hspace{1cm} (4.3)

where, \( W_s \) is the work required to form a gas-free cavity of area \( A \), \( W_1 \) is the work required to balance the counterforce of the liquid on the microscopic bubble of an initial size \( V_G' \) that prevents the bubble from collapsing onto itself and the work \( W_2 \) causes the bubble to expand in the liquid from its initial size \( V_G' \) to its final size \( V_G \). If \( \sigma \) denotes the surface tension of the liquid-gas interface, then,

\[ W_s = \sigma A \]  \hspace{1cm} (4.4)

The \( n \) molecules vaporizing into the cavity under isothermal conditions would be under a constant pressure equal to the vapor pressure \( p_v \) of the liquid (or of the volatile component in the liquid mixture). Although liquid-vapor equilibrium is a dynamic process in which the transfer of gas molecules would be occurring in both directions across the interface, it can be assumed for simplicity that the net number of molecules entering the bubble cavity, \( n \) are doing so through a semi-permeable membrane. If \( V_G' \) is the volume inside the (imaginary) membrane enclosing \( n \) gas molecules at pressure \( p_v \), the maximum possible work \( W_1 \) provided by the \( n \) molecules in the bubble of volume \( V_G' \) and at pressure \( p_v \) to counteract the force of the surrounding liquid (or imaginary membrane) maintained at pressure \( p_0 \) is:

\[ W_1 = (p_v - p_0)V_G' \]  \hspace{1cm} (4.5)

If the gas bubble expands from a volume \( V_G' \) to \( V_G \) (with the corresponding gas pressure inside the bubble changing from \( p_v \) to \( p \)), with the total number of gas
molecules in the bubble, \( n \), held constant, the maximum work done on the environment, \( W_2 \), can be expressed, using integration by parts, as:

\[
W_2 = \int_{V_0}^{V_G} (p - p_0) dV = pV_G - p_VV'_G - p_0(V_G - V'_G) - \int_{p_V}^{p} V dp
\]  

(4.6)

The chemical potential of the \( n \) gas molecules in the bubble would vary as \( d\mu = (V/n)dp \). Since the gas bubble is in chemical equilibrium with the surrounding metastable liquid, the chemical potential of the gas at the pressure \( p_V \), that is \( \mu' \) is the same as that of the gas in the external liquid, that is \( \mu'' \). Using this information, the expression for \( W_2 \) becomes:

\[
W_2 = pV_G - p_VV'_G - p_0(V_G - V'_G) - n(\mu' - \mu'')
\]

Substituting the values of \( W_S \), \( W_1 \) and \( W_2 \) into equation (1), \( W \) can be expressed as:

\[
W = \sigma 4r - (p - p_0)V_G + n(\mu' - \mu'')
\]  

(4.7)

Equation (4.7) is the fundamental equation for minimum reversible work of critical nucleus formation for homogeneous nucleation of vapor bubbles from a metastable liquid phase. For a spherical nucleus of radius \( r \), equation (4.7) becomes:

\[
W = 4\pi r^2 \sigma + \frac{4}{3}\pi r^3 (p_0 - p) + n[\mu'(p,T_0) - \mu''(p_0,T_0)]
\]  

(4.8)
4.5. Small Departures from Unstable Equilibrium for a Critical Bubble

The embryos or clusters that are precursors to bubbles in supersaturated liquids are microscopically small regions in the liquid where the local density is lower than the bulk density of the liquid. Considering the embryos as spherical clusters of ideal gas having radius \( r \) and containing \( n \) molecules, the following expression holds:

\[
\frac{4}{3} \pi r^3 p = nkT
\]  
(4.9)

For an ideal gas, one can also write:

\[
\mu'(p, T_o) - \mu'(p_c, T_o) = kT \ln \left( \frac{p}{p_c} \right)
\]  
(4.10)

Since for the critical nucleus, we have \( \mu'(p_c, T_0) = \mu''(p_0, T_0) \) the equation for \( W \) for a spherical nucleus of radius \( r \), i.e., equation (4.8), can be written as:

\[
W = 4 \pi r^2 \sigma + \frac{4}{3} \pi r^3 \left( p_0 - p \right) + nkT_0 \ln \left( \frac{p}{p_c} \right)
\]  
(4.11)

The work of embryo formation is a function of two variables, the radius \( r \) of the embryo and the pressure \( p \) of the gas in the embryo. At \( r=r_c \), chemical and mechanical equilibrium prevails and \( p=p_c \). Using this information, we can write an expression for the minimum work for critical nucleus formation at \( r=r_c \) as:

\[
W_c = \frac{4}{3} \pi r_c^2 \sigma
\]  
(4.12)

For small departures from the unstable equilibrium (corresponding to the critical radius), the above expression for the free energy can be expanded in a Taylor series. The first order derivatives would vanish at equilibrium and terms of an order
higher than the second can be ignored. For small departures from equilibrium $W(r,p)$ can now be expressed approximately as:

$$W(r,p) = \frac{4}{3} \pi r_c^2 \sigma - 4 \pi \sigma (r-r_c)^2 + \frac{2}{3} \frac{r_c^3}{p_c} \left(p-p_c\right)^2$$

(4.13)

The first and second order derivatives of $W(r,p)$ with respect to $r$ are:

$$\frac{dW}{dr} = -8\pi \sigma \left(r-r_c\right)$$

(4.14)

and

$$\frac{d^2W}{dr^2} = -8\pi \sigma$$

(4.15)

These equations will be used in the next section.


According to Gibbs (J.W.Gibbs 1961), the critical nucleus would correspond to an aggregate of the new phase of a size for which the work of formation (or free energy of formation) is a maximum. An increase in the size of such an aggregate or nucleus will lead to its further growth, while a decrease in the size of the nucleus will lead to its annihilation.

Zeldovich, in his seminal work on phase transitions, described the evolution of spontaneously arising bubbles from a metastable liquid, considering explicitly both thermodynamically determined transitions and random effects (Y.B.Zeldovich 1992). He began by considering a system in which the nuclei of a new phase (e.g. bubbles in a
metastable liquid) may be of different sizes. He plotted the dimension of the nucleus on the abscissa and the free energy on the ordinate. His construction is shown in Figure 4.1.

Zeldovich designated the critical region as a region in which the values of the free energy differed from the maximum free energy by less than or equal to $kT$. He assumed that motion along the abscissa took place in discrete jumps of $\pm \lambda$, where $\lambda$ denotes the length of the mean free path (see Figure 4.2). The frequency of jumps was determined by the probabilities $q_+$ and $q_-$ of a jump to the right and left (over a distance $+\lambda$ or $-\lambda$). Considering all nuclei to be discretely distributed according to their sizes over the nodes of the axis at a distance $\lambda$ from each other, he expressed the change in the number of nuclei $Z(n)$ at the nth node as:

$$\frac{\partial Z(n)}{\partial t} = -Z(n)[q_+(n) + q_-(n)] + Z(n-1)q_+(n-1) + Z(n+1)q_-(n+1) \quad (4.16)$$

Denoting the equilibrium number of nuclei by $b(n)$ and using this quantity to eliminate the $q_-$ terms from equation (4.16), designating the remaining quantity $q_+$ in equation (4.16) by $q$ and turning from a discrete distribution of nodes $Z(n)$ to a continuous distribution, $Z(x)$, Zeldovich obtained the fundamental equation:

$$\frac{\partial Z}{\partial t} = -D\frac{\partial}{\partial x} \left( q \frac{Z}{b} \right) \quad (4.17)$$

where the quantity $D=q\lambda^2$ is the diffusion coefficient. In the absence of external forces, all the points of the abscissa are constant, so that $b$ is constant, and Equation (4.17) reduces to Fick’s law:
\[
\frac{\partial Z}{\partial t} = D \frac{\partial^2 Z}{\partial x^2}
\]  \hspace{1cm} (4.18)

In order to account for the effect of random variations or fluctuations on the
distribution of nuclei, Zeldovich assumed that at the initial time, the system contains a
number \( N \) of nuclei of exactly the same size. He argued that in the absence of random
fluctuations, in an idealized system, the \( N \) nuclei, which were identical at initial time,
would stay identical after a time interval \( t \). However, in any real system, because of
the presence of fluctuations, the distribution at time \( t \) would be smeared in comparison
with the distribution at initial time due to diffusion although the center of gravity of the
smeared distribution would stay identical to the center of gravity of the non-smeared
distribution at time \( t \). Using this information, Zeldovich, derived an expression for the
diffusion coefficient \( D \) as:

\[
D = \frac{kT w}{-dW/dx}
\]  \hspace{1cm} (4.19)

where \( w(x, T_{\text{crit}}) = \frac{\partial x}{\partial t} \) denotes the change in size of the nucleus in the time interval, \( t \),
under the influence of macroscopic forces alone.

Expanding the work of formation of the nucleus, \( W \), around the critical radius
in a Taylor series, Zeldovich expressed the equilibrium number of nuclei, \( b \), in the
following form:

\[
b = b(x_{\text{crit}}) \exp \left[ -\frac{d^2W(x-x_{\text{crit}})^2}{dx^2 \frac{2kT}{kT}} \right]
\]  \hspace{1cm} (4.20)
W is the reversible work of critical nucleus formation and can be expressed, following
equations (4.1) and (4.12) as:

\[ W = \frac{16\pi\sigma^3}{3\Delta P^2} \]  

(4.21)

where \( \sigma \) is the interfacial tension between the stable gas in the bubble and the
surrounding metastable liquid phase and \( \Delta P \) is the pressure difference across the
bubble interface (which is discussed in greater detail in section 4.7).

Finally, equating the energy dissipated in the liquid during cavitation to the
work performed per unit time by the forces of surface tension and by external forces
causing stretching of the liquid, Zeldovich derived an expression for the number of
bubbles formed in 1 cm\(^3\) of the liquid in 1 second:

\[ J = \frac{(\Delta PkT)(\sqrt{\sigma/kT})}{(\mu d^2)} e^{(-16\pi\sigma^3/3\Delta P\mu_d^2)} \]  

(4.22)

where \( \mu \) is the viscosity of the liquid and \( d \) is the linear size of a molecule of liquid.

The salient steps in the derivation of the Zeldovich theory of phase transitions
are enumerated above, since the theory forms the cornerstone of the classical
clarified the theory of Zeldovich and extended it to account for hydrodynamic and
inertial constraints on the rate of bubble nucleation in simple liquids. Katz and his
coworkers (Blander, Hengstenberg et al. 1971; Blander and Katz 1975; Blander 1979)
further extended it to account for diffusional constraints in multi-component liquid
mixtures. The derivation of Kagan and the extension of Katz et. al. will be discussed
below in detail, since the nucleation rate calculations for this work are based on their theory.

Kagan began by writing an expression for the flow of nuclei along a phase axis $n$:

$$J = \dot{n}f_n - D \frac{\partial f_n}{\partial n}$$  \hspace{1cm} (4.23)

Here, $f_n$ is a distribution function which denotes the number of nuclei in unit volume containing $n$ molecules in the cavity. The dimensions of $f_n$ are $L^{-3}$. Then the total number of nuclei in unit volume can be given by the normalizing condition

$$\int f_n dn \cdot \dot{n}$$ is the derivative of $n$ with respect to time $t$, i.e. $\dot{n} = \frac{dn}{dt}$ and so has the units of $T^{-1}$. The dimensions of $J$ are thus $L^{-3}T^{-1}$. $J$ determines the number of supercritical nuclei formed per unit time per unit volume, since only such nuclei can grow into macroscopic gas bubbles. The term $\dot{n}f_n$ determines the macroscopic (hydrodynamic) transfer of nuclei which is related to the decrease and subsequent dissolution of a bubble if $r<r_c$ and to the growth of a bubble if $r>r_c$. The quantity $D$ is the diffusion coefficient and is exactly equivalent to the diffusion coefficient in the Zeldovich theory of phase transitions described above. It has the units of $T^{-1}$ in equation (4.23) (which corresponds to $\lambda$ being dimensionless in the Zeldovich theory). The quantity $D \frac{\partial f_n}{\partial n}$ describes the transfer of nuclei as a result of the fluctuations or smearing due to random microscopic forces.
For the case of quasi-stationary distribution of nuclei in a liquid, \( J \) can be taken to be constant and equation (4.23) can be solved using the integrating factor approach for ordinary differential equations. The integrating factor used is \( \exp\left(-\int \frac{n}{D} \, dn\right) \) and the distribution function \( f_n \) can now be expressed as:

\[
f_n = \exp\left(\frac{\dot{n}}{D} \int \frac{1}{D} \exp\left(-\int \frac{n}{D} \, dn\right) \, dn \right) - \int \left(\frac{\dot{n}}{D} \int \frac{1}{D} \exp\left(-\int \frac{n}{D} \, dn\right) \, dn\right) \, dn + C
\]  

(4.24)

Now, the number of nuclei in unit volume containing a very large number of molecules would be negligibly small. In fact, we can write:

\[
n \to \infty \quad f_n \to 0
\]

Applying the boundary condition to equation (4.24), we get:

\[
C = J \int_0^{\infty} \frac{1}{D} \exp\left(-\int \frac{n}{D} \, dn\right) \, dn
\]  

(4.25)

Substituting for \( C \) in equation (4.24), we can write \( f_n \) as:

\[
f_n = J \exp\left(\frac{\dot{n}}{D} \int \frac{1}{D} \exp\left(-\int \frac{n}{D} \, dn\right) \, dn \right) - \int \left(\frac{\dot{n}}{D} \int \frac{1}{D} \exp\left(-\int \frac{n}{D} \, dn\right) \, dn\right) \, dn
\]  

(4.26)

In order to obtain the value of the diffusion coefficient, \( D \), Kagan made use of the fact that the number of supercritical nuclei formed per unit time and unit volume, \( J \), is 0 for a phase in a stable state. When \( J = 0 \), equation (4.23) can be rewritten as:

\[
D = \frac{\dot{n}}{\left(\frac{d \ln f_{n0}}{dn}\right)}
\]  

(4.27)

where \( f_{n0} \) denotes the distribution function of bubbles from a stable liquid.

But
\[ f_{n0} \simeq e^{-W/kT_0} \quad (4.28) \]

Substituting this value of \( f_{n0} \) in equation (4.27),

\[ D \simeq \frac{\dot{n}kT_0}{\langle dW/dn \rangle} \quad (4.29) \]

which is equivalent to equation (4.19) in the Zeldovich theory. Substituting this value of \( D \) in \( \frac{\dot{n}}{D} \), we get:

\[ \frac{\dot{n}}{D} = \frac{1}{kT_0} \frac{dW}{dn} \]

Substituting this value of \( \frac{\dot{n}}{D} \) in equation (4.26), we get:

\[ f_n \simeq J \exp\left\{ -\frac{W(n)}{kT_0} \right\} \int_n^\infty \frac{1}{D} \exp\left\{ \frac{W(n)}{kT_0} \right\} dn \quad (4.30) \]

When \( r << r_c \), \( f_n \) is virtually the same as \( f_{n0} \). If \( n' \) denotes a certain fixed value of \( n << n_c \), equation (4.30) can be written in terms of \( J \) as:

\[ J \simeq f_{n0} \exp\left\{ -\frac{W(n')}{kT_0} \right\} \int_{n'}^\infty \frac{1}{D} \exp\left\{ \frac{W(n)}{kT_0} \right\} dn \quad (4.31) \]

However,

\[ f_{n0} = Ae^{-W/kT_0} \]

where \( A \) is generally taken to be \( N_0 \) which denotes the number of molecules in unit volume of liquid. Equation (4.31) thus reduces to:
\[ J \cong N_0 \frac{1}{\int_0^\infty D \exp \left( \frac{W(n)}{kT_0} \right) dn} \] (4.32)

Normally, the reversible work of formation of a critical nucleus, \( W \), is much greater than \( kT_0 \). Also, \( W \) has a maximum at \( r=r_c \), so the exponential under the integration sign will have a sharp maximum at the point \( n=n_c \). The pre-exponential factor, \( 1/D \), on the other hand, is far less sensitive to \( r \) (or \( n \)) as compared to the exponential term. It can therefore be evaluated at \( n=n_c \), and taken out from under the integration sign without a loss of accuracy. Doing this and changing from integration with respect to \( n \) to integration with respect to \( r \), we get:

\[ J \cong N_0 D_c \left( \frac{dr}{dn} \right) \frac{1}{\int_r^{\infty} \exp \left( \frac{W(r)}{kT_0} \right) dr} \] (4.33)

where \( r'<<r_c \). The fundamental quantity, \( D \), now needs to be determined at \( r=r_c \). For this, we make use of equation (9) and recall that for a critical bubble, \( \dot{n} \) is zero and also \( \frac{dW}{dn} \) is zero. Therefore an indeterminacy appears in equation (9). This indeterminacy is removed and we pass on from the independent variable \( n \) to the independent variable \( r \), and write:

\[ D_c = -\left( \frac{dn}{dr} \right) kT_0 \frac{1}{d^2W/dn} \] (4.34)
Now suppose that the vapor in the bubble (nucleus) is a perfect gas. The resulting rate of vaporization of molecules into the bubble from the supersaturated liquid can be expressed using the relation:

\[ \dot{n} = \frac{\pi \beta v_t r^2}{kT} \left( p_v - p \right) \] (4.35)

where \( v_t \) denotes the average thermal velocity of the vapor molecules impinging on the nucleus and is given by:

\[ v_t = \sqrt{\frac{8kT}{\pi m}} \] (4.36)

Here, \( m \) is the mass of a molecule. \( \beta \) is the condensation coefficient and for approximate calculations its value is taken to be 1 (Skripov 1974).

In order to assess the effect of hydrodynamics on the equation for nucleation rate, we may begin by considering a spherical aggregate of gas molecules of radius \( R \) growing in a very large volume of viscous Newtonian liquid. Figure 4.3 shows a schematic of the processes involved in the growth of an embryo. The growth of the bubble is impeded by viscous (and inertial) forces. The growing aggregate or cluster generates a velocity field and consequently a stress field that tends to retard the growth of the bubble. The rate of vaporization of the molecules into the bubble from the gas-liquid interface also impedes the nucleation rate. For mixtures, the rate of diffusion of the volatile component through the non-volatile material provides an additional impedance to the rate of bubble nucleation. Let \( t \) be the time measured from the instant of the formation of the aggregate and let \( r \) represent the radial coordinate. Considering
the center of the bubble to be motionless, the approximate equation of motion describing the dependence of radius of such a bubble on time, can be expressed in the following form:

\[
\rho r^2 \ddot{r} + \frac{3}{2} \rho r^2 \dot{r} = p - \frac{2\sigma}{r} - p_0 - \gamma \mu \frac{\dot{r}}{r}
\]  \hspace{1cm} (4.37)

where \(\rho\) is the density of the liquid, \(\mu\) is the viscosity of the liquid and \(\gamma\) is a numerical coefficient that has a value of \(\sim 4\).

Now, since

\[
\dot{r} = \frac{dr}{dt} = \frac{dr}{dr} \frac{dt}{dr}
\]

Substituting the value of \(p_r\) from equation (16) into equation (15), and using the relation above, we can write:

\[
\dot{n} = \frac{\pi \beta \nu r^2}{kT_0} \left\{ p_r(T_0) - p_0 - \frac{2\sigma}{r} - \gamma \mu \frac{\dot{r}}{r} \frac{dr}{dr} \right\}
\]  \hspace{1cm} (4.39)

We now take the derivative \(dn/dr\) at the point \(r=r_c\), and remember that at \(r=r_c\), \(p_V(T_0)=p_c\). We also recall the Laplace equation, which represents the condition for mechanical equilibrium for the critical bubble. Also, we remember that for a critical bubble, \(\dot{n}=0\) and therefore, \(\dot{r}=0\). Then,

\[
\left( \frac{dn}{dr} \right)_{r_c} = \frac{\pi \beta \nu r_c^2}{kT_0} \left\{ \frac{2\sigma}{r_c^2} \frac{\gamma \mu}{r_c} \frac{d\dot{r}}{d\dot{r}} \right\} - \rho r_c \left( \frac{d\dot{r}}{dr} \right)_{r_c}^2
\]  \hspace{1cm} (4.40)

Now, since we are treating the gas inside the bubble as a perfect gas, we can write \(pV=nkT\). Therefore,
\[
\frac{d}{dt}(nkT) = \frac{d}{dT}(pV)
\]

Hence, by definition, we can write:

\[
\dot{n} = \frac{1}{kT} \frac{d}{dT} \left( \frac{4}{3} \pi r^3 p \right)
\]  

(4.41)

Substituting the value of \( p \) from equation (16) and taking the derivative \( d\dot{n}/dr \) at the point \( r=r_c \), we get:

\[
\left( \frac{d\dot{n}}{dr} \right)_{r_c} = \frac{4 \pi r_c^2}{kT_0} \left( \frac{dr}{dr} \right)_{r_c} \left\{ \frac{4 \sigma}{3 r_c} + P_0 + \frac{1}{3} \gamma \mu \left( \frac{dr}{dr} \right)_{r_c} + \frac{2}{3} \mu r c^2 \left( \frac{dr}{dr} \right)_{r_c}^2 \right\}
\]  

(4.42)

If we now equate equations (4.40) and (4.42), we get the following cubic equation for \( (dr/dr)_{r_c} \):

\[
\frac{2}{3} \mu r c^2 \left( \frac{dr}{dr} \right)_{r_c}^3 + \left[ \frac{1}{3} \gamma \mu + \frac{2 \beta v r c}{4} \right] \left( \frac{dr}{dr} \right)_{r_c}^2 + \left[ \frac{\beta v r c}{4 r_c} + P_0 \right] \left( \frac{dr}{dr} \right)_{r_c} - \frac{\beta v r c}{2 r_c^2} = 0
\]  

(4.43a)

In dimensionless form, equation (4.43a) can be written as:

\[
\alpha' z^3 + \frac{8}{9} \alpha \left( \frac{27}{64} \alpha' \right) z^2 + \frac{2}{3} \left( \frac{\alpha + 3 - b}{b} \right) z - \frac{1}{2} = 0
\]  

(4.43b)

where, the dimensionless quantities in equation (4.43b) are defined as:

\[
z = \frac{\left( \frac{dr}{dr} \right)_{r_c}}{\frac{r_c}{\beta v_t}}
\]  

(4.44)

\[
\alpha = \frac{3 \beta v_t \gamma \mu}{8 \sigma}
\]  

(4.45)

\[
\alpha' = \frac{2 \beta^2 v_t^2 r c}{3 \sigma}
\]  

(4.46)
\[ b = \frac{2\sigma}{r_c P_c} \quad (4.47) \]

Equation (4.43a) (or 4.43b) can be solved to determine \((d\dot{n}/dr)_c\). This value can be substituted in Equation (4.34) to obtain \(D_C\) and both the values of \(D_C\) and \((d\dot{n}/dr)_C\) can be substituted in Equation (4.33) to obtain \(J\). The result obtained will account for the limitations of viscosity and inertia on the nucleation rate.

Note that the coefficient of the inertial term in Kagan’s paper has been incorrectly reported as 1/3 in the literature (instead of 2/3 as in equation 4.46 above).

Since inertia is not expected to be important at the low Reynold’s number flow conditions at which we are operating, we obtain a particular solution of equation 4.43(a) for the case when viscosity of the fluid is the only factor limiting the rate of growth of precursor embryos to critical nuclei sizes and beyond. The criterion justifying neglect of the inertia terms has been reported as \(\omega'/\omega^2 < 1\) in the literature, however the physical basis of making such an assumption is not clear. Blander (Blander 1979) suggests that the criterion justifying neglect of inertia terms should be \(\omega' = 0\).

For the case where the inertia terms (i.e. those containing \(\omega'\)) can be neglected, equation 4.43(a) becomes:

\[ \frac{8}{9} \alpha \omega^2 + \frac{2}{3} \left( \omega'^2 \frac{3-b}{b} \right) z - \frac{1}{2} = 0 \quad (4.48) \]

Equation (4.48) is a quadratic equation in \(z\) and can be easily solved analytically to give:
\[ z = \frac{3}{8} \left\{ -\frac{1}{\omega} \left( \frac{\omega + 3b}{b} \right) + \sqrt{\left( \frac{1}{\omega} \left( \frac{\omega + 3b}{b} \right) \right)^2 + \frac{4}{\omega}} \right\} \]  

(4.49)

Equating this expression for \( z \) with the right hand side of equation (4.44), we get:

\[ \left( \frac{dn}{dr} \right)_{r=rc} = 12 \pi \beta v \sigma 1 \frac{1}{kT_0 b} \left( \frac{\omega + 3b}{b} \right) + \sqrt{\left( \frac{\omega + 3b}{b} \right)^2 + 4\omega} \]

(4.50)

Substituting this value of \( (dn/dr)_{r=rc} \) in equation (4.34), we can evaluate \( D_C \) as:

\[ D_C = \frac{3 \beta v}{2} \frac{1}{b} \left( \frac{\omega + 3b}{b} \right) + \sqrt{\left( \frac{\omega + 3b}{b} \right)^2 + 4\omega} \left( \frac{dn}{dr} \right)_{r=rc} \]

(4.51)

The above expression for \( D_C \) is substituted in Equation (4.33). The integral in equation (4.33) can be evaluated using the method of steepest descent.

According to the method of steepest descent, for an integral of the general form:

\[ I(s) = \int_C g(z) e^{sf(z)} dz \]

where \( s \) is real, large and positive, and \( C \) is the contour of the integral, we can write:

\[ I(s) \approx g(z_0) e^{sf(z_0)} \left| sf''(z_0) \right|^{1/2} \int_{-\infty}^{\infty} e^{-t^2/2} dt \]

Noting that \( \int_{-\infty}^{\infty} e^{-t^2/2} dt \) is just a gauss error integral equal to \( \sqrt{2\pi} \), we finally obtain,

\[ I(s) \approx \frac{\sqrt{2\pi} g(z_0) e^{sf(z_0)}}{\left| sf''(z_0) \right|^{1/2}} \]
Also, noting that $s=1/kT_0$ is real, large and positive, $f(z) = W(r) = (4/3)\pi r_c^2 \sigma$ and $f''(z) = W''(r) = -8\pi \sigma$, we finally get the expression for $J$ for the viscosity-limiting case.

$$J = 3N_0 \frac{\beta v_f}{b} \frac{\sigma}{kT_0} \frac{1}{\left(\frac{\omega+3b}{b}\right) + \left(\frac{\omega-3b}{b}\right)^2 + 4\omega} e^{-1/3K}$$  \hspace{1cm} (4.52)

where,

$$K = \frac{4\pi r_c^2 \sigma}{kT_0}$$

4.7 Evaluation of $\Delta P$ in the expression for reversible work of critical nucleus formation

As explained in the previous section, the work required for critical nucleus formation can be expressed in the following form:

$$W = \frac{16\pi \sigma^3}{3\Delta P^2}$$  \hspace{1cm} (4.21)

The composition of the gas phase can be assumed to be pure CO$_2$ since the solubility of PS in CO$_2$ is negligible. The composition of the polymer rich phase can be determined from the equality of the chemical potential of CO$_2$ in the gas (vapor) phase and the liquid (polymer) phase.

The construction for evaluation of $\Delta P$ is shown in Figure 4.4. Blowing agent chemical potential is plotted vs. pressure for the case of 1.0 wt% CO$_2$ dissolved in PS. The point of intersection of the two curves corresponds to saturation conditions (the
binodal). $p_E$ is the ambient pressure (i.e. the pressure of the surrounding liquid). $p^*$ is the pressure inside the critical nucleus. The difference in the chemical potentials at $p_E$ provides the driving force for nucleation. Once the liquid phase becomes metastable in any vapor-liquid system undergoing transition in the direction of stable liquid (or liquid mixture) to stable vapor (or vapor mixture), the ambient pressure on the liquid, $p_0$, is less than the pressure on it at equilibrium (Blander and Katz 1975). The Poynting correction accounts for the fact that the metastable liquid is at an actual pressure $p_0$ that is different from the saturation pressure $p^*$ of the liquid corresponding to vapor-liquid equilibrium. The Poynting correction factor can be expressed as:

$$
\exp\left\{\frac{\dot{V}_1 dp}{RT}\right\}
$$

where $\dot{V}_1$ is the partial molar volume of the condensed phase. The Poynting correction factor can become significant for situations when $p^*$ is much different from $p_0$ since it is an exponential function of pressure. If the condensed phase is not near its critical point, the volume of the liquid usually does not show a pronounced dependence on pressure and temperature, and in that case the liquid can be considered as incompressible and the Poynting correction takes the following simple form (Prausnitz, Lichtenthaler et al. 1999):

$$
\exp\left(\frac{\dot{V}_1 (p_0 - p^*)}{RT}\right)
$$

For the PS-CO$_2$ system, $\dot{V}_1$ can be evaluated using the following relation (Sanchez, I.C and Lacombe, R.H., 1978):
\[
\dot{V}_1 = \frac{\partial \mathcal{V}}{\partial N_1}_{T,P,N_2} = n_1^0 v_1 \left[ \tilde{v} + \varphi_2 \frac{d\tilde{v}}{d\varphi_1} \right] \quad (4.53)
\]

where \( V \) is the volume of the mixture. The term \( \frac{d\tilde{v}}{d\varphi_1} \) can be evaluated as:

\[
\frac{d\tilde{v}}{d\varphi_1} = -\psi \tilde{T} P^* \beta \quad (4.54)
\]

where \( \beta \) is the isothermal compressibility of the mixture. \( \tilde{T} P^* \beta \) can be expressed by the following relation:

\[
\tilde{T} P^* \beta = \frac{1}{v \left[ 1/(\tilde{v} - 1) + 1/r - 2/\tilde{v} \tilde{T} \right]} \quad (4.55)
\]

\( \psi \) is a dimensionless function defined by:

\[
\psi = \left[ \tilde{\rho} \left( v \left( \frac{1}{r_1} - \frac{1}{r_2} \right) + \left( \varphi_1^2 - \nu \varphi_2^2 \right) X_1 \right) - v \left( \frac{1}{r_1^0} - \frac{1}{r_2^0} \right) + \frac{\tilde{P} \tilde{v}}{\tilde{T}} (v - 1)(\varphi_1 + \nu \varphi_2) \right] \left( \varphi_1 + \nu \varphi_2 \right)^2 \quad (4.56)
\]

\( X_1 \), which characterizes the interaction between the solute and the solvent, is given as:

\[
X_1 = \frac{\Delta P^* v_1^*}{kT} \quad (4.57)
\]

Figure 4.5 depicts the difference between \( p_{\text{sat}} \) and \( p^* \) on the application of the Poynting correction. Although the absolute value of the Poynting correction is small, the effect of this correction on the nucleation rate is significant, since the nucleation rate, \( J \), varies with \( \Delta P \) as \( \exp(-1/\Delta P^2) \).
4.8. Surface Tension of the PS-CO$_2$ system

The surface tension of the PS-CO$_2$ system was measured by Li et al. at 200°C using axisymmetric drop shape analysis (Li, Lee et al. 2004). For conditions for which the surface tension data is not available, Density Gradient Theory can be used to compute the interfacial tension of the polystyrene – carbon dioxide interface. The method is described in detail by Harrison et al. and Li et al. (Harrison, Johnston et al. 1996; Li, Lee et al. 2004). Their implementation of the method is described in brief below. The binary system of interest is the PS-CO$_2$ system. The subscript 1 is used to designate CO$_2$, while the subscript 2 is used to denote PS in the expressions that follow.

The SLEOS parameters that characterize the PS-CO$_2$ system are available in Sanchez. The SLEOS parameters vary only slightly with temperature so that accounting for these variations only causes small discrepancies in the surface tension calculations. In the SLEOS formulation, a real fluid is completely characterized by three molecular parameters $T^*$, $P^*$, and $\rho^*$. $\rho^*$ is the close-packed density of the disordered fluid (which is about 10% smaller than the crystalline (ordered) density of the corresponding fluid). $T^*$ can be determined by the expression:

$$T^* = \frac{\varepsilon^*}{k}$$  \hspace{1cm} (4.58)

where $\varepsilon^*$ denotes the nearest neighbor mer interaction energy and $k$ is the Boltzmann constant. The characteristic pressure $P^*$ is defined as:

$$P^* = \frac{\varepsilon^*}{\nu^*}$$  \hspace{1cm} (4.59)
where, \( v^* \) denotes the close-packed mer volume. Note that the characteristic pressure \( P^* \) is equal to the cohesive energy density (CED) of the fluid, since,

\[
CED = \frac{\Delta E_{\text{vap}}}{V} = \frac{\rho \varepsilon^*}{r v^*} \equiv P^*
\]

(4.60)

where \( \Delta E_{\text{vap}} \) is the energy required to convert 1 mol of the fluid from the close-packed state (reduced density, \( \tilde{\rho} = 1 \)) to a vapor of vanishing density (\( \tilde{\rho} = 0 \)) and \( V \) is the mixture volume. Pair-wise additivity of the characteristic pressures in the close-packed mixtures is assumed. Thus,

\[
P^* = \phi_1 P_1^* + \phi_2 P_2^* - \phi_1 \phi_2 \Delta P^*
\]

(4.61)

where

\[
\Delta P^* = P_1^* + P_2^* - 2P_{12}^*
\]

(4.62)

\( \Delta P^* \) is the only parameter in the SLEOS that characterizes a binary mixture.

Sanchez and Lacombe found it convenient to characterize the interaction between the polymer and the gas phase in terms of a dimensionless parameter, \( \zeta \), which measures the deviation of \( P_{12}^* \) from the geometric mean.

\[
\zeta = \frac{P_{12}^*}{(P_1^* P_2^*)^{1/2}}
\]

(4.63)

Equation 4.76 therefore becomes:

\[
\Delta P^* = P_1^* + P_2^* - 2\zeta(P_1^* P_2^*)^{1/2}
\]

(4.64)

Sato et. al. used the interaction parameter \( k_{ij} \) to characterize a binary mixture. The interaction parameter, \( k_{ij} \), is simply \( 1 - \zeta \) in the Sanchez-Lacombe notation.

Following Sato’s notation, we can write equation (4.64) as:
\[
\Delta P^* = P_1^* + P_2^* - 2(1 - k_T)(P_1^* P_2^*)^{1/2} \tag{4.65}
\]

According to the density gradient theory, for a phase-separated binary system, the interfacial tension can be expressed as:

\[
\gamma = 2^{1/2} \left[ k_{11}^{1/2} + k_{22}^{1/2} \left( \frac{\Delta \rho_m}{\Delta \rho} \right) \right] \rho \Delta \alpha^{1/2} d\phi \tag{4.66}
\]

Here, \( \Delta \alpha \) is the change in the interfacial free energy across the interface. It is defined as the difference between the actual free energy in the interfacial region and that which would exist if each phase existed, with corresponding bulk phase properties, to a dividing line of zero thickness.

\[
\Delta \alpha = \frac{\phi_i}{v_{m,i}} \mu_i^e - \frac{\phi_i}{v_{m,2}} \mu_2^e \tag{4.67}
\]

In the above equation, \( g \) is the Gibbs free energy density of a homogeneous system for a given composition within the interfacial region, \( \mu_1^e \) and \( \mu_2^e \) are the equilibrium chemical potentials of the two components comprising the binary system and \( v_{m,i}^* \) are the characteristic monomer volume defined as:

\[
v_{m,i}^* = \left( \frac{MW_i^*}{\rho_i^*} \right) / (DP) \tag{4.68}
\]

where \( MW_i \) refers to the molecular weight of species \( i \), and \( DP \) is the degree of polymerization.

The Gibbs free energy density, \( g \), can be expressed as:

\[
g = -\tilde{\rho} P^* + \frac{P}{\tilde{\rho}} + kT \left[ \frac{(1/\tilde{\rho} - 1)\ln(1 - \tilde{\rho})}{v_0} + \frac{1}{v} + \frac{\phi_1 \ln \phi_1}{v_1} + \frac{\phi_2 \ln \phi_2}{v_2} \right] \tag{4.69}
\]
Here,

\[
\frac{1}{v^*_0} = \phi_1 \left( \frac{P^*_1}{kT_1^*} \right) + \phi_2 \left( \frac{P^*_2}{kT_2^*} \right)
\]  

(4.70)

\[
\frac{1}{v^*_i} = \frac{\phi_1}{v^*_1} + \frac{\phi_2}{v^*_2}
\]  

(4.71)

and

\[
v^*_i = \frac{MW_i}{\rho_i^*}
\]  

(4.72)

\(\phi_i\), the volume fraction of each component, is defined as:

\[
\phi_i = \frac{(w_i / \rho_i^*)}{\sum (w_j / \rho_j^*)}
\]  

(4.73)

where \(w_i\) is the weight fraction of each component.

Figure 4.6 shows the variation of macroscopic surface tension with temperature for the PS-CO\(_2\) system as obtained from reference (Leung, Park et al. 2006). The surface tension obtained by either experimental measurements or by gradient theory as described above is too high for the bubble nucleation rate to have a non-zero realistic value.

Tolman’s approximation (Tolman 1949) to account for the curvature dependence of surface tension has been invoked in this work to override the capillary approximation. In order to obtain values of the parameter \(\delta\), which would give a nucleation rate of the same order as ones observed experimentally, experimentally observed bubble densities are matched (to within an order of magnitude) with theoretically predicted values at the centerline for the temperature of interest. On first trial, the matching is only an approximation and is not exact. If a constant value of \(\delta\) is
used throughout the die (for a specific inlet melt temperature) and the nucleation rates across the die cross-section are predicted at the die exit (including hydrodynamic and diffusional constraints to the rate of homogeneous nucleation for the PS-CO$_2$ system), nucleation rate profiles as shown in Figure 4.7 are obtained. The curvature dependence of surface tension for the small critical nuclei is expressed using the following simple expression given by Tolman.

\[
\log \frac{\sigma}{\sigma_0} = \int_{\infty}^{r} \left( \frac{2\delta}{r^2} \right) dr
\]  

(4.74)

\[
\frac{\sigma}{\sigma_0} = \frac{1}{1 + \frac{2\delta}{r}}
\]  

(4.74a)

We have used $\delta$ as a fitting parameter in the equation following the “bubble-density-matching-approach” discussed above. The variation of $\delta$ with absolute temperature for the PS-CO$_2$ system is shown in Figure 4.8. The radii of the critical nucleus corresponding to these values of $\delta$ were found to be ~ 3.05 to 3.20 nm for the processing conditions studied. The curvature dependent surface tension was found to increase with an increase in temperature as against the macroscopic surface tension which decreases with increasing temperature (see Figure 4.9).

Equation (4.74) is strictly valid only in the limit when $\delta/r \ll 1$, which is not the case here. A more exact form of the relationship between $\delta$ and $r$ is given by the following expression:
\[
\log \frac{\sigma}{\sigma_0} = \int_0^\infty \frac{r^2}{1 + [2\delta/r][1 + \delta/r + \delta^2/(3r^2)]} e^{-r} dr
\]  

(4.75)

\[
\Gamma = \frac{\rho' - \rho''}{(\rho' - \rho'')} = \delta \left[ \frac{1 + \delta}{r^2} + \frac{1}{3} \delta^2 \right]
\]

\(\Gamma\) is known as the superficial density and Tolman defines it as the difference – per unit area of the boundary surface – between the actual amount of fluid in the two-phase system and the amount which it would contain if the liquid and vapor phases retained uniform densities to the Gibbs surface of tension as the dividing surface between the phases. The quantities \(\rho'\) and \(\rho''\) refer to the bulk densities of the homogeneous condensed phase and the vapor phase respectively.

Both equations 4.74 and 4.75 were evaluated numerically for \(\delta = 5.3\) nm and \(\delta = 8.45\) nm (corresponding respectively to the extremes of temperature, 240°C and 140°C in the processing window). The function in the integral (for \(\delta = 8.45\) nm) is plotted against the radius of the critical nucleus in Figure 4.10. The function in the integral for \(\delta = 5.3\) nm follows a similar trend and therefore a plot of the function is not reproduced here. Although the approximate equation under-evaluates the function for all values of the radii, the trends of the evaluated functions are remarkably similar. For a critical nucleus radius of 3.0 nm, the numerically evaluated value of the integral for the approximate equation (Equation 4.74) and the Exact equation (Equation 4.75) is not more than 17%. Since the approximate equation (Equation 4.74) is easier to use analytically, this equation has been used for evaluating the curvature-dependence of the surface tension in this work.
4.9. Diffusional Constraints on Nucleation Rate

A bubble can only grow by the addition of more vapor molecules to it from the liquid phase. The rate of bubble growth (or shrinkage) with the addition (or subtraction) of bubbles is slowest near the critical size. Blander et. al. (Blander and Katz 1975) write the following relation for the net rate of vaporization of molecules into a bubble:

\[ \dot{n} = \frac{A}{\sqrt{2\pi nkT}} (p_r - p) \]  

(4.76)

At the critical size, the net rate of vaporization of molecules into the bubble \((dn/dt)\) is zero and \(p = p_V\).

At steady state the net flux of molecules diffusing to the gas-liquid interface from the liquid would be balanced by the net flux of molecules released into the bubble. This steady state condition for the net flux of molecules at the gas liquid boundary can be written as:

\[ D \left( \frac{\partial C}{\partial R} \right)_{R=r_c} = \frac{(p_r - p)}{\sqrt{2\pi nkT}} \]  

(4.77)

At distances sufficiently removed from the bubble wall, the bulk liquid has the concentration \(C_0\). \(C_0\) is the equilibrium concentration at a vapor pressure equal to the ambient pressure \(p_0\). Thus,

As \(r \to \infty\), \(C \to C_0\)
Solving the mass transport equation for the transfer of bubbles into the vapor and taking account of the above boundary conditions, Blander et al. (Blander and Katz 1975) derived a relation that accounts for diffusion as an impedance to the steady state nucleation rate:

\[ J_D = \frac{J}{1 + \delta_D} \]  

(4.78)

where \( \delta_D \) is the factor that accounts for the impedance arising from the diffusion of the volatile component into the interface and can be expressed as (Blander, Hengstenberg et al. 1971; Blander and Katz 1975; Blander 1979):

\[ \delta_D = \frac{2\sigma (dp/dC)p_v}{D\sqrt{2\pi nkT(p_v - p_0)}} \]  

(4.79)

where \( D \) is the diffusion coefficient of the volatile solute in the solvent. For a solution for which the Henry’s law is obeyed, \( (dp/dC) = p/C \) where \( p \) is the pressure and \( C \) is the concentration of volatile constituent in the in the liquid mixture (number per unit volume). \( \delta_D \) can then be written as:

\[ \delta_D = \frac{2\sigma}{D\sqrt{2\pi nkT(C_V - C_0)}} \]  

(4.80)

where, \( C_V \) is the concentration of solute in equilibrium with the gaseous solute at pressure \( p_v \).
4.10. Calculation of Diffusional Constraint on Nucleation Rate

In order to obtain an approximate idea of the importance of the diffusional constraint on the rate of homogeneous nucleation for the polystyrene-carbon dioxide system, the first step is to estimate $C_V$ and $C_0$ for the PS-CO$_2$ system in the Henry’s law limit, which, in turn, requires solubility data of CO$_2$ in polystyrene under the conditions of interest. A number of investigators have studied the diffusion and solubility of simple gases and volatile liquids in glassy and rubbery polymers as well as in polymer melts. Newitt and Weale (Newitt and Weale 1948) were probably the first investigators to obtain experimental data for the solubility and diffusion coefficient of carbon dioxide in molten polystyrene for temperatures ranging from 403°K to 463°K and pressures varying from 80 to 300 atm. They found that Henry’s law held for reasonably high pressures for this system and that no appreciable effect of pressures on gas diffusivities could be observed. Durrill and Griskey (Durrill and Griskey 1966; Durrill and Griskey 1969) obtained experimental data for the dissolution and diffusion behavior of CO$_2$ in PS at 462 K and for pressures up to 20 atm. They also found that the Henry’s law regime held for the dissolution of CO$_2$ in PS up to 20 atm and that pressure had a small effect on the diffusivity of CO$_2$ in PS under the conditions studied. Additionally, they showed that the available solubility data for a number of gases (CO$_2$ among them) in Polystyrene could be represented in terms of a linear relationship between the log of the Henry’s law constant and either the Lennard Jones force constant ($\varepsilon/k$) or the critical temperature ($T_c$) of the solute.
Later, Stern et. al. (Stern, Mullhaupt et al. 1969) found that the solubility data for a number of solutes in amorphous polyethylene over a wide range of temperatures could be represented as a linear relationship between the log of the Henry’s law constant and \((T_c/T)^2\). Stiel and Harnish (Stiel and Harnish 1976) followed an approach similar to that of Stern et. al. (Stern, Mullhaupt et al. 1969) to correlate solubility data for several gases and volatile liquids in molten polystyrene. They used a highly accurate chromatographic measurement technique to obtain solubility data for temperatures ranging from 408 to 503 K and pressures from 1 to 4 atm. They also found that for all solutes studied the data was in substantial agreement with a linear correlation of the following form:

\[
\ln \left( \frac{1}{K_p} \right) = A + B \left( \frac{T_c}{T} \right)^2
\]  

(4.81)

where \(K_p\) is a Henry’s law constant. However, CO\(_2\) was not among the solutes that Stiel and Harnish (Stiel and Harnish 1976) studied.

Recently, Sato et. al. (Sato, Yurugi et al. 1996; Sato, Takikawa et al. 2001) have carried out solubility measurements for the PS-CO\(_2\) system for temperatures ranging from 373.15 to 473.15 K and for pressures up to 20 MPa. They propose the following correlation to describe the solubility behavior of CO\(_2\) in PS:

\[
\ln \left( \frac{1}{K_p} \right) = 6.498 + 2.380 \left( \frac{T_c}{T} \right)^2
\]

(4.82)

Average absolute deviations of their Henry’s law constants as obtained by the above correlation deviated from ones obtained by experimental solubility measurements by
less than 2.2 % for the PS-CO$_2$ system. The critical temperature $T_c = 304.1$ K for carbon dioxide was used to obtain the above correlation. Henry’s constants, $K_p$, in the above equation, have the units of [kg MPa cm$^{-3}$ (STP)]. The Henry’s constant $K_p$ relates the solubility of CO$_2$ in PS and the pressure through the following relation (Stiel, Chang et al. 1985; Han 1987):

$$py_1 = K_p V_1^0$$

(4.83)

where $y_1$ is the mole fraction of the solute in the vapor phase and $V_1^0$ is the solubility (cm$^3$ solute/kg polymer at 273.15 K and 1 atm).

Using the above information, $C_V$ and $C_0$ were computed in the equation for $\delta_D$.

In order to compute the diffusion coefficient of CO$_2$ in PS, the approach of Areerat et. al. (Areerat, Funami et al. 2004) was followed. The mutual diffusion coefficient of a small solute molecule in a polymer melt can be estimated from the following relation proposed by Vrentas and Duda (Vrentas and Duda 1977):

$$D_{mutual} = \frac{x_1 D_1 + x_2 D_2 \left( \frac{\partial \mu_1}{\partial n_1} \right)_{T,P}}{RT}$$

(4.84)

where $x_1$ and $x_2$ refer to the mole fractions of the small solute and the polymer melt respectively, $D_1$ and $D_2$ are the self-diffusivities of the solute and of the polymer respectively and $\mu_1$ is the chemical potential of the small molecules in the polymer. For the PS/CO$_2$ system, since the self-diffusivity of the bulky PS chain-molecule is always much lesser than the self-diffusivity of the small CO$_2$ molecule, $x_1 D_2 << x_2 D_1$, and the equation above can be simplified as:
The self-diffusion coefficient of CO\textsubscript{2} in PS, D\textsubscript{1} or D\textsubscript{self} can be computed using the following expression, which is a modification of the theories of Maeda and Paul (Maeda and Paul 1987) and Fujita (Fujita 1961).

\[
D_{self} = RTA\exp\left[\frac{-B}{(\hat{V}_{mix}^{0} - \hat{V}_{mix}^{0})}\right] 
\]  \hspace{1cm} (4.86)

In the above equation, \(\hat{V}_{mix}\) refers to the specific volume of the PS-CO\textsubscript{2} mixture. The density of the single phase PS-CO\textsubscript{2} mixture, \(\rho\), can be evaluated using SLEOS:

\[
\rho = \rho^{0}\tilde{\rho}
\]

And then, \(\hat{V}_{mix}^{0} = 1/\rho\).

\(\hat{V}_{mix}^{0}\) refers to the occupied specific volume of the PS-CO\textsubscript{2} solution at absolute zero temperature. It depends on the weight fraction of CO\textsubscript{2} in polymer as follows:

\[
\hat{V}_{mix}^{0} = (1-w)\hat{V}_{poly}^{0} + w\hat{V}_{CO_{2}}
\]  \hspace{1cm} (4.87)

where \(w\) is the weight fraction of CO\textsubscript{2} in the mixture and \(\hat{V}_{poly}^{0}\) and \(\hat{V}_{CO_{2}}\) represent the occupied specific volume of the pure polymer and the pure gas alone.

\(\hat{V}_{poly}^{0}\) and \(\hat{V}_{CO_{2}}\) can be obtained from a knowledge of the Van der waals volume, \(V_{w}\), and through the use of the approximate equation suggested by Bondi (Bondi 1968):

\[
\hat{V}_{poly}^{0} \simeq 1.3V_{w}
\]
Value for $\dot{V}_{CO_2}$ obtained in this way is 25.61 cm$^3$/mol. A group contribution method has to be used to evaluate $V_w$ for polymers – Sugden (Sugden 1927) has reported a value of 66.88 cm$^3$/mol for $V_w$ (for PS) while Bondi has reported a value of 62.8 cm$^3$/mol for $V_w$. The corresponding values for $\dot{V}^0_{poly}$ (for PS) are 86.94 cm$^3$/mol and 81.64 cm$^3$/mol respectively. We have used a value of $\dot{V}^0_{poly} = 81.64$ cm$^3$/mol for our calculations.

In order to obtain $\left( \frac{\partial \mu}{\partial \ln x_1} \right)_{T,P}$, a derivative of equation (3.12) with respect to ln($x_1$) needs to be taken, where $x_1$ refers to the mass fraction of component 1 (same as w in the equation above). $\left( \frac{\partial \mu}{\partial \ln x_1} \right)_{T,P}$ can now be expressed as:

$$\left( \frac{\partial \mu}{\partial \ln x_1} \right)_{T,P} = \left( \frac{\partial \mu}{\partial \ln \phi_1} \right)_{T,P} \left( \frac{\partial \ln \phi_1}{\partial \ln x_1} \right)_{T,P} = \left[ 1 + \phi_1 \left( \frac{M_{w_2}\rho_2^* - M_{w_1}\rho_1^*}{M_{w_1}\rho_1^*} \right) \right] \left( \frac{\partial \mu}{\partial \ln \phi_1} \right)_{T,P}$$

(4.88)

where $\phi_1$ is the volume fraction of CO$_2$ in PS, $\rho_1^*$ and $\rho_2^*$ represent the characteristic densities of the CO$_2$ and PS respectively and $M_{w_1}$ and $M_{w_2}$ denote the average molecular weights of CO$_2$ and PS respectively. The chemical potential of CO$_2$, $\mu_1$, was evaluated for different values of ln($\phi_1$), and the term $\left( \frac{\partial \mu}{\partial \ln \phi_1} \right)_{T,P}$ was numerically calculated at the temperature and pressure of interest as shown in the figure.
\( D_{\text{mutual}} \) obtained by substitution of all the above values into equation (4.85) yields a value of \( \sim 10^{-9} \text{m}^2/\text{s} \) for \( \text{CO}_2 \) in PS at 200°C and 30.22 bar pressure. It is now possible to compute \( \delta_D \) by writing equation (4.80) in the following alternate form:

\[
\delta_D = \frac{2\sigma}{D\sqrt{2\pi MR}(C_v - C_0)}
\]

where \( \sigma \) has the units \( \text{J/m}^2 \), \( D \) is expressed in \( \text{m}^2/\text{s} \), \( M \) in kg/mol, \( T \) in K and \( C_v \) and \( C_0 \) are expressed in the units of moles solute/m³ solution. Figure 4.11 shows a plot of \( \delta_D \) for different values of temperature. As can be easily seen from the figure, \( \delta_D \) is large for all temperatures and contributes to the decrease in nucleation rate by at least three orders of magnitude.

### 4.11. Calculation of Viscosity Constraint on Nucleation Rate

The viscosity constraint on the rate of homogeneous nucleation can be computed using equation (4.52):

\[
J = 3N_0 \beta V_t \left[ \frac{\sigma}{kT_0} \frac{1}{(\omega + \frac{3b}{b})^{(\omega + \frac{3b}{b})} + \left(\frac{\omega - \frac{3b}{b}}{b}\right)^2 + 4\omega} \right] e^{-1/3K}
\]

(4.52)

In the absence of any impedance from viscous forces (that is, \( \omega = 0 \)), equation (4.52) would have the following form:

\[
J = \frac{N_0 \beta V_t}{2} \left[ \frac{\sigma}{kT_0} e^{-1/3K} \right]
\]

(4.90)

A plot of \( J/J_n \) for different radial cross-sections in the die can now give an estimate of the importance of viscous forces on the rate of homogeneous nucleation. Such a plot is
presented as Figure 4.12. As can be seen from the figure, viscosity can impede the rate of homogeneous nucleation along the centerline (where the viscosity is the highest) by ten orders of magnitude.

4.11. Time lag of Nucleation

While the location of the binodal is within the extrusion foaming die and quite far removed from the die exit (see Fig 3.6), the first observable nuclei appear only very close to the die exit for all processing conditions studied in this work. Figure 4.13 shows the nucleation rate along the die length at 200°C for constant values of delta corresponding to specific inlet melt temperatures. The figure also illustrates the relative importance of the diffusional and viscous constraints on the bubble nucleation rate along the centerline. The combined effect of viscous and diffusional constraints is to reduce the rate of bubble nucleation at the centerline by thirteen orders of magnitude. Figure 4.14 shows that bubble nucleation is so small right down-stream of the saturation surface (the binodal) that it cannot be observed experimentally. There is a certain delay period (which is referred to here as the time lag of nucleation) between the PS-CO₂ solution crossing the binodal and the first observable nuclei appearing in the system. At 200°C temperature and 10 rpm screw rotation rate, the calculated time lag is ~ 8.1 milliseconds at the centerline and ~ 13.1 milliseconds at r/R=0.88. This time lag is about three-four orders of magnitude higher than the one observed for bubble nucleation in low-molecular weight liquids.
Figure 4.1: Plot of free energy vs. dimension of the nucleus. The dimension of the nucleus can be its radius, volume or the number of molecules in it.
Figure 4.2: The motion along the phase axis takes place in discrete jumps of $\pm \lambda$. $\lambda$ has the dimensions of the value plotted on the x-axis of Figure 1.
Gas inside bubble at $T,p$

Outside Liquid maintained at $T_0,p_0$

Bubble of volume $V_0$

Bubble of volume $V_0'$

Direction of molecular vaporization into the bubble

Direction of diffusion of molecules into the bubble

Direction for Bubble Growth

Figure 4.3 Processes involved in the growth of an embryo. The growth of the bubble is impeded by viscous (and inertial) forces. The rate of vaporization of the molecules into the bubble from the gas-liquid interface also impedes the nucleation rate (especially in boiling nucleation). For mixtures, the rate of diffusion of the volatile component through the non-volatile material provides an additional impedance to the rate of bubble nucleation.
Figure 4.4: Plot showing blowing agent chemical potential vs. pressure for the case of 1.0 wt% CO\textsubscript{2} dissolved in PS at 200°C temperature. The point of intersection of the two curves corresponds to saturation conditions (the binodal). p\textsubscript{E} is the ambient pressure (i.e. the pressure of the surrounding liquid). p* is the pressure inside the critical nucleus. The difference in the chemical potentials at p\textsubscript{E} provides the driving force for nucleation.
Figure 4.5: Difference between $p_{\text{sat}}$ and $p^*$ on the application of the Poynting correction.
Figure 4.6: The variation of macroscopic surface tension with temperature for the PS-CO₂ system.

\[ y = -0.0025654 \ln(x) + 0.0398260 \]

\[ \text{Log. (surface tension)} \]

\[ R^2 = 0.9965563 \]
Figure 4.7: Nucleation rate at the die exit for which delta has been approximated.
Figure 4.8: The variation of $\delta$ with absolute temperature for the PS-CO$_2$ system.
Figure 4.9: Variation of curvature-dependent surface tension with temperature.
Figure 4.10: Value of the integral in equations (4.74) and (4.75) for various $r$ (delta = 8.45 nm).
Figure 4.11: Effect of diffusional constraints on the rate of nucleation.
Figure 4.12: Effect of viscosity constraint on the rate of nucleation.
**Figure 4.13**: Nucleation rate along the die centerline (200°C) for constant values of delta corresponding to specific temperatures. $J$ refers to the nucleation rate without hydrodynamic or diffusional constraints. $J_\mu$ refers to the nucleation rate accounting for only the high-viscosity constraint. $J_\mu,D$ refers to the nucleation rate accounting for both the viscosity and diffusional constraints on the rate of nucleation.
Figure 4.14: The time lag of nucleation – defined here as the time period which elapses between the PS-CO2 solution crossing the binodal and the first nuclei appearing in the system – is ~ 8.1 milliseconds at the centerline and ~ 13.1 milliseconds at r/R=0.88
CHAPTER 5

CONCLUSIONS AND FUTURE WORK

5.1. Main Results from this Work

An internally consistent viscoelastic scaling approach has been developed to scale up the shear viscosity of the fluid that accounts for the temperature, pressure as well as concentration dependence of the shear viscosity in a dynamic way along each cell element in the mesh of the foaming die. The pressure drop values predicted by the simulations give good qualitative (and even semi-quantitative) agreement with experimentally obtained pressure drop values under nearly identical flow conditions.

Simulations have been performed for the flow of a polymer diluent solution through an abrupt axisymmetric contraction extrusion foaming die. The axial profiles of the basic field variables: pressure, temperature and velocity – are obtained for different radial sections of the capillary die. From knowledge of the pressure and
temperature fields and using the SLEOS, the location of the saturation curves (also referred to as “the surface of incipient nucleation” in this work) in the foaming die are estimated. The shape of the surface of nucleation onset is compared with the handful of experimental data that have been reported in the literature and differences between the computed and measured profiles are discussed in detail. Also, the pressure drop rate and the temperature rise rate have been computed across the surface of incipient nucleation and their implications on the final foam morphology have been discussed.

5.2. Future Work

Measurement and subsequent incorporation of normal stress functions and extensional stresses for polymer – blowing agent solutions into the simulation can improve the model predictions. Also, once the time lag of nucleation for PS-CO₂ mixture is evaluated, use of a multiphase model to simulate the flow of the two-phase polymer gas mixture downstream of the surface of incipient nucleation will enhance the predictions. The next step would be to estimate the rate of bubble nucleation from knowledge of the hydrodynamics and the basic field variables – pressure, temperature and velocity of the PS-CO₂ mixture in the die. Finally a suitable bubble growth model will be incorporated in the simulation to predict the microstructure of the final foam.
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APPENDIX A

EXAMPLE OF A USER DEFINED FUNCTION

#include "udf.h"

DEFINE_PROPERTY(cross_ap_200, cell, thread)
{
    real eta_cross;
    real temp = C_T(cell, thread);
    real pressure = C_P(cell, thread);
    real strain_mag = C_STRAIN_RATE_MAG(cell, thread);
    real strain_term;
    real index_1;
    real ts = 473.15;
    real c1 = 3.11;
    real c2 = 142.83;
    real at1;
    real at;
    real ap;
    real n = 0.246248525;
    real eta_zero = 3295.011762;
    real tau = 25224.85724;
    real c1g_mix = 13.67;
    real c2g_mix = 32.50;
    real ap2;
    real ap3;
    real ap1;
    real a1 = 0.29e-06;
    real tgmix = 362.82;
    real tgmixp = tgmix + a1*pressure;

    at1 = (-c1*(temp - ts))/(c2 + temp - ts);
    at = pow(10, at1);

    at1 = (-c1*(temp - ts))/(c2 + temp - ts);
    at = pow(10, at1);
ap2 = (-c1g_mix*(temp - tgmixp))/(c2g_mix+(temp - tgmixp));
ap3 = (-c1g_mix*(temp - tgmix))/(c2g_mix+(temp - tgmix));
ap1 = ap2 - ap3;

if (pressure < 101325)
ap = 1.;
else if (pressure > 24000000)
ap = 1.;
else
    ap = pow(10,ap1);

index_1 = 1.-n;

strain_term = pow(((eta_zero*strain_mag)/tau),index_1);

eta_cross = (eta_zero*(at)*(ap))/(1+strain_term);

return eta_cross;
}
Figure B.1: 240°C, 10 rpm screw rotation rate, 1 wt% CO₂ in PS
Figure B.2: 220°C, 10 rpm screw rotation rate, 1 wt% CO₂ in PS

Figure B.3: 200°C, 10 rpm screw rotation rate, 1 wt% CO₂ in PS
**Figure B.4:** 180°C, 10 rpm screw rotation rate, 1 wt% CO$_2$ in PS

**Figure B.5:** 160°C, 10 rpm screw rotation rate, 1 wt% CO$_2$ in PS
Figure B.6: 140°C, 10 rpm screw rotation rate, 1 wt% CO₂ in PS