Mass transfer from bubbles and drops suspended in a liquid

by

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Abstract

The objective of this dissertation is the study of different phenomena related to the dissolution of bubbles and drops in liquids and to their influence on the dynamics of buoyant plumes. While the motivation for the work has been the massive oil spill caused by the Deepwater Horizon accident in the Gulf of Mexico in 2010, the results presented are of a fundamental nature and, therefore, of a broader relevance and applicability. The dissertation is divided into two main parts, the first one devoted to the study of single drops and bubbles, the second one to collective phenomena involving drops and bubbles.

The first problem considered is that of the dissolution of a single two-component drop. Assuming phase equilibrium at the interface between the drop and the surrounding ambient liquid, we can accurately capture the dissolution rate of each component despite the difficulty introduced by the mutual interference of the drop components in determining their chemical potential and, therefore, their solubility. In the course of this work, we discovered a new memory term in this type of diffusive processes which arises when the interface concentration is time-dependent. This realization has motivated us to extend the study of this effect to the case of gas bubbles in the chapter that follows.

In the second part of the dissertation we broaden the scope of our study by focusing
on a larger scale. Instead of single drops or bubbles, we study the collective behavior of buoyant plumes constituted by bubbles or drops. The collective rise of these entities lifts the ambient liquid forming a rising plume. An intrusion layer can form at a certain depth when the ambient liquid density is stratified. The intrusion layer is due to the insufficient buoyancy provided by the discrete phase. As the plume rises, its buoyancy decreases by the entrainment of the ambient liquid. At a certain height above the source, which we term the neutral height, the buoyancy of the plume vanishes while the accumulated momentum does not. Thus, the plume continues to rise to the so-called peel height, before falling back to form an intrusion. An important fact, which does not seem to have been previously recognized in the literature, is that the intrusion height is usually above the neutral height. This fact is due the entrainment of additional ambient liquid during the inertial rise above the neutral level. Once it reaches the peel height, therefore, the mean density of the plume liquid is less than that at the neutral height so that the intrusion forms above the neutral height. This realization explains why the measured intrusion heights are found so often to be significantly above the theoretical predictions. Another interesting effect identified in our study is the importance of the drop or bubble material dissolved in the liquid in maintaining, at least partially, the buoyancy lost with the dissolution of the drops or bubbles.

Since, in the modeling of plumes, we have used an averaged form of the balance equations, we have devoted the last chapter of the work to the general problem of averaging in multiphase flow obtaining a general expression for the non-convective fluxes of mass, momentum and energy. The main result is the elucidation of the role played by the total mixture flux in determining the specific fluxes for each phase.
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6.2 The unit normals are defined to be directed out of the corresponding phase.
List of Symbols

Chapter 2

$\gamma_k^C, \gamma_k^D$ Activity coefficient for component $k$ ($k = a, b, c$) in the continuous (host liquid) phase and disperse (drop) phase

$\mu_k^C, \mu_k^D$ Chemical potentials of component $k$ in the continuous (host liquid) phase and disperse (drop) phase

$\rho_k^i$ Density of drop constituent $k$ ($k = a, b$) in the host liquid before the insertion of the drop

$\rho_k$ Density (or mass concentration) of component $k$ in the host liquid

$\rho_{sf}^k$ Thermodynamic equilibrium surface concentration of component $k$ in the host liquid

$\rho_{sat}^k$ Saturation density for drop constituent $k$ in the host liquid

$\rho_0^k$ Density of the pure constituent $k$ of the drop

$\sigma$ Surface tension coefficient

$D_k$ Mass diffusivity of component $k$ in the host liquid

$m_k$ Mass of component $k$ inside drop

$M_k$ Molecular mass for component $k$

$n_k^D$ Mole amount of component $k$ in the disperse (drop) phase

$p$ Pressure

$R_G$ Perfect gas constant

$r$ Distance from the drop center

$R$ Drop radius, given by (2.12)

$Sh_k$ Sherwood number for component $k$

$T$ Temperature

$v_k$ Molar volume for component $k$

$x_k^C, x_k^D$ Mole fraction of the drop constituent $k$ in the continuous (host liquid) phase (2.15) and disperse (drop) phase (2.14)
Chapter 3

$\alpha, \beta$ Dimensionless surface tension given by (3.24)

$\rho_g'$ Density of gas dissolved in the liquid before the insertion of bubble

$\rho_g$ Density of gas dissolved in the liquid

$\rho_0'$ Gas density inside bubble under the pressure $p_\infty^0$

$\rho_{sat}$ Density of gas dissolved in the liquid at saturation under the pressure $p_\infty^0$

$\omega$ Angular frequency of the ambient pressure field

$d$ Solubility parameter defined in (3.3)

$D$ Mass diffusivity of bubble in the liquid

$K$ Henry’s law constant

$m_g$ Mass of bubble

$M_g$ Molecular mass of the gas

$p_\infty$ Ambient pressure in the liquid

$p_\infty^0$ Time-averaged ambient pressure in the liquid

$p_g$ Pressure inside bubble

$P_*$ Pressure oscillation amplitude

$Pe$ Ratio of the average bubble radius to the diffusion penetration length given by (3.22)

$R$ Bubble radius

$R_e$ Characteristic bubble radius given by (3.19) at threshold condition

$t_{diff}$ Characteristic time scale over which $\rho_g$ varies appreciably

$t_{diss}$ Total dissolution time of bubble

$T$ Temperature
Chapter 4

$\alpha_e$  Entrainment coefficient
$\beta_b$  Bubble volume fraction
$\Gamma$  Plume number, defined by (4.32)
$\lambda_s b$  Radius of the plume region in which the salinity difference with the ambient liquid is localized
$\rho$  Plume density
$\rho_a$  Ambient liquid density
$\rho_g$  Gas density
$\rho_w$  Water density

$b$  Plume half width
$B_b$  Buoyancy due to bubbles, given by (4.15)
$B_s$  Buoyancy due to salinity, given by (4.14)
$D$  Plume source diameter
$F_b$  Buoyancy flux due to bubble, given by (4.10)
$F_s$  Buoyancy flux due to salinity, given by (4.9)
$Fr$  Froude number, defined by (4.25)
$g$  Gravity
$h_p$  Peel height, i.e. the level at which the plume momentum varnishes
$h_i$  The intrusion layer height
$h_n$  Neutral buoyancy height, i.e. the level at which the plume buoyancy varnishes
$h_l$  Position of the lower edge of the intrusion layer
$H_c$  Characteristic plume height used in previous literature, given by (4.47)
$L_b$  Height reached by the plume in this buoyancy-dominated limit, given by (4.21)
$L_m$  Height reached by the plume in this momentum-dominated limit, given by (4.23)
$m$  Plume volume flux, given by (4.2)
$M$  Plume momentum flux, given by (4.13)
$N$  The Brunt-Väisälä frequency, given by (4.7)
$p_{atm}$  Atmospheric pressure
$Q_b$  Gas flow rate
$S$  Ratio of characteristic height for momentum-dominated plume to that of buoyancy-dominated plume, given by (4.33)
$U_N$  Dimensionless bubble slip velocity used in previous literature, given by (4.46)
$V_N$  Dimensionless bubble slip velocity in our model, given by (4.31)
$w$  Vertical liquid velocity
$w_b$  Bubble slip velocity
$z_E$  Height of the flow-establishment zone
Chapter 5

\( \alpha_e \) Entrainment coefficient

\( \beta_b, \beta_d \) Bubble/Drop volume fraction

\( \delta \) Solubility parameter of bubble

\( \Theta_b, \Theta_d \) Ratio of characteristic time for the plume, \( N^{-1} \), to the dissolution time \( t_{\text{dslv}} \), given by (5.66), (5.55) for bubble and drop, respectively

\( \lambda_s b \) Radius of the plume region in which the salinity difference with the ambient liquid is localized

\( \Lambda_b, \Lambda_d \) Density mixing coefficient, accounts for the capability of the dissolved material to provide buoyancy, given by (5.65), (5.54) for bubble and drop, respectively

\( \xi_b, \xi_d \) Density coefficient of dissolved constituent, for bubble and drop, respectively

\( \xi_s \) Density coefficient for dissolved salinity

\( \rho \) Plume density

\( \rho_a \) Ambient liquid density

\( \rho_b, \rho_d \) Bubble/Drop density

\( \rho_{0b}, \rho_{0d} \) Bubble/Drop density at plume source

\( \rho_{d,\text{dslv}} \) Density of dissolved drop constituent in the plume liquid

\( \rho_s \) Dissolved salt concentration by mass

\( \rho_{sa} \) Ambient salinity density

\( \rho_r \) Ocean water density at the source of the plume

\( \rho_w \) Pure water density

\( A \) Plume cross-section area

\( b \) Plume half width

\( B_d \) The buoyancy due to the discrete drops, given by (5.25)

\( B_{d,\text{dslv}} \) The buoyancy due to the dissolved drop components, given by (5.27)

\( B_s \) Buoyancy due to salinity, given by (5.26)

\( d \) Bubble/Drop diameter

\( D \) Diffusivity of bubble/drop component in the ambient liquid

\( F_d \) The buoyancy flux due to the discrete drops, given by (5.22)

\( F_{d,\text{dslv}} \) The buoyancy flux due to the dissolved drop components, given by (5.21)

\( F_s \) Buoyancy flux due to salinity, given by (5.20)

\( g \) Gravity
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$h_d$</td>
<td>Mass transfer coefficient between drop and ambient liquid</td>
</tr>
<tr>
<td>$h_i$</td>
<td>The intrusion layer height</td>
</tr>
<tr>
<td>$h_n$</td>
<td>Neutral buoyancy height, i.e. the level at which the plume buoyancy varnishes</td>
</tr>
<tr>
<td>$h_p$</td>
<td>Peel height, i.e. the level at which the plume momentum varnishes</td>
</tr>
<tr>
<td>$H_{total}$</td>
<td>Total water depth</td>
</tr>
<tr>
<td>$L_r$</td>
<td>Characteristic plume length scale, given by (5.46)</td>
</tr>
<tr>
<td>$m$</td>
<td>Plume volume flux, given by (5.15)</td>
</tr>
<tr>
<td>$m_d$</td>
<td>Mass flux of discrete drops, given by (5.34)</td>
</tr>
<tr>
<td>$m_{d,\text{dlsv}}$</td>
<td>Mass flux of dissolved drop constituent, given by (5.35)</td>
</tr>
<tr>
<td>$M$</td>
<td>Plume momentum flux, given by (5.24)</td>
</tr>
<tr>
<td>$n_d$</td>
<td>Drop number density</td>
</tr>
<tr>
<td>$N$</td>
<td>The Brunt-Väisälä frequency</td>
</tr>
<tr>
<td>$P_{\text{atm}}$</td>
<td>Atmospheric pressure</td>
</tr>
<tr>
<td>$Q_{b, d}$</td>
<td>Bubble/Drop flow rate</td>
</tr>
<tr>
<td>$t_{\text{dlsv}}$</td>
<td>Characteristic drop dissolution time</td>
</tr>
<tr>
<td>$v_d$</td>
<td>Volume of a single drop</td>
</tr>
<tr>
<td>$V_N$</td>
<td>Dimensionless bubble/drop slip velocity, given by (5.56)</td>
</tr>
<tr>
<td>$w$</td>
<td>Vertical liquid velocity</td>
</tr>
<tr>
<td>$w_b, w_d$</td>
<td>Bubble/Drop slip velocity</td>
</tr>
<tr>
<td>$w_r$</td>
<td>Characteristic plume velocity scale, given by (5.47)</td>
</tr>
</tbody>
</table>
Chapter 6

$\alpha_j$ Volume fraction of the $j$-phase
$\gamma$ The (vector) contribution of the surface forces
$\theta_j$ The volume source of $q_j$
$\mu_1$ Viscosity of the continuous phase
$\tilde{\mu}_j$ Possibly modified fluid viscosity for phase $j$
$\phi_j$ The non-convective flux of $q_j$

c_{pj}$ The constant-pressure specific heat for phase $j$
$Ca$ Capillary number
$g$ The volume source of momentum per unit mass
$h$ Heat transfer coefficient
$m$ Drop mass
$N_S$ The numbers of drops on the surface of the averaging volume
$N_V$ The numbers of drops inside the averaging volume
$q_j$ Generic quantity of arbitrary tensorial order belonging to the $j$-th phase
$r_d$ Drop radius
$S_j$ The portion of $S$ occupied by the $j$-th phase
$T_j$ Temperature for phase $j$
$u_d$ Drop velocity
$u_j$ The $j$-th phase velocity
$V_j$ Part of $V$ occupied by the $j$-th phase
$w_d$ Magnitude of the drop-fluid relative velocity
Chapter 1

Introduction

Mass transfer in multiphase flow is a fundamental process with many occurrences in science and technology, such as fluidized beds in gas-solid or liquid-solid applications, bubble/drop columns in chemical and environmental engineering, solvent extraction in the chemical industry, the PUREX process in nuclear fuel reprocessing, etc. The design and implementation of such processes requires the precise knowledge of the momentum and mass transfer within the systems.

The motivation for the present study of mass transfer from bubbles and drops arose from the Deepwater Horizon accident which occurred in 2010. This accident caused immense damage to the local economy and it also had a devastating environmental impact on the ecosystem. We address several specific problems relevant for mass transfer processes in the context of this accident.

During the Deepwater Horizon accident, the uncontrollable blowout caused $10^7$ kg/day of hydrocarbon release on average for several months, with 25% of the total hydrocarbon outflow – 10% of the liquid phase and 90% of the gaseous phase (Reddy and Arey, 2012) – consisting of components soluble in the ocean water (Ryerson et al., 2011). Large number of gas bubbles (Joye et al., 2011; Camilli et al., 2010; Valentine,
and crude oil droplets (Diercks et al., 2010; Hazen and Dubinsky, 2010) leaked out of the broken pipe.

The usage of dispersant decreased the number of large droplets and breaking them up into smaller ones, therefore making dissolution a more relevant process in the deep ocean (Kujawinski et al., 2011). As a result, a considerable fraction of the crude oil droplets dissolved in the deep ocean, leaving the remaining heavy hydrocarbon components to rise the surface (see Fig 1.1, 1.2). The dissolved aromatic hydrocarbons have a huge impact on the oceanic ecosystem in the entire water column (Camilli et al., 2010; Barron, 2012). In order to better predict the fate of different components of oil droplets and gas bubbles, and evaluate the impact of the dissolved material on the ecosystem, it is important to understand the mechanism of mass transfer between multicomponent drops/bubbles and ambient water. In this effort, it is natural to start by considering single drops and single bubbles.

Mass transfer between a stationary single component bubble and the ambient liquid has been described in a classical study (Epstein and Plesset, 1950a). For a multicomponent bubble, Henry’s law provides an adequate approximation to the process (see e.g. Kabalnov et al., 1998). The Epstein-Plesset framework has been also applied to the dissolution of a single component drop. While, for a single component drop, the dissolved concentration at the drop surface is constant in time and equal to the solubility of the drop liquid, for a multicomponent drop, the mutual interaction of the constituents causes the surface concentration to change in time as the composition of the drop varies due to the different dissolution rates of the constituents. This phenomenon greatly complicates the analysis of the dissolution which, for this reason, has not been sufficiently investigated. In chapter 2, we focus on this problem. In
this chapter, we present a thermodynamically consistent analysis of this situation, for both growing and dissolving drops, with and without an initial concentration of the drop constituents in the host liquid. In some cases the results, which have important implications also for solvent extraction processes in the chemical and environmental remediation industries, show major deviations from the predictions of recent approximations, based on the Epstein-Plesset theory (Su and Needham, 2013).

In the course of the analysis of multicomponent drop dissolution, we realized that a phenomenon not included in the Epstein-Plesset theory of bubble dissolution, namely history effects, could be important in some circumstances. For a gas bubble at rest in a liquid, such effects arise when the concentration of dissolved gas at the bubble surface, dictated by Henry’s law, depends on time. In chapter 3, we consider several such situations. An oscillating ambient pressure field causes rectified diffusion of gas into or out of the bubble. Unlike previous investigators, who considered thin boundary layers, we study this process for conditions when the diffusion length is larger than the bubble radius. It is found that history effects are important in determining the threshold conditions. Under a static ambient pressure, the time dependence of the gas concentration can arise due to the action of surface tension, which progressively increases the gas pressure as the bubble dissolves or, when the bubble contains a mixture of two or more gases, due to the different rates at which they dissolve. In these latter cases history effects prove mostly negligible for bubbles larger than a few hundred nanometers, but are important for smaller bubbles.

Observations have shown the presence of hydrocarbon intrusion layers at depths around 25 m, 265 m, 865 m, and 1175 m below the surface (Spier et al., 2013) (see Fig 1.3). Most light soluble alkanes such as methane, ethane, propane, butane (Camilli
Figure 1.1: Schematic of oil carbon and natural gas product partitioning in the marine environment from Ryerson et al. (2011).
Figure 1.2: Evaporated hydrocarbon composition after 2 d (A; blue bars), surface oil slick composition after 2 d (B; black bars), and dissolved hydrocarbon composition (C; red bars). (D) Schematic (not to scale) of hydrocarbon mass flows in the marine environment from Ryerson et al. (2012a).
et al., 2010; Valentine, 2010; Kessler and Valentine, 2011) and hydrocarbons such as benzene, toluene, ethylbenzene, and xylene (so called "BTEX") remained in a deep layer close to the ocean floor between 1100 \sim 1300 \text{m}, with a much smaller fraction found in the other carbon rich layers higher up in the water column (Diercks et al., 2010; Camilli et al., 2010). On the other hand, (alkylated) aromatics with longer chains were also present at higher elevations (see Fig. 1.4).

The carbon rich layers persisted in the deep ocean for months, and they gave a particularly serious contribution to the devastating damage to ecosystem at the depth where they concentrated (Churchill et al., 2015; D’elia et al., 2016; Fisher et al., 2014). As researchers in fluid mechanics, we will not focus on the biological aspects. Instead, we are more interested in the fundamental physics behind the intrusion phenomenon: how are the carbon-rich layers formed? what determines their levels? what role does mass transfer play in this process?

Chapters 4 and 5 are devoted to the study of the origin of the first intrusion layer for a bubble/drop plume in a stratified ambient liquid. Chapter 4 studies the case of a bubble plume rising without dissolution in a stratified quiescent liquid paying particular attention to the effect of conditions at the plume source. The analysis is based on a cross-sectionally averaged model of the plume. It is found that the source parameters (diameter, momentum flux, liquid and gas mass fluxes) have a strong effect on the predicted intrusion and peel heights. In attempting a comparison with existing data, it is pointed out that models of this type can only predict what we term the \textit{neutral height}, i.e. the depth at which the plume buoyancy vanishes. what is actually measured, however, is the intrusion height which occurs at a higher level. Recognizing this difference permits us to explain why the reported intrusion height
Figure 1.3: The ratio of the frequency of detectable compounds in each of the four identified plumes compared to the observed frequency overall depths is shown for aromatic hydrocarbons. The more water-soluble compounds (shown in red) are found at higher frequencies in the deepwater plumes compared to plumes closer to the surface from Spier et al. (2013).
Figure 1.4: Contour plots of different groups of hydrocarbons within a 45 km radius of the blowout. These contour plots were used for preliminary identification of plume locations. Low molecular weight compounds with higher solubilities appear to be found more frequently in deeper plumes than less soluble higher molecular weight compounds from Spier et al. (2013).
lies so frequently so much above the theoretical predictions, and brings our results in line with observations.

With the background of chapter 4, chapter 5 includes the effect of dissolution for a bubble plume rising in a stratified quiescent liquid. Dissolution phenomenon of liquid drops are also included. Unlike previous researchers, we consider the liquid density change due to dissolved material. Dissolution greatly decreases the plume buoyancy provided by the bubbles. Nevertheless, the dissolved material can have an effect on the ambient liquid density and partially balance the loss of buoyancy due to the shrinking bubble size. It is found that these two factors can be represented by two dimensionless groups, and their influence on the plume dynamics are extensively studied for bubble plume generated by a point source. We show that under most situations the plume behavior can be accurately captured by the values of these dimensionless groups evaluated at the source.

In chapters 2 and 3 we have studied the mass transfer from a single drop or bubble, and in chapters 4 and 5 we have studied the collective behavior of many bubbles by utilizing an integral model with a Gaussian or top-hat profiles of the relevant fields. The problems studied in these chapters represent strong simplifications of situations occurring in reality. More realistic models must address the momentum, mass and heat exchange with the surround liquid of huge numbers of drops and bubbles. Resolving the momentum, mass and energy equations for both phases is computationally prohibitive. It is thus necessary to have a recourse to averaged formulations of the relevant equations. The averaging process introduces more unknowns than the number of averaged equations available, which, therefore, constitute a mathematically unclosed system. This is a well known problem, and many attempts have been made to address
it (Prosperetti and Tryggvason, 2009a). In spite of all these work, several open issues remain. In chapter 6, we address some of these issues by providing a theoretically consistent analysis of the unclosed terms. More specifically, we examine the modeling of non-convective fluxes (e.g. stress, heat flux and others) as they appear in the general, unclosed form of the volume-averaged equations of multiphase flows. By appealing to the difference between slowly and rapidly varying quantities, it is shown that the natural closure of these terms leads to the use of a single, slowly-varying combined average flux, common to both phases, plus rapidly-varying local contributions for each phase. The result is general and only rests on the hypothesis that the spatial variation of the combined average flux is adequately described by a linear function of position within the averaging volume. No further hypotheses on the nature of the flow (e.g., about specific flow regimes) prove necessary. The result agrees with earlier ones obtained by ensemble averaging and is illustrated with the example of disperse flows and discussed in the light of some earlier and current literature.
Chapter 2

Multicomponent dissolution

2.1 Introduction

The dissolution of a multi-component drop in a host liquid is a fundamental process with many occurrences in science and technology. Liquid-liquid extraction (also known as solvent extraction) is a basic process in the chemical industry, important enough to deserve its own journal, Solvent Extraction and Ion Exchange. Examples of applications are the production of chemical compounds, such as pharmaceuticals, the separation of heavy organics and metals, waste purification and many others (see e.g. Rydberg et al., 2004). Another example is the PUREX process used for nuclear fuel reprocessing (see e.g. Taylor, 2015). Proteins, enzymes and other biological material can be extracted from biological fluids by this process (see e.g. Ahuja, 2000). The process is used in the food industry and the recent intense interest in ionic liquids has given an even greater impetus to research in this area (see e.g. Fukumoto, Yoshizawa, and Ohno, 2005).

The mass exchange between the drop and the host liquid is driven by the differences

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1This chapter is based on the paper “Dissolution and growth of a multicomponent drop in an immiscible liquid.” by Chu & Prosperetti (Journal of Fluid Mechanics, vol. 798, pp. 787-811, 2016.)
in the concentration of the solutes at the drop surface and in the host liquid. With the customary assumption of local thermodynamic equilibrium, the surface concentration follows from the equality of the chemical potentials across the drop interface. In general, this condition is difficult to express in an analytic form and, for this reason, several approximations can be found in the literature as will be discussed in section 2.4. The intent of the present chapter is to compare the results of a precise treatment of the interface condition with the results of approximations. It will be shown that, in some cases, the benefit stemming from the use of simplified treatments exacts a steep price in terms of accuracy.

We focus here on ternary system consisting of two miscible components \( a \) and \( b \), constituting the drop, and a third component \( c \), the host liquid, in which the other two are only sparingly soluble. A recent paper on a system of this type is a study by Su and Needham (2013) which proposes a seemingly straightforward adaptation of the method used by Epstein and Plesset (1950b) to model the dissolution or growth of a gas bubble in an undersaturated or oversaturated liquid. In that case, Henry’s law prescribes the gas concentration at the bubble surface. Su & Needham simply followed the analysis of Epstein & Plesset assuming that the concentration of each one of the drop components on the host-liquid side of the drop interface equals the solubility of that component in the host liquid adjusted, at every instant, by multiplication by the volume fraction of that component in the drop. While this represents an approximate way to deal with the condition of equality of chemical potentials mentioned before, it does not have a fundamental basis.

We study both situations in which the initial concentration of the two drop constituents in the host liquid does or does not vanish. The latter case proves particularly
interesting as shown in section 2.7. Although our focus is on ternary systems, similar methods can be used and results expected for quaternary and higher-order system.

We start by deriving an equation for the mass flow rate out of a multicomponent drop dissolving in an immiscible liquid in section 2.2. It is shown that the classic result of Epstein and Plesset (1950b) for the mass flux at the drop surface acquires a memory term when the concentration of the drop constituents varies in time. The law that governs the concentration of the diffusing substances at the drop surface is described in section 2.3 and some approximations in section 2.4. The implications for drop dissolution times are demonstrated numerically in sections 2.5 to 2.7. In particular, section 2.5 presents a comparison of the present theory with an approximate model in which the drop is treated as an ideal solution.

2.2 The diffusion problem

A liquid drop consisting (mostly) of two miscible components, indicated by superscripts $a$ and $b$, is instantaneously brought into contact with a large volume of a third liquid $c$ in which the drop liquids are sparingly soluble; the host liquid $c$ is sparingly soluble in $a$ and $b$. Before the insertion of the drop, its components may be present with small and uniform concentrations $\rho^i_a$ and $\rho^i_b$ in the host liquid. Depending on these initial values of concentration, the drop constituents diffuse into or out of the drop.

We follow the original work of Epstein and Plesset (1950b) and assume that the drop remains spherical, that it does not move relative to the host liquid and that the mutual diffusion of its constituents is fast enough to ensure that it remains well-mixed throughout the process. Sphericity prevails when the drop is small enough that surface
tension is important and, for small drops, buoyancy-induced motion is also negligible. The time scale for diffusion throughout a small drop is faster than the rate at which its radius changes, which justifies the assumption of a spatially uniform drop composition. Furthermore, the rate of dissolution is small enough that the radial convection of the host liquid can also be neglected. Thus, each component of the drop will satisfy the diffusion equation which, because of the spherical symmetry of the problem, is

\[
\frac{\partial \rho_a}{\partial t} = \frac{D_a}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \rho_a}{\partial r} \right),
\]

in which \(\rho_a\) is the density (or mass concentration) of component \(a\) in the host liquid, \(D_a\) is the mass diffusivity of that component and \(r\) is the distance from the drop center. Here we have focused on the \(a\)-component of the drop, but entirely equivalent expressions can be written down for the other component \(b\). In general, in a multi-component diffusion problem, the diffusive flux of one component is affected by that of the other ones (see e.g. Taylor and Krishna, 1993). However, since in our case the drop constituents are only sparingly soluble in the host liquid, this interaction can be neglected as we have done in writing (2.1).

Far from the drop the concentrations in the host liquid remain equal to their initial values \(\rho_{ai}\) so that

\[
\lim_{r \to \infty} \rho_a(r, t) = \rho_{ai}.
\]

At the surface of the drop \(r = R(t)\) the concentration is prescribed:

\[
\rho_a(R, t) = H(t) \rho_{ai}^{sf}(t) + (1 - H(t)) \rho_{ai},
\]

where the Heaviside function \(H(t)\) enforces the fact that the boundary condition is applied instantaneously at \(t = 0^+\), the concentration being \(\rho_{ai}^{sf}\) at earlier times.
The manner in which the thermodynamic equilibrium surface concentration $\rho_a^{sf}(t)$ is calculated is the focus of this chapter and is described in the next section. The rate at which the component $a$ diffuses into or out of the drop is given by

$$\frac{dm_a}{dt} = 4\pi R^2(t) D_a \frac{\partial \rho_a}{\partial r} \bigg|_{r=R(t)}.$$ \hspace{1cm} (2.4)

In order to solve the mathematical problem posed by (2.1), (2.2) and (2.3) it is convenient to define $u_a(r, t) = r[\rho_a(r, t) - \rho_i^a]$ in terms of which (2.1) becomes

$$\frac{\partial u_a}{\partial t} = D_a \frac{\partial^2 u_a}{\partial r^2},$$ \hspace{1cm} (2.5)

subject to

$$\lim_{r \to \infty} u_a = 0,$$ \hspace{1cm} (2.6)

and to the boundary condition deriving from (2.3)

$$\lim_{r \to R} u_a = RH(t) \left( \rho_a^{sf}(t) - \rho_i^a \right).$$ \hspace{1cm} (2.7)

Upon taking the Laplace transform (denoted by a tilde) and solving the resulting differential equation we find

$$\tilde{u}_a(r, s) = \tilde{u}_a|_{r=R} e^{-\sqrt{s/D_a}} (r-R).$$ \hspace{1cm} (2.8)

In keeping with the neglect of the convective term in the diffusion equation, we have treated $R$ as a fixed parameter in this derivation. In terms of $\tilde{u}_a$ we have

$$\frac{\partial \tilde{\rho}_a}{\partial r} \bigg|_{r=R} = - \left[ \frac{\tilde{u}_a(R, s)}{R^2} + \frac{1}{R} \frac{s\tilde{u}_a(r, s)}{\sqrt{D_a s}} \right]_{r=R},$$ \hspace{1cm} (2.9)
which can be inverted with the result

\[
\frac{\partial \rho_a}{\partial r} \bigg|_{r=R} = \frac{\rho^i_a - \rho^{sf}_a(0)}{\sqrt{\pi D_a t}} + \frac{\rho^i_a - \rho^{sf}_a(t)}{R} - \int_0^t \frac{d\rho^{sf}_a(\tau)}{d\tau} \frac{d\tau}{\sqrt{\pi D_a(t-\tau)}}. \tag{2.10}
\]

The first term in the right-hand side is due to the discontinuity of the boundary condition at \( t = 0 \). It is interesting to rewrite this equation identically as

\[
\frac{\partial \rho_a}{\partial r} \bigg|_{r=R} = \left[ \rho^i_a - \rho^{sf}_a(t) \right] \left( \frac{1}{\sqrt{\pi D_a t}} + \frac{1}{R} \right)
- \int_0^t \frac{d\rho^{sf}_a(\tau)}{d\tau} \left[ \frac{1}{\sqrt{\pi D_a(t-\tau)}} - \frac{1}{\sqrt{\pi D_a t}} \right] d\tau. \tag{2.11}
\]

The first term in the right-hand side is the only term occurring – correctly – in the original theory of Epstein and Plesset (1950b), in which \( \rho^{sf}_a \) is a constant, but also in its adaptation by Su and Needham (2013), in which, however, it is not.

The knowledge of the masses \( m_a \) and \( m_b \) of the two drop constituents enables us to calculate the drop radius from

\[
\frac{4}{3} \pi R^3(t) = \frac{m_a(t)}{\rho^0_a} + \frac{m_b(t)}{\rho^0_b}, \tag{2.12}
\]

where \( \rho^0_{a,b} \) are the densities of the pure constituents of the drop. The third component of the system, namely the host liquid, is also soluble in the drop constituents but, for the liquids considered in this chapter, this solubility is very small and we have neglected it in writing this equation. We include a comment in section 2.6 below to justify this approximation quantitatively. Since the focus of the chapter is on the calculation of the surface concentrations, volume changes upon mixing are also neglected for simplicity.
2.3 The surface concentration

Since the dissolution process is very slow, one may assume that thermodynamic equilibrium prevails at the drop surface. In the case of a bubble of a sparingly soluble, essentially perfect gas, such as the problem studied by Epstein and Plesset (1950b), equilibrium implies Henry’s law which (aside from surface tension effects) prescribes a constant value for the concentration of the dissolving substance at the bubble surface. In multi-component liquid systems the situation is more complex.

Thermodynamic equilibrium in a two-phase, three-component system requires that the chemical potentials $\mu_k$ of each one of the three components, $k = a, b, c$, have the same value in both phases (see e.g. Landau and Lifshitz, 1980):

$$\mu_k^D(p, T, x_a, x_b, x_c) = \mu_k^C(p, T, x_a, x_b, x_c), \quad k = a, b, c.$$  \hspace{1cm} (2.13)

Here the index $k$ denotes the component and the superscripts $D$ and $C$ the disperse (drop) and continuous (host liquid) phase; $p$ is the pressure, $T$ the temperature, and $x_a$, $x_b$, and $x_c$ are the mole fractions of the drop constituents (indices $a$, $b$) and of the continuous phase, or host liquid (index $c$), which satisfy the relation $x_a + x_b + x_c = 1$.

For a well-mixed drop the mole fraction of the $a$ component can be expressed as

$$x_a^D = \frac{m_a / M_a}{m_a / M_a + m_b / M_b + m_c / M_c},$$  \hspace{1cm} (2.14)

and similarly for the $b$ component; the $M$’s are the molecular masses. The mole fractions on the side of the drop surface exposed to the continuous phase are expressed in terms of the mass concentrations $\rho_k^{sf}$ as:

$$x_a^C = \frac{\rho_a^{sf} / M_a}{\rho_a^{sf} / M_a + \rho_b^{sf} / M_b + \rho_c^{sf} / M_c},$$  \hspace{1cm} (2.15)
in which the superscript $sf$ denotes equilibrium values at the drop surface.

The other two requirements of equilibrium, namely the equality of temperature and pressure, have already been used in writing (2.13). The latter condition implies the neglect of surface tension, which has a very minor effect in liquid-liquid systems except when the drop is exceedingly small and the curvature of its interface very large. This situation occurs only for a very brief time near the end of a dissolution process or near the beginning of growth and, therefore, neglect of the surface tension correction will not introduce significant errors.

The Gibbs phase rule states that, at equilibrium, the number of thermodynamic degrees of freedom of a system equals the number of components minus the number of phases plus 2 (see e.g. Landau and Lifshitz, 1980). Thus, with three components and two phases in equilibrium (the drop and the ambient liquid), the present system has three thermodynamic degrees of freedom. Since we assume temperature and pressure to remain fixed, these effectively reduce to one; we will make repeated use of this fact in the following.

The chemical potential of a solution is expressed in terms of the activity $a_k$ of the $k$ component as $\mu_k = \mu_k^0(p, T) + R_G T \log a_k$, with $\mu_k^0(p, T)$ the chemical potential of the pure fluid and $R_G$ the perfect gas constant. For an ideal solution the activity equals the mole fraction, $a_k = x_k$. Non-ideal behavior is usually accounted for by introducing an activity coefficient $\gamma_k$ through the definition $a_k = \gamma_k x_k$. As a consequence of the equality of temperature and pressure in the two phases, the condition of equality of the chemical potentials reduces then to

\[(x_k \gamma_k)^D = (x_k \gamma_k)^C, \quad k = a, b, c.\]  

(2.16)
This is the fundamental relation specifying the composition of the two phases on
the host-liquid side (superscript C) of the drop interface. While expressions for the
activity coefficients based on fundamental principles are not available, several semi-
empirical models exist (see e.g. Taylor and Krishna, 1993). In this study we use
the UNIQUAC model, which gives fairly accurate results for many liquid-liquid and
gas-liquid systems; this model is summarized in Appendix A.

It follows directly from (2.15) written for the a and c components that

\[
\rho_{sf}^a = \frac{M_a x_a^C \rho_{sf}^c}{M_c x_c^C \rho_c^0} \approx \frac{M_a x_a^C}{M_c x_c^C} \rho_c^0. \tag{2.17}
\]

In the last step, in view of the sparingly soluble nature of the components a and b in c,
we have approximated \(\rho_{sf}^c\) by the density \(\rho_c^0\) of the pure host liquid. Thus, by (2.16),
we have

\[
\rho_{sf}^b = \frac{M_a \gamma_a^D x_a^D}{M_c \gamma_c^C x_c^C} \rho_c^0. \tag{2.18}
\]

This relation, and the analogous one for \(\rho_{sf}^b\), enable us to calculate the interface
densities as functions of the mole fraction of the corresponding component in the
drop.

By definition, the solubility of component a in component c is the saturation
density \(\rho_{a}^{sat}\) of a in c in the absence of b, and similarly for the solubility of b in c.
These quantities therefore follow from (2.17) as

\[
\rho_{a}^{sat} \approx \frac{M_a [x_a^C]_{x_b^D=0}}{M_c [x_c^C]_{x_b^D=0}} \rho_c^0, \tag{2.19}
\]

and similarly for \(\rho_{b}^{sat}\), here again we have approximated \(\rho_{sf}^c\) by \(\rho_c^0\).
2.4 Approximations

As mentioned in the Introduction, the difficulty of expressing the activity coefficient in a convenient form has prompted the use of several approximations.

Upon taking the ratio of (2.18) and (2.19) we have

$$\frac{\rho_a^{sf}}{\rho_a^{sat}} = \frac{\gamma_a^D x_a^D [x_c^C]_{x_b^D=0}}{\gamma_a^C x_c^C [x_a^C]_{x_b^D=0}}.$$  \hspace{1cm} (2.20)

When the main drop components are only sparingly soluble in the continuous phase, $[x_c^C]_{x_b^D=0} \simeq 1$ and also $x_c^C \simeq 1$ so that the previous relation becomes

$$\frac{\rho_a^{sf}}{\rho_a^{sat}} \simeq \frac{\gamma_a^D}{\gamma_a^C [x_a^C]_{x_b^D=0}} x_a^D.$$  \hspace{1cm} (2.21)

An approximation widely used in the literature consists in taking the fraction in the right-hand side to be a constant, which amounts to the linearization of the correct condition in the neighborhood of a specific composition. If the approximation is to be used over the entire range of drop compositions, it is necessary to take the fraction essentially equal to 1, which is equivalent to treating the solution as ideal. Indeed, when there is no $b$ component, $x_a^D$ reaches its maximum $[x_a^D]_{x_b^D=0}$ and the surface concentration becomes equal to the solubility $\rho_a^{sf} = \rho_a^{sat}$, so that

$$\left[ \frac{\gamma_a^C x_c^C}{\gamma_a^D} \right]_{x_b^D=0} = [x_a^D]_{x_b^D=0} \simeq 1,$$  \hspace{1cm} (2.22)

where the last step is accurate when the host liquid is only sparingly soluble in the $a$ component as we assume. This argument then leads to (see e.g. Uribe-Ramirez and Korchinsky, 2000; Adekojo Waheed, Henschke, and Pfenning, 2002; McCray and
This linear relation is shown by the dashed lines in figures 2.1, 2.3 and 2.4.

To deal with the case of small $x_a^D$, it is common to introduce the distribution, or partition, coefficient of the compound $a$ between the drop phase and the host liquid $c$ defined so that $x_a^C = K_{ac} x_a^D$. Since, as is evident from the equilibrium condition (2.14), $K_{ac} = \gamma_a^C / \gamma_a^D$, (2.21) becomes

$$\frac{\rho_a^{sf}}{\rho_a^{sat}} \simeq \frac{x_a^D}{[x_a^D]_{x_b^D=0}} \simeq x_a^D,$$

(2.24)

which is also used in the literature with both $K_{ac}$ and $[x_a^C]_{x_b^D=0}$ taken as constants.

Another approximation introduced in Su and Needham (2013) consists in equating the right-hand side of (2.21) to the volume fraction of the $a$ component in the drop, which may be written as

$$\frac{\rho_a^{sf}}{\rho_a^{sat}} \simeq \frac{v_a x_a^D}{v_a x_a^D + v_b x_b^D + v_c x_c^D} = \frac{x_a^D}{x_a^D + (v_b/v_a) x_b^D + (v_c/v_a) x_c^D}.$$

(2.25)

If all the molar volumes $v_k$ (especially $v_b$ and $v_a$, since $x_c^D \ll 1$) are close to each other, since the mole fractions sum to 1, this approximation becomes essentially the same as (2.23).

While we have explicitly referred to the $a$ component, entirely analogous approximations are in current use for the $b$ component as well.
Figure 2.1: Equilibrium density of ethyl acetate (left) and butyl acetate (right) at the surface of a drop consisting of ethyl acetate and butyl acetate in water as functions of the respective mole fractions in the drop. The solid lines are the result of the theory leading to (2.17) while the dashed lines are the predictions of (2.23).

<table>
<thead>
<tr>
<th>System</th>
<th>$\rho^0$ (kg/m$^3$)</th>
<th>$\mu$ (mPa·s)</th>
<th>$\sigma$ (mN/m)</th>
<th>$D_{exp}$ (mm$^2$/s)</th>
<th>$D_{calc}$ (mm$^2$/s)</th>
<th>$\rho_{exp}$(sat) (kg/m$^3$)</th>
<th>$\rho_{calc}$(sat) (kg/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethyl acetate (a)</td>
<td>895</td>
<td>0.426$^c$</td>
<td>23.4$^g$</td>
<td>8.65$^a$</td>
<td>10.4</td>
<td>80$^a$</td>
<td>55.3</td>
</tr>
<tr>
<td>butyl acetate (b)</td>
<td>879</td>
<td>0.685$^g$</td>
<td>24.9$^g$</td>
<td>7.61$^a$</td>
<td>9.1</td>
<td>7.8$^a$</td>
<td>2.2</td>
</tr>
<tr>
<td>water (c)</td>
<td>995</td>
<td>0.890</td>
<td>72</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>acrylonitrile (a)</td>
<td>800</td>
<td>0.342$^c$</td>
<td>27.3$^c$</td>
<td>12.3$^{h,i}$</td>
<td>12.1</td>
<td>68.9$^b$</td>
<td>68.3</td>
</tr>
<tr>
<td>propanenitrile (b)</td>
<td>772</td>
<td>0.411$^d$</td>
<td>26.7$^c$</td>
<td>13.6$^i$</td>
<td>11.8</td>
<td>103$^c$</td>
<td>121.3</td>
</tr>
<tr>
<td>water (c)</td>
<td>995</td>
<td>0.890</td>
<td>72</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>toluene (a)</td>
<td>870</td>
<td>0.553$^c$</td>
<td>27.9$^c$</td>
<td>-</td>
<td>10.8</td>
<td>-</td>
<td>38.6</td>
</tr>
<tr>
<td>heptane (b)</td>
<td>680</td>
<td>0.397$^c$</td>
<td>19.7$^c$</td>
<td>-</td>
<td>9.76</td>
<td>-</td>
<td>112.7</td>
</tr>
<tr>
<td>perfluorocyclic oxide (c)</td>
<td>1,764</td>
<td>1.396$^e$</td>
<td>15.0$^f$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2.1: Physical properties used in the calculations. For the diffusivities we compare the experimental value, when available, with the result of equation (2.40); for the solubilities we compare the experimental value with the prediction of the UNIQUAC model as given by (2.19). The references are as follows: $^a$(Su and Needham, 2013), $^b$(Yalkowsky, He, and Jain, 2010), $^c$(Riddick, Bunger, and Sakano, 1986), $^d$(Wohlfarth (2009), $^e$(Reed and Taylor, 1959), $^f$(Kaisers, Kelly, and Busch, 2003), $^g$(Haynes, 2014), $^h$(Anonymous, 2014), $^i$(Anonymous, 2005).
2.5 Comparison with simplified theories

Before proceeding with the calculation of drop dissolution or growth, we compare the surface concentration from the theory of section 2.3 with the surface concentration according to the approximation (2.23) in a few cases; we avoid the last step in (2.23) using the correct value for \( x^D_{a} \) rather than replacing it by 1. As noted at the end of the previous section, the approximation used by Su and Needham (2013) is fairly close to (2.23) so that the results that we show here are representative also of those that can be obtained using (2.25).

The physical properties used in the calculations of this and the following sections are given in Table 2.1 with appropriate references. In the case of solubilities and diffusivities we show both measured values (where available) and the values predicted by the models we use (UNIQUAC for solubilities and equation (2.40) for diffusivities) to give an idea of their validity. For the diffusivities the comparison is reasonable; we use the experimental values where available. The comparison is also good for the solubilities of the second system, while we have been unable to find experimental values for the third one. For the first system, there is a rather large difference, which indicates some problems with the values of the basic UNIQUAC model in the literature. In any event, since the focus here is to show the difference between the present and the simplified approaches, valid conclusions will be drawn provided the same numerical values are used for both.

Our first example is for the system ethyl acetate (component \( a \)), butyl acetate (component \( b \)) in water (component \( c \)), which is one of the cases studied by Su and Needham (2013). Figures 2.1a and 2.1b compare the equilibrium concentrations \( \rho^{sf}_{a,b} \) of the two organic components at the drop surface as functions of their respective mole
fractions in the drop (solid lines) as given by (2.17), with the concentrations given by (2.23) (dashed lines). The lines stop at the maximum value of the mole fraction, namely $[x^D_a]_{x^D_b=0}$ in figure 2.1a and $[x^D_b]_{x^D_a=0}$ in figure 2.1b. The lines do not reach 1 because the solubility of water in the organic compounds, though small, is not zero.

It can be seen that there is a large difference between the two sets of results, both qualitative and quantitative. In particular, there are ranges of the drop composition in which the surface concentration is not a monotonic function of the amount of that component in the drop.

The mole fraction of water in the drop is shown in figure 2.2 as a function of the mole fraction of ethyl acetate in the drop. It is seen to grow up to a maximum of about 11% when the concentration of ethyl acetate reaches its maximum. This is a consequence of the greater solubility of water in ethyl as compared to butyl acetate.

In spite of the large differences shown in figure 2.1, it will be shown in section 2.6
**Figure 2.3:** Equilibrium density of acrylonitrile (left) and propanenitrile (right) at the surface of a drop consisting of acrylonitrile and propanenitrile in water as functions of the respective mole fractions in the drop. The solid lines are the result of the theory leading to (2.17) while the dashed lines are the predictions of (2.23).

**Figure 2.4:** Equilibrium density of toluene (left) and heptane (right) at the surface of a drop consisting of toluene and heptane in hexadecafluorooxonane as functions of the respective mole fractions in the drop. The solid lines are the result of the theory leading to (2.17) while the dashed lines are the predictions of (2.23).
(see in particular the first panel of figure 2.7) that the two models give comparable results for the dissolution times of a drop consisting of these two compounds in water. The reason is that ethyl acetate has a much larger solubility in water than butyl acetate, which leads to its rapid dissolution out of the drop. The drop dissolution time is therefore mostly determined by the residual, slowly dissolving butyl acetate as shown later in figure 2.6b. This is a general conclusion of our study: if the solubility or the diffusivity of a component $a$ is much larger than that of the other component $b$, component $a$ will quickly dissolve away and the surface concentration of the other component will remain very close to its saturation value $\rho_b^{sat}$ for the majority of the drop lifetime. In this case, whether the precise theory of section 2.3 or the approximations of section 2.4 are used, will make very little difference.

The two theories predict significant differences in drop dissolution times in the case of systems forming non-ideal solutions in which the components have comparable solubilities and comparable diffusivities in the continuous phase. One such case is that of acrylonitrile (or 2-propanenitrile, $C_3H_3N$, component $a$) and propanenitrile (or propionitrile, $C_3H_5N$, component $b$) in water (component $c$). Figure 2.3 present for this case information similar to that the previous in figure 2.1. The surface concentration of propanenitrile as given by the two models is fairly close, while that of acrylonitrile presents differences up to about 25%.

As a final example we consider a drop consisting of toluene (component $a$) and heptane (component $b$) in hexadecafluorooxonane (perfluorocyclic oxide, $C_8F_{16}O$, component $c$). The surface concentrations for this case are shown in figure 2.4. In the first panel it looks as if the mole fraction of toluene ranges all the way up to 1, but in fact this is not so – this is due only to the extremely small solubility of the third
component in toluene. Again, we note a substantial difference of the present more precise theory and the approximations of section 2.4.

2.6 Results for $\rho_{a,b}^i = 0$

We now show some numerical results to illustrate quantitatively the consequences of the dissolution process as predicted by the present theory in some specific cases. This section is devoted to situations in which the concentration of the drop components in the host liquid is initially zero; in the next section we consider the interesting differences introduced by a non-zero initial concentration. The numerical method used to integrate the mass diffusion equation (2.4) with $\partial \rho_{a,b}/\partial r|_{r=R}$ given by (2.10) is described in Appendix B.

As we have already remarked in section 2.5, conditions that lead to the strong prevalence of either one of the two main components of the drop over most of the drop lifetime will not show much difference between the present theory and (2.23) as, in this case, one deals essentially with a mono-component drop. This situation occurs, e.g., when the solubility of one of the two drop components in the host liquid is much greater than that of the other or when the diffusivities of the two components in the continuous phase are very different. Significant differences, however, are found when neither of these two conditions is satisfied. Another situation in which the two theories give significantly different results is when the initial concentration of the drop constituents in the host liquid is non-zero, as will be seen in the next section.

Since the drop constituents are only sparingly soluble in the continuous phase, we dispense with the Maxwell-Stefan theory of multi-component diffusion (see e.g. Wesselingh and Krishna, 2000) and simply use the binary diffusivities to calculate the
mass fluxes as already noted in section 2.2. For some substances these properties are not available; in these cases they have been estimated using equation (2.40) given at the end of Appendix A.

Our first example is a drop composed of ethyl acetate (component a) and butyl acetate (component b) with initial mole ratios \( n_D^a(0) : n_D^b(0) = 9 : 1 \) and \( n_D^a(0) : n_D^b(0) = 1 : 1 \) in water and an initial drop radius of 43 \( \mu m \). The use of a 9 : 1 mole ratio is suggested by the fact that ethyl acetate is much more soluble in water than butyl acetate. The 1 : 1 mole ratio is included here for comparison. Figures 2.5a, 2.5b compare the time dependence of the drop radius predicted by the theory of section 2.3 with that of the simplified model (2.23). The difference in the drop lifetime between the two models is about 19 s, or 15% for the \( n_D^a(0) : n_D^b(0) = 9 : 1 \) case shown in figure 2.5a.

We can understand the origin of the sharp transition in these curves by looking at the history of the interface concentrations of the drop constituents shown in figure 2.6a in which, again, the solid and the dashed lines correspond to the present theory and
It is seen here that the abrupt change in the slope of the lines in figure 2.5a corresponds to the near complete depletion of ethyl acetate which leaves behind the much more slowly dissolving butyl acetate. The position of this abrupt change shifts to the left if the amount of the more soluble component is decreased as can be seen in figure 2.5b.

The spike in the ethyl acetate concentration in figure 2.6a is due to the non-monotonic dependence of the surface concentration on the mole fractions pointed out earlier in connection with figure 2.1a. The butyl acetate concentration becomes essentially constant and equal to its saturation value after the other component has dissolved away. During this latter phase the two theories predict the same surface concentration, as expected. The time dependence of the moles of the two components in the drop is shown in figure 2.6b.

It is interesting to note the relatively large difference in the drop dissolution times in spite of the apparent close similarity of the predictions shown in this figure. In

![Figure 2.6: Time dependence of the surface concentration (left) and of the moles of the two constituents (right) for the case of figure 2.5a (ethyl acetate in red, curves marked $a$, butyl acetate in blue, curves marked $b$) according to the present theory (solid lines) and the model of (2.23) (dashed lines).](image-url)
the precise theory the surface concentration of ethyl acetate in the initial stages of the process is higher than according to the approximate theory (see figure 2.6a), which leads to a faster dissolution of this component and, ultimately, to the 15% difference in total drop dissolution time.

A summary of the drop dissolution times as functions of the drop composition for this system according to the two theories is shown in the first panel of figure 2.7. Since the theories are identical for a mono-component drop, the lifetime predictions coincide at the two ends of the graphs. It is seen here that, for this particular system, differences are small for the reasons already described (although they rise to about 50% when the butyl acetate is present in only trace amounts. Thus, it is not surprising that Su and Needham (2013) concluded that their approximate model was in reasonable agreement with their experiments although the comparison between theory and experiment of their figure 5 shows a small, but systematic, over-prediction of the dissolution times in qualitative agreement with the present results. A direct comparison of the present theory with the data of Su and Needham (2013) is not possible because, as shown in Table 2.1 and as already noted in section 2.5, there is a significant difference between the solubilities predicted by UNIQUAC and the measured ones. This difference indicates that the basic version of UNIQUAC that we use is not very accurate for this particular system and a more advanced version, or a different model such UNIFAC (see e.g. Magnussen, Rasmussen, and Fredenslund, 1981), might be more suitable.

Analogous graphs for the second system considered in section 2.5, namely acrylonitrile and propanenitrile in water, are shown in the second panel of figure 2.7 and for the third system, toluene and heptane in hexadecafluorooxonane, in the third panel; the initial drop diameter is, again, 43 μm. It is seen here that differences for the second
Figure 2.7: Drop lifetime according to the present theory (solid lines) and the model of (2.23) as function of the drop composition for an initial drop radius of 43 \( \mu \text{m} \). (a) ethyl acetate/butyl acetate/water; (b) acrylonitrile/propanenitrile/water; (c) toluene/heptane/hexadecafluoroocoxonane.
Figure 2.8: Normalized drop radius $R(t)/R_0$ vs. time according to the present theory (solid line) and the model of (2.23). The drop consists of a mixture of toluene (component $a$) and heptane (component $b$) in hexadecafluorooxonane with an initial mole ratio $n^D_a(0) : n^D_b(0) = 3 : 7$ and an initial drop radius of 43 $\mu$m.

Figure 2.8 shows the large differences in the predictions for the normalized drop radius $R(t)/R_0$ vs. time while figure 2.9 compares the predictions for the surface concentrations and moles of the two drop constituents. The rapid depletion of the more soluble heptane is predicted very similarly by both models. However, the difference between the predictions for toluene produce a large difference in the drop lifetime.

It is also of interest to study the magnitude of the three contributions accounting for the rate of diffusion of the material in the drop found by combining (2.11) and...
Figure 2.9: Time dependence of the surface concentration (left) and of the moles of the two constituents (right) for the case of figure 2.8 (toluene in red, curves marked $a$, heptane in blue, curves marked $b$) according to the present theory (solid lines) and the model of (2.23) (dashed lines).

Figure 2.10: Time dependence of the contributions $\dot{A}_a$, $\dot{B}_a$ and $\dot{C}_a$ defined in (2.26), (2.27) and (2.28), respectively, to the rate of mass loss of toluene from the drop of figures 2.8 to 2.9b; the asterisk indicates normalization by division by $\dot{A}(0)$. 

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(2.4), namely
\[
\dot{A}_a(t) = 4\pi R(t) D_a \left[ \rho_i^a - \rho_s^a(t) \right],
\] (2.26)
\[
\dot{B}_a(t) = \frac{4\pi R^2(t) D_a}{\sqrt{\pi D_at}} \left[ \rho_i^a - \rho_s^a(t) \right],
\] (2.27)
\[
\dot{C}_a(t) = 4\pi R^2(t) D_a \left| \int_0^t \frac{d\rho_s^a(\tau)}{d\tau} \left[ \frac{1}{\sqrt{\pi D_at - \tau}} - \frac{1}{\sqrt{\pi D_at}} \right] d\tau \right|.
\] (2.28)

The time evolution of these terms, normalized by division by $\dot{A}_a(0)$, is shown with semi-logarithmic axes in figure 2.10 for the toluene component of the case of figures 2.8 and 2.9; the asterisk on the symbols labelling the curves indicates that these

![Figure 2.11: Time dependence of the contributions $A_a$, $B_a$ and $C_a$ defined as the integrals of (2.26), (2.27) and (2.28)), to the rate of mass loss of toluene from the drop of figures 2.8 to 2.9b; the asterisk indicates normalization by division by $m_a(0)$.

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Figure 2.12: Sherwood number (defined in (2.29)) vs. time for the toluene component (a) and the heptane component (b) of the toluene/heptane drop in hexadecafluorooxonane of figures 2.8 to 2.11 (initial mole ratio $n_D^a(0) : n_D^b(0) = 3 : 7$, initial drop radius of 43 µm). The results of the approximate theory (first two terms of (2.30)) nearly superpose on the dashed line.

are normalized values. The results for the other component, heptane, are similar. It is seen that the dominant term is $\dot{A}_a$. The singularity in the denominator of $\dot{B}_a$ at $t = 0$ causes this term to dominate for very small times, but its importance quickly decreases and the integral term $\dot{C}_a$ is the least important contribution. It must therefore be concluded that the major contributor to the quantitative differences found in this study is not due to this new term but, rather, to the way in which the surface concentrations are calculated.

Figure 2.11 shows the time integrals of these three terms, namely $A_a(t) = \int_0^t \dot{A}_a(\tau)d\tau$ etc., normalized by division by $m_a(0)$. The graphs confirm that most of the mass transfer is due to the first term $A_a(t)$. The integral term $C_a(t)$ accounts for
about 4% of the total.

As a final point of interest, we show in figure 2.12 an example of the time dependence of the effective Sherwood numbers for the two components, defined by

\[
Sh_{a,b} = \frac{2R(t)[-\partial \rho_{a,b}/\partial r]_{r=R}}{\rho_{s f}^{a,b}(t) - \rho^i_{a,b}},
\]

for the same case of figures 2.8 to 2.11, namely a drop composition in the ratio 3:7 of toluene to heptane. By (2.11), the Sherwood number equals

\[
Sh_a = 2 + \frac{2R(t)}{\sqrt{\pi D_a t}} + \frac{2R}{\rho_{s f}^a(t) - \rho^i_a} \int_0^t d\rho_{s f}^a(\tau) \left[ \frac{1}{\sqrt{\pi D_a (t - \tau)}} - \frac{1}{\sqrt{\pi D_a t}} \right] d\tau,
\]

with a similar expression for the \( Sh_b \). The second term vanishes as \( R \to 0 \) and therefore, for the approximate model (dashed line), which does not contain the integral, \( Sh_a \to 2 \). As shown in figures 2.9a and 2.10, however, the time derivative of the surface concentration becomes large and negative for small radius so that, for the complete model, the final value of \( Sh_{a,b} \) dips below 2.

\section{Results for \( \rho^i_{a,b} \neq 0 \)}

The picture described in the previous section becomes more complex when the initial concentration of the drop components in the continuous phase is non-zero. An interesting observation is that, in this case, it is possible for the ratio \( n^D_a/n^D_b \) of the two components in the drop to take on a constant value in the early stages of the process and to maintain it until the end. This phenomenon occurs because, in view of the single degree of freedom of the system (section 2.3), constancy of \( n^D_a/n^D_b \) implies constancy of the interface concentrations. As a consequence, when \( n^D_a/n^D_b \)
has stabilized, the time dependence of the integral term in (2.11),

\[
\frac{1}{\sqrt{\pi D_a t}} \int_0^t \frac{d\rho_a^{sf}(\tau)}{d\tau} \left[ \frac{1}{\sqrt{1 - \tau/t}} - 1 \right] d\tau,
\]

(2.31)
decreases faster than \(t^{-1/2}\). If the effect of this term (which anyway is small, as shown in the example of figures 2.10 and 2.11) is neglected, and if the diffusivities are not too different, with the aid of (2.14), we find from (2.4) and (2.11)

\[
\frac{d}{dt} \left( \frac{n_a^D}{n_b^D} \right) = \frac{\mathcal{M}_b}{\mathcal{M}_a} \frac{d}{dt} \left( \frac{m_a}{m_b} \right) \approx \frac{4\pi R^2}{\mathcal{M}_a m_b x_b^D} \left( \frac{1}{\sqrt{\pi D_b t}} + \frac{1}{R} \right) \Delta,
\]

(2.32)

where

\[
\Delta = D_a \mathcal{M}_b x_b^D \left( \rho_a^i - \rho_a^{sf} \right) - D_b \mathcal{M}_a x_a^D \left( \rho_b^i - \rho_b^{sf} \right).
\]

(2.33)

Thus, \((d/dt)(n_a^D/n_b^D) = 0\) when \(\Delta = 0\), i.e., when

\[
\frac{\rho_a^i - \rho_a^{sf}}{\rho_b^i - \rho_b^{sf}} = \frac{D_b \mathcal{M}_a x_a^D}{D_a \mathcal{M}_b x_b^D}.
\]

(2.34)

For given mass diffusivities and initial concentrations \(\rho_{a,b}^i\) in the continuous phase, the two sides of this equation are functions of the single degree of freedom determining the equilibrium concentrations and the equality may be satisfied for specific values of that parameter. When this happens, the ratio \(n_a^D/n_b^D = (\mathcal{M}_b/\mathcal{M}_a)m_a/m_b\) remains constant. Clearly, this condition can only be satisfied when both \(\rho_a^i - \rho_a^{sf}\) and \(\rho_b^i - \rho_b^{sf}\) have the same sign, i.e., for drops which absorb or lose both components at the same time. It is important to note that, unlike binary systems, \(\rho_{a,b}^i - \rho_{a,b}^{sf}\) can be positive even if the initial concentration is smaller than saturation as, when \(\rho^{sf}\) is a monotonic function of the mole fraction (as in the majority of cases), the saturation concentration is the maximum value of \(\rho^{sf}\).

It is easy to see that there must always be at least one root of (2.34) and, if there are
Figure 2.13: Graphs of $\Delta / D_a \mathcal{M}_b$, with $\Delta$ defined in (2.33), vs. the mole fraction of toluene for the toluene/heptane/hexadecafluorooxonane system. The zeros of this quantity are the equilibrium solutions given by (2.34). They are stable when the derivative is negative and unstable otherwise. The example on the left is for $\rho_i^a / \rho_{sat}^a = 0.9$, $\rho_i^b / \rho_{sat}^b = 0.5$ while that on the right is for $\rho_i^a / \rho_{sat}^a = 0.0026$, $\rho_i^b / \rho_{sat}^b = 0.1$.

several, their number must be odd. Indeed, for $x_a^D = 0$, $\Delta = D_a \mathcal{M}_b (x_b^D)_{max} \rho_i^i > 0$, with $(x_b^D)_{max}$ the value of $x_b^D$ when $x_a^D = 0$. On the other hand, when $x_a^D = 0$, $\Delta = -D_b \mathcal{M}_a (x_a^D)_{max} \rho_i^i < 0$ so that the function $\Delta(x_a^D)$ goes through zero at least once. When there is only one root, $d\Delta / dx_a^D$ evaluated at that root must be negative, which implies that the root is stable: a small increase in $x_a^D$ produces a negative value of $(d / dt)(n_a^D / n_b^D)$, which causes $x_a^D$ to decrease. If there is more than one root, the smallest and largest ones will be stable, while some of the intermediate ones will be unstable. The actual number of roots will depend on the initial concentrations $\rho_{a,b}^i$ in the host liquid.

Examples of the function $\Delta / D_a \mathcal{M}_b$ are shown in figure 2.13 for the system toluene/heptane/hexadecafluorooxonane. The example on the left is for $\rho_i^a / \rho_{sat}^a = 0.9$, $\rho_i^b / \rho_{sat}^b = 0.5$ while that on the right is for $\rho_i^a / \rho_{sat}^a = 0.0026$, $\rho_i^b / \rho_{sat}^b = 0.1$. The previous arguments do not apply when either one or both $\rho_{a,b}^i$ vanish. In these cases, $\rho_{a,b}^{sf} = 0$ and/or $\rho_{b}^{sf} = 0$ may be stable or unstable equilibrium points, possibly
in addition to others.

If we choose $\rho_{SF}^{s}$ as the single degree of freedom of the system, it is possible to plot $\rho_{SF}^{s}$ as a function of $\rho_{SF}^{a}$; the panels of figure 2.14 depict this functional dependence for the case of the toluene/heptane/hexadecafluorooxonane system of figure 2.4. The point where the curve intersects the horizontal axis corresponds to the solubility of component $a$ in the continuous phase, and similarly for the other component on the vertical axis.

The three panels of figure 2.14 differ in the initial concentrations $\rho_{i,a,b}$ of the drop components in the host liquid, the values of which are indicated by the dashed horizontal and vertical lines. The point where these lines intersect are marked by the upper case letter $A$ in figure 2.14(a), $B$ in figure 2.14(b) and $C$ and $\tilde{C}$ in figure 2.14(c). The diamond on the curves is the only solution of (2.34) existing for the specific values of $\rho_{i,a,b}$ used in these numerical examples. From the fact that, as noted before, $\rho_{i,a} - \rho_{SF}^{a} \text{ and } \rho_{i,b} - \rho_{SF}^{b}$ must have the same sign at the equilibrium point, it follows that this point must lie along the arc of the curve between the intersections with the horizontal and vertical lines $\rho_{SF}^{a} = \rho_{i,a} \text{ and } \rho_{SF}^{b} = \rho_{i,b}$.

The history of the drop growth or dissolution corresponds to the path of a point along the curves of figures 2.14. If there is only one equilibrium solution, it is stable and the path will be attracted by it: the growth, or dissolution, will eventually occur maintaining a constant value of $n_{DF}^{D}(t) / n_{DF}^{D}(t)$. As noted before, unstable solutions can only occur together with stable ones. In this case, each stable point will have its own domain of attraction and the drop composition will eventually drift towards one of the stable points depending on the initial drop composition.

A consideration of the plane $(\rho_{SF}^{a}, \rho_{SF}^{b})$ also permits one to deduce when and
Figure 2.14: The solid lines (the same in all three panels) are the surface concentration of heptane vs. that of toluene for the toluene/heptane/hexadecfluorooxonane system of figure 2.4. The vertical dashed lines denote the values of the initial concentrations in the host liquid and a diamond marks the (single for these parameter values) equilibrium solution (2.34). The points where the curve intersects the axes correspond to the solubility of the respective component in the host liquid. The drop dissolves when the intersection point of the initial concentrations is under the curve, as in panel (a), while it grows when it is outside as in panels (b) and (c). The model (2.23) replaces the curve by the inclined straight line (green) in (c). Drops placed in a liquid with initial concentrations falling between this line and the curve are erroneously predicted to grow.
Figure 2.15: Surface concentration of butyl acetate vs. that of ethyl acetate for the system ethyl acetate/butyl acetate/water. As shown in figures 2.1a and 2.1b, in this case the dependence of the surface concentrations on the drop composition is non-monotonic and this feature is responsible for the small loop in the left diagram which is enlarged in the right diagram.

how the drop will dissolve or grow in dependence of the initial concentrations in the continuous phase. Consider, for example, figure 2.14(a) and suppose that the initial drop composition is such that the surface concentration (which must be on the \((\rho_{s}^{af}, \rho_{s}^{bf})\) curve for equilibrium) is near the lower right corner, so that \(\rho_{s}^{af} (t = 0) > \rho_{i}^{a}\) while \(\rho_{s}^{bf} (t = 0) < \rho_{i}^{b}\). It is evident from (2.11) that component \(a\) will start to diffuse out of the drop while component \(b\) will diffuse in so that the drop composition moves up the curve until it eventually reaches the equilibrium point marked by a diamond in the figure. At this point \(\rho_{s}^{af}\) and \(\rho_{s}^{bf}\) exceed \(\rho_{i}^{a}\) and \(\rho_{i}^{b}\) and both components will diffuse out so that the drop ultimately shrinks to zero radius.

Arguments of this type lead to the conclusion that, when the intersection of the two lines \((\rho_{i}^{a}, \rho_{i}^{b})\) lies under the curve, both constituents of the drop ultimately diffuse out and the drop dissolves, and conversely when the intersection point lies outside the curve. When the host liquid is supersaturated with one or both components, as points \(C\) and \(\tilde{C}\) in figure 2.14(c), the drop grows as would be expected even without analysis. However, it will be noticed that it is possible for growth to occur even in a
host liquid undersaturated with both components of the drop as indicated by the point
B in figure 2.14(b). This is impossible in a binary system, but it becomes possible in a
ternary or higher-order system.

The approximate model of (2.23) replaces the curves in figures 2.14 by the in-
clined straight line (green) shown in panel (c). Drops placed in a liquid with initial
concentrations falling between this line and the curve are erroneously predicted to
grow.

These general conclusions may be expected to hold also for a non-spherical drop
such as, for example, a drop sinking or rising by buoyancy, provided that the drop
composition remains homogeneous, the two diffusivities in the host liquid are not
too different and history effects are negligible, as we have assumed. Indeed, by the
linearity of the diffusion equation, in these more general cases the rate of change of
the moles of each component must be proportional to $D_{a,b}(\rho_{a,b}^{i} - \rho_{a,b}^{sf}) / \mathcal{M}_{a,b}$, which
is the only feature of the specific solution for a stationary drop that we have used in
the previous argument.

The situation depicted in figures 2.14 is typical of systems in which the surface
concentration of each component is a monotonic function of the corresponding mole
fraction. The case in which the dependence of the surface concentrations on the mole
fractions is non-monotonic, as in the case of figure 2.1a, is more complex, although
the equilibrium points and their stability can be studied numerically similarly to
figure 2.13. The dependence of $\rho_{b}^{sf}$ on $\rho_{a}^{sf}$ for the ethyl acetate/butyl acetate/water
system is shown in figure 2.15. The small loop in the left panel (magnified in the right
panel) is due to the presence of the maxima in the curves of figures 2.1a and 2.1b.
2.8 Summary and conclusions

We have presented a consistent theory for the dissolution, or growth, of a multi-component, well-mixed spherical drop at rest in a host liquid. The theory incorporates in a proper way the constraints of thermodynamic equilibrium at the drop surface by the adoption of UNIQUAC, a widely used model for the parametrization of the activity coefficients of many chemical compounds.

The gradual change of the drop composition due to the different solubilities and diffusivities of its components in the host liquid causes a variation in time of the concentration of these components at the surface of the drop. This circumstance requires a modification of the classic theory of Epstein and Plesset (1950b), which introduces memory effects in the diffusive flux out of the drop as shown in (2.10).

For the case in which the drop constituents are already present in the host liquid at the beginning of the process, we have found that, whatever the initial composition, the mole ratio of the drop constituents will reach a steady constant value for both dissolution and growth. We have formulated a simple criterion to predict whether one or the other will take place in any specific situation. In suitable conditions, a drop can grow even when the concentration of both constituents in the host liquid is smaller than their respective saturation values. This observation can have significant implications for solvent extraction processes which are widely used in the chemical and environmental remediation industries.

The predictions of the theory have been compared with those of a simpler approach to the problem built on the assumption of independence of the activity coefficients from the drop composition. It is found that the predictions of the two theories are similar when the solutions are close to ideal or there is a large difference in the
solubilities, or diffusivities, of the drop constituents in the host liquid, unless initially the drop consists mainly of the more soluble component. When the solubilities and diffusivities are close, the differences can be substantial for any drop composition. Thus, an experimental confirmation of our results would require the use of liquids forming non-ideal solutions and having comparable solubilities and diffusivities in the host liquid. Furthermore, the drop should be small enough that the diffusion time of its constituents is smaller than the dissolution time so as to ensure spatial uniformity of its composition.

To the extent that the drop considered in this work is spherical and homogeneous, with no relative motion with respect to the host liquid, our model is idealized. However, in section 2.7, we have presented arguments to show that these conclusions are valid beyond the limits of the model, e.g. for a sessile or translating drop.

Although in this chapter we have only considered ternary system, the same general approach would apply more broadly to systems with more than three components. In particular, quaternary systems can be studied by the same method as the UNIQUAC model is known to give reasonable results for many such systems (see e.g. Chen et al., 2014).

**Appendix A – The UNIQUAC model**

There are several versions of the UNIQUAC model (see e.g. Taylor and Krishna, 1993; Tamura et al., 2000; Islam, Javvadi, and Kabadi, 2011) but, for the purposes of this chapter, the basic formulation of Abrams and Prausnitz (1975) and Anderson & Prausnitz (1978a, 1978b) is sufficient.

The activity coefficient $\gamma_a$ of a component $a$ is expressed as the product of a
combinatorial contribution $\gamma^c_a$ and a residual contribution $\gamma^r_a$, $\gamma_a = \gamma^c_a \gamma^r_a$. The combinatorial term is given by

$$\log \gamma^c_a = 1 - \frac{\Phi_a}{x_a} + \log \frac{\Phi_a}{x_a} - \frac{1}{2}zq_a \left(1 - \frac{\Phi_a}{\theta_a} + \log \frac{\Phi_a}{\theta_a}\right).$$

(2.35)

Here $\Phi_a$ is the volume fraction of the $a$-component:

$$\Phi_a = \frac{x_ar_a}{x_ar_a + x_br_b + x_cr_c},$$

(2.36)

with the $r$’s model parameter related to the molecular volumes of each substance. The quantity $\theta_a$ is the area fraction of the component expressed in a similar way:

$$\theta_a = \frac{x_aq_a}{x_aq_a + x_bq_b + x_cq_c},$$

(2.37)

with the parameters $q$ other pure-component molecular structure constants. The residual contribution is expressed as

$$\gamma^r_a = q_a \left(1 - \log \frac{\sum k q_k x_k \tau_{ka}}{\sum k q_k x_k} - \sum k \frac{q_k x_k \tau_{ak}}{\sum \ell q_\ell x_\ell \tau_{k\ell}}\right),$$

(2.38)

in which the summations are over the three components $a$, $b$ and $c$. The quantities $\tau_{k\ell}$ are expressed as

$$\log \tau_{k\ell} = -\frac{A_{k\ell}}{T},$$

(2.39)

in which the $A$’s are binary interaction parameters. The coordination number $z$ in (2.35) is taken equal to 10. The value of the other model parameters are given in Tables 2.2 and 2.3 for all the compounds used in the numerical examples given in this chapter. The numerical calculation of the liquid-liquid equilibrium line was effected using the method of Prausnitz et al. (1980) and Islam, Zavvadi, and Kabadi (2012).

For some liquids we have been unable to find values of the binary diffusivities in
### Table 2.2: Values of the parameters $r$ and $q$ of the UNIQUAC model used in this work. The references are $^a$Sørensen & Arlt (1980) Part 2, $^b$Sørensen & Arlt (1980) Part 3.

<table>
<thead>
<tr>
<th>Component $^{a,b}$</th>
<th>$r$</th>
<th>$q$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethyl acetate</td>
<td>3.4786</td>
<td>3.116</td>
</tr>
<tr>
<td>butyl acetate</td>
<td>4.8274</td>
<td>4.196</td>
</tr>
<tr>
<td>acrylonitrile</td>
<td>2.3144</td>
<td>2.052</td>
</tr>
<tr>
<td>propanenitrile</td>
<td>2.5445</td>
<td>2.264</td>
</tr>
<tr>
<td>toluene</td>
<td>3.9228</td>
<td>2.968</td>
</tr>
<tr>
<td>heptane</td>
<td>5.1742</td>
<td>4.396</td>
</tr>
<tr>
<td>perfluorocyclic oxide</td>
<td>8.3279</td>
<td>7.600</td>
</tr>
<tr>
<td>water</td>
<td>0.920</td>
<td>1.400</td>
</tr>
</tbody>
</table>

### Table 2.3: Values of the binary interaction parameters $A$ used in equation (2.39) of the UNIQUAC model used in this work. The references are $^a$Arce, Alonso, and Vidal (1999), $^b$Sørensen & Arlt (1980) Part 2, $^c$Sørensen & Arlt (1980) Part 3.

<table>
<thead>
<tr>
<th>System</th>
<th>$A_{ab}$ (K)</th>
<th>$A_{ba}$ (K)</th>
<th>$A_{ac}$ (K)</th>
<th>$A_{ca}$ (K)</th>
<th>$A_{bc}$ (K)</th>
<th>$A_{cb}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethyl acetate+butyl acetate + water (298.15 K)$^a$</td>
<td>-53.249</td>
<td>317.47</td>
<td>408.81</td>
<td>107.72</td>
<td>590.92</td>
<td>209.68</td>
</tr>
<tr>
<td>acrylonitrile+propanenitrile + water (298.15 K)$^b$</td>
<td>27.07</td>
<td>38.361</td>
<td>316.84</td>
<td>211.78</td>
<td>303.09</td>
<td>123.77</td>
</tr>
<tr>
<td>toluene+heptane</td>
<td>78.766</td>
<td>-48.020</td>
<td>10.969</td>
<td>253.79</td>
<td>8.7937</td>
<td>138.91</td>
</tr>
<tr>
<td>perfluorocyclic oxide</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

46
the continuous phase. In these cases we have used the following empirical relation giving the diffusivity of solute $A$ in solvent $B$ (Poling, Prausnitz, and O’Connell, 2000, p. 11.26):

$$D_{AB} = 1.55 \times 10^{-8} V_B^{0.87} T^{1.29} \sigma_B^{0.125} \frac{V_A^{0.42} \mu_B^{0.92} \sigma_A^{0.105}}{\mu_B \sigma_B^{0.125} \sigma_A^{0.105}}.$$  (2.40)

Here $V$ denotes the molar volume in g/mole, $T$ the absolute temperature in Kelvins, $\mu$ the viscosity in mPa s and $\sigma$ the surface tension in mN/m.

**Appendix B – Numerical method**

The equation to be solved is

$$\frac{dm_a}{dt} = 4\pi R^2(t) D_a \left[ \frac{\rho_{ia} - \rho_{ia}^{sf}(0)}{\sqrt{\pi D_a t}} + \frac{\rho_{ia}' - \rho_{ia}^{sf}(t)}{R} - \int_0^t \frac{d\rho_{ia}^{sf}(\tau)}{d\tau} \frac{d\tau}{\sqrt{\pi D_a(t - \tau)}} \right].$$  (2.41)

To deal with the singularity of the integrand we approximate the integral as

$$\int_0^{t^n+1} \frac{d\rho_{ia}^{sf}(\tau)}{d\tau} \frac{d\tau}{\sqrt{\pi D_a(t^n+1 - \tau)}} \approx \int_0^{t^n} \frac{d\rho_{ia}^{sf}(\tau)}{d\tau} \frac{d\tau}{\sqrt{\pi D_a(t^n+1 - \tau)}}$$

$$+ \frac{1}{\sqrt{\pi D_a}} \left[ \frac{d\rho_{ia}^{sf}}{dt} \right]_{t^n} \int_{t^n}^{t^n+1} \frac{d\tau}{\sqrt{\pi D_a (t^{n+1} - \tau)}}$$

$$= \int_0^{t^n} \frac{d\rho_{ia}^{sf}(\tau)}{d\tau} \frac{d\tau}{\sqrt{\pi D_a(t^n+1 - \tau)}} + 2\sqrt{\frac{t^{n+1} - t^n}{\pi D_a}} \left[ \frac{d\rho_{ia}^{sf}}{dt} \right]_{t^n+1}.$$  (2.42)

The derivative in the last term is evaluated at the same time level as $dm_a/dt$ in the left-hand side of (2.41), which confers to the procedure a desirable degree of implicitness.

The approximation implicit in the last step depends on the time scale $T_a$ of variation of $\rho_{ia}^{sf}$. To estimate $T_a$, we use the result of Epstein and Plesset (1950b) weighing by
the initial mass fraction of the more soluble component, say component $a$:

$$T_a = \frac{m_a(0)}{m_a(0) + m_b(0)} \frac{R_0^2}{D_a |\rho_{ia} - \rho_{ia}^s| / \rho},$$  \hspace{1cm} (2.43)

where $\rho$ is the average initial density of the drop. Provided $t^{n+1} - t^n \ll T_a$ the approximation is justified. For completeness we now describe the remaining steps of the calculation.

From (2.17) we write $d\rho_{sf}^a / dt \equiv \dot{\rho}_{sf}^a$ in the form

$$\dot{\rho}_{sf}^a = \dot{x}_a^D \frac{d}{dx_a^D} \left( \frac{M_a x_a^C}{M_a x_a^C \rho_c^0} \right),$$  \hspace{1cm} (2.44)

with a similar equation for $\dot{\rho}_{sf}^b$ obtained by interchanging the indices $a$ and $b$. The derivative of the quantity in parentheses is calculated numerically due to the very complex functional dependence of the quantities involved upon $x_a^D$. The derivative $\dot{x}_a^D$ is then expressed in terms of $\dot{m}_a$ and $\dot{m}_b$ by using the relation of this quantity with the auxiliary parameter $\tilde{x}_a^D = \left( m_a / M_a \right) / \left( m_a / M_a + m_b / M_b \right)$. This step expresses $\dot{\rho}_{sf}^a$ in terms of a linear combination of $\dot{m}_a$ and $\dot{m}_b$, and a relation with a similar structure is obtained for $\dot{\rho}_{sf}^b$. Upon substitution into the last term of (2.42) and the analogous relation for the other component we are left with a linear system of two equations in the two unknowns $\dot{m}_a$ and $\dot{m}_b$ which can be readily solved and integrated.

To execute the first time step, which is affected by the singularity at $t = 0$ in the first term in the right-hand side of (2.41), we use the approximation

$$\int_0^{\Delta t_1} 4\pi R^2(t) D_a \frac{\rho_{ia}^i - \rho_{ia}^s(0)}{\sqrt{\pi D_a t}} dt \approx 8\pi R^2(0) D_a [\rho_{ia}^i - \rho_{ia}^s(0)] \sqrt{\frac{\Delta t_1}{\pi D_a}},$$  \hspace{1cm} (2.45)

where $\Delta t_1$ is the first time step. At this point the procedure previously described can be started. As a rough check we have used different values for $\Delta t_1$ finding that the
results at later times were essentially unaffected. In order to check the accuracy of this entire numerical calculation, we repeated it with time steps of several different magnitudes to prove convergence.
Chapter 3

History effect ¹

3.1 Introduction

Dependence on past history is one of the distinctive features of diffusive processes. In this chapter we study the consequences of this dependence on the mass exchange between a gas bubble and the ambient liquid super- or under-saturated with dissolved gas. The driver for the exchange is the difference between the concentration of the diffusing species at the surface of the bubble and in the surrounding liquid. The former is dictated by the bubble internal pressure according to Henry’s law. We consider the limit of small radial velocities, which enables us to omit the effects of convection focusing specifically on diffusion and the attendant history phenomena. We first develop a general theory (section 3.2) followed by some general scaling considerations (Section 3.2), and then illustrate its consequences for cases in which the ambient pressure oscillates (section 3.4) or is constant (sections 3.5 and 3.6), finding strong effects in the former situation and small ones in the latter two.

¹This chapter is based on the paper "History effects on the gas exchange between a bubble and a liquid." by Chu & Prosperetti (Physical Review Fluids, vol. 1, 064202, 2016.)
pressure field is well known in the acoustics literature where it is referred to as rectified diffusion (see e.g. Eller and Flynn, 1965; Crum, 1980; Brenner, Hilgenfeldt, and Lohse, 2002). The adjective “rectified” refers to the fact that a net inflow of gas dissolved in the liquid becomes possible in certain conditions. This phenomenon is due to the alternating expansion and contraction of the bubble, which causes the pressure of the gas contained in it to oscillate. Due to Henry’s law, the concentration of dissolved gas in the liquid at the bubble surface also oscillates and, if it becomes sufficiently small during expansion, the resulting diffusive influx may be large enough to balance the mass lost during contraction when the pressure rises.

A very complete theory of rectified diffusion has been developed by Fyrillas and Szeri (Fyrillas and Szeri, 1994) for conditions in which the diffusion layer, of order \( \sqrt{D/\omega} \) (with \( D \) the gas diffusivity in the liquid and \( \omega \) the angular frequency of the ambient pressure field) is much thinner than the bubble radius. In this limit, the alternating thinning and thickening of the diffusive boundary layer at the bubble surface plays a dominant role in determining the mass transfer. Here we focus on the opposite limit, in which the frequency is low and the diffusion layer is much thicker than the bubble radius. A situation of this type might be encountered, for example, in the case of bubbles present in a liquid the container for which is subject to mechanical vibrations; examples of other possible occurrences are low-frequency acoustic fields or bubbles in a turbulent liquid flow. Under these conditions there is no diffusive boundary layer and rectified diffusion is only dependent on the difference in the surface area of the bubble upon expansion and contraction.

The bubble-liquid mass exchange in a constant pressure field was first studied in a by-now classic paper by Epstein & Plesset (Epstein and Plesset, 1950b) who
treated the problem of the dissolution or growth of a gas bubble in a liquid under- or super-saturated with gas. More recently their approach has been extended to the dissolution or growth of single-component drops in an immiscible liquid (Duncan and Needham, 2004; Duncan and Needham, 2006) and to the study of nanodrops and nanobubbles (Lohse and Zhang, 2015). As long as surface tension and dynamical effects are negligible, whatever the bubble radius, the gas pressure in the bubble balances the constant ambient pressure and the dissolved gas concentration at the bubble surface remains constant according to Henry’s law. With surface tension, however, the bubble internal pressure comes also to depend on the bubble radius and, therefore, it changes as the bubble grows or dissolves.

Epstein & Plesset (Epstein and Plesset, 1950b) did not explicitly account for the time-dependence of this effect, assuming an instantaneous adjustment of the dissolved gas concentration to the changing boundary condition and, in so doing, they omitted history effects. This situation is considered explicitly in section 3.5 with the conclusion that their procedure is essentially justified as long as the bubble is larger than a few hundred nanometers. Another situation in which the dissolved gas concentration at the bubble surface depends on time, considered in section 3.6, is that of a multi-component bubble the constituents of which dissolve and diffuse at different rates. Here again history effects prove of relatively minor importance.

History effects have also been studied in a very recent paper (Peñas-López et al., 2016) focusing, however, on situations different from those considered here, namely the response of the bubble when the ambient pressure undergoes jump discontinuities, and rectified diffusion in the limit of small-amplitude oscillations. The method of investigation is similar, except for the use of a modified time variable (a point which
we briefly consider in the Appendix). This chapter also contains several interesting observations on the nature of the approximations made in the mathematical model.

The phenomena studied in this chapter are similar to those considered in chapter 2. In that case, the time dependence of the surface concentration of the diffusing species is a consequence of their mutual interaction as the composition of the drop varies in time.

### 3.2 Analysis

We follow the formulation of Epstein & Plesset. \cite{Epstein:1950:EP} according to which a bubble, containing an incondensible gas at a pressure \( p_g \), is instantaneously exposed to an infinite liquid medium containing the same gas dissolved with a uniform concentration \( \rho_i^g \). The ambient pressure in the liquid is \( p_\infty \) and diffusion and pressure variation are so slow that mechanical equilibrium may be assumed at the bubble surface, according to which

\[
p_g = p_\infty + \frac{2\sigma}{R}, \tag{3.1}
\]

where \( \sigma \) is the surface tension coefficient and \( R \) the bubble radius. As in Epstein and Plesset \cite{Epstein:1950:EP} we assume that the bubble remains spherical and that it does not move relative to the host liquid.

The liquid concentration \( \rho_s^{gf} \) of the dissolved gas at the bubble surface is determined by Henry’s law as

\[
\rho_s^{gf} = K(T)p_g, \tag{3.2}
\]

in which \( K(T) \) is a function of the absolute temperature \( T \). The difference \( \rho_s^{gf} - \rho_i^g \) sets up a diffusive flux \( -D\nabla \rho_g \) which causes inflow or outflow of gas from the
bubble; $D$ is the mass diffusivity of the gas in the liquid. In order to characterize the solubility of the gas it is useful to follow Epstein and Plesset (1950b) introducing a parameter

$$\frac{\rho_{\text{sat}}}{\rho_b^0} = \frac{K(T)R_G T}{M_g}, \quad (3.3)$$

with $\rho_{\text{sat}}$ the density of gas dissolved in the liquid at saturation under the pressure $p_\infty^0$, $\rho_b^0$ the density of the free gas at the same pressure $p_\infty^0$, $R_G$ the universal gas constant, $T$ the absolute temperature and $M_g$ the molecular mass of the gas.

For a bubble undergoing spherically symmetric motion, the convection-diffusion equation for the density $\rho_g$ of gas dissolved in the liquid may be written as

$$\frac{\partial \rho_g}{\partial t} = 1 \frac{1}{r^2} \frac{\partial}{\partial r} \left[ Dr^2 \frac{\partial \rho_g}{\partial r} - R^2 \dot{R} (\rho_g - \rho_g^i) \right] , \quad (3.4)$$

in which $R = R(t)$ is the bubble radius, $\dot{R} = dR/dt$ and $r$ is the distance from the bubble center. For motions taking place on a time scale $\omega^{-1}$ sufficiently long that the diffusion length $\sqrt{\pi D/\omega}$ exceeds the radius, the characteristic length for the gradient is the bubble radius itself and we have the estimate

$$\frac{R^2 \dot{R} (\rho_g - \rho_g^i)}{Dr^2 \partial \rho_g / \partial r} \sim \frac{R^2 \dot{R}}{r^2 D} , \quad (3.5)$$

in which the second fraction may be considered a Péclet number. Thus, the last term in (3.4) will be negligible compared with the diffusion term provided the Péclet number is small, which we assume. In an oscillating pressure field, if the bubble radius changes by $\Delta R$ during the time $\omega^{-1}$, $\dot{R} \sim \omega \Delta R$ and $R \dot{R} / D \sim (R^2 \omega / D)(\Delta R / R)$. The first factor is the square of the ratio of the radius to the diffusion length and is essentially the square of the parameter $Pe$ introduced later in (3.22).

On the basis of these considerations and assumptions we drop the convective
term. Furthermore, as in the previous chapter we define \( u(r, t) = r[\rho_g(r, t) - \rho_g^i] \) to recover the simpler diffusion equation

\[
\frac{\partial u}{\partial t} = D \frac{\partial^2 u}{\partial r^2},
\]

(3.6)

which will be used in this chapter. This is the standard approximation made in a majority of papers on the present subject and, most recently, in Peñas-López et al. (2016). Some further considerations on these issues will be found in the next section.

The boundary conditions are

\[
\rho_g(R(t), t) = H(t)\rho_g^{sf}(t) + (1 - H(t)) \rho_g^i, \quad \lim_{r \to \infty} \rho_g = \rho_g^i, \quad (3.7)
\]

where the Heaviside function \( H(t) \) enforces the fact that the boundary condition is applied instantaneously at \( t = 0^+ \), the concentration being \( \rho_g^i \) at earlier times. The initial condition is

\[
\rho_g(r, 0) = \rho_g^i. \quad (3.8)
\]

The rate at which \( m_g \), the mass of gas contained in the bubble, varies is given by

\[
\frac{dm_g}{dt} = 4\pi R^2(t) D \frac{\partial \rho_g}{\partial r} \bigg|_{r = R(t)}. \quad (3.9)
\]

Unlike Epstein & Plesset, we allow here \( p_\infty \) to be time-dependent but to vary so slowly that the quasi-equilibrium condition (3.1) is very nearly satisfied at every instant. The condition for the validity of this approximation is that the frequency be much smaller than the bubble resonance frequency, of the order of \( \sqrt{3p_\infty/(\rho R^2)} \). Ordinarily this condition is much less stringent than the previous one related to the neglect of convective terms.

In response to the changing ambient pressure, the bubble radius will also change.
If the gas in the bubble can be described by the ideal gas law, the bubble radius satisfies the relation

\[ p_g \left( \frac{4}{3} \pi R^3 \right) = \frac{m_g}{M_g} R_G T, \quad (3.10) \]

in which \( p_g \) is given by (3.1). In view of the assumed slow variation of the pressure, the gas will behave essentially isothermally so that \( T \) can be considered to be a constant.

In principle, with a significant amount of vapor in the bubble, several new effects become important: the mutual diffusion of the gas and vapor, latent heat and temperature variations both in the gas-vapor mixture and in the liquid. As the focus of this chapter is to study the effect of the time dependence of the dissolved gas concentration at the bubble surface, we disregard these complications here simply noting that a constant vapor pressure contribution can be simply added to the left-hand side of (3.1) if necessary.

Following the work of Epstein & Plesset and many other investigators Subramaniam and Weinberg (1980), Weinberg, Onorato, and Uhlmann (1980a), and Weinberg, Onorato, and Uhlmann (1980b), in the solution of the mathematical problem posed by (3.6), (3.7) and (3.8) we will treat \( R \) as a parameter. Tao (Tao, 1978; Tao, 1979) tried to improve on this approximation but his method of solution leads to infinite series that must be truncated introducing errors that are difficult to quantify. A better approach was developed in a recent paper (Peñas-López et al., 2016) by the introduction of a modified time variable. The radius of a dissolving bubble decreases very slowly for a significant fraction of its lifetime; it is only near the end of the process that it varies rapidly. In this case, as shown in the Appendix, the difference with our procedure is small. In the case of an oscillating pressure field, the error is of the order of \( \Delta R/R \), and therefore it is of the same order as that introduced by the neglect of convection,
as explained in the next section. Hence, treating the radius in a parametric way is consistent with the other approximations made in this study.

We take the Laplace transform (denoted by a tilde) and solve the resulting differential equation to find

\[ \tilde{u}(r, s) = \tilde{u}|_{r=R} e^{-\sqrt{s/D}(r-R)}. \]  

(3.11)

In terms of \( \tilde{u} \) we have

\[ \frac{\partial \tilde{\rho}}{\partial r} \bigg|_{r=R} = - \left[ \frac{\tilde{u}(R, s)}{R^2} + \frac{1}{R} \frac{s \tilde{u}(r, s)}{\sqrt{Ds}} \right] \bigg|_{r=R}, \]

(3.12)

which can be readily inverted. When the result is inserted into (3.9) we find

\[ \frac{dm_g}{dt} = 4\pi R^2(t)D \left[ \frac{(\rho^i_g - \rho^s \rho^f_g(0))}{\sqrt{\pi Di}} + \frac{(\rho^i_g - \rho^s \rho^f_g(t))}{R} - \int_0^t \frac{d\rho^s \rho^f_g(\tau)}{d\tau} \frac{d\tau}{\sqrt{\pi D(t-\tau)}} \right]. \]

(3.13)

The first term in the right-hand side is due to the discontinuity of the boundary condition at \( t = 0 \). If \( \rho^s \rho^f_g \) is independent of time, this result coincides with that of Epstein and Plesset (1950b). The last term is due to the variation in time of the surface concentration, which is a consequence of the time dependence of the bubble pressure caused by the variation of the ambient pressure, surface tension or other factors. The difference with Epstein and Plesset (1950b) is even more evident upon re-writing this equation identically as

\[ \frac{dm_g}{dt} = 4\pi R^2(t)D \left[ (\rho^i_g - \rho^s \rho^f_g(t)) \left( \frac{1}{\sqrt{\pi Di}} + \frac{1}{R} \right) - \int_0^t \frac{d\rho^s \rho^f_g(\tau)}{d\tau} \frac{d\tau}{\sqrt{\pi D(t-\tau)}} - \frac{1}{\sqrt{\pi Di}} \right] \right]. \]

(3.14)

The first term in the right-hand side is the only term occurring in the original theory of Epstein and Plesset (1950b).
After a discussion of orders of magnitude in the next section, we illustrate the effect of the new memory term in (3.13) or (3.14) for the case in which the time dependence of $\rho_s^{sf}$ is due to the time dependence of the ambient pressure, in a constant pressure field, to the effect of surface tension or to the presence of different gases.

### 3.3 Scaling

It was shown in the previous section that the convective term of the diffusion equation is small compared with the diffusion term provided the Péclet number is small. We now turn to a consideration of the other term in the convective derivative, namely $\partial \rho_s / \partial t$. Proceeding as for the convective term, the ratio of the two terms in the convective derivative can be estimated as

$$\frac{(R^2 / r^2) \dot{R} \partial \rho_s / \partial r}{\partial \rho_s / \partial t} \sim \frac{\dot{R} t_{\text{diff}}}{R},$$

(3.15)

in which $t_{\text{diff}}$ is the characteristic time scale over which $\rho_s$ varies appreciably.

In a static pressure field $t_{\text{diff}}$ can be estimated as $R^2 / D$, while $\dot{R}$ will be of the order of the initial radius $R_0$ divided by the total dissolution time $t_{\text{diss}}$ which, for a mono-component bubble, is of the order of $R_0^2 / [dD(1 - \rho_i^g / \rho_{\text{sat}})]$ according to Epstein & Plesset. In this way we find

$$\frac{(R^2 / r^2) \dot{R} \partial \rho_s / \partial r}{\partial \rho_s / \partial t} \sim \left(1 - \frac{\rho_i^g}{\rho_{\text{sat}}} \right) d,$$

(3.16)

a result previously given in Iliinski, Wilson, and Hamilton (2008). In this case, therefore, it is consistent to neglect the convective term provided $d$ is small or the liquid is nearly saturated with gas.

The situation is different in an oscillating pressure field with frequency $\omega$ because,
in this case, the previous estimate of \( \dot{R} \) is only applicable provided \( \omega t_{\text{diss}} \) is less than 1, i.e., at very low frequencies. When \( \omega t_{\text{diss}} > 1 \), the proper time scale for both \( \dot{R} \) and \( \partial \rho_{g} / \partial t \) is just \( 1/\omega \) and the ratio of the two terms is of the order

\[
\frac{(R^2 / r^2) \dot{R}}{\partial \rho_{g} / \partial t} \approx \frac{\dot{R}}{\omega} \approx \frac{\Delta R}{R},
\]

(3.17)

with \( \Delta R \) of the order of the oscillation amplitude of the radius. When the radius changes are small, the convective term is of higher order and can be neglected, which justifies the linearization of the diffusion equation. In this case, the boundary condition at the moving bubble surface can be treated as a domain perturbation as shown in one of the cases treated in Peñas-López et al. (2016). When \( \Delta R \sim R \), however, the two terms of the convective time derivative are of a comparable order and, therefore, the ratio of \( \partial \rho_{g} / \partial t \) to diffusion is also of the order of the Péclet number. In these conditions, when this number is small, it would be consistent to just use the steady-state diffusion equation treating time simply as a parameter. In this quasi-steady approximation, the only surviving term in the equation (3.13) for \( dm_{g} / dt \) would then be the middle one, proportional to \( 1/R \), and all effects explicitly dependent on time, including history, will be of the order of the Péclet number and, hence, small. When \( \Delta R / R \) is not small, omission of the convective term in spite of the retention of \( \partial \rho_{g} / \partial t \) is unjustified from a purely mathematical viewpoint. A pragmatic justification for our procedure is that it enables us to explicitly identify the presence of history effects and to estimate their magnitude. Furthermore, as will be shown in the next section in connection with figure 3.7, the effect of the magnitude of the ratio \( \Delta R / R \) is rather
small, which lends further justification to the simplification adopted in this chapter.

### 3.4 Mass transfer in an oscillating ambient pressure

Bubble growth (or delayed dissolution) by rectified diffusion is a fundamentally non-linear process. Firstly, for equal positive and negative ambient pressure changes, the bubble radius increases more upon expansion than it decreases upon contraction due the non-linearity of the pressure-volume relation. (A contributing factor is the non-linearity of the Rayleigh-Plesset equation governing the radial motion, which is neglected here). Thus, the surface area when the bubble expands and absorbs gas from the surroundings is larger than when it contracts and loses gas. Secondly, upon expansion, the diffusion boundary layer at the bubble surface is stretched and thins, which increases the inward-directed mass flux while, when it contracts, the boundary layer thickens and the outward-directed mass flux decreases. In the limit considered here this second process, as well as inertia, are negligible and the phenomenon rests solely on the difference in the surface areas upon expansion and contraction of the bubble.

We focus on the threshold conditions separating bubble growth from dissolution and consider sinusoidal ambient pressure oscillations writing

\[ p_\infty(t) = p_\infty^0 \left(1 - P^* \sin \omega t\right), \]  

(3.18)

with \( P^* \) the dimensionless pressure amplitude. A length \( R_e \) useful to characterize the bubble size can be defined by

\[ \frac{4}{3} \pi R_e^3 p_\infty^0 = \frac{\langle m_g \rangle}{M_g} \mathcal{R} \mathcal{G} T, \]  

(3.19)

in which \( \langle m_g \rangle \) is the average mass of gas in the bubble, which is a constant in steady
threshold conditions. We set

\[ t_\ast = \omega t, \quad R_\ast = \frac{R(t)}{R_e}, \quad p_\ast(0) = \frac{p_\infty(t)}{p_\infty}, \quad \rho_s^f = \frac{\rho_s^f}{\rho_{sat}}, \quad (3.20) \]

with \( \rho_{sat} = K(T)p_\infty^0 \). In dimensionless form the mass transfer equation (3.13) is

\[
\frac{dm_\ast}{dt_\ast} = \frac{3}{\pi} d \frac{1}{Pe} R_\ast^2 \left[ \frac{\rho_g^i - \rho_g^f(0)}{\sqrt{t_\ast}} + \frac{\rho_g^i - \rho_g^f(t)}{Pe \rho_{sat}} - \int_{t_\ast}^{t_\ast + 2\pi/\omega} \frac{d\rho_g^f(t_\ast)}{d \tau_\ast} \frac{d\tau_\ast}{\sqrt{t_\ast - \tau_\ast}} \right],
\]

(3.21)
in which \( m_\ast = m_g/\langle m_g \rangle \) and \( d \) is the solubility parameter defined earlier in (3.3).

An important parameter appearing in this equation is

\[
Pe = \frac{R_e}{\sqrt{\pi D/\omega}},
\]

(3.22)

which is the ratio of the average bubble radius to the diffusion penetration length. The bubble internal pressure is non-dimensionalized in the same way:

\[
p_\ast = \frac{p_g}{p_{sat}} = p_\infty + \frac{\alpha}{R_\ast} = p_\infty + \frac{\beta}{Pe R_\ast},
\]

(3.23)

where

\[
\alpha = \frac{2\sigma}{\rho_p^0 R_e}, \quad \beta = Pe \alpha.
\]

(3.24)

We thus see that the problem contains 5 parameters, namely \( \rho_g^i, Pe, P*, d \) and \( \alpha \) (or \( \beta \)). At threshold conditions, any one of them will be a function of the remaining 4.

Threshold conditions for rectified diffusion are identified by the requirement that no net mass transfer occurs over a complete cycle of pressure oscillations:

\[
\int_{t_\ast}^{t_\ast + 2\pi/\omega} \frac{1}{Pe} R_\ast^2 \left[ \frac{1}{\rho_g^i - \rho_g^f(t)} + \int_{t_\ast}^{t_\ast + 2\pi/\omega} \frac{d\rho_g^f(t_\ast)}{d \tau_\ast} \frac{d\tau_\ast}{\sqrt{t_\ast - \tau_\ast}} \right] dt = 0.
\]

(3.25)

Here we have omitted the transient term proportional to \( t^{-1/2} \) in (3.21), the effect of
which decreases with time.

Before turning to the results it is useful to note that, as a consequence of the equation of state,

\[
\frac{[1 - P_\ast \sin t_\ast + \alpha/R_\ast(t_\ast)]R_\ast^3(t_\ast)}{1 + \alpha} = \frac{m_g(t)}{\langle m_g \rangle}.
\]  

(3.26)

According to this relation, the bubble radius responds to both the external pressure and changes in the bubble contents. Consider the beginning of a pressure cycle in which the pressure falls. Until the pressure inside the bubble becomes close to the saturation value corresponding to the gas content of the liquid, gas keeps diffusing out of the bubble and the radius expands less than it would in the absence of diffusion. When the ambient pressure is low enough, gas starts diffusing into the bubble and the radius expands more than it would without diffusion. This expansion period which, due to the area effect mentioned before, is crucial for rectified diffusion, becomes longer and longer as the pressure amplitude is increased. When the ambient pressure starts rising, the increased mass of gas in the bubble limits the bubble compression and, therefore, decreases the mass loss. Since these effects depend on diffusion, which is a slow process, one may expect their influence to decrease as frequency is increased. These considerations help to interpret the results that we now describe. For definiteness we present numerical results for the case of air and water at 22 °C, for which \( d = 0.02 \).

We begin by neglecting surface tension effects so that, with \( d \) fixed, the free parameters reduce to 3, namely the water super- or under-saturation \( \rho_g^1/\rho_{sat} \), the dimensionless radius \( Pe = R_e/\sqrt{\pi D/\omega} \) and the dimensionless pressure amplitude \( P_\ast \). Figure 3.1 is a graph of the threshold amplitude \( P_\ast \) vs. the parameter \( Pe \) for
Figure 3.1: Dimensionless rectified diffusion threshold amplitude $P_*$ vs. dimensionless bubble radius $Pe = R_e/\sqrt{\pi D/\omega}$ for different values of the liquid under-saturation $\rho_i^g/\rho_{sat}$; surface tension effects not included.
different values of the under-saturation $\rho_s^i/\rho_{sat}$. It is clear from (3.26) that, in the absence of surface tension, the radial oscillations become larger and larger as $P_e$ approaches 1. This circumstance makes a precise determination of the threshold numerically delicate in this range and, for this reason, our exploration of the parameter $P_e$ does not extend all the way to 1, and the dimensionless radius $R_e/\sqrt{\pi D/\omega}$ does not extend to 0. This difficulty becomes more acute with increasing $\rho_s^i$ as then the amplitude of the mass fluxes also becomes very large.

Moreover, the range of the horizontal axis is limited by the requirement that $R_e$ be smaller than $\sqrt{\pi D/\omega}$ for the present approximations to be justified as discussed in section 3.2.

The results of figure 3.1 conform with the analysis provided before in connection with (3.26). The threshold amplitude increases with increasing under-saturation (i.e., decreasing gas content in the liquid), and also increases as the frequency decreases due to the increasing importance of diffusive effects.

Additional insight into these results is provided by figures 3.2 and 3.3. The former shows the amplitude of the mass oscillations $\Delta m_g = m_{g,\text{max}} - m_{g,\text{min}}$ normalized by $\langle m_g \rangle$, while the latter is the non-dimensional radius excursion, $\Delta R / R_e$, with $\Delta R = R_{\text{max}} - R_{\text{min}}$, both as functions of the parameter $Pe$. Each line corresponds to one value of $\rho_s^i/\rho_{sat}$. As expected, the mass amplitude rapidly increases as the frequency is decreased reaching 100% of the mean value in the parameter range covered by the figure. Balancing the increasing mass losses taking place at low frequency requires an increased mass inflow, which in turns requires a large area increase and a significant radial amplitude. Conversely, as the frequency increases, mass losses are reduced, the radial amplitude becomes more tightly connected with
Figure 3.2: (Left) Dimensionless oscillation amplitude of the mass of gas in the bubble vs. the dimensionless bubble radius $Pe = \frac{R_e}{\sqrt{\pi D/\omega}}$ for different liquid under-saturations as in figure 3.1; surface tension effects are not included.

Figure 3.3: (Right) Dimensionless oscillation amplitude of the bubble radius vs. the dimensionless bubble radius $Pe$ for different liquid under-saturations as in figure 3.1; surface tension effects are not included.

the ambient pressure oscillations and the radial oscillation amplitude decreases.

A cross-plot of the quantities of the previous two figures is provided in figure 3.4 in which each line is the dimensionless amplitude of the mass oscillations, $\Delta m_g/\langle m_g \rangle$, vs. the non-dimensional radius excursion $\Delta R/R_e$, for fixed $\frac{\rho_g^i}{\rho_{sat}}$. The range of the curves is the same as in the previous three figures, with $P_*$ increasing and the frequency decreasing as the lines are traversed from the lower left to the upper right. Again we see that, at the higher frequencies, the amplitude of the mass oscillations is small while that of the radial oscillations remains substantial. As the frequency decreases and the pressure amplitude increases, the amplitude of the mass oscillations increases substantially, the more the greater the gas content of the liquid. In considering these results it should be kept in mind that, unless $Pe$ is very small, the first and last term in the bubble mass equation (3.13) tend to lose accuracy as $\Delta R/R$ approaches or exceeds 1, as explained in the section 3.2. A more precise calculation should include
Figure 3.4: Dimensionless oscillation amplitude of the mass of gas in the bubble vs. dimensionless amplitude of the radial oscillations for different values of the liquid under-saturation $\frac{\rho_g^i}{\rho_{sat}}$ as in figure 3.1. The pressure amplitude increases from the lower left to the upper right; surface tension effects not included.
Figure 3.5: (Left) Dimensionless mean bubble radius over a complete oscillation period vs. the dimensionless bubble radius $Pe = \frac{R_e}{\sqrt{\pi D/\omega}}$ for different liquid under-saturations as in figure 3.1; surface tension effects not included.

Figure 3.6: (Right) Dimensionless bubble radius vs. time over one complete period of the ambient pressure oscillations. Solid line: $Pe = 0.065$, $\frac{\rho^i_s}{\rho_{sat}} = 0.8$ and $P_s = 0.86$; dashed line: $Pe = 0.36$, $\frac{\rho^i_s}{\rho_{sat}} = 0.8$ and $P_s = 0.74$; dash-dotted line: $Pe = 0.36$, $\frac{\rho^i_s}{\rho_{sat}} = 0.5$ and $P_s = 0.93$.

the effect of convection, which would preclude the possibility of an analytic solution comparable to (3.13) and, therefore, the explicit identification of history effects.

Figure 3.5 is a graph of $\langle R \rangle / R_e$ vs. $R_e / \sqrt{\pi D/\omega}$. The dependence on frequency tends to become weaker as frequency increases because, with the decreasing amplitude of mass fluxes, relatively small-amplitude oscillations are sufficient to provide the area changes necessary to preserve the mean bubble mass so that a small amount of non-linearity (which is responsible for the difference between $\langle R \rangle$ and $R_e$) is sufficient. This regime is achieved later, of course, as the under-saturation increases and $\frac{\rho^i_s}{\rho_{sat}}$ becomes smaller. The fact that $\langle R \rangle / R_e > 1$ in this parameter range suggests that the nature of the oscillations is such that the bubble radius is larger than $R_e$ during a substantial fraction of the oscillation period. The trend is reversed at low frequencies, where $\langle R \rangle / R_e < 1$. Here the compressive phase is longer than the expansion phase,
but the mass gained during the latter balances that lost during the former. These considerations are illustrated in figure 3.6 in which \( R/R_e \) is plotted over a complete cycle for several values of \( \rho_g^i/\rho_{sat} \), \( Pe \) and \( P_* \). The solid line, for \( Pe = 0.065 \), \( \rho_g^i/\rho_{sat} = 0.8 \) and \( P_* = 0.858 \), is typical of the radius response at low frequency. One observes a marked asymmetry with respect to the maximum, with a compression phase much longer than the expansion phase due to the slowness of mass diffusion out of the bubble. On figure 3.5 this situation corresponds to the decreasing part of the curves on the left. The asymmetry is much less marked for the larger frequency examples for \( Pe = 0.36 \). The dashed line is for \( \rho_g^i/\rho_{sat} = 0.8 \) and \( P_* = 0.74 \) and the dash-dotted line \( \rho_g^i/\rho_{sat} = 0.5 \) and \( P_* = 0.93 \). The liquid is very under-saturated in the last case and the amplitude necessary to ensure threshold conditions correspondingly larger. These curves are strikingly different from those found when the liquid inertia is important (see e.g. Prosperetti and Hao (1999)), in which case the expansion phase is usually much longer than the contraction phase.

It is also of interest to consider the relative magnitude of the second and third terms in (3.13) in the course of an oscillation. A few examples are shown in figures 3.7(a) to (d). Here the solid line is the quasi-steady term \( (\rho_g^i - \rho_g^{sf})/R \) while the dashed line is the memory integral; both terms are nondimensionalized by division by \( \rho_{sat}/R_e \). When the parameter \( Pe = R_e/\sqrt{\pi D/\omega} \), which is essentially the Péclet number, is small (figures 3.7(a) and (b)), the history term is smaller than the quasi-steady term, as expected. As \( Pe \) increases (figures 3.7 (c) and (d)), the relative magnitude of the history effect increases, again as expected. It was argued in section 3.2 that the expression for the history effect given in (3.13) gradually loses accuracy as \( \Delta R/R_e \) increases. However, it can be noted in panels (c) and (d), for the same values of \( Pe \)
Figure 3.7: The normalized quasi-steady (second) term of (3.13) (solid line) and the history term in the course of one oscillation period at threshold conditions. The two panels in the first line are for $Pe = 0.15$, $\Delta R / R = 0.95$, $\rho_i^j / \rho_{sat} = 0.90$, $P_* = 0.69$, and $Pe = 0.17$, $\Delta R / R_c = 2.0$, $\rho_i^j / \rho_{sat} = 0.70$, $P_* = 0.92$; those in the second line for $Pe = 0.43$, $\Delta R / R_c = 0.47$, $\rho_i^j / \rho_{sat} = 0.90$, $P_* = 0.54$, and $Pe = 0.43$, $\Delta R / R_c = 1.03$, $\rho_i^j / \rho_{sat} = 0.70$, $P_* = 0.82$. 

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but $\Delta R / R_e = 0.47$ and $1.03$, that the relation between the two terms is comparable, which suggests a limited influence of the magnitude of $\Delta R / R_e$. The difference in the vertical scales is mostly due to the different liquid saturation as can be seen by comparing with the figures in the first line.

These results are strongly dependent on the history effect as shown by comparing figure 3.1, obtained from the full equation (3.21), with figure 3.8; this latter figure has been generated by omitting the history term so that (3.25) is replaced by

$$\int_{t_1}^{t_2} \frac{2\pi}{\omega} \left[ R_s \left( \rho_{g*}^i - \rho_{g*}^e(t) \right) \right] dt = 0. \quad (3.27)$$

The lines are essentially horizontal, suggesting an independence of the threshold amplitude from frequency, except at very low frequency. This trend can be readily explained by recalling that at large frequencies the alternating mass exchange with the liquid has a negligible effect on the oscillation amplitude. In these conditions,
the area difference between contraction and expansion and, therefore, the net mass inflow into the bubble, only comes to depend on the pressure amplitude. A certain degree of under-saturation requires a corresponding net mass inflow and, therefore, a certain area change and a certain pressure amplitude. This argument can be given a quantitative form by noting that, in this limit, (3.31) can be approximated as

\[ [1 - P_\ast \sin t_\ast]R_\ast^3(t_\ast) \approx 1. \tag{3.28} \]

Thus, remembering also that \( \rho_{g\ast}^{\ast s f} = 1 - P_\ast \sin t_\ast \), (3.27) gives

\[ \rho_{g\ast}^{\ast i} \int_0^{2\pi/\omega} [1 - P_\ast \sin t_\ast]^{-1/3} dt_\ast = \int_0^{2\pi/\omega} [1 - P_\ast \sin t_\ast]^{2/3} dt_\ast, \tag{3.29} \]

which can be solved to give \( P_\ast \) vs. \( \rho_{g\ast}^{\ast i} \) independently of frequency. This relation is graphed in figure 3.9. This exclusive dependence on pressure amplitude becomes less accurate as the mass fluxes become larger with decreasing frequency.

We now turn to a consideration of the effects of surface tension, the most important of which – of increasing importance as the bubble radius becomes smaller – is to inhibit the radial expansion. Thus it may be expected that, as a consequence, the threshold for rectified diffusion will be generally larger and exhibit a much stronger dependence on the radius than that shown in figure 3.1. This expectation is borne out by figure 3.10 which is comparable to figure 3.1 except for the fact that the parameter \( \beta \), defined in (3.24), equals 0.1, rather than 0, and that the liquid gas content needs to be significantly increased to allow for a threshold in the presence of the strong surface-tension-induced over-pressure. To give an idea of the orders of magnitude of actual physical quantities we may note that, for water and air, with \( D = 2 \times 10^{-9} \)
Figure 3.10: Dimensionless rectified diffusion threshold amplitude $P^*$ vs. dimensionless bubble size $Re/\sqrt{\pi D/\omega}$ for different values of the liquid under-saturation $i_g/\rho_{sat}$ with surface tension effects included. The parameter $\beta = 2\sigma/(p^0_\infty \sqrt{\pi D/\omega})$ equals 0.1.
m²/s and σ = 0.07 N/m, β = 0.1 corresponds to a frequency

\[ \frac{\omega}{2\pi} = \frac{1}{2} D \left( \frac{\beta p_0^0}{2\sigma} \right)^2 \approx 10 \text{ Hz} \]  

while Pe ~ 0.3, for example, would correspond to Re ~ 30 μm. It is not surprising to see such a strong effect of surface tension for a this small radius.

A direct comparison of the threshold with and without surface tension, β = 0.01 and β = 0, is given in figure 3.11 for \( \rho_g^i / \rho_{sat} = 0.9 \). The smaller value of β as compared with figure 3.10 causes smaller differences which, however, remain significant.

### 3.5 Mass transfer in a constant pressure field

We now turn to the case of a constant pressure field \( p_\infty \), the original situation studied in Epstein and Plesset (1950b). Now it is convenient to use the initial bubble radius \( R(0) \) as scale and we set \( R_\ast(t) = R(t) / R(0) \). The analog of (3.26) is now

\[
\frac{[1 + \alpha / R_\ast(t)] R_\ast^3(t)}{1 + \alpha} = \frac{m_g(t)}{m_g(0)}. \tag{3.31}
\]

with \( \alpha \) given by (3.24).

Figure 3.12 shows the time to complete dissolution as a function of the gas content of the liquid for three values of the parameter \( \alpha \), 1.42, 0.142 and 0.0142 which, in water at 22 °C, would correspond to initial radii of 1, 10 and 100 μm. For dissolution to be possible it is necessary that \( \rho_g^i / \rho_{sat} < 1 + \alpha \) and the dissolution becomes markedly slower as the limiting value is approached until it diverges when it is attained. The difference due to the removal of the history term (dashed line) is very small and only visible for the smallest bubble. In the other cases, the effect of the surface-tension over-pressure is so small over the major fraction of the bubble lifetime that that the
Figure 3.11: Comparison of the dimensionless rectified diffusion threshold amplitude $P_*$ vs. the dimensionless bubble size $R_e/\sqrt{\pi D/\omega}$ with and without surface tension effects for $\rho_g^i/\rho_{sat} = 0.9$; the parameter $\beta$ is defined in (3.24).
Figure 3.12: Dimensionless time to complete dissolution of gas bubbles with different initial radii as a function of the gas content of the liquid; the ambient pressure is constant. The dashed lines show the results when the history term is omitted.
Figure 3.13: Fractional contributions of the three terms in (3.13) to the dissolution time of an air bubble in water with an initial radius of 1 µm. In ascending order the lines show the contributions of the history term, of the term proportional to $t^{-1/2}$ and of the term inversely proportional to $R$. The top dashed line is the contribution of this last term in the absence of history effects.
Figure 3.14: Dimensionless time for growth up to 10 times the initial radius of an air bubble in water as a function of the liquid super-saturation; the initial bubble radius is 1 µm. The dashed line is the result in the absence of the history term in (3.13).
two results with and without memory effects are indistinguishable within the thickness of the lines. It is somewhat surprising that the slight difference between the two theories is seen to increase with the degree of saturation as one would expect that faster dissolution would increase the significance of the memory term. While this is true, the effect becomes secondary compared to the influence of the memory term over the longer bubble lifetime produced by a greater amount of dissolved gas. Even so, the effect remains small, mostly of the order of a fraction of a percent. Figure 3.13 shows the relative importance of the three terms in (3.13). Figure 3.14 illustrates the effect of the memory term on the time to growth up to 10 times the initial radius.

3.6 A multicomponent bubble

As a last example of a situation in which the boundary condition at the bubble surface is time-dependent, we consider a bubble consisting of a mixture of two different gases, denoted by indices $a$ and $b$, each one with its own solubility and diffusivity. This problem has been considered in Weinberg, Onorato, and Uhlmann (1980b) in the limit in which one of the gases is insoluble and in Weinberg and Subramaniam (1980) under the assumption of a constant dissolved gas mole fraction at the bubble surface; in neither work are history effects considered. The latter authors compared the results of a numerical simulation, including convection and the time-dependence of the surface concentration and of the boundary, with their quasi-steady approximate solution finding a reasonable agreement between them. In this analysis we neglect surface tension and assume that the binary diffusivity in the gaseous phase is sufficiently rapid for the two constituents to remain fully mixed in the bubble interior.

The masses $m_a$ and $m_b$ of each component of the gas mixture are each determined
by an equation of the form (3.13), after which the bubble radius follows from Dalton’s law and the equation of state (3.10) as

\[
\left(\frac{4}{3}\pi R^3\right) (p_a + p_b) = \left(\frac{4}{3}\pi R^3\right) p_\infty = \left(\frac{m_a}{M_a} + \frac{m_b}{M_b}\right) \mathcal{R}_G T. \tag{3.32}
\]

For a numerical example we consider the case of a bubble consisting of a mixture of nitrogen (component \(a\)) and \(\text{CO}_2\) in water at 20 °C under a constant 101.3 kPa ambient pressure; at the initial instant there are no gases dissolved in the water. The values of the parameter \(d\) defined in (3.3) are \(d_a = 0.04\) and \(d_b = 0.80\), respectively, and the respective diffusivities \(D_a = 1.88 \times 10^{-9} \text{ m}^2/\text{s}\) and \(D_b = 1.92 \times 10^{-9} \text{ m}^2/\text{s}\). On the basis of the time scale for the dissolution of a mono-component bubble, it was shown in section 3.2 that neglect of convection was legitimate for small \(d\). For the present case of a multi-component bubble it is the less soluble gas which determines the dissolution time and, therefore, the fact that \(d_b\) is not small does not introduce a significant error. The left panel in figure 3.15 shows the percent difference between the predicted lifetimes with and without the history effect as a function of the nitrogen mole fraction \(x_{N_2}\) initially present in the bubble. A maximum of about 4% is found for \(x_{N_2} \simeq 2 \times 10^{-3}\). The right panel, in which the solid line includes the history effect, is a comparison of the actual lifetimes in the range of small \(x_{N_2}\). The more significant differences are limited to the range of small \(x_{N_2}\) because \(\text{CO}_2\) dissolves much faster than nitrogen. Thus, when the nitrogen amount is not small, the \(\text{CO}_2\) dissolves very quickly and the situation becomes similar to that of a single-component nitrogen bubble except for a very short initial period.
3.7 Summary

Henry’s law dictates the concentration of dissolved gas at the surface of a gas bubble in a liquid. When the bubble internal pressure changes, either in response to a varying ambient pressure, because of surface tension in the presence of radius changes, or for other causes, the dissolved gas concentration becomes time-dependent and the history effects characteristic of all diffusive processes appear. In order to focus on these effects, we have considered the limit in which the diffusive layer is much thicker than the bubble radius and the frequency of the pressure variation is much slower than the bubble resonance frequency. Not surprisingly we have found that, when the dissolution or growth take place under a constant ambient pressure, so that the sole agent of the internal pressure variation is the changing radius, history effects are small. In the last example considered, in which the bubble consists of the mixture of two gases, history effects can be somewhat larger but they amount to a few percent at most.
When the internal pressure changes in response to variations of the ambient pressure, however, the history effect on rectified diffusion can be more important. In this case, the different frequency response of the gas inflow/outflow and surface area increase/decrease during the pressure cycle are important. Since the former is a relatively slow process, at low frequency there are large mass exchanges with the liquid which require large expansions and contractions of the bubble. At higher frequency, changes in the surface area become the dominant effect and the oscillation amplitude is smaller.

While several experimental data exist when the situation in which the diffusion length $\sqrt{D/\omega}$ is much smaller than the bubble radius, we have been unable to find corresponding results for the opposite limit which is the one we have studied in this chapter. At high frequency, pressure-radiation forces can be relied upon to maintain the bubble position offsetting buoyancy, but at low frequency this option is not available. One possibility might be to trap the bubble under a horizontally positioned porous screen.

**APPENDIX – AN ESTIMATE OF THE ERROR IN (3.12)**

In the convection-diffusion equation let

$$x = \frac{r}{R}, \quad u(x, t) = x \left( \rho_s - \rho_i^g \right),$$

(3.33)

to find

$$\frac{\partial u}{\partial t} + \frac{\dot{R}}{R} \left( \frac{1}{x^3} - 1 \right) \left( x \frac{\partial u}{\partial x} - u \right) = \frac{D}{R^2} \frac{\partial^2 u}{\partial x^2}.$$ 

(3.34)
The second term in the left-hand side can be estimated as before and neglected at low frequency. In terms of the new time variable

\[
\tau = \int_0^t \frac{dt'}{R^2(t')},
\]

(3.35)

the equation then becomes (approximately)

\[
\frac{\partial u}{\partial \tau} = D \frac{\partial^2 u}{\partial x^2}.
\]

(3.36)

Upon taking the Laplace transform and solving with the appropriate boundary condition we find

\[
\tilde{u}(x,s) = \tilde{u}(x = 1, s)e^{-\sqrt{s/D}(x-1)},
\]

(3.37)

from which

\[
\frac{1}{x} \left( \frac{\partial \tilde{u}}{\partial x} - \tilde{u} \right) = -\frac{s\tilde{u}(x = 1, s)e^{-\sqrt{s/D}(x-1)}}{x\sqrt{sD}} - \frac{\tilde{u}(x = 1, s)e^{-\sqrt{s/D}(x-1)}}{x^2}.
\]

(3.38)

Upon inverting the transform we find

\[
\frac{1}{x} \left( \frac{\partial u}{\partial x} - u \right) = -\frac{1}{x} \int_0^\tau u(x = 1, \theta) e^{(x-1)^2/4D(\tau - \theta)} \frac{d\theta}{\sqrt{\pi(\tau - \theta)}}
\]

\[
-\frac{1}{x} \int_0^\tau u(x = 1, \tau - \theta)e^{(x-1)^2/4D\theta} \frac{d\theta}{2\sqrt{\pi D\theta^3}}.
\]

(3.39)

We are interested in the value of this quantity at \(x = 1\). For the first term we recall the boundary condition (3.7) to find

\[
\frac{du(x = 1, \theta)}{d\theta} = d(\theta) \left[ \rho^{sf}_g(0) - \rho^{i}_g \right] + H(\theta) \frac{\partial \rho^{sf}_g}{d\theta},
\]

(3.40)
from which
\[
\left[ \frac{1}{x} \int_0^\tau \frac{du(x=1,\theta)}{d\theta} e^{(x-1)^2/4D(\tau-\theta)} \frac{d\theta}{\sqrt{\pi(\tau-\theta)}} \right]_{x=1} = -\frac{\rho_s^f(0)-\rho_s^i}{\sqrt{\pi D\tau}} - \int_0^\tau \frac{d\rho_s^f}{d\theta} \frac{d\theta}{\sqrt{\pi D(\tau-\theta)}}.
\]  
(3.41)

For the second term we set
\[
\eta = \frac{x - 1}{2\sqrt{D(\tau - \theta)}},
\]  
(3.42)
to find
\[
\frac{1}{x} \int_0^\tau u(x=1,\tau - \theta) \frac{x-1}{2\sqrt{\pi D\theta}} e^{(x-1)^2/4D\theta} d\theta = \frac{1}{x\sqrt{\pi}} \int_0^{\infty} \frac{d\rho_s^f}{d\theta} u \left( x = 1, \tau - \frac{(x-1)^2}{4D\eta^2} \right) e^{-\eta^2} d\eta.
\]  
(3.43)

Upon evaluating at \( x = 1 \) this is simply
\[
\left[ \frac{1}{x} \int_0^\tau u(x=1,\tau - \theta) \frac{x-1}{2\sqrt{\pi D\theta^3}} e^{(x-1)^2/4D\theta} d\theta \right]_{x=1} = u(x=1,\tau) = \rho_s^f(\tau) - \rho_s^i.
\]  
(3.44)

In conclusion we have found
\[
\left[ \frac{\partial \rho_s}{\partial r} \right]_{r=R} = \left[ \frac{1}{x} \frac{\partial u}{\partial x} - \frac{u}{x^2} \right]_{x=1} = -\frac{1}{R} \left[ \frac{\rho_s^f(0)-\rho_s^i}{\sqrt{\pi D\tau}} + \rho_s^f(\tau) - \rho_s^i + \int_0^\tau \frac{d\rho_s^f}{d\theta} \frac{d\theta}{\sqrt{\pi D(\tau-\theta)}} \right],
\]  
(3.45)

which differs from the earlier results only by the substitution of the original time variable \( t \) by the modified time variable \( \tau \).

We note that, by the first mean value theorem, for some \( \tau_m \) with \( 0 \leq \tau_m \leq t \),
\[
R\sqrt{\tau} = R(t) \sqrt{\int_0^t \frac{dt'}{R^2(t')}} = R(t) \sqrt{\frac{t}{R^2(t_m)}}.
\]  
(3.46)

If the radius is constant, this is just \( \sqrt{t} \) and (3.13) is recovered. The radius of a dissolving bubble in a constant pressure field decreases very slowly for a dominant
fraction of the bubble lifetime. In this case, therefore, the difference between using $t$ or $\tau$ will not be large. For an oscillating bubble with a radius varying between $R_e - \Delta R$ and $R_e + \Delta R$, identifying (3.46) with $\sqrt{t}$ introduces an error bounded by $(1 - \Delta R / R_e) / (1 + \Delta R / R_e)$ and $(1 + \Delta R / R_e) / (1 - \Delta R / R_e)$ which will be small provided $\Delta R / R_e$ is small.
Chapter 4

Bubble plumes in a stratified ambient

4.1 Introduction

Multiphase plumes occur in a number of situations such as the aeration or de-stratification and mixing of water bodies (see e.g. Wüest, Brooks, and Imboden, 1992; Imteaz and Asaeda, 2000; Sahoo and Luketina, 2006; Boegman and Sleep, 2012), submarine volcanic eruptions (see e.g. Baumberger et al., 2014), metal processing (see e.g. Zhang, Eckert, and Gerbeth, 2007) and others. A recent occurrence is the major oil spill caused by the Deepwater Horizon accident in the Gulf of Mexico in 2010 (McNutt et al., 2012; Reddy et al., 2012; Ryerson et al., 2012b).

The behavior of bubble plumes is strongly influenced by the degree of stratification of the ambient liquid. In the absence of stratification, the plume reaches fully-developed conditions as found e.g. in Milgram (1983), Leitch and Baines (1989), and Bombardelli et al. (2007) and (Seol, Bryant, and Socolofsky, 2009). The situation

1This chapter is based on the paper "Bubble plumes in a stratified environment: Source parameters, scaling, intrusion height, and neutral height." by Chu & Prosperetti (Physical Review Fluids, vol. 2(10), 104503, 2017.)
is markedly different if the ambient liquid is stably stratified as, in that case, with sufficient depth, the plume rises to a maximum height, the peel height. Due to the accumulated momentum in the plume, this height is greater than the level of neutral buoyancy, termed the intrusion, or trap, height (figure 4.1). The plume liquid falls back down from the peel height to the intrusion height giving rise to a complex structure that has stimulated the development of so-called double-plume models (McDougall, 1978; Socolofsky, Bhaumik, and Seol, 2008), which have also proved useful in the study of fountains (see e.g. Bloomfield and Kerr, 2000; Hunt and Burridge, 2015). In these models, the ascending inner region of the plume is surrounded by a descending region between the peel height and the intrusion height. We prefer not to adopt a model of this type to avoid the appearance of additional empirical parameters lacking a solid experimental and physical basis. Our model focuses on the inner core of the plume which is not significantly affected by the slowly descending liquid surrounding it. In view of the low velocity of this outer section of the plume, it maybe expected that our prediction of the highest level reached by the ascending liquid, the peel height, will remain fairly accurate. If the water is deep enough the pattern can repeat with the appearance of more than one peel and intrusion heights (see e.g. Asaeda and Imberger, 1993; Socolofsky and Adams, 2005).

Other important features determining the plume dynamics are the depth and the horizontal extent of the ambient liquid. Limitations on both quantities permit the coupling of surface waves with the plume buoyant motion sometimes resulting in sloshing of the liquid surface and meandering of the plume (see e.g. Murai and Matsumoto, 2000; Rensen and Roig, 2001; Simiano et al., 2006; Neto, Zhu, and Rajaratnam, 2008; Simiano et al., 2009). If the depth is comparable with the hydrostatic head
Figure 4.1: Schematic representation of the formation of intrusion when the plume liquid, after exhausting its upward momentum at the peel height \( h_p \), falls back to the intrusion height \( h_i \).

\[
p_{atm}/(\rho_w g) \quad (\text{with } p_{atm} \text{ the atmospheric pressure, } \rho_w \text{ the water density and } g \text{ the acceleration of gravity}),
\]

the expansion of the bubbles as they rise and respond to the decreasing hydrostatic pressure impacts the plume behavior (see e.g. McDougall, 1978; Asaeda and Imberger, 1993). With stratification, this effect is smaller for water depths shallower than \( p_{atm}/(\rho_w g) \) or, for deeper water bodies, up to the first peel height.

The effect of bubble size has been considered by several investigators including (Wüest, Brooks, and Imboden, 1992; Asaeda and Imberger, 1993; Lemckert and Imberger, 1993; Socolofsky and Adams, 2005), all of whom focused on the size-dependent slip velocity of the bubbles relative to the surrounding liquid. Of course, the assumption of equal-size bubbles is a simplification. Several investigators have developed models to predict the bubble size distribution in an underwater blow-out.
(recent references are (Bandara and Yapa, 2011; Zhao et al., 2016)), but these models do not seem to have yet been incorporated into full plume models.

Most of the theoretical work on the dynamics of bubble plumes is based on an integral formulation of the balance equations (see e.g. McDougall, 1978; Milgram, 1983; Asaeda and Imberger, 1993; Lemckert and Imberger, 1993; Wüest, Brooks, and Imboden, 1992; Zheng, Yapa, and Chen, 2003; Bombardelli et al., 2007) following the classic approach used for single-phase plumes (see e.g. Priestley and Ball, 1955; Morton, Taylor, and Turner, 1956; Morton, 1959). An important result achieved in this work is the identification of the dimensionless quantities having the greatest influence on the plume behavior. More recently, two-fluid models or Lagrangian-Eulerian models based on Navier-Stokes equations with large-eddy turbulence models have been developed (see e.g. Buscaglia, Bombardelli, and García, 2002; Fraga et al., 2016; Yang et al., 2016; Fraga and Stoesser, 2016). Ref. Tomas et al. (2016) compared these more recent models with the integral approach and found a good agreement on several fundamental aspects of the plume behavior.

A question faced by researchers interested in integral formulations is the modeling of inlet conditions at the plume source. In the case of single-phase plumes, and bubble plumes in an unstratified environment, the inlet conditions have a negligible influence on the ultimate behavior of the plume (see e.g. Lee and Chu, 2003; Bombardelli et al., 2007). As recognized by Morton and Middleton (1973), this conclusion does not hold in a stratified environment where, however, the concept of virtual origin proves useful in the case of single-phase plumes. Researchers on bubble plumes in stratified environments have dealt with the problem of inlet conditions by using educated guesses based on approximating the starting flow as similar to that in a
single-phase plume (see e.g. Wüest, Brooks, and Imboden, 1992; Liro, Adams, and Herzog, 1992; Crounse, Wannamaker, and Adams, 2007).

In this chapter we present an attempt at a more general modeling of the inlet conditions, such as momentum and mass flow rates, in the context of a horizontally integrated plume model. We find that, as these conditions are varied, the results for the scaled peel and intrusion heights are significantly affected. A second point of the chapter is the recognition that what is commonly considered as the intrusion height in integral models is actually not directly comparable with the intrusion height observed in experiments. The difference between these two quantities explains why the experimental intrusion height is often found to lie significantly above the theoretical prediction. Once this difference is appreciated, our results are found to be in line with experiment. In formulating our model, we assume that cross-flow is negligible. This was the situation in the conditions of the Deepwater Horizon accident in which the measured cross-flow velocity at depth was of the order of a few centimeters per second (Ryerson et al., 2012b). A significant cross-flow would introduce substantial changes in the fluid mechanics of the plume (Murphy et al., 2016). It appears, however, that the integral model can be adapted to describe this situation as well (Lee and Chu, 2003), although we do not attempt to do so.

### 4.2 Mathematical model

Since our objective here is to focus on the effect of the plume inlet conditions, we use a standard, horizontally-integrated, quasi-one dimensional model for an axisymmetric, vertically-oriented plume. The liquid is assumed to be vertically stratified with a density \( \rho_a(z) \) (\( z \) is the vertical coordinate positive upward measured from the plume
source) and there is no cross-flow. A similar model has been used by many previous authors (see e.g. Morton, Taylor, and Turner, 1956; Morton, 1959; Morton and Middleton, 1973; McDougall, 1978; Wüest, Brooks, and Imboden, 1992; Hunt and Kaye, 2005; Crounse, Wannamaker, and Adams, 2007); our work differs from theirs in its focus on the conditions at the plume source. Some comments on the derivation of the equations of the model are provided in Appendix; here we simply state them.

The statement of conservation of the liquid volume is

\[
\frac{dm}{dz} = 2\pi b(z)\alpha_e w(z),
\]  

(4.1)

with

\[
m(z) = \int_A (1 - \beta_b)wdA \simeq \int_A wdA,
\]  

(4.2)

where \(b(z)\) is the local radius of the plume and \(w(z)\) the vertical liquid velocity; \(m\) is the liquid volume flow rate in the plume. In the last step of (4.2) we have neglected the bubble volume fraction \(\beta_b\) which is usually small. In the derivation of (4.2) from the principle of conservation of mass the liquid density appears both inside the integral and in the right-hand side. We have cancelled it invoking a Boussinesq-type approximation based on the assumption that the difference between the liquid density inside and outside the plume has negligible effects on the mass balance.

In the right-hand side of (4.1) we have made the usual entrainment hypothesis which establishes a proportionality relation between the entrainment velocity of the ambient fluid and the plume vertical velocity. The proportionality constant is the entrainment coefficient \(\alpha_e\). For a Gaussian profile of the plume fields (density, velocity etc.), the values of this parameter encountered in the literature are between 0.07 and 0.11 (Carazzo, Kamiski, and Tait, 2006). This range is supported by the recent DNS
simulations of single-phase plumes in Reeuwijk et al. (2016) who, however, found a
dependence on distance from the source. The recent LES numerical simulations of
bubble plumes in Yang et al. (2016) also find that $\alpha_e$ depends on distance from the
source. The mean value over the entire height of the simulation reported by these
authors is 0.086 and over the fully developed region 0.067. In the literature on integral
models of bubble plumes frequently used values are $\alpha_e = 0.083 – 0.085$ (Turner, 1986;
Hunt and Kaye, 2005; Asaeda and Imberger, 1993).

With the neglect of diffusion at the plume edge, the balance equation for the
dissolved salt concentration $c$ can be written as

$$\frac{d}{dz} \int_A (1 - \beta_b) \rho_w (c - c_a) dA + \frac{d c_a}{dz} \int_A (1 - \beta_b) \rho_w dA = 0, \quad (4.3)$$

in which $c_a$ is the concentration in the ambient liquid. Upon setting

$$\frac{\rho - \rho_w}{\rho_w} = \xi c, \quad (4.4)$$

where $\rho_w$ is the density of pure water and $\xi$ a constant, we have

$$\frac{\rho - \rho_a}{\rho_a} = \xi (c - c_a), \quad (4.5)$$

and the previous equation may be rewritten as

$$\frac{d}{dz} \int_A (1 - \beta_b) \rho_w \frac{\rho - \rho_a}{\rho_w} g \rho w dA = N^2 \rho_w \int_A (1 - \beta_b) \rho_w dA, \quad (4.6)$$

with

$$N^2 = - \frac{g}{\rho_w} \frac{\partial \rho_a}{\partial z}, \quad (4.7)$$

the Brunt-Väisälä frequency. As before, we invoke the Boussinesq approximation and
the smallness of $\beta_b$ to rewrite this equation in the approximate form

$$\frac{dF_s}{dz} = -N^2 m, \quad (4.8)$$

where the buoyancy flux due to salinity, $F_s$, is defined by

$$F_s = \int_A \rho \frac{\rho_a - \rho}{\rho_w} g\omega dA. \quad (4.9)$$

Although we have explicitly referred to a density stratification due to salinity, these expressions are also applicable to the case of thermal stratification with an obvious re-interpretation of the symbols. Temperature would have an effect also on gas solubility, which is not considered here, and on the gas density. Given the small range of temperatures encountered in the deep ocean (Ridgway, 1969), both effects are minor.

The buoyancy flux due to the bubbles is defined similarly to (4.9) as

$$F_b = \int_A \rho \frac{\rho_g - \rho}{\rho_w} g(\omega + w_b) \beta_b dA \simeq g \int_A (\omega + w_b) \beta_b dA = gQ_b, \quad (4.10)$$

in which $\rho_g \ll \rho$ is the gas density and $Q_b$ is the gas flow rate injected at the plume source. In the present chapter we assume that the change in the bubble volume is negligible, an assumption that is justified for plumes in shallow water or for a fraction of the plume development in deep water as noted before. With this approximation $Q_b$ remains constant so that the counterpart of (4.8) for the bubble buoyancy flux is simply

$$\frac{dF_b}{dz} = 0. \quad (4.11)$$

The bubbles exert a drag force on the liquid which, since the acceleration to which they are subjected is very small, essentially balances the buoyancy force acting on
them. Thus, the force exerted by the bubbles on the liquid can be replaced by their buoyancy in the liquid momentum equation. The liquid momentum equation then becomes (see the Appendix)

\[
\frac{dM}{dz} = B_b + B_s ,
\]

(4.12)

where

\[
M = \int_A (1 - \beta_b)w^2 dA \simeq \int_A w^2 dA ,
\]

(4.13)

\[
B_s = \int_A \frac{\rho_a - \rho}{\rho_w} g dA ,
\]

(4.14)

\[
B_b = \int_A \beta_b \frac{2\rho - \rho_a - \rho_s}{\rho_w} g dA \simeq \int_A \beta_b g dA .
\]

(4.15)

Here \(M\) can be identified with the momentum flow rate per unit mass of the liquid, \(B_s\) with the buoyancy due to salinity (or temperature) and \(B_b\) with the buoyancy due to bubbles. In defining the momentum flow rate \(M\) we have assumed a unit value for the so-called momentum amplification factor (Milgram, 1983). The commonly used value for this parameter is about 1.1 (see e.g. Milgram, 1983; Socolofsky, Bhaumik, and Seol, 2008). Its inclusion would introduce another empirical parameter without altering significantly our results.

The two terms in the plume momentum equation (4.12) have opposite signs because the rising plume liquid is saltier and therefore heavier than the surrounding liquid. A level therefore is reached where \(dM/dz = 0\); we may term this the neutral height. Above this level, the plume gets progressively heavier than the surrounding fluid, starts to slow down and, after reaching the peel height, it falls back. Representing this final stage in an integral model requires the adoption of a double-plume model.
such as that developed, e.g., in McDougall (1978) and (Socolofsky, Bhaumik, and Seol, 2008). In the framework of the present model one simply observes that, as the plume rises toward the peel height, it slows down and its cross section increases to conserve mass until it diverges at the peel height, where its momentum vanishes.

As pointed out in Morton, Taylor, and Turner (1956) and (Turner, 1986), the neutral height, where \( \frac{dM}{dz} = 0 \), represents an estimate of the lower edge of the intrusion layer which, experimentally, is identified by observing the level at which the liquid falling back from the peel height expands horizontally. The reason why this is a lower bound is that this falling liquid is lighter than the plume liquid at the neutral level due to the lighter liquid entrained on the way to the peel height. This observation has important implications for the comparison of theory and experiment as will be shown below in section 4.6.

In summary, in integral form the equations of the model are given by (4.1), (4.8), (4.11) and (4.12). Further progress requires an assumption on the distribution of the fields over the plume cross section. Following approximations common in the literature we assume either a top-hat or a Gaussian form. For the top-hat model (see e.g. Morton and Middleton, 1973) we have

\[
m = \pi wb^2, \quad M = \pi w^2 b^2, \quad F_s = \pi w \frac{\rho - \rho_a}{\rho_w} g (\lambda_s b)^2,
\]

(4.16)

where \( \lambda_s b \) is the radius of the plume region in which the salinity difference with the ambient liquid is localized. After substitution of (4.16) into the governing equations
(4.1), (4.8) and (4.12) we find

\[
\frac{dm}{dz} = 2\sqrt{\pi} \alpha_c \sqrt{M}, \tag{4.17}
\]

\[
\frac{dM}{dz} = \frac{Q_b g}{w + \omega_b} + \frac{F_s}{w}, \tag{4.18}
\]

\[
\frac{dF_s}{dz} = -mN^2. \tag{4.19}
\]

Analogous expressions for the Gaussian profile are given in the Appendix, where it is also shown that, after appropriate normalization, the dimensionless form of these equations, on which our numerical results are based, is the same for the top-hat and the Gaussian profiles.

### 4.3 Single-phase plume

For purposes of orientation it is useful to consider the single-phase plume first. Furthermore, when the bubble rise velocity is very small, the bubbly mixture behaves essentially like a homogeneous lighter liquid and the single-phase results are directly applicable.

Two important limit cases are those of a plume dominated by the salinity buoyancy flux \( F_{s0} \) or by the momentum \( M_0 \) injected by the source. In the former case the momentum equation (4.12) is unimportant and the order of magnitude of the height \( L_b \) reached by the plume in this buoyancy-dominated case is dependent on the mass (4.17) and buoyancy (4.19) equations. The characteristic time scale is \( N^{-1} \) so that \( w \sim L_b N \) and, from the two equations, we have the estimates

\[
\frac{m_0}{L_b} \sim 2\pi \alpha_c b L_b N, \quad -\frac{F_{s0}}{L_b} \sim -m_0 N^2, \tag{4.20}
\]
with \( b \sim 2\alpha e L_b \) (the plume radius) estimated from the classical solution for a single-phase plume in a uniform ambient. The minus sign in the left-hand side of the second equation arises from the fact that, for \( z \simeq L_b \), \( M \simeq 0 \). Here and in the rest of the chapter the index 0 denotes values at the source. Upon eliminating \( m_0 \) between these two relations, we find

\[
L_b = \left( \frac{F_{s0}}{4\pi\alpha e^2 N^3} \right)^{1/4}, \tag{4.21}
\]

where the equal sign defines the quantity in the left-hand side.

In the momentum-dominated case, it is the buoyancy equation that plays a minor role. If, on the basis of (4.9) and (4.14), we use the estimate \( F_s \sim wB_s \sim L_m NB_s \), we obtain from the momentum equation (4.12)

\[
-\frac{M_0}{L_m} \sim \frac{F_s}{L_m N}, \tag{4.22}
\]

where the minus sign arises for the same reason as in the previous case; \( L_m \) is the height reached by the plume in this momentum-dominated limit. Upon substituting the estimate of \( F_s \) found from this equation into (4.21), we find

\[
L_m = \left( \frac{M_0}{4\pi\alpha e^2 N^2} \right)^{1/4}. \tag{4.23}
\]

These results agree with those given in Morton, Taylor, and Turner (1956). The ratio \( (L_m/L_b)^8 \) is the parameter \( S \) previously introduced in the literature (see e.g. List, 1982)

\[
S = \left( \frac{L_m}{L_b} \right)^8 = \left( \frac{M_0 N}{F_{s0}} \right)^2. \tag{4.24}
\]

Upon using (4.16) we see that \( M_0 N / F_{s0} \propto \rho w w_0 N / [(\rho - \rho_a)g] \) so that \( \sqrt{S} \) can be seen as the ratio of the mean rate of change of the plume momentum to the reduced gravity force. Large and small values of \( S \) correspond therefore to strong and weak
accelerations of the plume liquid, respectively.

The Froude number, defined by

\[ Fr = \frac{w}{\sqrt{2\lambda_s b g (\rho_a - \rho) / \rho}}, \]

is often used to represent the ratio of inertia and buoyancy of the plume (see e.g. Wüest, Brooks, and Imboden, 1992). In a uniform ambient, \( Fr \) reaches an asymptotic value as the plume becomes fully developed (see e.g. Morton, Taylor, and Turner, 1956). For a top-hat profile this asymptotic value can be deduced from the results of Morton, Taylor, and Turner (1956) and is

\[ Fr_\infty = \sqrt{\frac{5\lambda_s}{16\alpha_e}}. \]

The result for a Gaussian profile is recovered by substituting \( \alpha_e \) by \( \alpha_e / \sqrt{2} \) as can be seen upon comparing (4.17) and (4.80). If the Froude number at the source is larger than this asymptotic value, the plume is termed forced while, if it is smaller, it is termed “lazy” (Hunt and Kaye, 2005). The inverse square of the ratio of the source Froude number to the asymptotic value

\[ \Gamma = \frac{5\lambda_s^2}{8\alpha_e} \frac{b_0 g (\rho_{a0} - \rho_0) / \rho_0}{w_0^2}, \]

can then be used to characterize the strength of the source. By using (4.16) we may re-express this quantity as

\[ \Gamma = \frac{5}{8\sqrt{\pi\alpha_e}} \frac{F_{so} m_0^2}{M_0^{5/2}}. \]

Forced plumes correspond to \( \Gamma < 1 \) and lazy ones to \( \Gamma > 1 \). An alternative way to regard the dimensionless parameter \( \Gamma \) is as the ratio of two length scales, one, \( L_Q \),
characterizing the inlet dimension for a unit Froude number and one, $L_M$, for the actual Froude number. Up to numerical factors of order 1 we have

\[ L_Q \sim \frac{b_0}{\alpha_e} \sim \frac{m_0}{\alpha_e \sqrt{M_0}}, \quad L_M \sim \frac{b_0}{\alpha_e Fr} \sim \left( \frac{M_0^{3/2}}{\alpha_e F_{r0}} \right)^{1/2}, \] (4.29)

from which (4.28) follows upon forming the ratio $(L_Q/L_M)^2$ (Hunt and Kaye, 2005).

While $S$ and $\Gamma$ both contain buoyancy and momentum, the key difference between the two is the presence of the characteristic time $N$ in the former. As a consequence, $S$ compares the rate of change of the plume velocity with the gravitational acceleration, rather than the plume velocity with the characteristic fall velocity (or the plume kinetic energy with the gravitational potential energy) as $\Gamma$ does. Thus, $S$ embodies the effect of forces, while $\Gamma$ compares energies.

The mathematical model described in the previous section can be solved analytically for a single-phase plume. The solution is somewhat involved and is given in the Appendix. Here we simply quote results for the peel height found in the two limit cases considered above for a plume generated by a point source, which are $h_p/L_m = 1.43$ for $S$ large (momentum dominated) and $h_p/L_b = 2.57$ for $S = 0$ (buoyancy dominated), respectively. The latter result agrees with that given in Morton (1959) (see also (Turner, 1979; Scase, Caulfield, and Dalziel, 2006)) while the former one can be recovered by accounting for the different normalizations. The results also agree with those of List (1982) upon taking $\alpha_e = 0.12$ in the definitions of $L_b$ and $L_m$ as in that paper. For the buoyancy-dominated case the neutral height is found to be $h_n/L_b = 1.95$, while it vanishes for a point source in the momentum-dominated case. The appearance of constants of order one in these relations supports the scaling arguments used to deduce (4.21) and (4.23).
4.4 Bubble plumes

In a bubble plume the total buoyancy flux at the source is the sum of the salinity component $F_{s0}$ and the bubble component $Q_{bg}$. Unless the gas flow rate is very small, the latter dominates so that source buoyancy flux can be approximated by $Q_{bg}$. With this approximation, the length scale (4.21) for buoyancy dominated plumes becomes

$$L_b = \left( \frac{Q_{bg}}{4\pi\alpha_e^2N^3} \right)^{1/4}. \quad (4.30)$$

Another important parameter affecting the bubble plume is the drag exerted by the bubbles on the liquid, which is dependent on the bubble-liquid slip velocity $w_b$. With $N^{-1}$ as the characteristic time scale, an appropriate dimensionless measure of this velocity is

$$V_N = \frac{w_b}{L_bN} = \left( \frac{4\pi\alpha_e^2w_b^4}{NQ_{bg}} \right)^{1/4}, \quad (4.31)$$
as suggested, e.g., in McDougall (1978) and (Socolofsky and Adams, 2005).

The parameter $\Gamma$ characterizing the source strength needs to be modified similarly replacing $F_{s0}$ by $Q_{bg}$. According to (Bombardelli et al., 2007), the asymptotic value of the Froude number for a bubble plume in a uniform ambient liquid is given by $\sqrt{3\lambda_b/8\alpha_e}$. However, in the literature, the normalization most frequently used is the same as for the single-phase case (see e.g. McDougall, 1978; Seol, Bryant, and Socolofsky, 2009; Socolofsky, Bhaumik, and Seol, 2008) and, accordingly, we define $\Gamma$ as

$$\Gamma = \frac{5}{8\alpha_e \sqrt{\pi M_0^{5/2}}} Q_{bg}m_0^2. \quad (4.32)$$

By using (4.16) for a top-hat profile we see that $\Gamma \propto (Q_{bg}/[w_0(\alpha_e w_0^2 b_0)])$, which may be seen as proportional to the ratio of the buoyancy force acting on the gas, of the
order of $\rho (Q_g / N) g$, to the rate at which the momentum of the entrained liquid, of the order of $\rho \alpha_e w_0^2 b^2 / N$, increases as shown by (4.1).

Finally, we replace $F_{s0}$ by $Q_b g$ in the definition (4.24) of the parameter $S$ writing

$$S = \left( \frac{M_0 N}{Q_b g} \right)^2. \quad (4.33)$$

Rewriting this expression as $\sqrt{S} = \rho M_0 N / (\rho Q_b g)$, we see that $\sqrt{S}$ represents the rate of change of the plume momentum to the buoyancy force on the gas and has, therefore, a physical meaning similar to that in the single-phase case. Alternatively, since $Q_b / N$ is the total amount of gas injected during the characteristic time $N^{-1}$, $S$ may also be interpreted as the ratio of the momentum flux to the buoyancy force. Buoyancy-dominated plumes, therefore, are characterized by small values of $S$. It may also be noted that

$$\Gamma \sqrt{S} = \frac{5}{8 \sqrt{\pi \alpha_e}} N m_0^2 \left( \frac{b_0 / \alpha_e}{\sqrt{\pi} \bar{w}_0 / N} \right), \quad (4.34)$$

with the last step appropriate for a top-hat profile. Recalling that $b \sim \alpha_e z$, we see that $\Gamma \sqrt{S}$ may be interpreted as the ratio of the virtual source height to the distance travelled by the plume liquid during the time $N^{-1}$.

In order to go beyond the scaling analysis and calculate precise numerical values it is useful to recast the model equations in dimensionless form using the dimensionless independent variable

$$z^* = \frac{z}{L_b}, \quad (4.35)$$

and the definitions

$$m^* = \frac{m}{\pi N L_b (2 \alpha_e L_b)^2}, \quad M^* = \frac{M}{\pi (NL_b)^2 (2 \alpha_e L_b)^2}. \quad (4.36)$$
\[ B_b^* = \frac{B_b}{\pi (2\alpha e L_b)^2 N^2 L_b}, \quad F_s^* = \frac{F_s}{\pi N L_b (2\alpha e L_b)^2 N^2 L_b}. \] (4.37)

The combination \(2\alpha e L_b\) is of the order of the plume diameter at the height \(L_b\) above the source. In this way the equations become

\[ \frac{dm^*}{dz^*} = \sqrt{M^*} \] (4.38)

\[ \frac{dM^*}{dz^*} = B_b^* + B_s^* = \frac{1}{M^* / m^* + V_N} + \frac{m^* F_s^*}{M^*} \] (4.39)

\[ \frac{dF_s^*}{dz^*} = -m^*. \] (4.40)

Here we have used the relation \(w^* = M^* / m^*\), which is an immediate consequence of (4.16). The corresponding inlet conditions can be expressed in terms of the dimensionless parameters introduced earlier with the results

\[ m_0^* = \frac{2}{\sqrt{3}} S^{5/8} \Gamma^{1/2}, \quad M_0^* = S^{1/2}. \] (4.41)

Since, as already noted, the buoyancy flux at the inlet is dominated by the bubbles, we will solve these equations with the initial condition

\[ F_{s0}^* = 0. \] (4.42)

The liquid in the rising plume is always heavier than the surrounding liquid, and the buoyancy flux due to salinity vanishes at the source. Thus, \(F_s^*\) is always negative and monotonically increases in magnitude.

As mentioned in the Introduction, the inlet conditions used in previous theoretical work adopting the integral model (see e.g. McDougall, 1978; Crounse, Wannamaker, and Adams, 2007) are equivalent to taking \(S = 0\), i.e., a totally buoyancy-driven plume.
with no inlet liquid momentum, and $\Gamma = 1$, which is appropriate asymptotically for fully developed plumes in an unstratified environment. This procedure was justified by the results of Morton, Taylor, and Turner (1956) and (Liro, Adams, and Herzog, 1992) which suggest that the plume behavior is only weakly dependent on the inlet conditions. While this is approximately true in unstratified environments, we find that the finiteness of the peel and intrusion heights in the presence of stratification causes inlet conditions to acquire a greater importance. This result is similar to the case of fountains in which the height reached by the liquid is also finite, not because of stratification, but because of the strong effect of gravity (Hunt and Burridge, 2015).

4.5 Results

As formulated, the solution to the mathematical problem embodied in (4.38), (4.39), (4.41) and (4.42) depends on three parameters, the dimensionless bubble velocity, $V_N$, the ratio of the bubble buoyancy to the momentum flux, $S$, and the source strength $\Gamma$. It is therefore not possible to present a comprehensive parametric study of the system. Rather, we focus on some limit cases which help illuminate the physical contents of the model, the role of the parameters and their interaction.

To begin with, for very small $S$, i.e., for plumes dominated by buoyancy effects, rather than momentum, and the source strength $\Gamma$ small enough (forced plume) that $M_0^*$ is large, no parameters are left to characterize the inlet conditions and the solution only depends on $V_N$. Figure 4.2 shows the dimensionless peel height $h_p/L_b$ (left) and the dimensionless neutral height $h_n/L_b$ for this case, which is equivalent to a point source with the entire buoyancy provided by the bubbles.

The peel height is a decreasing function of $V_N$ because large values of the bubble
Figure 4.2: Dimensionless peel height $h_p / L_b$ (upper curve) and neutral height $h_n / L_b$ for $S = 0$ as functions of the dimensionless bubble rise velocity $V_N$ defined in (4.31). The parameter $\Gamma$ has no influence when $S = 0$. The neutral height is the level at which the plume momentum attains its maximum value.
Figure 4.3: Left: Dimensionless peel height for $S = 0.1, 1$ and 10, in increasing order at the right of the diagram. Right: Dimensionless neutral height for $S = 0, 0.1, 1$ and 10, in decreasing order at the right of the diagram. The solid and dashed lines correspond to $\Gamma = 10^{-3}$ and $\Gamma = 10^{-1}$.

rise velocity imply that the bubbles are unable to exert a strong drag force on the liquid and lift it. The decreasing drag causes the rise velocity and entrainment to decrease as well, with the consequence that the neutral height also decreases with increasing $V_N$. The maximum effect of the bubble buoyancy occurs when the drag is so strong that the bubbles and the liquid form a homogeneous, relatively light bubbly mixture. In this case $w_b \ll w$ or $V_N \ll M^*/m^*$ and the momentum equation (4.39) reduces to

$$\frac{dM^*}{dz^*} = \frac{F_s^*}{w^*} + 1,$$

which has the same form as for a single phase plume with $F^*$ replaced by $F^* + 1$; the solution is given in the Appendix. When $V_N$ is much greater than the liquid velocity $w^* = M^*/m^*$, the weak bubble drag has the consequence that (4.39) becomes identical to the momentum equation for a single-phase plume with the peel height tending to become independent of $V_N$ as shown later in figure 4.7.

In most of the available experiments there was no injection of liquid at the source
which results in small values of $S$ (see next section). However this parameter would not be necessarily small with liquid injection. As $S$ increases, the peel height increases because of the increasing injection of momentum by the source as shown in the left panel of figure 4.3. The dependence of the peel height on $\Gamma$ is also stronger, which reflects the increasing importance of the mass flux. This dependence is the stronger the larger $S$, i.e., the initial momentum. The neutral height (right panel), on the other hand, is a decreasing function of $S$ because large $S$ implies strong entrainment which lowers the level at which the plume density equals the density of the surrounding liquid. Indeed, as can be seen from figure 4.3, the largest neutral height occurs for $S = 0$. The dependence on $\Gamma$ is weaker than for the peel height, which implies that the plume ascent up to the neutral height is dependent more on momentum than on mass flux, at least in the parameter range to which these figures refer.

The panels in figure 4.4 show the profiles of the momentum flow rate, mass flow rate, plume radius and salinity buoyancy flux for a fairly large bubble velocity, $V_N = 2.54$, a small source strength, $\Gamma = 0.01$ and several values of $S$. The plume source is located at $z^* = 0$. Since the total buoyancy (bubbles + salinity) is fairly small, the momentum flux exhibits a very weak growth up to its maximum (i.e., the neutral height), and then decreases to zero at a faster and faster rate as the peel height is approached. The mass flux remains however finite as the vanishing velocity is balanced by an increase of the plume radius at the peel height where, in fact, it diverges as shown in the third panel. The buoyancy flux due to salinity is negative as explained after (4.42). The larger the momentum effects compared to buoyancy, i.e., the larger $S$, the larger $M^*, m^*, b^*$ and $|F^*_s|$. 

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Figure 4.4: Vertical distribution of the dimensionless momentum flux $M^*$, dimensionless mass flux $m^*$, dimensionless plume radius $b^*$ and dimensionless salinity buoyancy flux $F_s^*$ for $V_N = 2.54$, $\Gamma = 0.01$ and $S = 0.1, 1$ and 10. The plume source is at $z^* = 0$. In these cases, the total buoyancy (bubbles + salinity) is fairly small. Note the divergence of the plume radius as the peel height is approached. The buoyancy flux due to salinity is negative as the plume liquid becomes progressively heavier than the ambient liquid.
The analysis presented in the Appendix for single-phase plumes brings into evidence the importance of the combination

$$\phi = \frac{m^*_0}{(S + 1)^{3/8}} = \frac{2}{\sqrt{5}} \Gamma^{1/2} \frac{S^{5/8}}{(S + 1)^{3/8}} = \frac{m_0 N^{1/2}}{(4\pi\alpha_e^2 M_0^3)^{1/4}}.$$  \hspace{1cm} (4.44)

As noted in section 4.4, the single-phase definitions (4.24) and (4.28) of $S$ and $\Gamma$ can be adapted to the two-phase case simply by replacing $F_0$ by $Q_{bg}$.

For small $S$, $\phi \approx m^*_0$ while, for large $S$, $\phi \propto \sqrt{S}^{1/2}$; the physical meaning of this combination was discussed earlier in connection with (4.34).

For a lazy plume generated by a source injecting a finite mass of fluid with a small momentum, the main agent lifting the liquid is the bubble buoyancy. In this case $S$ is small, but $\Gamma$ large enough that $m^*_0 \propto \sqrt{S}^{5/4} \propto \phi$ is finite (see Eq. (4.41)).

Figure 4.5, in which the three families of lines correspond to different values of $S^{5/4} \Gamma$ and the two curves in each family differ by the value of $S$, refers to this case. The peel height (left panel) mainly depends on $V_N$ and $m^*_0$. The weakness of the dependence

![Figure 4.5: Dimensionless peel height (left) and neutral height for a “lazy” plume generated by a source injecting a finite mass of fluid with small momentum. The pairs of curves correspond to $m^*_0 \propto S^{5/4} \Gamma = 0.1$, 1 and 10. The two curves in each family are, in ascending order, for $S = 10^{-4}$ and $S = 5 \times 10^{-4}$.](image)
on $S$ becomes particularly evident for small $V_N$, in which case the plume behaves like a single homogeneous medium, and agrees with the analysis of the Appendix for the single-phase case (see in particular Eq. (4.67)). As $V_N$ increases, the two-phase nature of the plume becomes more evident and a dependence on $S$ begins to appear. The behavior of the neutral height (right panel in figure 4.5) is similar, as suggested by (4.68) and the analysis in the Appendix.

Conversely, when the source momentum is large, $S$ is large and momentum dominates. In this case $\phi \propto \sqrt{\Gamma S^{1/2}} \propto \sqrt{b_0/(w_0/N)}$. The analysis for single-phase plumes presented in the Appendix suggests that the proper normalization of the peel height should be in terms of $L_m$, the characteristic length for the momentum-dominated case defined in (4.23), rather than $L_b$, with a difference by a factor $S^{1/8}$. The left panel of figure 4.6 shows the peel height plotted in this way. For large $V_N$, the single-phase case is recovered and the grouping of the curves in terms of $\Gamma \sqrt{S}$ is confirmed. Some difference however remains when $V_N$ is not large because, in this case, the first term in the right-hand side of the momentum equation cannot be neglected and the competition between bubble rise velocity and plume velocity comes into evidence. From the Appendix, in the case of a single-phase plume, the proper normalization of the neutral height is $S^{3/8} h_n / L_b$. The right panel of figure 4.6 shows the neutral height normalized in this way for the same cases as in the left panel. Unlike the peel height, however, we do not observe a good scaling for large $V_N$ because at the neutral height, with these parameters, the plume velocity $w^* = M^* / m^*$ in (4.39) is not small compared with the bubble velocity so that the two-phase nature of the plume is important.
Figure 4.6: Dimensionless peel height (left) and neutral height for large source momentum and finite \( \phi \); note that the normalization used for \( h_p \) and \( h_n \) is different from that of the previous figures for the reason described in the text. The three pairs of curves correspond to \( \sqrt{\Gamma S^{1/2}} = 0.1, 1 \) and 10. The solid lines are for \( S = 20 \) and the dashed lines for \( S = 1000 \).

When both \( \phi \) and \( S \) are large the dependence of the peel height (left panel, figure 4.7) on \( V_N \) is weak. Here the influence of \( V_N \) is limited to the very small values for which the bubble lift force is significant in spite of the large momentum. The parameter labelling the groups of curves in the figure is proportional to the inverse square of the normalized liquid velocity as suggested by (4.69) in the Appendix:

\[
S^{1/4} \Gamma = \left( \frac{\sqrt{5} \, m_0^*}{2 \, M_0^*} \right)^2 = \left( \frac{5 \lambda_s^2}{4 \omega_0^*} \right)^2. \tag{4.45}
\]

The large momentum causes a strong entrainment and the mean plume density quickly increases. The neutral height is therefore small, much smaller, in fact, than the peel height. The effect of \( V_N \) appears to be stronger for the neutral height than for the peel height, but this is an artifact of the different vertical scales in the two panels. Because of the different physics determining the two heights, the asymptotic independence on \( V_N \), clear in the left panel for the peel height, is only visible for large values of \( S^{1/4} \Gamma \).
Figure 4.7: Dimensionless peel height (left) and neutral height for large source momentum and large $\phi$ (which can be interpreted as large mass injection or strong stratification). The three groups of curves correspond to $S^{1/4}\Gamma = 10$, 100 and 1,000. The solid lines are for $S = 20$ and the dashed lines for $S = 1000$.

<table>
<thead>
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<th>$U_N$</th>
<th>$\Gamma$</th>
<th>$S \times 10^4$</th>
<th>$h_{i,n}/(Q_b\bar{g}/N^3)^{1/4}$</th>
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<td></td>
<td></td>
<td>(Yang et al., 2016) present</td>
</tr>
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<td>1.77</td>
</tr>
</tbody>
</table>

Table 4.1: Comparison between the present results for the neutral height $h_n$ (last column) and the numerical results for the intrusion height $h_i$ reported in Yang et al. (2016). The values of $S$, $\Gamma$ and dimensionless bubble rise velocity $V_N$ shown are obtained from the information given in the reference.
4.6 Comparison with experiment

We now consider how and to what extent the present theory can be compared with experiment and other theoretical analyses. In the presentation of results in the previous section it was useful to use the parameter $V_N$, defined in (4.31), to non-dimensionalize the bubble velocity and the parameter $L_b$, defined in (4.30), to nondimensionalize the neutral and trap heights because use of these parameters does not require the explicit adoption of a specific value for the empirical entrainment coefficient $\alpha_e$. However, in turning to actual data, it is preferable to follow most authors (see e.g. Socolofsky and Adams, 2005; Socolofsky, Bhaumik, and Seol, 2008; Crounse, Wannamaker, and Adams, 2007; Yang et al., 2016) and use a different dimensionless bubble velocity

$$U_N = \frac{w_b}{(Q_b g N)^{1/4}} = \frac{V_N}{(4\pi\alpha_e^2)^{1/4}},$$

and characteristic length

$$H_c = \left(\frac{Q_b g}{N^3}\right)^{1/4} = (4\pi\alpha_e)^{1/4}L_b.$$

To obtain the results described below we took $\alpha_e = 0.117$, which is equivalent to $\alpha_e = 0.083$ for a Gaussian profile; this is a value widely used in the literature (see e.g. Turner, 1986; Hunt and Kaye, 2005; Asaeda and Imberger, 1993) and close to the average value 0.086 reported in Yang et al. (2016). With this value of $\alpha_e$, $V_N/U_N \simeq 0.624$ and $L_b/H_c \simeq 1.60$.

We begin with a comparison with the numerical results of Yang et al. (2016) who carried out LES numerical simulations of bubble plumes in a stratified environment. These are the most suitable results we have found to compare with as, in their Table 1, these authors also report values for the source mass and momentum flow rates $m_0$, 

\[\text{Page 111}\]
Figure 4.8: Dimensionless intrusion height $h_i/H_c$ as a function of the dimensionless bubble velocity $U_N$ reported by several investigators; the dashed line is the theoretical prediction by Crounse, Wannamaker, and Adams (2007).
$M_0$, in addition to the gas flow rate $Q_b$ and bubble size. The results of the comparison are shown in Table 4.1. Our predictions are close, although they fall somewhat below the data reported in Yang et al. (2016) for reasons which will be addressed shortly.

Figure 4.8 shows a collection of experimental results for the intrusion height from various sources rendered dimensionless in terms of the characteristic quantities defined in (4.46) and (4.47); the original data, taken from the original papers, are shown in Table 4.2. The dashed line is the theoretical result of Crounse, Wannamaker, and Adams (2007) to which we return later. All the data shown in this figure refer to bubble plumes generated by injecting only gas, but no liquid, at the source. Taken literally, this would imply that the inlet quantities $m_0$ and $M_0$ of our model should both vanish and, with them, also $S$ and $\Gamma$. This conclusion, however, would be incorrect as no integral model can be expected to hold in the flow-establishment zone near the source where the self-similarity assumption does not apply.

One way to deal with this problem, proposed in Crounse, Wannamaker, and Adams (2007), consists in calculating effective values for $m_0$ and $M_0$ at the source from

$$m_0 = \frac{6}{5} \left( \frac{9\pi^2}{10} \frac{\alpha^4}{\rho g} Q_b g z_0^3 \right)^{1/3}, \quad M_0 = \left( \frac{81\pi}{100} \frac{\alpha^2}{\rho^2 g^2} Q_b^2 g^2 z_0^3 \right)^{1/3},$$

(4.48)

by taking $z_0 = 10D$, with $D$ the source diameter. These are the relations for a fully developed single-phase plume at a distance $z_0$ from a point source (see e.g. Reeuwijk et al., 2016). If these relations are converted to the parameters $\Gamma$ and $S$ of the present theory, we find $\Gamma = 1$ and

$$S = 270 \left( \frac{10\pi^2 \alpha^4 D^8}{3 \frac{\alpha^2}{\rho^2 g^2}} \right)^{1/3}.$$

(4.49)

The normalized intrusion height $h_i / H_c$ reported in figure 3 of the chapter by Crounse,
Table 4.2: Original data used to generate figure 4.8. The values of $Q_{bg}$ and $w_b$ for the data of AI (Asaeda and Imberger, 1993) have been obtained from the values of $P_N$ and $M_H$ given in Table 1 of that chapter; the value of $D$ shown corresponds to the maximum area reported to be ejecting bubbles in their experiment; $h_l$ and $h_i$ are the positions of the lower edge of the intrusion layer and the intrusion depth, respectively, reported in AI (Asaeda and Imberger, 1993); the other authors including SA (Socolofsky and Adams, 2005), R (Reingold, 1994), SBS (Seol, Bryant, and Socolofsky, 2009) only report $h_i$. The question mark indicates the tank depth; the depth of the liquid is not reported by these authors.

<table>
<thead>
<tr>
<th>Reference</th>
<th>ID</th>
<th>$N$ s$^{-1}$</th>
<th>$Q_{bg} \times 10^6$ m$^4$/s$^3$</th>
<th>$w_b$ m/s</th>
<th>$D$ mm</th>
<th>$h_l$ m</th>
<th>$h_i$ m</th>
<th>depth</th>
</tr>
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<td>5.968</td>
<td>0.080</td>
<td>4.570</td>
<td>0.132</td>
<td>0.240</td>
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<tr>
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<td>4.570</td>
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<td>0.468</td>
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<td>0.700</td>
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<td>0.360</td>
<td>66.300</td>
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<td>0.390</td>
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<td></td>
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<tr>
<td></td>
<td>g50a</td>
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<td>66.300</td>
<td>0.233</td>
<td></td>
<td>0.380</td>
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<td></td>
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<td>35.000</td>
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<td>0.225</td>
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<td>14</td>
<td>0.143</td>
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Table 4.3: Values of the dimensionless parameters $\Gamma$ and $S$ according to (4.52) for the Milgram procedure and to (4.49) for the procedure of Crounse et al. (in which case $\Gamma = 1$); $U_N$ is defined in (4.46). The column labelled “Exp” shows the normalized measured values; the quantities $h_1$ and $h_l$ are explained in the caption of the previous table; $h_n$ is the neutral height of the present theory. The last two pairs of columns show the dimensionless intrusion heights calculated according to the two procedures, uncorrected and corrected by the addition of the height of the flow-establishment zone (f.e.z.) estimated to be $5D$.

<table>
<thead>
<tr>
<th>Reference</th>
<th>ID</th>
<th>$\Gamma$ Milgram</th>
<th>$S$ Crounse et al.</th>
<th>$U_N$</th>
<th>$h_i/(Q_b g/N^3)^{1/4}$</th>
<th>$h_l/(Q_b g/N^3)^{1/4}$</th>
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<td>2.737</td>
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Figure 4.9: Dimensionless intrusion height $h_i/H_c$ as a function of the dimensionless bubble velocity $U_N$. The data points and the dashed line are the same as shown in figure 4.8. The solid lines are the results of the present theory for the neutral height, the lower one for $\Gamma = 1$ and $S = 0.01$ and the upper one for $S = 0$; this latter line is the same as shown with a different normalization in figure 4.2.
Wannamaker, and Adams (2007) is reproduced as the dashed line in figures 4.8 and 4.9 as a function of the dimensionless bubble velocity $U_N$. It is not straightforward to compare this result with the predictions of the present theory as there is some uncertainty as to the actual values of $D$ and $Q_b$ used by Crounse, Wannamaker, and Adams (2007) but, upon taking $S = 0.01$, we find the good match shown by the solid line in figure 4.9. If we use the data shown in their figure 6 of Crounse, Wannamaker, and Adams (2007), namely $U_N = 3$, $w_b = 0.12$ m/s and $N = 0.08$ s$^{-1}$, we find $Q_b = 3.27 \times 10^{-6}$ m$^3$/s = 196 mL/s which, for $S = 0.01$, corresponds to $D \simeq 21$ mm, which appears reasonable. The results of Yang et al. (2016) (upward triangles) and (Reingold, 1994) (squares) shown in figure 4.9 are between the line for $S = 10^{-2}$ and that for $S = 0$ (shown earlier in figure 4.2 and reproduced here with the present slightly different normalization) and can easily be fitted by the present model. However, there is no way to fit most of the other data. This situation might appear perplexing because the uppermost $S = 0$ line in figure 4.2 represents an upper boundary for the intrusion height as noted earlier in comparing figures 4.2 and 4.3. There are two observations to make in this connection.

In the first place, a proper comparison of these data with theory should allow for the presence of a flow-establishment zone traversing which the plume attains its ultimate self-similar structure as the liquid is gradually accelerated by the relatively weak drag exerted by the bubbles. A meaningful comparison with the present theory, which relies on the assumption of self-similarity, is only possible starting from the top of this zone. In this perspective, the proper values of $m_0$ and $M_0$ to be used in the theory are the values of these quantities at the top of this flow-establishment zone. This correction is not necessary if there is a significant liquid injection at the source,
as in the calculation of Yang et al. (2016), but it is a central problem when the liquid mass and momentum fluxes at the source vanish.

An estimate of the height of the flow-establishment zone can be attempted following (Milgram, 1983). This author gives two estimates for the height $z_E$ of the flow-establishment zone but only one of them applies in the vast majority of cases. According to this estimate, $z_E \simeq 5D$, which is also consistent with later work (see e.g. Lee and Chu, 2003). From this estimate, (Milgram, 1983) deduces a value of $M_0$ given by

$$M_0 \simeq \frac{2Q_b}{w_b} gz_E. \quad (4.50)$$

Upon using the top-hat relations (4.16) we then find

$$m_0 = b_0 \sqrt{M_0}, \quad (4.51)$$

in which, from the spreading rate of a single-phase jet (Reeuwijk et al., 2016), $b_0 \simeq \frac{1}{2} D + 2\alpha_e z_E$. With these results we can calculate the dimensionless parameters $S$ and $\Gamma$:

$$S = 100 \frac{D^2 N^2}{w_b^2}, \quad \Gamma = \frac{(1 + 20\alpha_e)^2}{60\alpha_e} \sqrt{\frac{w_b^2 D}{Q_b g}}, \quad (4.52)$$

from which we also find

$$\Gamma^{1/2} S^{-1/8} = \frac{(1 + 20\alpha_e)w_b}{8\sqrt{5}(4\pi \alpha_e^2 Q_b N)^{1/4}} = \frac{1 + 20\alpha_e}{8\sqrt{5}} V_N. \quad (4.53)$$

The second, and possibly more important, point is that, as noted in section 4.2, the neutral height predicted by the model should actually be considered as an estimate of the lower edge of the intrusion layer. The reason is that the descending liquid which settles at the intrusion depth is lighter than the ascending liquid due to the entrainment of the liquid between the neutral and peel heights as indicated in figure 4.10.
Figure 4.10: The liquid that falls back from the peel height $h_p$ to form the intrusion layer at $h_i$ is lighter than the ascending liquid due to the entrainment of the light liquid between the neutral height $h_n$ and peel heights. For this reason the intrusion height differs from the neutral height, which is the level at which the ascending liquid has the same density as the ambient liquid. Therefore, the neutral height underestimates the true intrusion height.
Figure 4.11: The vertical lines connect the data points of Asaeda and Imberger (1993) marking the lower edge of the intrusion layer and the intrusion height. The filled squares and diamonds are the corresponding predictions of the neutral height given by the present theory with and without the flow-establishment zone correction. The open triangle is the single data point reported by Seol, Bryant, and Socolofsky (2009), and the symbols above and below it are the present results with and without the flow-establishment zone correction.
Reference Asaeda and Imberger (1993) includes experimental results not only for the intrusion height, but also for the lower edge of the intrusion layer. These data are shown in Table 4.2 and in figure 4.11, where they are connected by a vertical line to the respective reported intrusion height. In this figure we show our predictions for the neutral height without correction for the zone of flow establishment by a filled diamond and with the correction by a filled square. We see that there is a good overall match between predictions and observations. The open triangle is the single data point reported in Seol, Bryant, and Socolofsky (2009), and the symbols above and below it are the present results with and without the establishment zone correction.

Ref. Asaeda and Imberger (1993) is the only data set reporting information not only on the intrusion height, but also on the position of the lower edge of the intrusion layer. This distinction appears to be very important not only for the data of Asaeda and Imberger (1993), but also for most of those of Socolofsky and Adams (2005) which fall well above predictions as shown by the crosses in figure 4.9. Other data are closer to the model predictions. One may conjecture that, in these cases, the thickness of the intrusion layer was relatively small. Unfortunately, in the absence of more complete information on the experimental observations, it is not possible to reach a firmer conclusion.

As we have shown, the comparison between the data of Yang et al. (2016) and our results in table 4.1 is close, which appears at variance with the distinction between intrusion and neutral heights that we just described. A plausible explanation is that the effective entrainment coefficient resulting from the LES simulation of Yang et al. (2016) in the plume establishment zone is larger than the average value we have used. As a consequence, at the lower level, more heavier liquid is entrained than estimated.
from the averaged value of $\alpha_e$. The final intrusion height would therefore be lower than that for the smaller $\alpha_e$ we have used, and therefore, closer to the neutral height that we have calculated.

4.7 Summary and conclusions

In this chapter we have developed a horizontally integrated model for bubble plumes in stratified environments which, unlike earlier models, includes the effects of inlet conditions. We have found that these conditions have a strong influence on the model predictions. By a suitable rescaling of the dependent and independent variables, the equations of the model take the same form for a top-hat and a Gaussian distribution of the flow fields over the plume cross section. We have also provided a scaling analysis which helps clarify the physical meaning of the main dimensionless parameters arising in the theory.

Unlike much earlier work (see e.g. Zheng, Yapa, and Chen, 2003; Socolofsky and Adams, 2005; Socolofsky, Bhaumik, and Seol, 2008), we were careful to make a distinction between the height at which the plume momentum attains its maximum value, which we term the neutral height, and the intrusion height reported in many experiments. We have argued that the neutral height represents an estimate of the lower edge of the intrusion layer, and cannot be taken to represent the measured intrusion height. This distinction proves critical when it is attempted to compare the results of our model, as well as those of earlier investigators, with experimental data, which would otherwise be found to fall inexplicably much above the theoretical predictions in many cases. Our results on this point are unaffected by the precise value of the entrainment coefficient which is a matter of some uncertainty as mentioned in
section 4.2.

Appendix A – Derivation of (4.12)

Upon integrating the liquid momentum equation over the plume cross-section we have

\[
\frac{d}{dz} \int_A (1 - \beta_b) \rho u_z^2 dA = \int_A [(1 - \alpha) (\rho_a - \rho) g + n f_{z,bub}] dA - \tau_t P ,
\]

in which \( f_{z,bub} \) is the force exerted by a bubble on the liquid, \( n \) is the bubble number density, \( \tau_t \) is the turbulent stress at the edge of the plume and \( P \) the perimeter of the plume. After a similar integration, the momentum equation for the bubble phase is

\[
\frac{d}{dz} \int_A \beta_b \rho_{bubble} u_{bubble}^2 dA = \int_A [\beta_b (\rho - \rho_{bubble}) g - n f_{z,bub}] dA .
\]

Upon adding these two equations and neglecting the density of the bubbles the result may be written as

\[
\frac{d}{dz} \int_A (1 - \beta_b) \rho u_z^2 dA = \int_A [\beta_b (2 \rho - \rho_a) g + (\rho_a - \rho) g] dA - \tau_t P .
\]

or approximately, upon setting \( \rho \simeq \rho_w , \)

\[
\frac{d}{dz} \int_A (1 - \beta_b) u_z^2 dA = \int_A \left[ \beta_b \frac{2 \rho - \rho_a}{\rho_w} g + \frac{\rho_a - \rho}{\rho_w} g \right] dA - \tau_t P ,
\]

which is (4.12) after dropping the small effect due to turbulent drag at the edge of the plume.
Appendix B – Solution for a single-phase plume in uniform ambient

The solution for a single-phase buoyant plume in a stratified ambient liquid has been worked out by Morton (1959) in the case in which the plume issues from a point-like source or, equivalently, the plume has a point-like virtual origin. Here we extend this solution to the case of a source of finite diameter. We assume a top-hat profile which permits us to write $B_s = F_s/w$ as directly follows from (4.16). In dimensionless form the governing equations are then (4.38), (4.39) and (4.40), with the first term in the right-hand side of (4.39) omitted, and inlet conditions $m^*_0, M^* = M_0^*$ and $F_s^* = F_{s0}^* = 1$. As noted in section 4.5, the solution that follows can also be applied to the case of (4.43) in which the bubbles rise so slowly that the bubbly mixture behaves like a light homogeneous liquid. For this application the two-phase $F_s^* + 1$, in which $F_s^*(0) = 0$, should be replaced by the present $F_s^*$ with $F_s^*(0) = 1$.

Upon multiplying (4.39) by $M^*$, (4.40) by $F_s^*$ adding and integrating we find

$$ (M^*)^2 + (F_s^*)^2 = (M^*(0))^2 + (F_s^*(0))^2 = S + 1, \quad (4.58) $$

with $S$ defined in (4.24). This relation shows that $M^*$ reaches a maximum value $\sqrt{S + 1}$ when $F_s^* = 0$, i.e., at the neutral height $h_n^*$. As the plume continues its rise by inertia $F_s^*$ turns negative and $M^*$ starts decreasing until it vanishes at the peel height $h_p^*$. By manipulating (4.38) and (4.39) we have

$$ 2m^* dm^* = \frac{\sqrt{M^*}}{\sqrt{S + 1 - (M^*)^2}} d(M^*)^2. \quad (4.59) $$
Upon integration, from the inlet to the neutral height we find

\[(S + 1)^{-3/4} \left[ m^*(h_n) - m_0^2 \right] = \beta \left( \frac{5}{4}, \frac{1}{2}, \frac{(M^*)^2}{S + 1} \right) - \beta \left( \frac{5}{4}, \frac{1}{2}, \frac{S}{S + 1} \right), \tag{4.60} \]

where \( \beta \) is the incomplete beta function. A further integration from the neutral height to the peel height gives

\[(S + 1)^{-3/4} \left[ m^*(h_p^*) - m^*(h_n^*) \right] = 2\beta \left( \frac{5}{4}, \frac{1}{2} \right) - \beta \left( \frac{5}{4}, \frac{1}{2}, \frac{(M^*)^2}{S + 1} \right) - \beta \left( \frac{5}{4}, \frac{1}{2}, \frac{S}{S + 1} \right). \tag{4.61} \]

With \( m^* \) known as a function of \( M^* \), we can find expressions for the neutral and peel heights from (4.38). The results are:

\[ \frac{h_p}{L_b} = \frac{1}{2} (1 - \sigma)^{-1/8} \left( I_1 + I_2 \right), \tag{4.62} \]

\[ \frac{h_n}{L_b} = \frac{1}{2} (1 - \sigma)^{-1/8} I_1, \tag{4.63} \]

where

\[ I_1(\sigma, \phi) = \int_{\sigma}^{1} \frac{dt}{\sqrt{(1 - t) [\phi^2 + \beta(\frac{5}{4}, \frac{1}{2}, t) - \beta(\frac{5}{4}, \frac{1}{2}, \sigma)]}}, \tag{4.64} \]

\[ I_2(\sigma, \phi) = \int_{0}^{1} \frac{dt}{\sqrt{(1 - t) [\phi^2 + 2\beta(\frac{5}{4}, \frac{1}{2}) - \beta(\frac{5}{4}, \frac{1}{2}, t) - \beta(\frac{5}{4}, \frac{1}{2}, \sigma)]}} \tag{4.65} \]

with \( \sigma = S/(S + 1) \) and \( \phi \) defined in (4.44). As the parameter \( t \) ranges from 0 to 1, the incomplete beta function \( \beta(\frac{5}{4}, \frac{1}{2}, t) \) ranges from 0 to \( \beta(\frac{5}{4}, \frac{1}{2}) \approx 1.748 \). The integrals can be simplified when \( \phi \) is large to find

\[ I_1 \approx \frac{2}{\phi \sqrt{S + 1}}, \quad I_2 \approx \frac{2}{\phi}. \tag{4.66} \]
For small $S$ (but $\Gamma$ large enough that $\phi$ is large) (4.62) and (4.63) become

\[
\frac{h_p}{L_b} \approx \frac{2}{\phi} = \sqrt{\frac{5}{\Gamma S^{5/4}}},
\]

(4.67)

\[
\frac{h_n}{L_b} \approx \frac{1}{2\phi} = \frac{1}{2} \sqrt{\frac{5}{\Gamma S^{5/4}}} = \frac{1}{2} \frac{h_p}{L_b}.
\]

(4.68)

For large $S$, on the other hand, (4.62) and (4.63) give

\[
\frac{h_p}{L_b} \approx \frac{S^{1/8}}{\phi} = \frac{\sqrt{5}}{2\sqrt{\Gamma S^{1/4}}},
\]

(4.69)

\[
\frac{h_n}{L_b} \approx \frac{1}{\phi S^{3/8}} = \frac{\sqrt{5}}{2\sqrt{\Gamma S^{5/4}}},
\]

(4.70)

We recognize here the same combinations of $S$ and $\Gamma$ encountered before, with $S^{1/2}\Gamma$ appropriate for momentum-dominated plumes and $S^{5/4}\Gamma$ for buoyancy-dominated plumes.

For a point source $\Gamma = 0$. In this case, for $S = 0$, $\sigma = 0$ and $\phi = 0$. The numerical evaluation of the integrals gives $I_1 \approx 3.91$ and $I_2 \approx 1.24$. With these values we find the results for the neutral height quoted at the end of section 4.3. For large $S$, $I_1 \to 0$ while $I_2 \approx 2.86$. 

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Appendix C – Gaussian profiles

Assume

\[ w(r, z) = w(r = 0, z)e^{-r^2/b^2} \]  \hspace{1cm} (4.71)

\[ \frac{\rho(r, z) - \rho_a(z)}{\rho_w} \frac{\rho(r = 0, z) - \rho_a}{\rho_w} e^{-r^2/(\lambda_s b)^2} \]  \hspace{1cm} (4.72)

\[ \beta_b(r, z) = \beta_b(z)e^{-r^2/(\lambda_b b)^2} . \]  \hspace{1cm} (4.73)

Then we have

\[ m = \pi wb^2 , \]  \hspace{1cm} (4.74)

\[ M = \frac{1}{2} \pi w^2 b^2 , \]  \hspace{1cm} (4.75)

\[ B_f = \pi (\lambda_s b)^2 \frac{\rho - \rho_a}{\rho_w} g , \]  \hspace{1cm} (4.76)

\[ F_s = \pi \frac{\lambda_s^2}{1 + \lambda_s^2} wb^2 \frac{\rho - \rho_a}{\rho_w} g , \]  \hspace{1cm} (4.77)

\[ B_b = \pi \beta_b g (\lambda_b b)^2 , \]  \hspace{1cm} (4.78)

\[ F_b = B_b \left( \frac{w}{1 + \lambda_b^2} + w_b \right) = Q_b g , \]  \hspace{1cm} (4.79)

with \( w, \rho \) and \( \beta_b \) evaluated on the axis of the plume. Similar expressions have also been obtained e.g. in Wüest, Brooks, and Imboden (1992) and Socolofsky, Bhaumik, and Seol (2008) for bubble plumes, Morton (1959) for single-phase plumes and Lai et al. (2016) for a descending particle plume.
With the Gaussian profiles, the dimensional governing equations become

\[
\frac{dm}{dz} = 2\alpha_e \sqrt{2\pi M}, 
\]

(4.80)

\[
\frac{dM}{dz} = B_b + B_s s = \frac{Q_b g}{w/(1 + \lambda_b^2) + w_b} + (1 + \lambda_s^2) \frac{F_s}{w} 
\]

(4.81)

\[
\frac{dF_s}{dz} = -m N^2. 
\]

(4.82)

Since \( F_s < 0 \), increasing \( \lambda_s \) decreases the peel height. An intuitive view at the dimensional momentum equation would show that increasing \( \lambda_s \) will decrease the peel level, whereas increasing \( \lambda_b \) will increase the peel level.

We can recast the dimensionless version of these equation in a form identical to the one used before with the following definitions:

\[
m^* = \frac{m}{\pi \sqrt{2(1 + \lambda_b^2)} N L_b (2\alpha_e L_b)^2}, \quad M^* = \frac{M}{\pi (1 + \lambda_b^2) N^2 L_b^2 (2\alpha_e L_b)^2}, 
\]

(4.83)

\[
B^*_b = \frac{B_b}{\pi \sqrt{2(1 + \lambda_b^2)} N^2 L_b (2\alpha_e L_b)^2}, \quad F^*_s = \frac{F_s}{\pi \sqrt{2(1 + \lambda_b^2)} N^3 L_b^2 (2\alpha_e L_b)^2}, 
\]

(4.84)

\[
V_N = \frac{1 + \lambda_b^2}{\sqrt{2(1 + \lambda_b^2)}} \frac{w_b}{N L_b}, 
\]

(4.85)

in which

\[
\tilde{L}_b = \left( \frac{1 + \lambda_b^2}{[2(1 + \lambda_s^2)]^{3/2}} \right)^{1/4} L_b, \quad z^* = \frac{z}{\tilde{L}_b}. 
\]

(4.86)

Upon redefining the parameters \( S \) and \( \Gamma \) according to

\[
S = \frac{8(1 + \lambda_s^2)}{(1 + \lambda_b^2)^2} \left( \frac{M_0 N}{Q_b g} \right)^2, 
\]

(4.87)
\[ \Gamma = \frac{5 (1 + \lambda_b^2) \ Q_b \ g \ m_0^2}{2^{11/2} \sqrt{\pi} \ \alpha \ M_0^{5/2}}, \]  

(4.88)

the previous expressions (4.41) for \( m_0^* \) and \( M_0^* \) are recovered. The \( \Gamma \) defined in Morton and Middleton (1973) for single-phase Gaussian plumes is twice as large as that defined here with \( \lambda_b \) replaced by \( \lambda_s \). We adopt this slightly different definition so that the form of the dimensionless equations is the same as for the top-hat profile.
Chapter 5

Effect of dissolution in bubble/drop plume

5.1 Introduction

In the previous chapter, we have adopted an integral model to study bubble plumes in a stratified ambient, in which the gas was modeled as insoluble the bubble compressibility was neglected. As a result, bubble volume remained the same at different vertical elevations.

The model is appropriate for bubble plumes at large depths when the bubble size does not change much from source to intrusion height. This model is justified when the focus is on the plume behavior between the source and the first intrusion height for a very deep water column, because size of the bubbles do not change much in the region of interest. The model is also applicable in very shallow water layers with very strong stratification, a situation often encountered in laboratory experiments.

However, the hydrostatic effect is non-negligible in other situations. One refinement of the bubble plume model introduced in the previous chapter is the consideration of the bubble volume change. Another refinement of the model is the inclusion of mass
exchanges between the bubbles and the ambient water. Other refinements include the consideration of drops, in addition to bubbles, and the study of the effects of bubble/drop dissolution on the plume dynamics.

The inclusion of this effect is motivated by their importance in the Deepwater Horizon accident in 2010. It was observed that low chain hydrocarbons both in the liquid phase (benzene, toluene, ethylbenzene, xylenes, so called BTEX) and in the gas phase (methane, ethane, propane, butane) dissolved completely in the deep ocean as crude oil drops and natural gas bubbles rose (Ryerson et al., 2012b). As a result, several carbon rich intrusion layers were formed, with an observed persistence for months (Spier et al., 2013).

At high pressure and low temperature, there is a possibility for certain gases, such as $\text{CO}_2$ and $\text{CH}_4$, to form hydrates. Hydrate formation, however, is not a universal phenomenon and it occurs only in restricted ranges of pressure and temperature. Furthermore, there are modeling uncertainties which prevent a physically realistic study of their influence on the dynamics and dissolution of the bubbles (Warzinski et al., 2014). In view of these uncertainties, and since the present study is devoted to the elucidation of the basic processes of plume dynamics in the presence of mass exchange, we neglect hydrate formation.

There are several numerical studies that incorporated gas dissolution in bubble plumes. Wüest, Brooks, and Imboden (1992) have studied the dissolution of an oxygen bubble plume in a stratified lake with an integral model based on the entrainment hypothesis. They also carried out systematic study of source conditions (such as initial bubble radius, oxygen volume rate, initial plume area, etc). However, their calculations are based on a measured stratification profile which limits the general
applicability of the results. Zheng and Yapa (2002) have studied dissolution in
bubble plume at 700 m depth and they found that dissolution is more important than
expansion due to pressure decrease as bubble travel upwards. They have provided
an empirical formulation for mass transfer coefficient of non-spherical bubbles in
liquid. Besides, their study showed that there exist a negligible difference in results
using ideal and non-ideal gas models in their conditions. Buscaglia, Bombardelli, and
Garci’a (2002) have studied oxygen and nitrogen bubble plumes in a 77 m reservoir
with uniform ambient including bubble dissolution and bubble slip. They carried out
RANS study and compared the results with those of an integral model, including
bubble slip and dissolution, finding a good match. Crounse, Wannamaker, and Adams
(2007) studied dissolution of carbon dioxide bubble plume with the double plume
model, and compared with lab experimental results. Their model gave prediction
in general agreement with the data although with large scatter. As in the previous
chapter, we use a single plume model rather than a double plume model. A comment
on this aspect of our work can be found on page 86.

None of the previous studies considered the effect of dissolved material on the
plume liquid and consequent change in buoyancy (Yapa et al., 2012). The only study
that includes this effect is by Domingos and Cardoso (2013), who however, were
interested in a somewhat different phenomenon in which a chemical reaction played a
significant role, different from that of dissolution. Furthermore, in their study, bubbles
were treated as passive scalars neglecting their slip velocity. These differences are
reflected in the model that they adopted and limit the applicability of their results to
the type of bubble plumes considered in this chapter.

In this chapter, we quantify the effect of density change due to bubble and drop
dissolution on the plume dynamics under various situations. We find that the results for the peel and intrusion heights are significantly affected by the dissolution rate and density modification of the plume liquid.

5.2 Mixture liquid density

The molar volume of the mixture of two liquids is described as Landau and Lifshitz (1969)

\[ V_m = (1 - x)V_1 + xV_2, \]  

(5.1)

where \( x \) is the mole fraction of the solute, component 2, \( V_1 \) and \( V_2 \) are the partial molar volumes of the two components.

For ideal mixing, the previous relation reduces to

\[ V_{m}^{id} = (1 - x)V_{1}^{id} + xV_{2}^{id}, \]  

(5.2)

where \( V_{1}^{id} \) and \( V_{2}^{id} \) are the molar volume of the pure components.

The difference between the ideal molar volumes and the partial molar volumes, so called the excess molar volumes, are defined by

\[ V_{1}^{E} = V_{1} - V_{1}^{id} \]  

(5.3)

\[ V_{2}^{E} = V_{2} - V_{2}^{id} \]  

(5.4)

\[ V_{m}^{E} = V_{m} - V_{m}^{id} = (1 - x)V_{1}^{E} + xV_{2}^{E}. \]  

(5.5)

According to the Redlich-Kister expansion (Prausnitz, Lichtenthaler, and Azevedo,
1998), the excess molar volume can be approximated as

\[ V_m^E = 4x(1-x)(V_m^E)_{\text{max}}, \quad (5.6) \]

where \((V_m^E)_{\text{max}}\) is the maximum absolute value of \(V_m^E\) in the range \(0 < x < 1\).

Thus when \(x \ll 1\), (5.5), (5.6) show that

\[ V_m \simeq 4x(1-x)(V_m^E)_{\text{max}} + (1-x)V_1^{id} + xV_2^{id} \quad (5.7) \]

\[ \simeq V_1^{id} + x[4(V_m^E)_{\text{max}} + V_2^{id} - V_1^{id}] \quad (5.8) \]

\[ \simeq V_1^{id} + x[V_2^{id} - V_1^{id}]. \quad (5.9) \]

The last step is justified by the fact that \((4(V_m^E)_{\text{max}})/|V_2^{id} - V_1^{id}| \ll 1\) when \(V_1^{id} \neq V_2^{id}\), which is experimentally valid for most binary mixtures (Valtz et al., 2004). When \(V_1^{id} = V_2^{id}\), the excess molar volume will be 0 for obvious reason. Based on the above, we can neglect the excess molar volume in liquid mixing with an acceptable error. The preceding argument justifies the use of the ideal mixing rule (5.2).

For dilute solutions, when the concentration of component 2 is very small in the mixture, we have \(x \ll 1\), the expression for mixture density can be further simplified.
In terms of molar masses $\mathcal{M}_1$, $\mathcal{M}_2$, the mixture density is

$$
\rho = \frac{(1 - x)\mathcal{M}_1 + x\mathcal{M}_2}{V_m} = \frac{\mathcal{M}_1}{V_1} \frac{1 - x(\mathcal{M}_1 - \mathcal{M}_2)/\mathcal{M}_1}{1 - x(V_1 - V_2)/V_1} \quad (5.10)
$$

$$
\simeq \frac{\mathcal{M}_1}{V_1} [1 + x(\mathcal{M}_2/\mathcal{M}_1 - V_2/V_1)] \quad (5.11)
$$

$$
= \rho_1 + \left(1 - \frac{\rho_1}{\rho_2}\right) x\rho_1 \frac{\mathcal{M}_2}{\mathcal{M}_1} \quad (5.12)
$$

$$
= \rho_1 + \left(1 - \frac{\rho_1}{\rho_2}\right) \rho_{2,\text{dslv}}. \quad (5.13)
$$

In this equation, in principle, $\rho_1$, $\rho_2$ are to be understood as the densities calculated from the partial molar volumes. However, on the basis of the argument leading to (5.9), we will use this equation with the densities of the pure components. Notice that $\rho_1 \frac{\mathcal{M}_2}{\mathcal{M}_1} = \frac{\mathcal{M}_2}{V_1} \simeq \frac{\mathcal{M}_2}{V_m} = \rho_{2,\text{dslv}}$ is approximately the dissolved density of component 2 in the mixture. The approximation omits the higher order terms of $x$.

The above derivation can be easily extended to ternary and higher order mixtures, provided that one component is dominant in the mixture and other components are dilute. It is evident from (5.13) that: if $\frac{\rho_1}{\rho_2} > 1$, the mixture density will be lighter than component 1.

### 5.3 Integral model for bubble and drop plumes

We begin by presenting the equations appropriate for a drop plume because, as will be explained in next section, the same equations apply for bubble plumes in deep water. After this we consider the case of bubble plume in shallow water. The theoretical framework of the current study is essentially the same as in the previous chapter, with the exception that it incorporates bubble/drop dissolution and the consequent liquid
density modification.

### 5.3.1 Drop plume

For a drop plume, the statement of conservation of the liquid volume is

\[
\frac{dm}{dz} = 2\pi b(z) \alpha_c w(z).
\]  

(5.14)

The liquid volume flux is

\[
m(z) = \int_A (1 - \beta_d) w dA \simeq \int_A w dA,
\]  

(5.15)

where \(b(z)\) is the local radius of the plume and \(w(z)\) the vertical liquid velocity. \(\beta_d\) is the drop volume fraction; notice that \(\beta_d \ll 1\) due to the rapid dilution when plume rise after the zone of establishment region.

Based on section 5.2 the liquid mixture density can be linearly related to the dissolved concentration provided the solution is not too dense, see in section 5.2 (also see in Domingos and Cardoso (2013))

\[
\rho = \rho_a + \xi_d \rho_{d,dslv} + \xi_s (\rho_s - \rho_{sa}),
\]  

(5.16)

where \(\rho_{d,dslv}\) is the dissolved drop density, and \(\rho_s\) is the dissolved salt concentration by mass, \(\rho_{sa}\) is the ambient salinity density. The ambient density is written as \(\rho_a = \rho_w^0 + \xi_s \rho_{sa}\) where \(\rho_w\) is the pure water density, and \(\xi_s = \frac{\partial \rho}{\partial \rho_s}|_{\rho_s=0}\). \(\xi_d\) is the analogous quantity of the dissolved the drop material and can expressed as (see section 5.2),

\[
\xi_d = 1 - \frac{\rho_r}{\rho_{\rho_d}}
\]  

(5.17)
in which \( \rho_r \) is the ocean water density at the source of the plume, and \( \rho^0_d \) is pure drop density at plume source.

With the neglect of diffusion at the plume edge, the balance equation for the dissolved salt concentration \( \rho_s \) can be written as

\[
\frac{d}{dz} \int_A (1 - \beta_d) \rho w (\rho_s - \rho_{sa}) dA + \frac{d \rho_{sa}}{dz} \int_A (1 - \beta_d) \rho w dA = 0, \tag{5.18}
\]

As in the previous chapter, by invoking the Boussinesq approximation and the smallness of \( \beta_d \), we rewrite this equation in the approximate form

\[
\frac{d F_s}{dz} = -N^2 \rho_r, \tag{5.19}
\]

where the buoyancy flux due to salinity is given by

\[
F_s = \int_A \left( \frac{\rho - \tilde{\rho}_d \rho_d,_{d,\text{slv}} - \rho_a}{\rho} \right) g w dA. \tag{5.20}
\]

Notice that when drop dissolution is excluded \( \rho_{d,\text{slv}} = 0 \), this equation reduces to the form used in the previous chapter. \( N = \sqrt{-g/\rho_r \partial \rho_a / \partial z} \) is the stratification strength of ambient water density. Although in this chapter we specifically refer to stratification due to salinity, the same analysis would apply to stratification due to temperature. In this case, in principle, one should include the effect of temperature on solubility, gas pressure and other material properties. In practice, given the small temperature range in deep ocean (Ridgway, 1969), it is likely that these effects would play a minor quantitative role.

The buoyancy fluxes due to the dissolved drop components and the discrete drops
are defined similarly to (5.20) by

\[ F_{d,\text{slv}} = \int_A -\frac{\zeta_d \rho_d \Phi_{d,\text{slv}}}{\rho} g w \, dA, \quad (5.21) \]

\[ F_d = \int_A \rho - \rho_d \frac{\beta_d}{\beta} g(w + w_d) \beta_d \, dA, \quad (5.22) \]

in which \( \rho_d \) is the drop density.

The liquid momentum equation is

\[ \frac{dM}{dz} = B_d + B_s + B_{d,\text{slv}}, \quad (5.23) \]

where

\[ M = \int_A (1 - \beta_d) w^2 \, dA \simeq \int_A w^2 \, dA. \quad (5.24) \]

\[ B_d = \int_A \frac{\rho - \rho_d}{\rho_r} \beta_d g \, dA. \quad (5.25) \]

\[ B_s = \int_A \frac{\rho_d - (\rho - \zeta_d \rho_{d,\text{slv}})}{\rho_r} g \, dA, \quad (5.26) \]

\[ B_{d,\text{slv}} = \int_A -\frac{\zeta_d \rho_{d,\text{slv}}}{\rho_r} g \, dA, \quad (5.27) \]

The integral form of the mass conservation equation for the drop phase can be derived as explained in the appendix 4.7 in the previous chapter starting from

\[ \partial_t (\beta_d \rho_d) + \nabla \cdot (\beta_d \rho_d v_d) = n_d \frac{d (\rho_d v_d)}{dt} = \pi n_d d DSh (\rho_d - \rho_{sat}), \quad (5.28) \]

\( \rho_d \) and \( v_d \) are the density and volume of a single drop. \( n_d = \frac{\beta_d}{v_d} \) is the drop number.
density. The drop Sherwood number $Sh$ is

$$Sh = \frac{h_d d}{D},$$

(5.29)

where $D$ is the diffusivity of drop component in the ambient liquid, $d$ is the drop diameter, $h_d$ is the mass transfer coefficient between drop and ambient liquid.

Since the density dissolved in the ambient liquid is typically much less than the saturation density $\rho_{sat}$, in order of magnitude, we can neglect $\rho_{d,dslv}$ with respect to $\rho_{sat}$ to estimate the mass loss rate for a single drop

$$\frac{d (\rho_d v_d)}{dt} \simeq -\pi d D Sh \rho_{sat}.$$  

(5.30)

A characteristic drop dissolution time $t_{dslv}$ can then be found by substituting the initial value for the drop related quantities into the above equation

$$\frac{\rho_{d0} v_{d0}}{t_{dslv}} \simeq \pi d_0 D Sh_0 \rho_{sat0}.$$  

(5.31)

to get

$$t_{dslv} = \frac{\rho_{d0} d_0^2}{\rho_{sat0} 6 D Sh_0}.$$  

(5.32)

After integration over the plume cross-section, we have

$$\partial_z m_d = -Q_{d,dslv} = \pi n_d A_d D Sh (\rho_{d,dslv} - \rho_{sat}) = -\partial_z m_{d,.dslv},$$

(5.33)

where

$$m_d = \int \beta_d \frac{\rho_d}{\rho_r} w dS = \int \beta_d \frac{\rho_d}{\rho_r} (w + w_d) dS,$$

(5.34)

$$m_{d,dslv} = \int \frac{\rho_{d,dslv}}{\rho_r} w dS = \int \frac{\rho_{d,dslv}}{\rho_r} w dS,$$

(5.35)
are the drop mass flux of the drop constituents in the discrete phase and continuous phase, respectively. The drop constituent mass conservation states that

$$m_d + m_{d, dslv} = m_{d0}, \quad (5.36)$$

so that the total drop constituents mass flux is conserved; $m_{d0}$ is the total drop mass flux at the source. Throughout this chapter, the index 0 appended to any quantity indicates the corresponding value at the source.

### 5.3.2 Top-hat profile

In summary, in integral form the equations of the model are given by (5.14), (5.23), (5.19) and (5.33). Further simplification requires an assumption on the distribution of relevant fields over the plume cross section.

As in the previous chapter we assume a top-hat profile for which we have

$$m = Aw, \quad M = Aw^2, \quad F_s = \lambda_s^2 Aw \left( \frac{\rho - \rho_d \rho_{d, dslv}}{\rho_r} \right) g.$$  \quad (5.37)

$$m_d = \frac{\rho_d}{\rho_r} Q_d, \quad m_{d, dslv} = \frac{\rho_{d, dslv}}{\rho_r} Aw, \quad Q_d = A \beta_d (w + w_d). \quad (5.38)$$

where $\lambda_s b$ is the radius of the plume region in which the salinity difference with the ambient liquid is localized. For simplicity, we take $\lambda_s = 1$ in the following. $A = \pi b^2$ is the plume cross-section area. $Q_d$ is the drop volume flow rate.
For top-hat profile, \( m_d, m_{d,d,slv} \) are related with \( F_d, F_{d,d,slv} \) in the following way

\[
F_d = \frac{\rho_r - \rho_d}{\rho_d} m_d g, \quad (5.39)
\]

\[
F_{d,d,slv} = -\xi_{d} g m_{d,d,slv} = -\xi_{d} g (m_{d0} - m_d), \quad (5.40)
\]

with their ratio

\[
\frac{F_{d,d,slv}}{F_d} = -\frac{\xi_{d} \rho_d}{\rho_r - \rho_d} \frac{m_{d0} - m_d}{m_d}. \quad (5.41)
\]

Upon substitution of (5.37), (5.38) into the governing equations (5.14), (5.19), (5.23) and (5.33) we find

\[
\frac{dm}{dz} = 2\sqrt{\pi \alpha_c} \sqrt{M}, \quad (5.42)
\]

\[
\frac{dM}{dz} = \frac{F_d}{w + w_d} + \frac{F_s + F_{d,d,slv}}{w}, \quad (5.43)
\]

\[
\frac{dF_s}{dz} = -MN^2, \quad (5.44)
\]

\[
\frac{dm_d}{dz} = \frac{6m_d D}{\rho_d d^2(w + w_d)} Sh(\rho_{d,d,slv} - \rho_{sat}), \quad (5.45)
\]

in which \( Sh \) is defined in (5.29). \( F_d \) and \( F_{d,d,slv} \) are given by (5.39), (5.40) respectively.

In a situation in which a significant amount of drop ejected into a small amount of liquid, the liquid will become quickly saturated within a distance of a few diameters from the source. Since the focus of this work is on the large structure of the plume, we are justified in assuming \( \rho_{d,d,slv} = \rho_{sat} \) at the source. As the plume rises and entrains ambient liquid, the highly concentrated solution will gradually start to dilute, and
much above the source the dilution will be so strong that $\rho_{d,dslv} \ll \rho_{sat}$.

5.3.3 Scaling

As described in previous chapter, we use $L_r, w_r$ to scale the droplet plume size and velocity, respectively, with their expression given by

$$L_r = \left( \frac{F_0}{4\pi\alpha^2 N^3} \right)^{1/4},$$

$$w_r = NL_r = \left( \frac{F_0 N}{4\pi\alpha^2} \right)^{1/4},$$

in which $F_0 = \frac{p_r - p_d}{\rho_r} Q_{d0} \Phi$ is the plume buoyancy flux at the source, which is provided by the drops in this case.

Scaling of the plume mass flux, momentum flux and salinity flux $m, M, F_s$ are the same as described in the previous chapter. As for the drop related quantities, we use the values at the source for normalization. More specifically, we write the dimensionless drop diameter, density, mass flux, solubility and dissolved concentration as $d^* = d/d_0, \rho_{d}^* = \rho_{d}/\rho_{d0}, m_{d}^* = m_{d}/m_{d0} = \rho_{d}^*(d^*)^3, \rho_{sat}^* = \rho_{sat}/\rho_{sat0}, \rho_{d,dslv}^* = \rho_{d,dslv}/\rho_{sat0}, \rho_{sat0}$ is the drop solubility at the source.

Furthermore,

$$\rho_{d,dslv}^* = \frac{m_{d,dslv}}{A_{w} \rho_{sat0}} = \frac{m_{d0}}{m_{r}} \frac{\rho_{r}}{\rho_{sat0}} \frac{1 - m_{d}^*}{m^*} = \Phi_d \frac{1 - m_{d}^*}{m^*},$$

where $m_r = A_{r} w_r$ is the reference plume volume flux, $A_r = \pi (2\alpha_c L_r)^2$ is the reference plume cross-section area.
The parameter $\Phi_d$, implicitly defined in (5.48) can be rewritten as

$$
\Phi_d = \frac{m_{d0}}{m_r \rho_{sat0}} \frac{\rho_r}{\rho_{sat0} w_r A_r} = \frac{\rho_{d0}}{\rho_{sat0}} \left( \frac{\rho_r - \rho_d}{\rho_r} \frac{Q_{d0} N^5}{4\pi \epsilon^2 \Omega^3} \right)^{1/4}.
$$

(5.49)

It should be noted that $\Phi_d \ll 1$ is found in practical cases as shown in Table 5.2.

The dimensionless equations become

$$
\frac{dm^*}{dz^*} = \sqrt{M^*},
$$

(5.50)

$$
\frac{dM^*}{dz^*} = \frac{m^*_d}{\bar{w}^* + V_N} + \Lambda_d \rho_d^* \frac{1 - m^*_d}{\bar{w}^*} + \frac{F^*_s}{\bar{w}^*},
$$

(5.51)

$$
\frac{dF^*_s}{dz^*} = -m^*,
$$

(5.52)

$$
\frac{dm^*_d}{dz^*} = \Theta_d \frac{Sh^* m^*_d}{\rho_d^*(\bar{w}^* + V_N)} \left( \Phi_d \frac{1 - m^*_d}{m^*} - \rho_{sat}^* \right),
$$

(5.53)

where

$$
\Lambda_d = -\xi_d \frac{\rho_{d0}}{\rho_r - \rho_{d0}},
$$

(5.54)

$$
\Theta_d = \frac{6\rho_{sat0} DSh_0}{\rho_{d0} N d_0^2},
$$

(5.55)

$$
V_N = \frac{w_d}{w_r},
$$

(5.56)

with specified source condition $m^*(0)$, $M^*(0)$ and $F^*_s(0) = 0, m^*_d(0) = 1$. Notice $Sh^* = Sh/\bar{Sh}$, where $\bar{Sh}$ is the drop Sherwood number at source. The assumption of the saturated dissolved concentration at the source mentioned after (5.48) implies the following relation

$$
\Phi_d \frac{1 - m^*_d}{m^*} \bigg|_{z^*=0} = 1
$$

(5.57)
The parameter $\Lambda_d$ accounts for the capability of the dissolved material to provide buoyancy. For drop plume, with the relation (5.17) derived in section 5.2, it equals 1. Therefore, with the present model, $\Lambda_d$ is not really a free parameter, although it may become one with a different mixing density model from (5.17). The parameter $\Theta_d$ represents the ratio of characteristic time for the plume, $N^{-1}$, to the drop dissolution time $t_{d_{slv}}$ given in (5.32).

For a single component drop

$$\rho_d^* = \rho_{sat}^* = 1,$$  \hspace{1cm} (5.58)

so that (5.50), (5.53) can be further simplified to

$$\frac{dM^*}{dz^*} = \frac{m_d^*}{w^* + V_N} + \frac{1 - m_d^*}{w^*} + \frac{F_{d}^*}{w^*'}, \hspace{1cm} (5.59)$$

$$\frac{dm_d^*}{dz^*} = \Theta_d \left( \frac{Sh^*m_d^*}{w^* + V_N} \right) \left( \Phi_d \frac{1 - m_d^*}{m^*} - 1 \right) \approx -\Theta_d \frac{Sh^*m_d^*}{(w^* + V_N)}. \hspace{1cm} (5.60)$$

Notice that the fact $\Phi_d \ll 1$ is used in the last step, which is found in the present situations.

Apart from the initial conditions, the important dimensionless parameters are $\Theta_d, \Lambda_d, V_N, \frac{L_r}{H_{total}}, \Phi_d$. To avoid the complexity of dealing with so many parameters, in presenting results in the following section we focus on a point source plume for which $m^*(0) = 0, M^*(0) = 0$.

It may also be noted that as the drops rise, the rise velocity and Sherwood number will generally vary. These laws of variation, therefore, also influence the results, as will be described in 5.4.3.
5.3.4 Bubble plume

The governing equations for the bubble plume can be obtained similarly to those for a drop plume by replacing the drop related quantities by the corresponding bubble related quantities. The dimensional governing equations for a bubble plume have essentially the same form as (5.14), (5.23), (5.19) and (5.33). The source bubble buoyancy flux is now

\[ F_0 = \frac{(\rho_r - \rho_b)}{\rho_r Q_{b0} g} \]

Using same forms of \( L_r, w_r \) given in (5.46), (5.47) to scale the bubble plume equations, we thus obtain the dimensionless equations for bubble plumes: The dimensionless equations become

\[
\frac{dm^*}{dz^*} = \sqrt{M^*}, \tag{5.61}
\]

\[
\frac{dM^*}{dz^*} = \frac{m_b^*}{w^* + V_N} + \Lambda_b \rho_b^* \frac{1 - m_b^*}{w^*} + \frac{F_s^*}{w^*}, \tag{5.62}
\]

\[
\frac{dF_s^*}{dz^*} = -m^*, \tag{5.63}
\]

\[
\frac{dm_b^*}{dz^*} = \Theta_b \frac{Sh_b^* m_b^*}{\rho_b^* (w^* + V_N)} \left( \Phi_b \frac{1 - m_b^*}{m_b^*} - \rho_{\text{sat}}^* \right), \tag{5.64}
\]

where

\[
\Lambda_b = -\tilde{g}_b \frac{\rho_b}{\rho_r - \rho_b}, \tag{5.65}
\]

\[
\Theta_b = \frac{6 \rho_{\text{sat}} DSh_0}{\rho_b N \tilde{d}_0^2}, \tag{5.66}
\]

\[
V_N = \frac{w_b}{w_r}, \tag{5.67}
\]

These equations differ from the corresponding ones for a drop plume shown above in the fact that the parameter \( \Lambda_b \) is usually smaller than one. Furthermore, when bubbles
expand due to hydrostatic effect, the normalized density of bubbles becomes smaller than 1 as they rise.

The parameter $\Phi_b$ according to (5.49) is

$$\Phi_b = \frac{m_{b0}}{m_r \rho_{sat0}} = \frac{\rho_{b0}}{\rho_{sat0}} \left( \frac{\rho_r - \rho_b}{\rho_r} \frac{Q_{b0} N^5}{4\pi \alpha_c^2 g^3} \right)^{1/4}.$$  (5.68)

The gas solubility is related to ambient pressure according to Henry’s law as $\rho_{sat} = M_g c_{sat} = K_H M_g P$, where $K_H$ is the Henry’s law constant, $M_g$ is the bubble molar mass and $c_{sat}$ is the saturation concentration of the gas in ambient water. For a perfect gas, we also have

$$\frac{\rho_{sat0}}{\rho_{b0}} = K_G T \mathcal{R}_G,$$  (5.69)

$$\rho_{b0}^* = \rho_{sat}^* = P^*.$$  (5.70)

where $\mathcal{R}_G$ and $T$ are ideal gas constant and ambient temperature. The pressure $P^* = P/P_0$ is normalized by the pressure at the source, and can be expressed as

$$P^* = 1 - \frac{\rho_a g z}{P_0} = 1 - \frac{L_r}{H_{total}} z^*,$$  (5.71)

where $H_{total} = H + H_{atm}$, with $H$ the plume source depth, and $H_{atm} = P_{atm}/\rho_w g \approx 10$ m where $P_{atm}$ is the atmosphere pressure.

### 5.4 Drop plumes and deep water bubble plumes

When the peel height reached by the bubbles, $L_r$ is much smaller than the total water depth $H_{total}$, a case we refer to as deep ocean, the hydrostatic effect on the bubble expansion is negligible so that $\rho_{b0}^* = \rho_{sat}^* = P^* = 1$. For the case of drops, this is
always true due to incompressibility.

Upon using different lengths \( (Q_b g / 4\pi\alpha_c^2 N^3)^{1/4} \) and \([((\rho_r - \rho_d) / \rho_r Q_d g / 4\pi\alpha_c^2 N^3])^{1/4}\) to scale the bubble plume and drop plume respectively, we obtain similar dimensionless governing equations for the bubble plume and drop plume. Moreover, it can be observed that \( \Phi \ll 1 \) is generally satisfied for both bubbles and drops under typical situations provided that ambient stratification is strong enough to form intrusions before the plume rises to the surface. Therefore, for drop plumes (5.51), (5.53) become

\[
\frac{dM^*}{dz^*} = m^*_d \frac{1 - m^*_d}{w^*} + \frac{F^*_s}{w^*},
\]

(5.72)

\[
\frac{dm^*_d}{dz^*} = -\Theta_d \frac{Sh^* m^*_d}{(w^* + V_N)}.
\]

(5.73)

According to the mixing model in equation (5.72) derived from section 5.2, the parameter \( \Lambda_d \) equals 1, however, for other mixing models, it may take different values, and therefore, we retain it in equation (5.72).

Similarly for bubble plumes in deep ocean (5.62), (5.64) become

\[
\frac{dM^*}{dz^*} = m^*_b \frac{1 - m^*_b}{w^*} + \frac{F^*_s}{w^*},
\]

(5.74)

\[
\frac{dm^*_b}{dz^*} = -\Theta_b \frac{Sh^* m^*_b}{(w^* + V_N)}.
\]

(5.75)

The parameter \( \Theta \) for bubble and drop plumes has similar form but with different correlations for slip velocity and Sherwood number. However, as shown in section 5.4.4, the source values for \( V_N, Sh \) are a good approximation also for the variable \( V_N, Sh \). In this sense, the different empirical correlations of \( V_N, Sh \) for bubbles and for drops have a negligible influence on the parameter study carried out below. In
other words, once proper dimensionless variables are used, the results for drop plumes are essentially the same for bubble plumes in deep water except for the different parameter ranges of $\Lambda, \Theta$ ($\Lambda = 1$ for drop plume).

For this reason, the following sections perform parameter study on bubble plumes only, but one can easily obtain similar results for drop plumes thereafter.

The effect of source mass flux and momentum flux on the plume dynamics have been discussed in the previous chapter. For simplicity, we focus on plumes generated by a point source in the present work, in which case $m^*(0) = 0, M^*(0) = 0$.

Apart from the initial conditions, for a related problem the important dimensionless parameters are $\Lambda, \Theta$. The importance of these two parameters has been documented in Domingos and Cardoso (2013), who use the buoyancy frequency parameter $G$ that is related with $\Lambda$ by $G = 1 - \Lambda$.

5.4.1 Numerical parameter range

In developing the applications that follow, for the typical values for the various quantities involved we use the values given in tables 5.1 and 5.2. Table 5.1 shows the material properties of typical soluble bubble and drop components. Table 5.2 is based on reported measurements concerning the Deepwater Horizon accident (Socolofsky, Adams, and Sherwood, 2011). In all the examples, we take the entrainment coefficient $\alpha_e = 0.11$.

5.4.2 Small slip velocity

For small enough bubbles, the rise velocity is much smaller than the plume velocity, and therefore, $w_b \ll w$, then $V_N \ll w^*$. In this case mass transfer is purely diffusive
Table 5.1: Material properties for typical water-soluble gas under standard conditions. \( D = 10^{-9} \text{ m}^2/\text{s}, \) \( \mathcal{R}_G = 8.31 \text{ m}^3 \text{ Pa/K/mol}, \) \( \rho_r = 1027 \text{ kg/m}^3, \) \( T = 293\text{K}, \) \( P_0 = 1.5 \times 10^7 \text{ Pa}, \) \( N = 1.5 \times 10^{-3} \text{s}^{-1}, \) \( \delta = K_H \mathcal{R}_G T. \)

<table>
<thead>
<tr>
<th>Gas</th>
<th>( K_H ) (10^{-5} mol/m^3/pa)</th>
<th>( M_g ) (g/mol)</th>
<th>Liquid density (10^3 kg/m^3)</th>
<th>( \delta )</th>
<th>( \zeta )</th>
<th>( \Lambda_b )</th>
<th>( \Theta_b/\text{Sh}_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH_4</td>
<td>2.10</td>
<td>16</td>
<td>0.422</td>
<td>0.0511</td>
<td>-1.43</td>
<td>0.137</td>
<td>0.205</td>
</tr>
<tr>
<td>C_2H_6</td>
<td>3.54</td>
<td>30</td>
<td>0.547</td>
<td>0.0862</td>
<td>-0.879</td>
<td>0.158</td>
<td>0.345</td>
</tr>
<tr>
<td>C_3H_8</td>
<td>2.90</td>
<td>44</td>
<td>0.581</td>
<td>0.0706</td>
<td>-0.768</td>
<td>0.203</td>
<td>0.278</td>
</tr>
<tr>
<td>C_4H_10</td>
<td>2.50</td>
<td>58</td>
<td>0.601</td>
<td>0.0609</td>
<td>-0.708</td>
<td>0.246</td>
<td>0.243</td>
</tr>
<tr>
<td>C_2H_4</td>
<td>7.30</td>
<td>28</td>
<td>0.568</td>
<td>0.178</td>
<td>-0.809</td>
<td>0.136</td>
<td>0.71</td>
</tr>
</tbody>
</table>

Table 5.2: Typical plume parameters with \( \alpha_c = 0.11, \) \( \delta = 0.1 \)

<table>
<thead>
<tr>
<th>( Q_{b} ) (m^4/s)</th>
<th>( N ) (10^{-3} s^{-1})</th>
<th>( L_r ) (m)</th>
<th>( w_r ) (m/s)</th>
<th>( H_{total} ) (m)</th>
<th>( L_r/\text{H}_{total} )</th>
<th>( \Phi_{b} = \frac{m_{b0}}{\rho_r \rho_{sat}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.04</td>
<td>0.4</td>
<td>448</td>
<td>0.179</td>
<td>1500</td>
<td>0.299</td>
<td>7.32E-05</td>
</tr>
<tr>
<td>0.09</td>
<td>2.7</td>
<td>131</td>
<td>0.354</td>
<td>1500</td>
<td>0.0874</td>
<td>9.75E-04</td>
</tr>
</tbody>
</table>

so that \( Sh = 2 \) and \( Sh^* = 1. \)

It is convenient to replace the variable \( z^* \) with \( m_{b}^* \) so that (5.61)~(5.63) become

\[
\frac{dm^*}{dm_{b}^*} = -\frac{(M^*)^{3/2}}{\Theta_{b}m_{b}^*m_{*}^*},
\]

\[
\frac{dM^*}{dm_{b}^*} = -\frac{m_{b}^* + \Lambda_b(1 - m_{b}^*) + F_{s}^*}{\Theta_{b}m_{b}^*},
\]

\[
\frac{dF_{s}^*}{dm_{b}^*} = \frac{M^*}{\Theta_{b}m_{b}^*},
\]

\[
\frac{dz^*}{dm_{b}^*} = -\frac{M^*}{\Theta_{b}m_{b}^*m_{*}^*}.
\]

With the condition \( F_{s}^* = 0, \) \( M^* = 0, \) \( m_{*}^* = 0 \) at the source, we obtain the
following solution

\[ m^* = \sqrt{\frac{2}{\Theta_b} \int_{m_b^*}^{1} \frac{M^*(\mu_b)^{3/2}}{\mu_b} d\mu_b}, \quad (5.80) \]

\[ M^*(m_b^*) = \frac{1}{1 + \Theta_b^2} \left\{ \Theta_b(1 - \Lambda_b) \left( \cos \theta - m_b^* \right) - \left( 1 + \Lambda_b \Theta_b^2 \right) \sin \theta \right\}, \quad (5.81) \]

\[ F^*_z(m_b^*) = -\Lambda_b + \frac{1}{1 + \Theta_b^2} \left[ \left( 1 + \Lambda_b \Theta_b^2 \right) \cos \theta + (1 - \Lambda_b) \left( \Theta_b \sin \theta - m_b^* \right)^2 \right] \]

where \( \theta = \log m_b^*/\Theta_b \). Notice that the bubble size \( d \) is implicitly included in the definition of \( \Theta_b \). The vertical distance \( z^* \) can be obtained in terms of \( m_b^* \) by substituting the above solution into (5.79), we can express the vertical distance \( z^* \) in terms of \( m_b^* \) as well.

The peel height \( h_p \) is the location when \( M^* = 0 \), in the nomenclature used in the previous chapter the location where \( \partial_z M^* = 0 \) is termed the \( h_n \).

It can be shown that \( M^* \) as a function of \( m_b^* \) oscillates between positive maximum and negative minimum values, which implies that it will cross the zero value, i.e. the plume reaches the peel height, for a positive value of \( m_b^* \). Thus in this model, the bubble can not dissolve completely below the peel height. At least a secondary plume structure can be expected.

Example of the dependence of peel height \( h_p \) and \( h_n \) on \( \Lambda_b, \Theta_b \) given by (5.80)~(5.82) are shown in Figure 5.1. Figure 5.1a shows the dependence of \( h_p, h_n \) on density mixing parameter \( \Lambda_b \) for different dissolution rates \( \Theta_b \). The density mixing parameter \( \Lambda_b \) represents the ability for dissolution to maintain total buoyancy. Neglect of the mixing density change corresponds to \( \Lambda_b = 1 \), which coincides with existing literature. The Figure, however, parameter \( \Lambda_b \) can have a very significant effect.
For insoluble bubbles $\Theta_b = 0$, $\Lambda_b$ has no effect on the plume, which is shown by the horizontal lines in Figure 5.1a, with the peel height $h_p = 2.6$ (Morton and Turner, 1956) as also found in the previous chapter. When $\Lambda_b = 1$ and $V_N$ negligible compared to $w^*$, $m_b^*$ has no influence on $M^*$ which implies that the peel height and neutral height would be independent of the parameter $\Theta_b$. Indeed, in Figure 5.1a, the curves corresponding to different $\Theta_b$ all cross at the same point when $\Lambda_b = 1$. For dissolving bubbles $\Theta_b > 0$, the total plume buoyancy increases with $\Lambda_b$, so do the peel height $h_p$ and $h_n$.

Figure 5.1b shows the dependence of $h_p$, $h_n$ on $\Theta_b$ for different density mixing efficiency $\Lambda_b$. For $\Lambda_b < 1$, the dissolved bubble component provides less buoyancy than the discrete bubble component. Therefore rapid dissolution (smaller $\Theta_b$) will
decrease the total plume buoyancy and thus decrease the plume peel height. Consequently $h_p$ decreases with $\Theta_b$. The converse trend will be found for $\Lambda_b > 1$. For very large $\Theta_b$, the bubbles dissolve very rapidly after release, and the total plume buoyancy becomes only dependent on the density mixing efficiency $\Lambda_b$.

5.4.3 Finite slip velocity

A review of the empirical Sherwood number correlations for bubbles can be found in Olsen et al. (2017). We choose the correlation for no-slip bubble surface given in Hughmark (1967) as bubbles easily get contaminated in seawater:

$$Sh = 2 + 0.95Re^{1/2}Sc^{1/3}. \quad (5.83)$$

In using this correlation to calculate the mass transfer coefficient, we neglect the small area increase of the bubbles due to their deformation, which could be included if needed by introducing a shape factor (Michaelides, 2006).

As for the bubble slip velocity, we use the empirical correlation given in Rodrigue (2004).

$$\frac{w_b}{w_c} = 0.0545F^{3/4}\left(1 + 1.31 \times 10^{-5}Mo^{11/20}F^{73/33}\right)^{21/176}\left(1 + 0.02F^{10/11}\right)^{10/11}. \quad (5.84)$$

where

$$Mo = \frac{g\mu^4}{\rho\sigma^3}, \quad F = g \left(\frac{\rho^5d^8}{\sigma\mu^4}\right)^{1/3}, \quad w_c = 1.53 \left(\frac{\sigma g \Delta \rho}{\rho^2}\right)^{1/4} \approx 1.53 \left(\frac{\sigma g}{\rho}\right)^{1/4}. \quad (5.85)$$

Notice that $w_c$ is a typical value of the plateau region in the bubble slip velocity correlation given in Clift, Grace, and Weber (1978); $Mo, F$ are the Morton and flow numbers respectively. It may be noted that $Sh, w_b$ and therefore, $Sh^*, V_N$ will evolve
in the course of the simulations according to relations (5.83), (5.84).

Sample results for this case can be seen in Figure 5.2. The values involved in the
definition of $\Theta_b$ are taken from table 5.2. Initial bubble sizes are chosen in the range
of from 1 to 20 mm, resulting in $1 < \Theta_b < 4$; the lines in each family correspond to
different values of $\Lambda_b$ in the range $-0.5 < \Lambda_b < 1.5$.

Small bubbles dissolve quickly: the bubble mass decreases rapidly (Figure 5.2a) and so does the normalized Reynolds number (Figure 5.2b); the Sherwood number $Sh$ tends to 2, so that $Sh^* \rightarrow 0$ (Figure 5.2c). With rapid dissolution, the bubble plume behaves like a single phase plume after the discrete bubbles are gone and $\Lambda_b$ dominates the plume momentum flux equation (5.74). Consequently, $\Lambda_b$ becomes the sole important parameter in this case, and therefore, the variation of $V_N$ and $Sh$ with height becomes secondary important. As the bubble radius increases, the rate of variation of all quantities shown decreases and they have not changed drastically by the time the bubbles reach the peel height where the curves terminate. These observations suggest that fixing $V_N$ and $Sh$ at their initial source values will result in a small error for all cases, for small bubbles because they dissolve quickly and for larger bubbles because dissolution will not have progressed very much by the time they reach the peel height. Of course, there will be an error size range in which corresponding to bubbles that barely reach the peel height where the variation of $V_N$ and $Sh$ are important. As found in Domingos and Cardoso (2013) for a different problem, however, this seems to be fairly narrow parameter window, we do not investigate it further.
Figure 5.2: Plume simulation details for different initial bubble size with bubble slip velocity given by (5.84). The red, blue, black curves are for $(\Theta_b, V_N) = (19.2, 0.63), (2.1, 0.69), (0.26, 0.92)$ respectively. Solid and dashed curves are for $\Lambda_b = 1.5, -0.5$, respectively.
5.4.4 Constant $V_N$ and $Sh$

As noted in the previous section, it is reasonable to approximate $V_N$ and $Sh$ using their initial values for either slow or fast dissolution. Under this assumption, the bubble plume momentum flux (5.74) and bubble mass flux equation (5.75) become

\[
\frac{dM^*}{dz^*} = \frac{m_b^*}{w^* + V_N(0)} + \Lambda_b \frac{1 - m_b^*}{w^*} + \frac{F_s^*}{w^*}
\]

\[
\frac{dm_b^*}{dz^*} = -T_s \frac{m_b^*}{w^* + V_N(0)}
\]

(5.86)

(5.87)

with point source conditions $m^*(0) = 0$, $M^*(0) = 0$ and $F_s^*(0) = 0$, $m_b^*(0) = 1$.

With this approximation, only three independent constant parameters $\Lambda_b$, $\Theta_b$, $V_N(0)$ govern the system. As described in the previous chapters, a large $V_N$ corresponds to weak buoyancy effect, and thus it results in smaller peel height. This trend can be seen in Figure 5.86.

Figure 5.3a shows the dependence of $h_p$, $h_n$ on the $\Lambda_b$ for $V_N(0) = 2$ with different $\Theta_b$. As in the previous case of 5.1a, also in this case we see the strong effect of the parameter $\Lambda_b$. We noticed that in Figure 5.3a that lines for different $\Theta_b$ all cross at a single point dependent on $\Lambda_b$, $V_N(0)$. We thus conclude that there exist a critical curve along which $\Lambda_b$ is a function of $V_N(0)$ such that, on this curve, $h_p$ does not depend on $\Theta_b$. Both $h_p$ and $h_n$ tend to increase with $\Theta_b$ to the right of this critical curve, and to decrease with $\Theta_b$ to the left of this critical curve. Figure 5.3b shows the dependence of $h_p$ on $\Theta_b$ for different $V_N(0)$, $\Lambda_b$, whereas Figure 5.3c shows the corresponding dependence for $h_n$. The negative dependence of $h_p$ on $V_N(0)$ to the left of the critical curve can be easily seen from Figure 5.3b, 5.3c.

A direct comparison of the results for constant and variable $V_N$ and $Sh$ is shown
Figure 5.3: Constant $V_N$, Sh model according to (5.86), (5.87).
in Figure 5.4a and 5.4b. The solid and dashed curves show results for variable and constant $V_N, Sh$, respectively. The negligible difference between solid and dashed lines over majority of the parameter range studied justifies the accuracy of keeping $V_N, Sh$ at their source values.

(a) $h_p, h_n$ vs. $\Lambda_b$. The red, blue, black curves are for $\Theta_b = 4, 1, 0.26$, respectively.

(b) $h_p, h_n$ vs. $\Theta_b$. The red, blue, black curves are for $\Lambda_b = 1.5, 1, -0.5$, respectively.

**Figure 5.4:** Solid and dashed curves are for $h_p, h_n$ obtained with time dependent $V_N, Sh$ according to (5.74), (5.75). Dash-dotted curves are obtained with constant $V_N, Sh$ according to (5.86), (5.87) (using the initial value with $w_b$ calculated from the Rodrigue relation).

### 5.5 Bubble plumes finite water depth

In shallow water, conditions may be such that no intrusion can be formed as the plume never reaches the neutral height. The minimum depth for the formation of intrusions depends on the stratification and deceases as stratification increases. Since our interest is the formation of intrusions, we focus on moderate water depths. Because the ambient pressure is limited, the gas density will be orders of magnitude smaller than the liquid density, and therefore, the parameter $\Lambda_b$ can be taken as 0.
The parameter \( \frac{L_r}{H_{total}} \) determines the relative change of the ambient hydrostatic pressure while bubbles rise from the source to the peel height. The relation between \( \frac{L_r}{H_{total}} \) and the ambient hydrostatic pressure was given in (5.71). In this case the bubble buoyancy varies not only because of dissolution but also because of bubble expansion due to the changing hydrostatic pressure.

Figures 5.5a, 5.5b show the \( h_p, h_n \) dependence on \( \Lambda_b \) and \( \Theta_b \) respectively, for different \( \frac{L_r}{H_{total}} \). It can be seen that increasing \( \frac{L_r}{H_{total}} \) will result in decreasing \( h_p, h_n \). Nevertheless, the dependence of \( h_p, h_n \) on \( \frac{L_r}{H_{total}} \) is pretty weak provided \( \frac{L_r}{H_{total}} \) does not become very large.

\[
\begin{align*}
(a) \ h_p \ vs. \ \Lambda_b. \ Solid \ and \ dashed \ curves \ are \ for \ \Theta_b = & 4, \ 0.26, \ \text{respectively.} \\
(b) \ h_p \ vs. \ \Theta_b. \ Solid \ and \ dashed \ curves \ are \ for \ \Lambda_b = & 1.5, \ -0.5, \ \text{respectively.}
\end{align*}
\]

**Figure 5.5:** Effect of \( \frac{L_r}{H_{total}} \) for variable \( V_N, \Theta_b, Re, Sh \). Red and blue curves are for \( L_r/H_{total} = 0.1, 0.3 \), respectively.

### 5.6 Conclusion

This paper has presented a numerical study of bubble and drop plumes in a stratified ambient with mass transfer between bubbles/drops and ambient liquid. In addition to
parameters with limited influence on the results, the effect of bubble/drop dissolution on the plume dynamics is described by two main dimensionless groups: one, $\Theta$, represents the bubble dissolution rate and the other, $\Lambda$, the density mixing efficiency. The latter parameter is very small in shallow water, but becomes influential in deep water where the hydrostatic pressure increases the ratio between the gas and liquid densities.

The density modification of the ambient liquid due to dissolution is found to have crucial importance in maintaining the total plume buoyancy while the bubble/drop size reduces due to dissolution. The results shown are particularly relevant for soluble bubbles in deep water, as the dissolution plays an important role.
Chapter 6

On flux terms in volume averaging

6.1 Introduction

Volume averaging is a standard method for the derivation of averaged equations of balance for the modelling of multiphase flows (see e.g. Nigmatulin, Lahey, and Drew, 1996; Whitaker, 1999; Prosperetti and Tryggvason, 2009b; Ishii and Ibiki, 2011). While the formal application of the method is relatively straightforward, the interpretation of the resulting equations is subtle. This is a crucial point as, in the absence of physical transparency, it becomes harder to develop physically relevant closures.

The specific aspect on which we focus in this note is the modelling of non-convective fluxes (e.g, stress, heat flux, diffusive flux) in the averaged balance equations. The basis of the approach is the recognition that, in a spatially non-homogeneous flow, simultaneously with the slow spatial dependence of the macroscopic averaged quantities, there is a faster, local spatial dependence of the microscopic fields. A procedure which takes into consideration this multi-scale nature of the actual situation

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1This chapter is based on the paper "On flux terms in volume averaging." by Chu & Prosperetti (International Journal of Multiphase Flow, vol. 80, pp. 176-180, 2016.)
Figure 6.1: Averaging volume in a two-phase system. The surface of the averaging volume, $S = S_1 + S_2$, consists of a portion $S_1$ in contact with phase 1 (continuous thick line) and a portion $S_2$ in contact with phase 2 (dashed thick line). Inside the averaging volume the two phases are separated by an interface $S_i$ (thin lines) which may consist of disjoint parts as in this figure.

results in a physically transparent form of the averaged equations (section 3) which, in turn, helps to close the equations as we show with the example of a disperse flow in section 4. Section 5 provides a discussion of the results in the context of the existing literature. Section 2 contains a very synthetic (“efficient”) derivation of the volume-averaged equations in the standard form in which they are usually presented.

6.2 The general averaged balance law

We consider for simplicity a general system consisting of two phases, denoted by indices 1 and 2, although extension of the procedure to the more general case of three or more phases is straightforward.
Figure 6.2: The unit normals are defined to be directed out of the corresponding phase.

We attach to each point \( x \) in space an averaging volume \( V(x) \) of fixed shape and orientation; \( V_j(x,t) \), with \( j = 1 \) or \( 2 \), denotes the (generally time-dependent) part of \( V \) occupied by the \( j \)-th phase so that \( V = V_1 + V_2 \). The surface \( S \) of \( V \) is also decomposed in the same way, \( S = S_1 + S_2 \), with \( S_j \) the portion of \( S \) occupied by the \( j \)-th phase (see figure 6.1). Inside \( V \) the two phases are separated by an interface \( S_i \), possibly consisting of disjoint parts as, e.g., in the case of droplets suspended in a continuous phase. It is important to keep in mind that the volume occupied by the \( j \)-th phase inside the averaging volume is bounded by \( S_j + S_i \) which, therefore, is a closed surface.

The volume average of a generic quantity \( q_j \) of arbitrary tensorial order belonging to the \( j \)-th phase is defined as

\[
\langle q_j \rangle(x,t) = \frac{1}{V_j(x,t)} \int_{V_j(x,t)} q_j(\vec{\xi},t) d^3 \vec{\xi},
\]

(6.1)

where \( x \) is the position of the averaging volume. Upon using the (generalized)
Reynolds transport theorem we have

\[
\frac{\partial}{\partial t} (V_j \langle q \rangle) = \int_{V_j} \frac{\partial q_j}{\partial t} d^3 \xi + \oint_{S_j + S_i} q_j \mathbf{v} \cdot \mathbf{n}_j dS,
\]

(6.2)

where \( \mathbf{v} \) is the local velocity of the integration surface and \( \mathbf{n}_j \) is the unit normal directed out of the \( j \)-th phase (figure 6.2). Since \( V \) is fixed, \( \mathbf{v} = 0 \) on \( S_j \) and we are left with

\[
\frac{\partial}{\partial t} (V_j \langle q \rangle) = \int_{V_j} \frac{\partial q_j}{\partial t} d^3 \xi + \int_{S_i} q_j \mathbf{v}_j \cdot \mathbf{n}_j dS_i,
\]

(6.3)

where \( \mathbf{v}_i \) is the velocity of the interface contained within \( V \). We assume that the quantity \( q_j \) satisfies a general balance equation of the form

\[
\frac{\partial q_j}{\partial t} = -\nabla \cdot (u_j q_j) + \nabla \cdot \phi_j + \theta_j,
\]

(6.4)

where \( u_j \) is the \( j \)-th phase velocity, \( \phi_j \) the non-convective flux of \( q_j \) and \( \theta_j \) the volume source of \( q_j \). Upon substituting into the first term in the right-hand side of (6.3) we find

\[
\frac{\partial}{\partial t} (V_j \langle q \rangle) = \int_{V_j} \left[ -\nabla \cdot (u_j q_j - \phi_j) + \theta_j \right] d^3 \xi + \oint_{S_j} q_j \mathbf{v}_j \cdot \mathbf{n}_j dS_i,
\]

(6.5)

or, upon using the divergence theorem,

\[
\frac{\partial}{\partial t} (V_j \langle q \rangle) + \int_{S_j} q_j \mathbf{u}_j \cdot \mathbf{n}_j dS_j = \int_{S_j} \phi_j \cdot \mathbf{n}_j dS_j + \int_{S_i} \left[ -q_j (u_j - \mathbf{v}_i) + \phi_j \right] \cdot \mathbf{n}_j dS_i + \int_{V_j} \theta_j d^3 \xi.
\]

(6.6)

Here we have separated the surface integrals over the interface (in the right-hand side) from those over the surface of the averaging volume (in the left-hand side).

Now we use the exact, purely geometric theorem (see e.g. Gray and Lee, 1977;
Prosperetti and Tryggvason, 2009b)

\[
\int_{S_j} \mathbf{\phi}_j \cdot \mathbf{n}_j dS_j = \nabla \cdot \int_{V_j} \mathbf{\phi}_j d^3 \xi = \nabla \cdot \left( V_j \langle \mathbf{\phi}_j \rangle \right),
\]

(6.7)

(actually valid for any vector or higher-order tensor) to rewrite this result as

\[
\frac{\partial}{\partial t} \left( V_j \langle q_j \rangle \right) + \nabla \cdot \left( V_j \langle q_j \mathbf{u}_j \rangle \right) = \nabla \cdot \left( V_j \langle \mathbf{\phi}_j \rangle \right) + \int_{S_i} \left[ -q_j (\mathbf{u}_j - \mathbf{v}_i) + \mathbf{\phi}_j \right] \cdot \mathbf{n}_j dS_i + V_j \langle \theta_j \rangle.
\]

(6.8)

Upon division by \( V \), assumed to be independent of \( x \) as already stated, and upon introduction of the volume fraction \( \alpha_j \) of the \( j \)-phase defined by

\[
\alpha_j = \frac{V_j}{V},
\]

(6.9)

we find the general averaged balance law

\[
\frac{\partial}{\partial t} \left( \alpha_j \langle q_j \rangle \right) + \nabla \cdot \left( \alpha_j \langle q_j \mathbf{u}_j \rangle \right) = \nabla \cdot \left( \alpha_j \langle \mathbf{\phi}_j \rangle \right)
\]

\[
+ \frac{1}{V} \int_{S_i} \left[ -q_j (\mathbf{u}_j - \mathbf{v}_i) + \mathbf{\phi}_j \right] \cdot \mathbf{n}_j dS_i + \alpha_j \langle \theta_j \rangle.
\]

(6.10)

### 6.3 Separation of scales

While (6.10) is formally exact, its physical transparency can be enhanced as we now show. We focus on the terms containing the non-convective flux \( \mathbf{\phi}_j \), namely

\[
\mathbf{\Phi}_j \equiv \nabla \cdot \left( V_j \langle \mathbf{\phi}_j \rangle \right) + \int_{S_i} \mathbf{\phi}_j \cdot \mathbf{n}_j dS_i.
\]

(6.11)

We show the development explicitly for \( j = 1 \); the results for \( j = 2 \) can be recovered by simply interchanging the indices 1 and 2.
Let us define

$$\bar{\phi} = \alpha_1 \langle \phi_1 \rangle + \alpha_2 \langle \phi_2 \rangle.$$  \hfill (6.12)

By its definition, this quantity captures the large-scale structure of the $\phi$ field and may be expected to be slowly varying over the scale of the averaging volume. Upon multiplying by $V$ (assumed independent of position) and taking the divergence we have

$$V \nabla \cdot \bar{\phi} = \nabla \cdot \left( V \langle \phi_1 \rangle \right) + \nabla \cdot \left( V \langle \phi_2 \rangle \right).$$  \hfill (6.13)

This relation permits us to re-write (6.11) with $j = 1$ as

$$\Phi_1 = V \nabla \cdot \bar{\phi} - \nabla \cdot \left( V \langle \phi_2 \rangle \right) + \int_{S_i} \phi_1 \cdot n_1 dS_i.$$  \hfill (6.14)

On the phase interface $S_i$ the conservation law of the generic quantity $q_j$ imposes a relation between $\phi_1$ and $\phi_2$ of the general form

$$(\phi_1 - \phi_2) \cdot n_1 = \gamma,$$  \hfill (6.15)

where $\gamma$ is a surface source term. For example, when $\phi$ is the stress, $\gamma$ would be a vector accounting for surface tension effects at the interface separating two fluids. For a liquid-vapor system, when $\phi$ is the heat flux, $\gamma$ would account for the latent heat effects associated to phase change, and so on. Upon using the fact that, on the interface $S_i$, $n_1 = -n_2$ as the normals are defined to be directed out of the corresponding phase (see figure 6.2), we can re-write (6.14) as

$$\Phi_1 = V \nabla \cdot \bar{\phi} - \nabla \cdot \left( V \langle \phi_2 \rangle \right) - \int_{S_i} \phi_2 \cdot n_2 dS_i + \int_{S_i} \gamma dS_i.$$  \hfill (6.16)
or, by the geometric theorem (6.7),

\[ \Phi_1 = V \nabla \cdot \Phi - \oint_{S_2 + S_i} \phi_2 \cdot n_2 dS + \int_{S_i} \gamma dS_i. \]  

(6.17)

Let us now set in this equation

\[ \phi_2 = \Phi + \phi'_2. \]  

(6.18)

By the definition of \( \Phi \), \( \phi'_2 \) captures the local small-scale fluctuations of the field \( \phi_2 \) in the averaging volume. The contribution of \( \Phi \) to the first integral in (6.17) is

\[ \oint_{S_2 + S_i} \Phi \cdot n_2 dS = \int_{V_2} \nabla \cdot \Phi dV. \]  

(6.19)

Since \( \Phi \) is slowly varying over the scale of the averaging volume, we approximate the volume integral as

\[ \oint_{S_2 + S_i} \Phi \cdot n_2 dS \simeq V_2 \nabla \cdot \Phi, \]  

(6.20)

which is equivalent to assuming that \( \nabla \cdot \Phi \) is essentially constant over the averaging volume \( V \) or that, equivalently, \( \Phi \) is adequately represented by a linear function of position inside \( V \). Upon substituting into (6.17) we then find

\[ \Phi_1 \simeq V \nabla \cdot \Phi - V_2 \nabla \cdot \Phi - \oint_{S_2 + S_i} \phi'_2 \cdot n_2 dS + \int_{S_i} \gamma dS_i, \]  

(6.21)

i.e.

\[ \Phi_1 \simeq V_1 \nabla \cdot \Phi - \oint_{S_2 + S_i} \phi'_2 \cdot n_2 dS + \int_{S_i} \gamma dS_i. \]  

(6.22)

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With this development the general averaged balance law (6.10) becomes

\[
\frac{\partial}{\partial t} (\alpha_1 \langle q_1 \rangle) + \nabla \cdot (\alpha_1 \langle q_1 u_1 \rangle) = \alpha_1 \nabla \cdot \vec{\phi} - \frac{1}{V} \oint_{S_2 + S_i} \phi_2 \cdot \mathbf{n}_2 dS + \frac{1}{V} \int_{S_i} \left[-q_1 (u_1 - v_i) \cdot \mathbf{n}_1 + \gamma\right] dS_i + \alpha_1 \langle \theta_1 \rangle,
\]

(6.23)

with a similar equation for the other phase. This is the main result of this work. It shows that both phases are acted upon by the same non-convective flux \(\vec{\phi}\) apportioned according to the respective volume fractions. The first surface integral in the right-hand side accounts for the local interaction between the phases and can be calculated as if the flow was locally uniform since its large-scale structure is captured by \(\vec{\phi}\).

### 6.4 An example: Disperse flow

Let us consider the application of the result (6.23) to the case of disperse flow in which drops or particles (phase 2) are suspended in a continuous phase (phase 1). The same result would apply to bubbles provided they maintain a constant volume as, in the derivation that follows (but not in the general argument of the previous section), we assume the two phases to be incompressible. For simplicity of exposition we use the word “drop” to designate any type of disperse entity.

In this application the interface \(S_i\) consists of the collection of the surfaces of the drops entirely contained in the averaging volume, plus the surfaces of the incomplete drops only part of which is in the averaging volume (see figure 6.1).

For momentum balance, for which \(q_j = \rho_j u_j\), \(\phi_j = \sigma_j\) is the stress tensor for phase \(j\). The total force exerted by the continuous phase on each complete drop (i.e.,
on each drop entirely contained within the averaging volume \( V \) is given by

\[
\mathbf{f}_t = \oint_{s_d} \mathbf{n}_d \cdot \sigma_1 ds_d = \oint_{s_d} \sigma_2 \cdot \mathbf{n}_d ds_d,
\]

(6.24)
in which \( s_d \) is the drop surface and \( \mathbf{n}_d \) is the outwardly directed unit normal. Actually \( \sigma_2 \cdot \mathbf{n}_d \) differs from \( \sigma_1 \cdot \mathbf{n}_d \) because of the effect of surface tension but, after integration over the entire drop surface, this contribution vanishes as surface tension does not exert any net force on the whole drop (see e.g. Prosperetti and Jones, 1984; Hesla, Huang, and Joseph, 1993). We write

\[
\mathbf{f}_t = \oint_{s_d} \sigma_2 \cdot \mathbf{n}_d ds_d = \oint_{s_d} (\sigma + \sigma'_2) \cdot \mathbf{n}_d ds_d \simeq v_d \nabla \cdot \sigma + \oint_{s_d} \sigma'_2 \cdot \mathbf{n}_d ds_d,
\]

(6.25)
where \( v_d \) is the drop volume. Note that the normal \( \mathbf{n}_d \) has the same direction as the normal \( \mathbf{n}_2 \) appearing in (6.23). The first term is the force due to the large-scale flow in which the drop is immersed and is akin to a pseudo-buoyancy force (see e.g. Jackson, 2000; Prosperetti and Tryggvason, 2009b), while the second one is responsible for the force due to the local conditions in the neighborhood of the drop such as drag, lift, added mass and others; we set

\[
\mathbf{f} = \oint_{s_d} \sigma'_2 \cdot \mathbf{n}_d ds_d.
\]

(6.26)
The situation of the drops only partially contained in the averaging volume is different as their contribution to \( S_i \) is not via integration over a closed surface. Thus, for example, the result of the integral analogous to (6.24) for these drops would depend on the absolute pressure level, which would introduce an unphysical feature in the modelling of incompressible flows. Furthermore, these drops contribute to the integration over \( S_2 \) in (6.23). The simplest way to deal with this situation probably is
to count the contribution of these drops proportionally to the fraction of their volume (or surface area) contained within the averaging volume. With this understanding we find for the second term in the right-hand side of (6.23)

$$\frac{1}{V} \int_{S_2 + S_i} \sigma'_2 \cdot n_2 dS = \frac{1}{V} \sum_d f_d = n\bar{f},$$

(6.27)

where the summation is over all the drops in the averaging volume, possibly weighted proportionally to their inclusion in the averaging volume as explained before. In the last step we have introduced the drop number density $n$ and the mean hydrodynamic force acting on the drops $\bar{f}$.

Assuming the density of the continuous phase to be constant and neglecting mass transfer phenomena across the drop interfaces, (6.23) becomes then

$$\rho_1 \left( \frac{\partial}{\partial t} (\alpha_1 \langle u_1 \rangle) + \nabla \cdot (\alpha_1 \langle u_1 u_1 \rangle) \right) = \alpha_1 \nabla \cdot \sigma - \frac{1}{V} \sum_d f_d$$

$$+ \frac{1}{V} \int_{S_i} \gamma dS_i + \alpha_1 \rho_1 g,$$

(6.28)

where $\gamma$ is the (vector) contribution of the surface forces and the volume source of momentum per unit mass has been written as $g$. The mean stress $\bar{\sigma}$ may be decomposed into pressure and viscous components and closed, e.g., as

$$\bar{\sigma}_{ij} = -\bar{p}\delta_{ij} + \bar{\tau}_{ij} = -\bar{p}\delta_{ij} + \mu_{eff} \left( \frac{\partial \bar{u}_i}{\partial x_j} + \frac{\partial \bar{u}_j}{\partial x_i} \right),$$

(6.29)

with $\mu_{eff}$ an effective shear viscosity and $\bar{u} = \alpha_1 \langle u_1 \rangle + \alpha_2 \langle u_2 \rangle$ as in (6.12). A diagonal term proportional to $\nabla \cdot \bar{u}$ is absent since the mixture is incompressible.
With these choices (6.28) becomes

$$\rho_1 \left( \frac{\partial}{\partial t} (\alpha_1 \langle u_1 \rangle) + \nabla \cdot (\alpha_1 \langle u_1 u_1 \rangle) \right) = -\alpha_1 \nabla \bar{p} + \alpha_1 \nabla \cdot \bar{\tau} - \frac{1}{V} \sum_d f_d$$

$$+ \frac{1}{V} \int_{S_i} \gamma dS_i + \alpha_1 \rho_1 \mathbf{g}. \quad (6.30)$$

The integral over $S_i$ is obviously difficult to model. If the area fraction occupied by the drops on the surface of the averaging volume is $\alpha_s$ we have, in order of magnitude,

$$\left| \frac{1}{V} \int_{S_i} \gamma dS_i \right| \sim \frac{\alpha_s S 2 \gamma}{V r_d} \quad (6.31)$$

where $S$ is the surface of the averaging volume, $\gamma$ the surface tension coefficient and $r_d$ the drop radius. The hydrodynamic force is very often dominated by drag so that, again in order of magnitude,

$$n \left| \bar{f} \right| \sim n \mu_1 r_d w_d, \quad (6.32)$$

with $w_d$ the magnitude of the drop-fluid relative velocity and $\mu_1$ the viscosity of the continuous phase. The ratio of these two terms is therefore

$$\frac{2(\alpha_s S/V)\gamma/r_d}{n \mu_1 r_d w_d} = \frac{2 \alpha_s S/ r_d^2}{nV \mu_1 w_d} = \frac{N_S}{N_V} \frac{2}{Ca}. \quad (6.33)$$

in which $N_S$ and $N_V$ are the numbers of drops on the surface of, and inside, the averaging volume, respectively, and $Ca = \mu_1 w_d / \gamma$ is a representative capillary number. One would typically expect $N_S < N_V$. Thus, provided the capillary number is not too small, the surface integral in (6.28) and (6.30) may be neglected.

The disperse phase can be treated in the same way except that, in the final result, one can take a step similar to the second one in (6.27) thus finding a momentum
equation for the “average drop” contained in the averaging volume, which it is
convenient to write in the Lagrangian form:

\[
\frac{d}{dt} \left( m u_d \right) = \nu_d \nabla \cdot \sigma + \tilde{f} + mg, \tag{6.34}
\]

where \( m \) and \( u_d \) are the drop mass and velocity. Surface tension causes deformation
of the drop but no translational motion, as noted before, and, accordingly, it has
been omitted. An alternative to the use of (6.34) is to write the equation for each
individual drop, thus adopting a Lagrangian description as is done, for example, in
the point-particle or discrete-element models (see e.g. Ferrante and Elghobashi, 2003;
Eaton, 2009; Deen et al., 2007).

The thermal energy balance can be treated in a similar way. For an incompressible
continuous phase with constant properties we would have \( q_1 = \rho_1 c_{p1} T_1 \), with \( c_{p1} \) the
constant-pressure specific heat and \( T_1 \) the temperature, while \( \phi_1 = -q_1 \) the heat
flux. In this case the analog of (6.25) is

\[
Q_t = \oint_{s_d} \left( -q - q_2' \right) \cdot n_d ds_d \simeq -\nu_d \nabla \cdot \bar{q} - \oint_{s_d} q_2' \cdot n_d ds_d, \tag{6.35}
\]

and, upon letting

\[
Q = -\oint_{s_d} q_2' \cdot n_d ds_d, \tag{6.36}
\]

we find the energy balance in the form

\[
\rho_1 c_{p1} \left( \frac{\partial}{\partial t} (\alpha_1 \langle T_1 \rangle) + \nabla \cdot (\alpha_1 \langle T_1 u_1 \rangle) \right) = -\alpha_1 \nabla \cdot \bar{q} - n \bar{Q}. \tag{6.37}
\]

Here we have neglected volume sources of internal energy such as viscous dissipation.
Furthermore, because of the neglect of phase change at the drop surface, the right-hand
side of the interface balance (6.15) vanishes.
The average heat flux can be closed as before as

\[ \overline{q} = -k_{\text{eff}} \nabla \overline{T}, \]  

(6.38)

with \( k_{\text{eff}} \) an effective conductivity and \( \overline{T} = \alpha_1 \langle T_1 \rangle + \alpha_2 \langle T_2 \rangle \) as in (6.12). The internal energy balance for the drops can be readily written down as before:

\[ \frac{d}{dt} (c_p m \overline{T}_d) = -\overline{\nu}_d \nabla \cdot \overline{q} + \overline{Q}. \]  

(6.39)

Similarly to the use of a drag coefficient in the closure of the interphase force, a heat transfer coefficient \( h \) can be used to close \( Q \):

\[ Q = h s_d (\langle T_1 \rangle - T_d). \]  

(6.40)

### 6.5 Discussion

The result (6.23) shows two significant features concerning the contribution of the non-convective flux \( \phi \) to the general averaged balance law. The first one is the appearance of the flux averaged over the entire mixture rather than over the individual phases. The second one is the presence of the volume fraction outside, rather than inside, the divergence operator.

In an earlier paper (Zhang and Prosperetti, 1997) we have derived the momentum and energy equations in a dilute fluid-particle flow by means of ensemble averaging. The results conform precisely with (6.28) and (6.37), respectively, with \( \overline{\sigma} \) and \( \overline{q} \) as in (6.29) and (6.38). The very different method of derivation lends considerable support to the validity of these results.

It is well appreciated in the literature that, in the pressure term of the momentum
equation, the volume fraction must be outside the gradient operator as in (6.30) in order to avoid unphysical results, e.g. in the case of a spatially non-uniform system on which no forces are acting (see e.g. Jackson, 2000; Prosperetti and Tryggvason, 2009b). However, the viscous term is often written as \( \nabla \cdot (\alpha_1 \langle \tau_1 \rangle) \). While this form agrees with the result of straight volume averaging as in the first term in the right-hand side of (6.10), the problem remains of closing \( \langle \tau_1 \rangle \) as well as the interface integral in (6.10). The first objective is often accomplished by simply setting

\[
\langle \tau_{1,ij} \rangle = \bar{\mu}_1 \left( \frac{\partial}{\partial x_j} \langle u_{1,i} \rangle + \frac{\partial}{\partial x_i} \langle u_{1,j} \rangle - \frac{2}{3} \nabla \cdot \langle u_1 \rangle \delta_{ij} \right),
\]

with \( \bar{\mu}_1 \) a possibly modified fluid viscosity. This is the choice made by a large number of investigators; representative examples of what could be a very long list are the model employed in the code MFIX (Benyahia, Syamlal, and O’Brien, 2012) as well as the studies by Deen et al. (2007), Janet, Liao, and Lucas (2015) and many others.

In a recent paper, Capecelatro and Desjardins (2013) derive a momentum equation for the continuous phase by a mollified form of volume averaging separating terms slowly and rapidly varying in space. Upon combining their equations (26), (27), (40) and (41) one finds that (upon omitting non-essential features) the contribution of the stress terms in the right-hand side of the fluid momentum equation can be written as

\[
-\alpha_1 \nabla \bar{p} + \alpha_1 \nabla \cdot \left[ \mu_{\text{eff}} \left( \nabla \bar{u}_1 + \nabla \bar{u}_1^T - \frac{2}{3} \nabla \cdot \bar{u}_1 \right) \right] - \frac{1}{V_c} \sum_i f_i,
\]

with the sum extended to the particles in the computational cell of volume \( V_c \) and \( f \) the hydrodynamic force on each particle. Here \( \bar{u}_1 \) is defined as “the volume-filtered [i.e., slowly varying] fluid velocity” and is therefore similar, although not exactly equal, to the slowly varying volumetric flux of the whole mixture \( \bar{u} \) introduced before in (6.29);
the last term is the same as (6.27). The derivation by Capecelatro and Desjardins (2013) confirms the presence of the volume fraction outside the divergence operator in spite of the (probably quantitatively) minor difference between $\tilde{u}_1$ and $\tilde{u}$.

The derivation of section 6.3 shows that the proper position of the volume fraction is outside the gradient operator not only for the momentum equation, but for all the balance laws. This is at variance with most of the models in current use (see e.g. Janet, Liao, and Lucas, 2015; Patil, Peters, and Kuipers, 2015, for some recent examples).

### 6.6 Conclusions

By taking advantage of the separation of scales between macroscopic and local microscopic fields, we have recast the mathematical form in which non-convective fluxes $\phi_j$ (e.g. stress, heat flux and others) appear in the volume-averaged equation of the $j$-th phase. We have shown that, in place of fields $\langle \phi_j \rangle$ averaged over the individual phases, it is preferable to use a single, globally averaged field $\bar{\phi} = \alpha_1 \langle \phi_1 \rangle + \alpha_2 \langle \phi_2 \rangle$, the action of which is apportioned according to the volume fraction of each phase as shown in (6.23). This step has several advantages.

In the first place, it provides a clear guidance as to how to interpret and use the terms containing $\phi_j$ in the unclosed form (6.10) of the general volume-averaged balance equation usually encountered in the literature.

Secondly, the derivation shows the much greater significance of the mixture flux compared to that of the individual phases. When the normal component of $\phi_j$ is continuous across the interface, while $\langle \nabla \cdot \phi_j \rangle \neq \nabla \cdot \langle \phi_j \rangle$ as differentiation and averaging do not commute, it can be shown that it is nonetheless true that $\alpha_1 \nabla \cdot \phi_1 + \alpha_2 \nabla \cdot \phi_2 = \nabla \cdot (\alpha_1 \langle \phi_1 \rangle + \alpha_2 \langle \phi_2 \rangle) \equiv \nabla \cdot \bar{\phi}$. Similarly, if some
quantity such as the temperature $T_j$ is continuous across the interface, it is true that

$$
\alpha_1 \langle \nabla T_1 \rangle + \alpha_2 \langle \nabla T_2 \rangle = \nabla (\alpha_1 \langle T_1 \rangle + \alpha_2 \langle T_2 \rangle) \equiv \nabla T.
$$

In the case of heat conduction, for example, this circumstance justifies the introduction of an effective thermal conductivity $k_{eff}$ of the mixture defined so that the mixture heat flux $\bar{q}$ is closed as

$$
\bar{q} = -k_{eff} \nabla \bar{T}
$$
as done before in (6.38) (see e.g. Sangani and Acrivos, 1983; Chang and Acrivos, 1986; Bonnecaze and Brady, 1990; Marchioro and Prosperetti, 1999).

A similar relation permits the introduction of an effective viscosity in a mean stress-volumetric flux closure relation (see e.g. Batchelor, 1970; Batchelor, 1974; Nunan and Keller, 1984). There is therefore a direct connection between the voluminous literature on effective properties of disperse systems (see e.g. Torquato, 2011) and the volume averaged equations.

Thirdly, the derivation clarifies the proper position of the volume fractions in the terms involving the divergence of the non-convective fluxes.

Our result is general and only rests on the hypothesis that the spatial variation of the combined average flux $\bar{\boldsymbol{\phi}}$ is adequately represented by a linear function of position within the averaging volume, which seems a rather mild assumption whenever the use of volume averaging is useful. No further hypotheses on the nature of the flow (e.g., about specific flow regimes) are necessary.

Finally, it is to be noted that the present results coincide with earlier ones obtained by the completely different method of ensemble averaging for the special case of a dilute suspension of spherical particles in a fluid (Zhang and Prosperetti, 1997). This coincidence, together with the difference between the methods of derivation, lends a strong support to their validity.
Chapter 7

Summary and Conclusions

We now proceed to a presentation of a summary of this work followed by an outlook and some conclusions.

7.1 Summary

In chapter 2, we have presented a consistent theory for the dissolution, or growth, of a multi-component, well-mixed spherical drop at rest in a host liquid. The theory incorporates in a proper way the constraints of thermodynamic equilibrium at the drop surface by the adoption of UNIQUAC, a widely used model for the parametrization of the activity coefficients of many chemical compounds. The gradual change of the drop composition due to the different solubilities and diffusivities of its components in the host liquid causes a variation in time of the concentration of these components at the surface of the drop. This circumstance requires a modification of the classic theory of Epstein and Plesset (1950b), which introduces memory effects in the diffusive flux out of the drop as shown in (2.10). The memory effects are found to be small in the dissolution/growth process of a multicomponent drop, however, they are not negligible.
when surface concentration changes rapidly with time as in the case of bubbles. The importance of this memory effects was further evaluated under several situations in chapter 3.

For the case in which the drop constituents are already present in the host liquid at the beginning of the process, we have found that, whatever the initial composition, the mole ratio of the drop constituents will reach a steady constant value for both dissolution and growth. We have formulated a simple criterion to predict whether one or the other will take place in any specific situation. In suitable conditions, a drop can grow even when the concentration of both constituents in the host liquid is smaller than their respective saturation values. This observation can have significant implications for solvent extraction processes which are widely used in the chemical and environmental remediation industries.

The predictions of the theory have been compared with those of a simpler approach to the problem built on the assumption of independence of the activity coefficients from the drop composition. It is found that the predictions of the two theories are similar when the solutions are close to ideal or there is a large difference in the solubilities, or diffusivities, of the drop constituents in the host liquid, unless initially the drop consists mainly of the more soluble component. When the solubilities and diffusivities are close, the differences can be substantial for any drop composition. Thus, an experimental confirmation of our results would require the use of liquids forming non-ideal solutions and having comparable solubilities and diffusivities in the host liquid. Furthermore, the drop should be small enough that the diffusion time of its constituents is smaller than the dissolution time so as to ensure spatial uniformity of its composition.
To the extent that the drop considered in this work is spherical and homogeneous, with no relative motion with respect to the host liquid, our model is idealized. However, in section 2.7, we have presented arguments to show that these conclusions are valid beyond the limits of the model, e.g. for a sessile or translating drop.

Although in this chapter we have only considered ternary system, the same general approach would apply more broadly to systems with more than three components. In particular, quaternary systems can be studied by the same method as the UNIQUAC model is known to give reasonable results for many such systems (see e.g. Chen et al., 2014).

In chapter 3, we utilized Henry’s law which dictates the concentration of dissolved gas at the surface of a gas bubble in a liquid. When the bubble internal pressure changes, either in response to a varying ambient pressure, because of surface tension in the presence of radius changes, or for other causes, the dissolved gas concentration becomes time dependent and the history effects characteristic of all diffusive processes appear. When the dissolution or growth take place under a constant ambient pressure, so that the sole agent of the internal pressure variation is the changing radius, we have found history effects are small. When the bubble consists of the mixture of two gases, history effects can be somewhat larger, especially for micron size bubbles, but they amount to a few percent at most. When the internal pressure changes in response to variations of the ambient pressure, however, the history effect on rectified diffusion can be more important. In this case, the different frequency responses of the gas inflow or outflow and surface area increase or decrease during the pressure cycle are important. Since the former is a relatively slow process, at low frequency there are large mass exchanges with the liquid which require large expansions and contractions.
of the bubble. At higher frequency, changes in the surface area become the dominant effect and the oscillation amplitude is smaller.

In chapter 4, we have developed a horizontally integrated model for bubble plumes in stratified environments which, unlike earlier models, includes the effects of inlet conditions. We have found that these conditions have a strong influence on the model predictions. By a suitable rescaling of the dependent and independent variables, the equations of the model take the same form for a top-hat and a Gaussian distribution of the flow fields over the plume cross section. We have also provided a scaling analysis which helps clarify the physical meaning of the main dimensionless parameters arising in the theory.

Unlike much earlier work (see e.g. Zheng, Yapa, and Chen, 2003; Socolofsky and Adams, 2005; Socolofsky, Bhaumik, and Seol, 2008), we were careful to make a distinction between the height at which the plume momentum attains its maximum value, which we term the neutral height, and the intrusion height reported in many experiments. We have argued that the neutral height represents an estimate of the lower edge of the intrusion layer, and cannot be taken to represent the measured intrusion height. This distinction proves critical when it is attempted to compare the results of our model, as well as those of earlier investigators, with experimental data, which would otherwise be found to fall inexplicably much above the theoretical predictions in many cases. Our results on this point are unaffected by the precise value of the entrainment coefficient which is a matter of some uncertainty as mentioned in section 4.2.

Chapter 5 has presented a numerical study of bubble and drop plumes in a stratified ambient with mass transfer between bubbles/drops and ambient liquid. In addition to
parameters with limited influence on the results, the effect of bubble/drop dissolution on the plume dynamics is described by two main dimensionless groups: one, \( \Theta \), represents the bubble dissolution rate and the other, \( \Lambda \), the density mixing efficiency. The latter parameter is very small in shallow water, but becomes influential in deep water where the hydrostatic pressure increases the ratio between the gas and liquid densities.

The density modification of the ambient liquid due to dissolution is found to have crucial importance in maintaining the total plume buoyancy while the bubble/drop size reduces due to dissolution. The results shown are particularly relevant for soluble bubbles in deep water, as the dissolution plays an important role.

Finally, in the last chapter, we have considered the problem of deriving averaged equations for dispersed multiphase flow. By taking advantage of the separation of scales between averaged and local microscopic fields, we have recast the mathematical form of the averaged equations in which non-convective fluxes \( \mathbf{\phi}_j \) (e.g. stress, heat flux and others) appear in the volume-averaged equation of the individual phases. We have shown that, in place of fields \( \langle \mathbf{\phi}_j \rangle \) averaged over the individual phases, it is preferable to use a single, globally averaged field \( \overline{\mathbf{\phi}} = \alpha_1 \langle \mathbf{\phi}_1 \rangle + \alpha_2 \langle \mathbf{\phi}_2 \rangle \), the action of which is apportioned according to the volume fraction of each phase as shown in (6.23). The result is general and only rests on the hypothesis that the spatial variation of the combined average flux \( \overline{\mathbf{\phi}} \) is adequately represented by a linear function of position within the averaging volume, which seems a rather mild assumption whenever the use of volume averaging is useful. No further hypotheses on the nature of the flow (e.g., about specific flow regimes) are necessary. Besides, the results coincide with earlier ones obtained by the completely different method of ensemble averaging for
the special case of a dilute suspension of spherical particles in a fluid (Zhang and Prosperetti, 1997). This coincidence, together with the difference between the methods of derivation, lends a strong support to their validity.

7.2 Conclusions and outlook

The general area of mass transfer in fluids is very important in many natural, and technological and industrial process. Much work of this field has been driven by applications, and it has led to considerable progress. However, even more progress can be expected from the application of work more closely focused on the basic principles of fluid dynamics, heat and mass transfer. In the present work, we have adopted point of this view in the analysis of a few specific problems, finding some interesting results. We have focused on fairly idealized situations, which are now ripe for more detailed investigations.

Our study of single drop and bubble should be complemented by accounting for relative velocity with respect to ambient fluid. In addition to enhanced convection, such a relative velocity would affect the droplet shape and its surface area. There are more complete models (Magnussen, Rasmussen, and Fredenslund, 1981, see e.g.) for calculation of the phase equilibrium and it would be interesting to see how their adoption compares with our results. Other interesting effects may derive from a spatially non-uniformity of the drop composition due, for example, to a diffusion time scale comparable to or slower than the time scale for dissolution. The dissolved material will change the density of the ambient fluid, leading to the possibility of natural convection which would have a strong effect on the dissolution rate (Soto et al., 2017). An examination of the effect of nearby drops/bubbles would be interesting to
ascertain the effect of the interaction of the concentration fields.

We have utilized a simple integral model to study bubble/drop plumes. It would be interesting to compare these results with those obtained by more resolved model, for example, of the point particle, Euler-Langrangian type. Turbulence would, of course, have a significant role, as shown in a recent work of Yang et al. (2016). Another effect of turbulence has not been considered in literature, is the break up of bubbles/drops, which, by increasing the surface area would result a faster dissolution. The converse process of coalescence may occur very near the plume source, but will rapidly loose importance as the plume expands and dilutes. A major factor in the dynamics of plumes is the precise mechanism by which they entrain the ambient fluid, which largely determines the intrusion height. Our treatment has been based on simplified hypothesis in which the entrainment rate is parametrized in terms of a single coefficient. The theoretical and experimental basis for this treatment has been insufficiently investigated, especially for multiphase plumes.

Possibly significant effects for bubble plumes with very deep sources that we have neglected include temperature, deviation from perfect gas law and its effects on gas solubility and gas density, and possible formation of hydrates for carbon dioxide, methane, and other alkanes. All of these problems render the area of mass transfer in multiphase plume of great scientific interest and practical significance.
References


Domingos, M. G. and S. S. Cardoso (2013). “Turbulent two-phase plumes with bubble-size reduction owing to dissolution or chemical reaction”. In: Journal of Fluid Mechanics 716, pp. 120–136.


emissions from the Deepwater Horizon spill constrain air-water partitioning, hydrocarbon fate, and leak rate”. In: *Geophysical Research Letters* 38.7.


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- Outstanding Bachelor Thesis award, Peking University, 2012
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