

LARGE-EDDY SIMULATION OF DEEP-WATER HYDROCARBON
PLUME DYNAMICS

by
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DEDICATION

This dissertation is dedicated to my parents, Changfa Peng and Jianzhen Sun.

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ABSTRACT

During a deep-water wellhead blowout incident, the dynamics of the released hydrocarbon plume is strongly affected by the gas dissolution and hydration process that weakens the bubble-induced buoyancy for driving the plume.

In this study, a new modeling strategy is developed to efficiently incorporate the gas dissolution and hydration effects into a fast Eulerian-Eulerian large-eddy simulation (LES) model. By simultaneously simulating the evolutions of the bubble mass concentration and number density functions, the average bubble size in each LES computational cell can be calculated locally. Based on the cell-averaged bubble diameter, the local gas dissolution rate and hydrate formation/decomposition rate and bubble rise velocity are parameterized, which are then used in the gas transport equations to model the evolution of the gas bubble field due to turbulent transport and gas dissolution and hydrate formation and decomposition.

In Chapter 2, the LES model is applied to simulate several blowout scenarios with different initial bubble sizes. The results show that the plumes that have smaller initial bubble sizes exhibit a faster relative bubble dissolution rate compared to the plumes with larger initial bubble sizes. As a result, the plumes with smaller bubbles also have lower peel and trap heights than those with larger bubbles. For comparison, a set of cases without

including the gas dissolution is also performed.

In Chapter 3, a multi-component gas dissolution model is implemented to study the contribution of dissolution from each component and the distribution of dissolved gas in each component. The results show the dissolution ratio for each gas component is different and the average dissolved gas are distributed at different altitude.

In Chapter 4, the hydrate formation and decomposition effect are considered in the LES model for hydrocarbon plumes with deeper release conditions. When the gas bubble is released under the equilibrium depth, the gas bubbles and ambient water compose the hydration shell surrounding the bubble surface under deep ocean conditions as well as the gas dissolution into the surrounding seawater and loses its upward buoyancy force throughout the plume's ascent. As the hydrates rise, the hydrates will dehydrate slowly and dissolve into ambient water.

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Chapter 1

INTRODUCTION

1.1 Background

The hydrocarbon plume released from a deep-water wellhead blowout is typically formed by a mixture of gas bubbles and oil droplets [58, 66, 100]. After being released from the wellhead, the initial flow momentum is quickly dissipated over a relatively small distance [10], and the gas and oil quickly break up into a large number of bubbles [103] and droplets [104], respectively. The multiphase hydrocarbon flow then continues to rise as a turbulent plume driven primarily by the buoyancy force induced by the gas bubbles, and interacts with the stably stratified seawater in a highly dynamic manner [40, 82]. In the case of a deep-water blowout, the gas bubbles can have sufficient time to interact with the surrounding seawater when rising through the ocean column. When rising towards higher elevation, two processes occur simultaneously and induce opposite effects [28, 106]: (i) the bubbles expand while rising due to the decrease of hydrostatic pressure; (ii) the gas dissolution and hydrate formation/decomposition the bubbles into the surrounding seawater causes the bubbles to shrink, which can significantly reduce the bubble-induced buoyancy for driving the plume. The combined effect of these two processes and the seawater stratification

govern the dynamics of the nearfield plume from a deep-water wellhead blowout.

Accurately quantifying the gas dissolution and hydrate formation/decomposition rate and its effect on the characteristics of the plume structure and material transport in a deep-water wellhead blowout is a difficult task. This is largely due to the technical challenges for measuring the detailed information inside the multiphase hydrocarbon plume in the deep-water environment [58]. To help understand the effect of bubbles on the plume dynamics, some studies have focused on measuring the flow and bubble dynamics in simple bubble-driven plumes in laboratory experiments [e.g., 51, 72, 92, 93]. In order to achieve fast prediction of the nearfield plume dynamics, many previous studies have devoted considerable efforts to developing and improving the one-dimensional integral plume modeling approach [e.g., 4, 24, 28, 83, 99, 106]. These integral models calculate the plume-integrated physical quantities as a function of the height by solving a set of one-dimensional ordinary differential equations derived from the cross-plume integration of the three-dimensional Navier–Stokes equations and material transport equations. The low computational cost associated with these models has made them valuable tools for quick modeling to support the decision making for rapid response to subsea wellhead blowout accidents.

Several studies have attempted to include the gas dissolution and hydrate formation/decomposition effect in the integral plume modeling framework. For example, [101, 106] included the methane bubble dissolution and hydrate formation/decomposition effect in the integral plume model by modeling the mass transfer and heat transfer of methane based on empirical parameterizations of mass transfer coefficient and bubble rise velocity. Their integral model was able to capture the effect of the gas dissolution and hydrate formation/decomposition on the vertical variations of the mean inner plume characteristics, such as

the reductions of bubble diameter, buoyancy flux, and momentum flux with the plume elevation. This model was further validated and upgraded with additional features added to the model [19, 98, 107]. [28] incorporated dissolution of multi-component gas bubbles (methane, ethane, propane, etc. all in one bubble) in both double-plume and Lagrangian plume integral models, and successfully modeled the nearfield plume dynamics under deep-water blowout conditions similar to those in the Deepwater Horizon accident.

In recent years, large-eddy simulation (LES) has become a powerful numerical tool for high-fidelity simulations of the turbulent flow physics in buoyant plumes [e.g., 17, 25, 27, 31, 35, 43, 95]. LES can model the time evolution of the plume structures with a wide range of scales of turbulent flow motions being resolved (down to the computational grid scale). While it still requires the unresolved subgrid-scale (SGS) effects to be modeled, LES can directly capture the turbulent flow and material transport phenomena above the computational grid scale, which can provide detailed plume field information to help assess, calibrate and improve the integral plume model [34, 97]. To model the multiphase plume flow from a subsea blowout using LES, the seawater flow is typically modeled as a continuous phase carrier flow governed by the filtered Navier–Stokes equations, while the gas bubbles and oil droplets are modeled as dispersed phases that are transported by the turbulent carrier flow. There are two major approaches for modeling the dispersed phase transport, i.e. the Lagrangian approach and the Eulerian approach [84]. In the Lagrangian approach, the motions of each particles are simulated based on Newton’s second law [e.g., 34, 35, 43]. In the Eulerian approach, the spatial distribution of a dispersed particle phase is described using an Eulerian concentration function, and its time evolution is modeled by solving an advection-diffusion equation to model the transport of the dispersed particles by

the turbulent plume flow [e.g. 17, 31, 32, 97]. In combination with the Eulerian approach for modeling the carrier flow, the former plume modeling approach is usually referred to as the Eulerian–Lagrangian approach, and the latter is referred to as the Eulerian–Eulerian approach.

While it may be straightforward to add additional equations in the Lagrangian approach to model the gas dissolution and hydrate formation/decomposition from individual bubbles to the surrounding seawater, the overall computational cost of the Eulerian–Lagrangian approach can be quite high when modeling the plume of a realistic-scale deep-water blowout event in which a huge number of Lagrangian particles need to be tracked simultaneously. Therefore, the application of the Eulerian–Lagrangian LES model has been mainly limited to the laboratory scale problem [e.g. 34, 35], in which the gas bubbles do not have sufficient time to dissolve mass into the water so that the gas dissolution and hydrate formation/decomposition effect is often not modeled. On the other hand, the Eulerian–Eulerian approach has been successfully applied to model plumes at realistic scales [e.g., 17, 96]. Note that in a typical Eulerian–Eulerian model with polydisperse particles, the distribution of each particle species (e.g., gas bubbles within the same discretized diameter bin) needs to be modeled by a separate Eulerian concentration function. As a result, if the bubbles in the plume from a deep-water blowout experience size reduction over a wide range of diameters due to gas dissolution and hydrate formation/decomposition, a large number of Eulerian concentration functions may need to be used to cover the diameter bins. For example, [54] developed an Eulerian–Eulerian LES model based on the multiple-bin approach (e.g. 17 bins of bubble sizes in their reported results) and applied it to simulate the bubble distribution in the ocean surface layer and the effect of air bubble dissolution on the air–sea

gas transfer.

This current study aims at developing a new cost-efficient approach to include the effect of gas bubble dissolution and hydrate formation/decomposition in the Eulerian–Eulerian LES model framework for deep-water hydrocarbon plumes. The basic turbulent flow and particle transport LES solver for modeling oceanic plumes is adopted from [95] and [96], which has been successfully applied to simulate multiphase buoyant plumes at both laboratory scale [e.g., 97] and field scale [e.g., 17]. In the current LES modeling approach, the evolutions of both the Eulerian mass concentration and bubble number density functions of the gas bubbles are simulated simultaneously, based on which the cell-averaged bubble equivalent diameter can be calculated. Then the cell-averaged gas mass transfer coefficient and bubble rise velocity are parameterized based on the bubble diameter, which are used for modeling the local cell-averaged rate of gas dissolution and hydrate formation/decomposition. The dissolution rate and hydrate formation/decomposition rate are then fed back to the Eulerian transport equation of the bubble mass concentration to account for the reduction of bubble mass due to gas dissolution into surrounding seawater.

1.2 Motivation and Dissertation Overview

The gas bubble dissolution and hydrate formation/decomposition effect are observed to be remarkable in the evolution of the deep ocean hydrocarbon plume. The current experimental study on the micro-scale effects and dynamics of the bubble evolution can reveal the mechanism and build the model of the single bubble dissolution and hydrate formation/decomposition. The lab-scale experiments on the plume dynamics cannot mimic the

real deep ocean's condition for the bubble evolution due to the scale limitation. On the other hand, the field data from the real ocean environment is expensive to obtain and is hard to control and repeat the ocean current condition. For the plume modeling, the integral model can get a rough result, but the detailed plume dynamics is hard to simulate. As mentioned above, modeling the dissolution and hydrate formation/decomposition effect of a single bubble under the large-eddy simulation frame is studied. The new model with LES simulations reveal how the gas bubble plumes interact with the environment.

The current dissertation is organized as follows. In chapter 2, the large-eddy simulation model for the effect of single component gas bubble dissolution is performed. This is a validation and reference test for the following simulations of the gas bubble buoyancy plume with dissolution effect. One important purpose of this simulation is to help validate the effectiveness of the single gas bubble evolution model under the LES framework. The large-eddy simulation for multi-component gas bubble dissolution is shown in chapter 3. The gas bubble dissolution effect is studied for the more general case and closer to the natural gas component. In chapter 4, the LES hydrocarbon plume with hydrate formation and decomposition in deep ocean conditions is studied. A summary of the current research and the future research plan are provided in chapter 5.

Chapter 2

LARGE-EDDY SIMULATION MODEL FOR THE EFFECT OF SINGLE COMPONENT GAS BUBBLE DISSOLUTION

2.1 Introduction

During a deep-sea oil wellhead blowout accident, the oil/gas mixed plume rises through the ocean driven by the buoyancy induced by gas bubbles. As the plume rises, it continuously loses its driving force as gas bubbles are dissolved by the ambient sea water. Accurately modeling the effect of gas dissolution is thus crucial for understanding plume dynamics and predicting the oil dispersion, which are key pieces of information needed for planning oil spill remediation. In this chapter, a fast Eulerian large-eddy simulation (LES) approach is used to model the effect of gas dissolution on plume dynamics. By simultaneously simulating the evolutions of the bubble mass concentration function and the number density field, the average bubble size in each LES computational cell can be calculated locally. Based on this information, the local gas dissolution rate and bubble rise velocity are computed, which are then used in the gas transport equations. This fast Eulerian LES model is able to capture the effect of gas bubble dissolution on the macroscopic plume

characteristics with reasonable computational cost.

To test the performance of the new Eulerian–Eulerian gas bubble dissolution modeling approach, the LES model is first applied to simulate a test case with methane bubbles and the results are compared to the integral model calculation reported from [106]. To further explore the effects of the gas bubble dissolution on the plume dynamics, a series of simulations are conducted with identical volumetric release rate of methane but four different initial bubble diameters. The variation of initial bubble diameter can affect both the gas dissolution rate and the bubble rise velocity, resulting in noticeable variation in the bubble-induced buoyancy force that affects the plume dynamics and material transport. Furthermore, for each initial bubble diameter, both a primary case with gas dissolution modeling and a reference case without gas dissolution effect are simulated to reveal the importance of including the gas dissolution effect in modeling the plume dynamics. In this study, systematic data analyses are performed and the plume statistics under different simulation conditions are compared.

The remainder of this chapter is organized as follows. Section 2.2 provides the detailed description on how to model the gas bubble dissolution effect in the Eulerian–Eulerian LES model. Section 2.3 shows the results of the test case in which the current LES result is compared to the integral model prediction. Then the LES model is applied to study the effect of initial bubble diameter on the gas dissolution and plume characteristics, and the simulation results are presented in section 4.3.2. Finally, the summary is presented in section 2.5.

2.2 Modeling gas bubble dissolution in Eulerian–Eulerian LES framework

2.2.1 Modeling gas mass transfer coefficient

As the gas bubbles from a deep-water blowout rise through the ocean column, they can experience considerable change of seawater hydrostatic pressure and temperature, which can affect the gas state in the bubbles and the gas mass transfer rate from the bubbles into the surrounding seawater. For simplification, in the current study the gas bubbles are assumed to be in thermal equilibrium with the surrounding seawater so that the temperature in a bubble is the same as the local seawater temperature around it. The bubble surface tension effect is also neglected so that the gas pressure inside the bubbles is assumed to be the same as the hydrostatic pressure in the surrounding seawater. The effect of dynamic pressure due to the motion of the bubble is also neglected because of the dominant contribution from the hydrostatic pressure in the deep-water environment. These simplifications allow us to focus on the development and test of the main methodology for modeling the gas dissolution effect in the Eulerian–Eulerian LES framework. These neglected effects can be included into the LES model framework in the future upon the success of the current gas dissolution model development.

In the current modeling framework, the gas dissolution rate is first modeled for single bubbles (details are given in this section and section 2.2.2), and then applied to the modeling of the plume by also taking into account the bubble number density (details are given in section 4.2.4). Due to the high ambient seawater pressure in the deep-water environment, the ideal gas law is not an accurate approximation for describing the state of the gas in the

bubbles, and the Peng–Robinson equation of state [64, 73] should be used instead [106],

$$p_b V_b = Z n_b R T, \quad (2.1)$$

where p_b is the pressure inside the bubble, V_b is the volume of a single bubble, Z is the compressibility factor of the gas, n_b is the number of moles of gas in a single bubble, R is the ideal gas constant, and T is the temperature inside the bubble (which is the same as the seawater temperature under the thermal equilibrium assumption). The key difference between Eq.(2.1) and the ideal gas law is the inclusion of the compressibility factor Z . For bubbles with a single type of gas under a given environment pressure, Z can be calculated by solving a cubic equation constructed based on the equation of state [64]. The details for determining Z is given in Appendix A.

In order to determine n_b , the evolutions of bubble mass concentration C_b (in kg/m^3) and number density N_b (in m^{-3}) are simulated simultaneously in the LES (details are given in section 4.2.4). Based on the local values of C_b and N_b and by neglecting the effect of the subgrid-scale bubble size variation, the average value of n_b in each LES computational cell can be calculated based on

$$n_b = \frac{C_b}{N_b M_g}, \quad (2.2)$$

where M_g is the molar mass of the gas. The cell-averaged single bubble volume within a local LES computational cell, V_b , can be calculated based on Eqs. (2.1) and (2.2) as

$$V_b = \frac{Z n_b R T}{p_b}, \quad (2.3)$$

and the corresponding equivalent bubble diameter (i.e. for a spherical shape with equal volume) is given by

$$d_e = \sqrt[3]{\frac{6V_b}{\pi}} = \sqrt[3]{\frac{6Zn_bRT}{\pi p_b}}. \quad (2.4)$$

The gas density in the bubble is given by

$$\rho_b \equiv \frac{n_b M_g}{V_b} = \frac{p_b M_g}{ZRT}. \quad (2.5)$$

Based on the equivalent bubble diameter d_e , the mass transfer coefficient K (in m/s) for gas dissolution from the bubble to the surrounding seawater can be calculated based on the parameterizations developed from empirical data. In this study, we employ a set of parameterizations for dirty bubbles (i.e. with the effect of surfactant included) for different ranges of d_e based on those used in [106] and [103]. In particular, for small bubbles in the range of $d_e < 4 \times 10^{-4}$ m with spherical shape [36, 61, 70, 103],

$$\frac{K}{D/d_e} = 0.552 \text{Re}_b^{1/2} \text{Sc}^{1/3}, \quad (2.6)$$

where d_e is in m, $\text{Sc} = \nu/D$ is the Schmidt number, ν is the kinematic viscosity of seawater (in m^2/s), D is the molecular diffusivity of the gas in the seawater (in m^2/s), $\text{Re}_b = w_r d_e / \nu$ is the particle Reynold's number, and w_r is the rise velocity (in m/s) of the gas bubbles relative to the surrounding seawater (which also depends on d_e). For bubbles in the range of $4 \times 10^{-4} \text{ m} < d_e < 5 \times 10^{-3} \text{ m}$ with spherical shape [88, 103],

$$\frac{K}{(Dw_r/d_e)^{1/2}} = \frac{2}{\sqrt{\pi}} \left[\left(1 - \frac{2.89}{\sqrt{\text{Re}_b}} \right) f_R \right]^{1/2}, \quad (2.7)$$

where f_R is the surface-flow retardation factor given by [88]

$$\log_{10} f_R = 0.5 \left\{ \tanh \left[3.9 \log_{10} \left(\frac{d_e}{d_0} \right) \right] - 1 \right\}, \quad (2.8)$$

with $d_0 = 8.7 \times 10^{-4}$ m. For bubbles in the range of 5×10^{-3} m $< d_e < 1.3 \times 10^{-2}$ m with elliptical shape [23, on page 196 underneath equation (7.50)],

$$\frac{K}{D^{1/2}} = A_0, \quad (2.9)$$

where $A_0 = 6.5 \text{ s}^{-1/2}$. For large bubbles in the range of $d_e > 1.3 \times 10^{-2}$ m with spherical cap shape [23, page 214, equation (8.29)],

$$\frac{K}{D^{1/2}} = \frac{B_0}{d_e^{1/4}}, \quad (2.10)$$

where $B_0 = 2.19 \text{ m}^{1/4} \text{ s}^{-1/2}$ (converted from the original equation in [23] with d_e in cm).

2.2.2 Modeling gas dissolution rate for single bubble

Using the modeled mass transfer coefficient K , the gas mass dissolution rate of a single bubble, α_b , can be modeled as [106]:

$$\alpha_b = A_b K (C_s - C_{dis}), \quad (2.11)$$

where α_b is in kg/s, K is in m/s, $A_b = \pi d_e^2$ is the bubble equivalent spherical surface area (in m²), C_s is the solubility of the gas in water (in kg/m³), C_{dis} is the concentration of

dissolved gas in the ambient water (in kg/m^3). The concentration field C_{dis} is modeled in the LES by solving a transport equation for the dissolved gas part, which is discussed in detail in section 4.2.4. The solubility is modeled as [106]

$$C_s = \left(\chi \frac{\rho}{M_w} \right) M_g, \quad (2.12)$$

where χ is the mole fraction of dissolved gas in water at equilibrium condition, ρ is the water density (in kg/m^3), M_w is the molar mass of water (in kg/mol), and M_g is the molar mass of gas (in kg/mol).

Considering the high pressure environment near the source of a deep-water blowout, here a modified Henry's law for non-ideal gas is applied to model χ [47, 52, 106]:

$$\chi = \frac{f^g}{H} \exp \left(-\frac{p_b V_m}{RT} \right), \quad (2.13)$$

where V_m is the gas molar volume (in m^3/mol), H is the Henry's law constant (in $\text{Pa}/\text{mol frac}$), and f^g is the fugacity of gas in gas phase (in Pa) given by [64]

$$f^g = p_b \exp \left[Z - 1 - \ln(Z - B) - \frac{A}{2\sqrt{2}B} \ln \left(\frac{Z + 2.414B}{Z - 0.414B} \right) \right], \quad (2.14)$$

in which A and B are the model coefficients involved in calculating the compressibility factor Z (see Eqs. (A.9) and (A.10) in Appendix A for more details). Note that Eq. (4.4) is valid for bubbles with a single gas component. If a bubble contains multiple gas components, a variant of Eq. (4.4) needs to be used to calculate the fugacity coefficient for each gas component (see Eq. (19) in [64]).

For methane bubble considered in this study, the Henry law constant H is parameterized as [12],

$$H = 1000 \exp \left(\alpha_0 + \frac{\alpha_1}{T} - \frac{\alpha_2}{T^2} + \frac{\alpha_3}{T^3} \right), \quad (2.15)$$

where the temperature T is in K, and the coefficients used in the parameterizations are $\alpha_0 = 5.1345$, $\alpha_1 = 7837 \text{ K}$, $\alpha_2 = 1.5090 \times 10^6 \text{ K}^2$, and $\alpha_3 = 2.060 \times 10^7 \text{ K}^3$. Note that for the sake of model simplification, the effect of salinity is not included in the current calculation, which may result in slight overestimation of H . For future extension of the model, the effect of salinity can be included using the Setchenow equation [11, 12, 39].

2.2.3 Large-eddy simulation model for multiphase hydrocarbon plume

In the current study, the seawater flow in and around the plume is modeled as a single-phase carrier flow and is simulated using the LES approach. The model uses a Cartesian coordinate system defined as $\mathbf{x} = (x, y, z)$, where x and y are the horizontal coordinates and z is the vertical coordinate. The carrier flow motions are modeled by solving the filtered Navier–Stokes equations [97],

$$\nabla \cdot \tilde{\mathbf{u}} = 0, \quad (2.16)$$

$$\frac{\partial \tilde{\mathbf{u}}}{\partial t} + \tilde{\mathbf{u}} \cdot \nabla \tilde{\mathbf{u}} = -\frac{1}{\rho_0} \nabla \tilde{P} - \nabla \cdot \boldsymbol{\tau}^d + \left(1 - \frac{\tilde{\rho}}{\rho_0} \right) g \mathbf{e}_z + \left(1 - \frac{\rho_b}{\rho_0} \right) \frac{\tilde{C}_b}{\rho_b} g \mathbf{e}_z + \left(1 - \frac{\rho_d}{\rho_0} \right) \frac{\tilde{C}_d}{\rho_d} g \mathbf{e}_z. \quad (2.17)$$

Here, the tilde denotes the variable resolved by the LES computational grid, $\mathbf{u} = (u, v, w)$ is the velocity vector of the carrier flow, ρ_0 is a reference seawater density, ρ is the local seawater density, P is the modified pressure, g is the gravitational acceleration, $\mathbf{e}_z$ is the unit vector in the vertical direction, $\boldsymbol{\tau} = (\widetilde{\mathbf{u}\mathbf{u}} - \tilde{\mathbf{u}}\tilde{\mathbf{u}})$ is the subgrid-scale stress tensor with $\text{tr}(\boldsymbol{\tau})$

being its trace and $\tau^d = \tau - [\text{tr}(\tau)/3]\mathbf{I}$ being its deviatoric part, $\mathbf{I}$ is the identity tensor, ρ_b is the density of gas in bubbles in local LES computational cell, C_b is the mass concentration of gas bubbles, ρ_d is the density of oil droplet, and C_d is the mass concentration of oil droplets. The last three terms in equation (4.25) are the buoyancy force due to water density fluctuations, gas bubble concentration and oil droplet concentration, respectively, which are all modeled based on the Boussinesq approximation [97].

Following previous LES studies [e.g. 17, 49, 59, 65, 96], the seawater stratification effect is modeled by considering a virtual potential temperature field θ governed by a filtered convection–diffusion equation

$$\frac{\partial \tilde{\theta}}{\partial t} + \nabla \cdot (\tilde{\mathbf{u}} \tilde{\theta}) = -\nabla \cdot \pi_\theta, \quad (2.18)$$

where $\pi_\theta = \tilde{\mathbf{u}} \tilde{\theta} - \tilde{\mathbf{u}} \tilde{\theta}$ is the SGS thermal flux. For the sake of model simplification, in the current study the salinity is assumed to be a constant and the LES-resolved seawater density field $\tilde{\rho}$ is assumed to vary linearly with the potential temperature as [e.g., 49, 59, 65, 96]

$$\tilde{\rho} = \rho_0[1 - \alpha_t(\tilde{\theta} - \theta_0)], \quad (2.19)$$

where α_t is the thermal expansion coefficient, and θ_0 is the reference potential temperature corresponding to the reference seawater density ρ_0 .

The evolution of the gas bubble field is described using two continuous Eulerian functions, i.e. the bubble number density function $N_b(\mathbf{x}, t)$ and the bubble mass concentration function $C_b(\mathbf{x}, t)$. The evolution of the bubble number density is modeled based on a filtered

transport equation

$$\frac{\partial \tilde{N}_b}{\partial t} + \nabla \cdot (\tilde{\mathbf{v}}_b \tilde{N}_b) = -\nabla \cdot \boldsymbol{\pi}_n + q_n, \quad (2.20)$$

where $\tilde{\mathbf{v}}_b$ is the Lagrangian transport velocity of bubbles, q_n is a volumetric source term (i.e. number of released bubbles per m^3 per second) representing the release of bubbles from a subsea blowout, and $\boldsymbol{\pi}_n = \widetilde{\mathbf{u}N_b} - \tilde{\mathbf{u}}\tilde{N}_b$ is the SGS flux of bubble number density due to SGS turbulent flow effects. In Eq. (4.28), the effects of bubble breakup and coalescence are neglected for the sake of model simplicity. The bubble transport velocity $\tilde{\mathbf{v}}_b$ is modeled as [17, 33, 97]

$$\tilde{\mathbf{v}}_b = \tilde{\mathbf{u}} + w_{r,b} \mathbf{e}_z + \frac{w_{r,b}}{g} \frac{D\tilde{\mathbf{u}}}{Dt}, \quad (2.21)$$

where $w_{r,b}$ is the rise velocity of bubbles relative to the surrounding carrier flow (see Appendix B for the parameterizations of $w_{r,b}$), and $D\tilde{\mathbf{u}}/Dt = \partial\tilde{\mathbf{u}}/\partial t + \tilde{\mathbf{u}} \cdot \nabla \tilde{\mathbf{u}}$ is the material derivative (or Lagrangian acceleration) of the carrier flow velocity.

The evolution of the bubble mass concentration field is modeled by solving a filtered transport equation similar to Eq. (4.28) but with the decrease of bubble mass due to the dissolution effect,

$$\frac{\partial \tilde{C}_b}{\partial t} + \nabla \cdot (\tilde{\mathbf{v}}_b \tilde{C}_b) = -\nabla \cdot \boldsymbol{\pi}_b + q_b - \tilde{\alpha}. \quad (2.22)$$

Here, $\boldsymbol{\pi}_b = \widetilde{\mathbf{u}C_b} - \tilde{\mathbf{u}}\tilde{C}_b$ is the SGS flux of bubble mass concentration, $q_b = \rho_{b,0} V_{b,0} q_n$ is the volumetric source term for the release of gas bubble mass, $\rho_{b,0}$ is the gas density in the bubbles at the release source, $V_{b,0}$ is the initial volume of a single bubble at the release source, q_n is the same source term for bubble number density as in Eq. (4.28), and $\tilde{\alpha} = \tilde{N}_b \tilde{\alpha}_b$ is the cell-averaged local gas mass dissolution rate (per unit volume) resolved by the LES

model. Applying Eq. (3.7) based on the LES-resolved quantities gives

$$\tilde{\alpha} = \tilde{N}_b \tilde{\alpha}_b = \tilde{N}_b \tilde{A}_b \tilde{K} \left(\tilde{C}_s - \tilde{C}_{dis} \right). \quad (2.23)$$

For the dissolved gas in the seawater, the concentration function $\tilde{C}_{dis}$ is modeled using

$$\frac{\partial \tilde{C}_{dis}}{\partial t} + \nabla \cdot \left(\tilde{\mathbf{u}} \tilde{C}_{dis} \right) = -\nabla \cdot \boldsymbol{\pi}_{dis} + \tilde{\alpha}, \quad (2.24)$$

where $\boldsymbol{\pi}_{dis} = \widetilde{\mathbf{u} \tilde{C}_{dis}} - \tilde{\mathbf{u}} \tilde{C}_{dis}$ is the SGS flux of mass concentration for the dissolved gas.

Unlike $\tilde{N}_b$ and $\tilde{C}_b$, the concentration $\tilde{C}_{dis}$ for the dissolved gas is transported as a passive scalar based on the carrier flow velocity $\tilde{\mathbf{u}}$. Note that the evolution equations for $\tilde{C}_b$ and $\tilde{C}_{dis}$ are coupled through the gas dissolution rate $\tilde{\alpha}$, which acts as a sink term in Eq. (4.27) and as a source term in Eq. (4.31).

In addition, we also simulate the transport of dye and oil droplets to model the effects of the plume on transporting materials. The evolution of the dye mass concentration field $\tilde{C}_{dye}$ is used to represent the transport of passive tracers, which is governed by the filtered transport equation

$$\frac{\partial \tilde{C}_{dye}}{\partial t} + \nabla \cdot \left(\tilde{\mathbf{u}} \tilde{C}_{dye} \right) = -\nabla \cdot \boldsymbol{\pi}_{dye} + q_{dye}, \quad (2.25)$$

where q_{dye} is a source term for the dye release and $\boldsymbol{\pi}_{dye} = \widetilde{\mathbf{u} \tilde{C}_{dye}} - \tilde{\mathbf{u}} \tilde{C}_{dye}$ is the SGS dye concentration flux. The transport of oil droplets is affected by both the carrier flow and the buoyancy-induced rise velocity of the oil droplets. The oil droplet mass concentration field

$\tilde{C}_d$ is modeled by solving the filtered transport equation

$$\frac{\partial \tilde{C}_d}{\partial t} + \nabla \cdot (\tilde{\mathbf{v}}_d \tilde{C}_d) = -\nabla \cdot \boldsymbol{\pi}_d + q_d, \quad (2.26)$$

where q_d is a source term for the oil droplet release, $\boldsymbol{\pi}_d = (\widetilde{\mathbf{u}C_d} - \tilde{\mathbf{u}}\tilde{C}_d)$ is the SGS flux of oil mass concentration, and $\tilde{\mathbf{v}}_d$ is the transport velocity of oil droplets (with non-negligible buoyancy effect) [e.g., 16, 21, 96],

$$\tilde{\mathbf{v}}_d = \tilde{\mathbf{u}} + w_{r,d} \mathbf{e}_z + \frac{w_{r,d}}{g} \frac{D\tilde{\mathbf{u}}}{Dt}. \quad (2.27)$$

The oil droplet rise velocity due to buoyancy is modeled as [22, 89, 97]

$$w_{r,d} = \begin{cases} w_{r,d}^S & \text{Re}_d < 0.2, \\ w_{r,d}^S (1 + 0.15 \text{Re}_d^{0.687})^{-1}, & 0.2 < \text{Re}_d < 750, \end{cases} \quad (2.28)$$

where $w_{r,d}^S$ is the oil droplet rise velocity given by Stokes' law as

$$w_{r,d}^S = \frac{(1 - \rho_d/\rho_0)gd_d^2}{18\nu}, \quad (2.29)$$

ρ_d is the oil density, d_d is the equivalent diameter of the oil droplet, ν is the kinematic viscosity of water, and $\text{Re}_d = w_{r,d}d_d/\nu$ is the oil droplet Reynolds number.

Following [95], [96], and [97], the filtered LES governing equations (4.25), (4.25), (4.28), (4.27), (4.31)–(4.32) are closed by parameterizing the SGS terms with proper turbulence closures. In particular, the SGS stress tensor τ^d is parameterized using the Lilly–

Smagorinsky eddy-viscosity type model [55, 76], $\tau^d = -2\nu_\tau \tilde{\mathbf{S}}$, where $\tilde{\mathbf{S}} = [\nabla \tilde{\mathbf{u}} + (\nabla \tilde{\mathbf{u}})^T]/2$ is the resolved strain rate tensor, $\nu_\tau = (c_s \Delta)^2 |\tilde{\mathbf{S}}|$ is the modeled SGS eddy viscosity, c_s is the Smagorinsky model coefficient, and Δ is the LES grid (filter) scale. In the current model, the value of c_s is determined dynamically during the simulation using the Lagrangian-averaged scale-dependent dynamic SGS model [8]. The SGS fluxes of the scalar quantities are then parameterized as $\pi_\theta = -(\nu_\tau/\text{Pr}_\tau) \nabla \tilde{\theta}$, $\pi_n = -(\nu_\tau/\text{Sc}_\tau) \nabla \tilde{N}_b$, $\pi_b = -(\nu_\tau/\text{Sc}_\tau) \nabla \tilde{C}_b$, $\pi_{dis} = -(\nu_\tau/\text{Sc}_\tau) \nabla \tilde{C}_{dis}$ and $\pi_{dye} = -(\nu_\tau/\text{Sc}_\tau) \nabla \tilde{C}_{dye}$, with a constant SGS Prandtl number $\text{Pr}_\tau = 0.4$ and SGS Schmidt number $\text{Sc}_\tau = 0.4$ [3, 14, 50, 57, 60, 85, 97]. The solution process and numerical schemes for solving the LES model equations are summarized in Appendix C.

2.3 LES gas dissolution model test

The basic coupled turbulent flow and scalar transport solver used in the current LES model has been tested against experimental data [14] and successfully applied to simulate oil and gas plume dispersion in the oceanic environment in several prior studies [e.g., 16, 21, 96]. The LES solver's performance has been further tested against laboratory experiments for bubble-driven plume [72] and oil jet in cross flow [62] in several recent studies [e.g., 1, 97]. Here we focus on testing the performance of the new LES model for capturing the gas dissolution effect.

In the test case, the physical parameters of the environmental and plume conditions were set to match with those used in the integral plume model computation in [106]. In

particular, the seawater temperature was assumed to vary linearly with the depth

$$T(z) = T_b + \gamma z, \quad 0 \leq z \leq L_z, \quad (2.30)$$

where γ is the vertical temperature gradient, T_b is the seawater temperature at the bottom of the simulation domain (i.e. at $z = 0$ m), and L_z is the domain height. Following [106], these parameters were set to be $\gamma = 0.02 \text{ K m}^{-1}$, $T_b = 284.15 \text{ K}$, and $L_z = 700 \text{ m}$. Following [106], a constant salinity of 35‰ was considered and the corresponding background density stratification was set up accordingly. In the test case, methane bubbles with a uniform initial equivalent diameter of $d_{e,0} = 12 \text{ mm}$ were released from a localized source at $z = 0$ m with a volume release rate of $Q_v^0 = 3.2752 \text{ normal m}^3/\text{s}$ (i.e. defined under normal condition at the sea level) [106]. The corresponding mass release rate of methane is $Q_c = 2.32 \text{ kg/s}$. Oil droplets with density $\rho_d = 893 \text{ kg/m}^3$ and diameter $d_d = 0.5 \text{ mm}$ were also released from the same source location with a mass release rate of 16.4 kg/s . In addition, the dye (i.e. passive tracer) was released from the source with a mass release rate of 1 g/s .

In the test case, a domain of $(L_x, L_y, L_z) = (700, 700, 700) \text{ m}$ was used for the LES. Three test runs with different grid numbers for the spatial discretization were considered, including a coarse-grid case with $N_x \times N_y \times N_z = 192 \times 192 \times 256$ points, a medium-grid case with $256 \times 256 \times 320$ points, and a fine-grid case with $320 \times 320 \times 384$ points. These three cases are named as LS-12D-L, LS-12D-M, and LS-12D-H, respectively. The simulation time steps used for these LES runs with different grid resolutions were $\Delta t = 0.2 \text{ s}$ for the coarse-grid case, and 0.1 s for the medium- and fine-grid cases. The simulation cases for the current test as well as for the results reported in section 4.3.2 are listed in Table 2.1.

Similar to the LES study reported in [97], we used the no-slip condition at the bottom boundary, the free-slip condition at the top boundary, and the periodic boundary conditions in the horizontal directions associated with the pseudo-spectral method. Note that [97] obtained good agreement with the laboratory experimental data of [72] by performing LES using a domain with an aspect ratio of $0.67 : 0.67 : 1$ (for $L_x : L_y : L_z$), which was found to be sufficient to avoid artificial effect from the periodic horizontal boundary conditions. The current domain aspect ratio of $1 : 1 : 1$ is expected to provide sufficient horizontal space for the expansion of the horizontal intrusion layers from the plume.

The general dynamics of multiphase buoyancy plume in stratified flow environment has been studied experimentally and numerically in prior studies [24, 53, 68, 72, 79, 83, 97]. Here the physical processes are briefly summarized. The multiphase plume consisting of methane bubbles, oil droplets and dye tracer is released from a localized source at the initial time $t = 0$ s. Due to the density difference between the methane bubbles and the ambient seawater, the buoyancy induced by the bubbles provides the main driving force for the multiphase plume to rise upwards. The turbulence eddies entrain the ambient seawater into the plume as it rises, and lifts the entrained seawater to higher elevations where the ambient seawater has smaller density due to the stable stratification. The density difference between the entrained and ambient seawater results in a downward force to act against the buoyancy induced by the bubbles. In the meantime, the methane in the bubbles gets dissolved continuously into the surrounding seawater, causing the plume to lose the buoyancy when rising. Once the plume reaches a height where the downward force due to entrained seawater can overcome the buoyancy from the remaining gas bubbles, the entrained seawater in the plume starts to slow down and eventually reaches the maximum rising elevation,

Table 2.1: List of large-eddy simulation cases. In the table, $d_{e,0}$ is the initial equivalent bubble diameter at the plume source.

Case	Gas dissolution	Stratification	$d_{e,0}$	Grid number	Time step
LS-12D-L	Modeled	linear	12 mm	$192 \times 192 \times 256$	0.2 s
LS-12D-M	Modeled	linear	12 mm	$256 \times 256 \times 320$	0.1 s
LS-12D0-M	Modeled ^a	linear	12 mm	$256 \times 256 \times 320$	0.1 s
LS-12N-M	Not modeled	linear	12 mm	$256 \times 256 \times 320$	0.1 s
LS-12D-H	Modeled	linear	12 mm	$320 \times 320 \times 384$	0.1 s
QS-3D	Modeled	quadratic	3 mm	$256 \times 256 \times 320$	0.1 s
QS-6D	Modeled	quadratic	6 mm	$256 \times 256 \times 320$	0.1 s
QS-12D	Modeled	quadratic	12 mm	$256 \times 256 \times 320$	0.1 s
QS-18D	Modeled	quadratic	18 mm	$256 \times 256 \times 320$	0.1 s
QS-3N	Not modeled	quadratic	3 mm	$256 \times 256 \times 320$	0.1 s
QS-6N	Not modeled	quadratic	6 mm	$256 \times 256 \times 320$	0.1 s
QS-12N	Not modeled	quadratic	12 mm	$256 \times 256 \times 320$	0.1 s
QS-18N	Not modeled	quadratic	18 mm	$256 \times 256 \times 320$	0.1 s

^aIn case LS-12D0-M, the methane is treated as ideal gas.

from where the heavier entrained seawater peels from the inner rising plume to form an annular plume that falls down along the outside of the inner rising plume [4, 79, 81].

Figure 2.1 shows the instantaneous plume flow and scalar fields for case LS-12D-M obtained from the LES. Here the contours on the (x, z) -plane across the centre of the plume are shown: (a) bubble mass concentration (in kg/m^3); (b) bubble number density (in m^{-3}); (c) bubble diameter (in mm); (d) bubble mass dissolution rate (in $\text{kg/m}^3\text{s}$); (e) mass concentration of dissolved gas in the water (in kg/m^3); (f) dye concentration (in g/m^3); (g) vertical velocity of plume flow (in m/s); (h) horizontal velocity of plume flow (in m/s); (i) oil droplets mass concentration (in kg/m^3).

In the Figure 2.1, the representative snapshots of the plume structure at $t = 8000\text{s}$ are shown, in which the contours of several key physical quantities obtained from the LES are shown on the (x, z) -plane across the plume center line. The LES model obtains the instantaneous bubble mass concentration C_b (Figure 2.1a) and number density N_b (Figure 2.1b) by solving their transport equations, based on which the local cell-averaged bubble diameter (Figure 2.1c) and bubble gas dissolution rate (Figure 2.1d) are modeled. The methane gas in the bubbles gets dissolved into the surrounding seawater at the modeled instantaneous gas mass dissolution rate, causing the bubble diameter to reduce with height from the source (Figure 2.1c). Consequently, the bubble mass concentration (Figure 2.1a) decreases as the plume rises, and becomes negligible above $z = 180\text{m}$. In the height range of $180\text{m} \lesssim z \lesssim 200\text{m}$, the bubble number density (Figure 2.1b) appears to be high due to the accumulation of tiny bubbles, which have negligible rise velocities and buoyancy effects. These tiny bubbles are found to be fully dissolved below $z = 200\text{m}$.

The plume dynamics can be seen from the contours of the vertical velocity w (Fig-

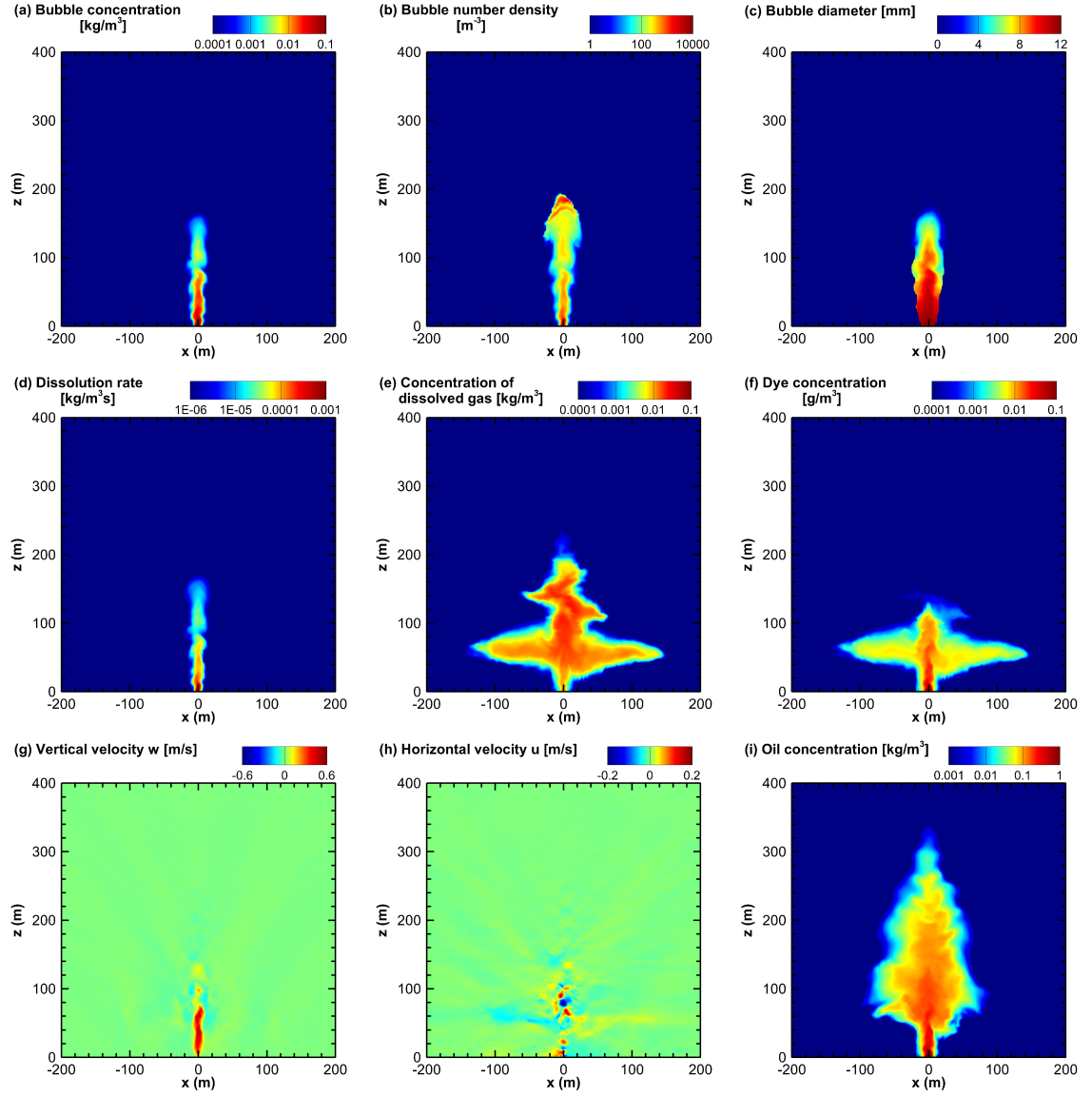


Figure 2.1: Instantaneous plume flow and scalar fields for case LS-12D-M obtained from the LES.

ure 2.1g) and horizontal velocity u (Figure 2.1h). The plume is released with zero initial velocity right at the source, but quickly reaches a noticeable vertical velocity due to the bubble-induced buoyancy. The horizontal gradient of the vertical velocity induces the shear instability and generates turbulent motions as the plume rises, causing the fluctuation of the horizontal velocity that entrains ambient seawater into the plume to rise together with the methane bubbles and oil droplets. Due to the stable stratification of the ambient environment, the seawater entrained at lower elevation has higher density than the surrounding environment when lifted to higher elevations by the plume, resulting in a downward force to the plume flow (i.e. the first Boussinesq term on the right-hand side of Eq. (4.25)). This downward force caused by density stratification increases as the entrained seawater rises while the buoyancy of bubbles decreases with height due to the continuous gas dissolution, which causes the plume to decelerate and eventually starts falling at around $z = 140\text{m}$. This maximum height of the plume rise is named the peel height [80]. The higher density seawater entrained into the plume at lower elevation detrains from the plume at the peel height to form an annular downward plume outside the inner rising plume, as indicated by the negative vertical velocity in Figure 2.1(g). The peeling process is unsteady due to the highly dynamic interactions and counter motions between the inner and outer plumes, which has been studied in detail in previous studies [72, 97].

During the strong peeling process, the dissolved methane (Figure 2.1e) and dye (Figure 2.1f) are carried by the detrained seawater to fall together along the downward outer plume, and then transported horizontally to form an intrusion layer at around $z = 60\text{m}$ where the detrained seawater reaches the new equilibrium height in density. Note that the dye concentration is negligible above $z = 140\text{m}$, indicating that most of the seawater

entrained and carried by the plume from lower elevation near the source gets detrained from the rising plume at the peel height at $z = 140\text{m}$. This is consistent with the large peeling fraction in deep-sea blowout condition reported in [82]. Note that when the remaining undissolved gas bubbles continue to rise up to $z = 200\text{m}$ (Figure 2.1b) before getting fully dissolved, they continue to contribute to the concentration of the dissolved gas (Figure 2.1e), allowing us to visualize the secondary peel and intrusion events above the primary peel height ($z = 140\text{m}$) that is not visible from the contours of the dye concentration (Figure 2.1f).

The oil droplets with 0.5mm diameter behave differently from other passive scalars (e.g., dye and dissolved gas) in the plume. Initially the oil droplets rise upwards along the narrow inner plume together with the bubbles and entrained seawater. At the peel height, the oil column expands horizontally due to the horizontal velocity associated with the peeling process. Additional entrainment of the oil droplet from the inner plume also occurs below the primary peel height (at $z = 140\text{m}$) due to the turbulence in the shear layer between the inner and outer plumes. The combined effect of the peeling and turbulent entrainment processes results in a noticeable expansion of the oil column starting from $z = 40\text{m}$. Different from passive scalars, the oil droplets have small but non-negligible rise velocity relative to the surrounding seawater flow. As a result, the oil droplets can escape from the falling outer plume and continue to rise slowly by its own buoyancy even after all the gas bubbles are fully dissolved. Similar behavior of the oil droplet plume was observed in the laboratory study of [15] in their Type-1a* plumes.

Figure 2.2 shows the mean bubble diameter inside the inner plume as a function of the vertical elevation. The LES results for three different simulation conditions are plotted:

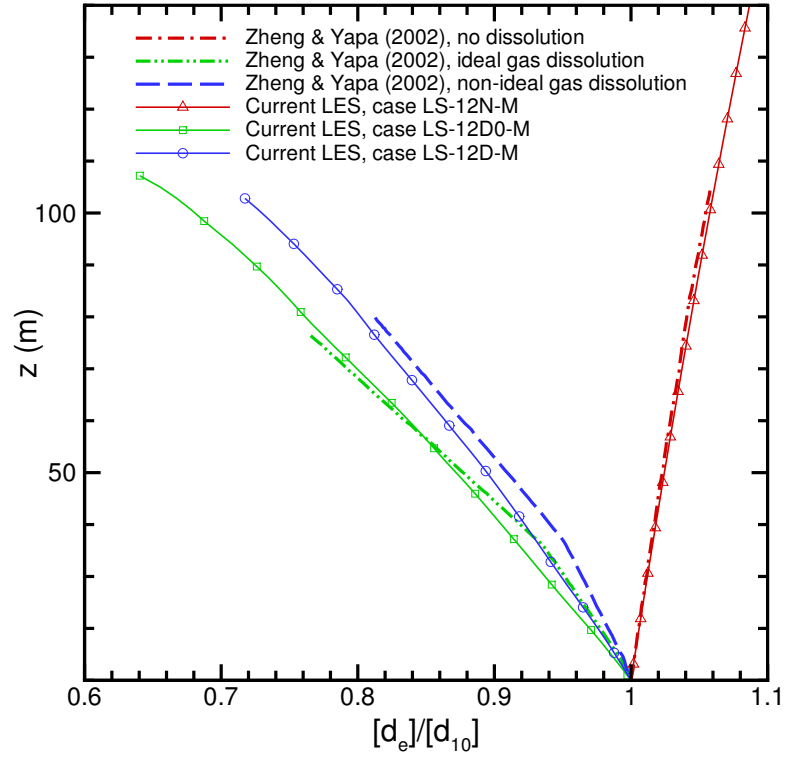


Figure 2.2: Variation of bubble diameter with height. The LES results for three different simulation conditions are plotted: case LS-12N-M, case LS-12D0-M, and case LS-12D-M.

case LS-12N-M (without gas dissolution), case LS-12D0-M (with gas dissolution based on ideal gas law), and case LS-12D-M (with gas dissolution based on non-ideal gas law). The corresponding integral model predictions from [106] are also plotted for comparison. The equivalent bubble diameter d_e is normalized by the reference diameter d_{10} at $z = 10$ m above the plume source.

Here the mean bubble diameter at the elevation z is estimated as

$$[d_e](z) = \left(\frac{6 \int_0^{b_i} \langle \tilde{C}_b \rangle 2\pi r dr}{\pi \rho_b \int_0^{b_i} \langle \tilde{N}_b \rangle 2\pi r dr} \right)^{1/3}, \quad (2.31)$$

where b_i is the radius of the averaged inner plume, and $\langle \tilde{C}_b \rangle$ and $\langle \tilde{N}_b \rangle$ are the time- and angular-averaged bubble mass concentration and number density, respectively. The predictions from the integral model of [106] are also included in Figure 2.2. Note that in [106], three different integral model computations were performed, including the primary case (Figure 2.1) with gas dissolution based on the modified Henry's law for non-ideal gas under the deep-water environment, as well as a case with gas dissolution based on the Henry's law for ideal gas and a case without gas dissolution. For comparison, the LES runs were performed accordingly by matching the physical parameters as well as the gas dissolution setting. Note that in the integral model of [106], the initial effect of heat transfer between the hot gas bubbles and the ambient seawater was included, resulting in the thermal shrinkage of the bubbles within the first few meters above the plume source. This effect is not included in the current LES model for the sake of model simplicity. Here the comparisons between the current LES model results and the integral plume model prediction by [106] are made for the region above the initial thermal shrinkage region, and the bubble diam-

eters shown in Figure 2.2 are normalized by the corresponding mean bubble diameter at 10m above the source in each case. Above this initial shrinkage region, the case without gas dissolution (i.e. case LS-12N-M) exhibits a monotonic increase of bubble diameter with height due to the reduction of the ambient hydrostatic pressure, while the cases (i.e. cases LS-12D-M and LS-12D0-M) with gas dissolution show a monotonic decrease of bubble diameter with height. The use of the regular Henry's law for idea gas in case LS-12D0-M results in an overestimation of the gas dissolution rate, causing the predicted bubble diameter to reduce more rapidly than that predicted in case LS-12D-M using the modified Henry's law for non-ideal gas. The current LES model shows good agreement with the integral model of [106] for modeling the gas bubble size variation due to gas dissolution and change of hydrostatic pressure. Considering the complexities associated with modeling the plume dynamics and gas mass transfer process, the overall agreement between the two models are considered to be satisfactory.

To test the grid resolution convergence of the LES model, here the simulation results from the cases LS-12D-L ($192 \times 192 \times 256$ grid points), LS-12D-M ($256 \times 256 \times 320$ grid points), and LS-12D-H ($320 \times 320 \times 384$ grid points) are compared.

Here Figure 2.3 shows the comparison of time- and angular-averaged plume flow and scalar fields from LES runs with different grid resolutions: (a–c) case LS-12D-L ($192 \times 192 \times 256$ grid points); (d–f) case LS-12D-M ($256 \times 256 \times 320$ grid points); (h–j) case LS-12D-H ($320 \times 320 \times 384$ grid points). For each LES case, the left panel shows the bubble mass concentration (in kg/m^3), the middle panel shows the vertical velocity of the plume flow (in m/s), and the right panel shows the oil droplets mass concentration (in kg/m^3).

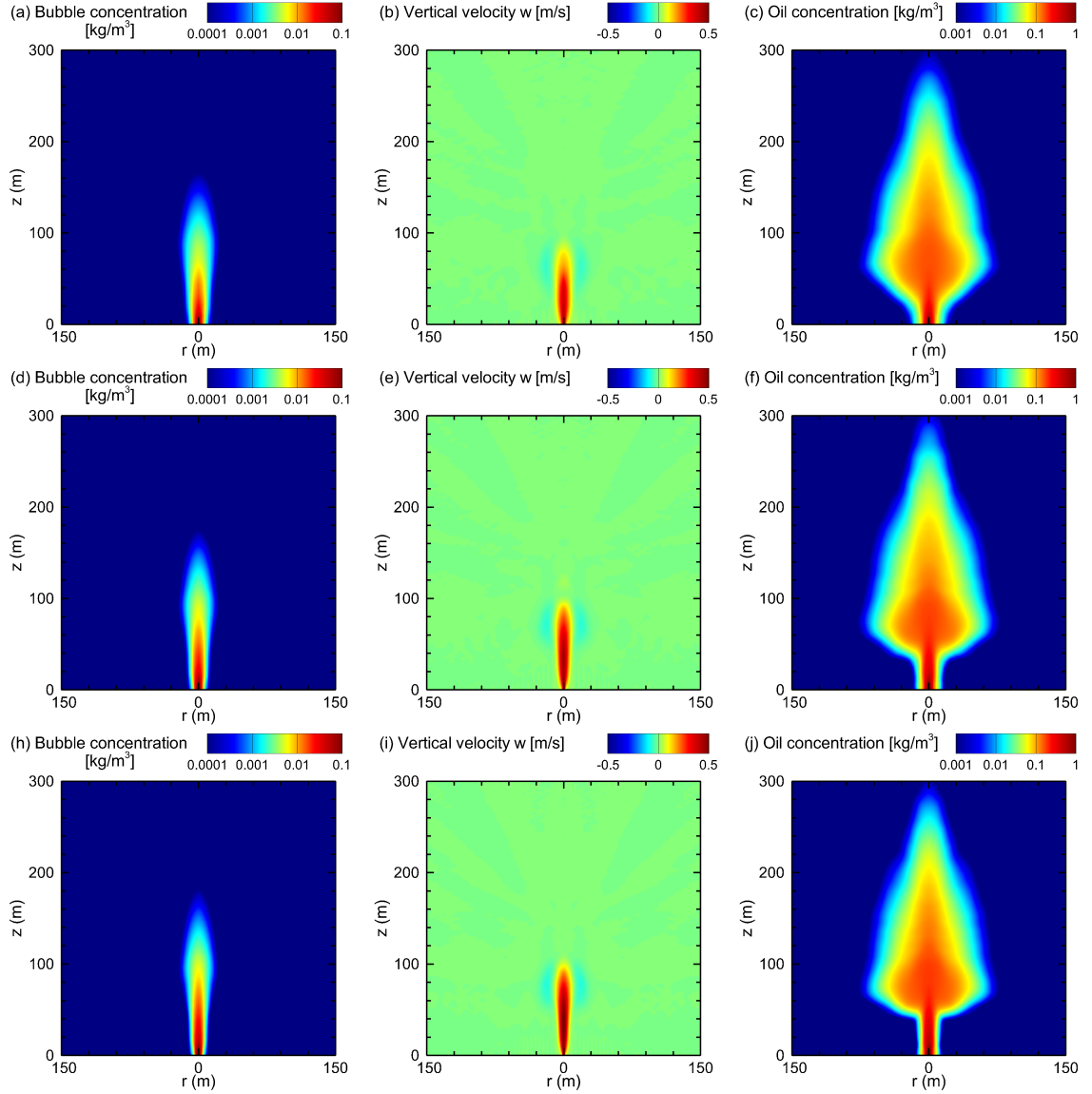


Figure 2.3: Comparison of time- and angular-averaged plume flow and scalar fields from LES runs with different grid resolutions: (a–c) case LS-12D-L; (d–f) case LS-12D-M; (h–j) case LS-12D-H.

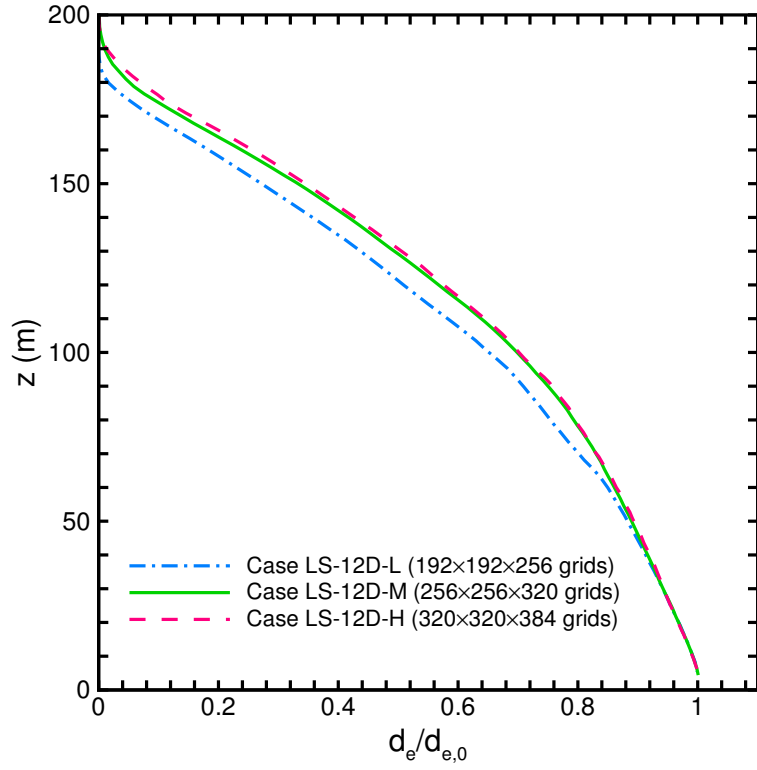


Figure 2.4: Vertical variation of bubble diameter along the center line of the time- and angular-averaged plume obtained from the LES runs with different grid resolutions: case LS-12D-L, case LS-12D-M, and case LS-12D-H.

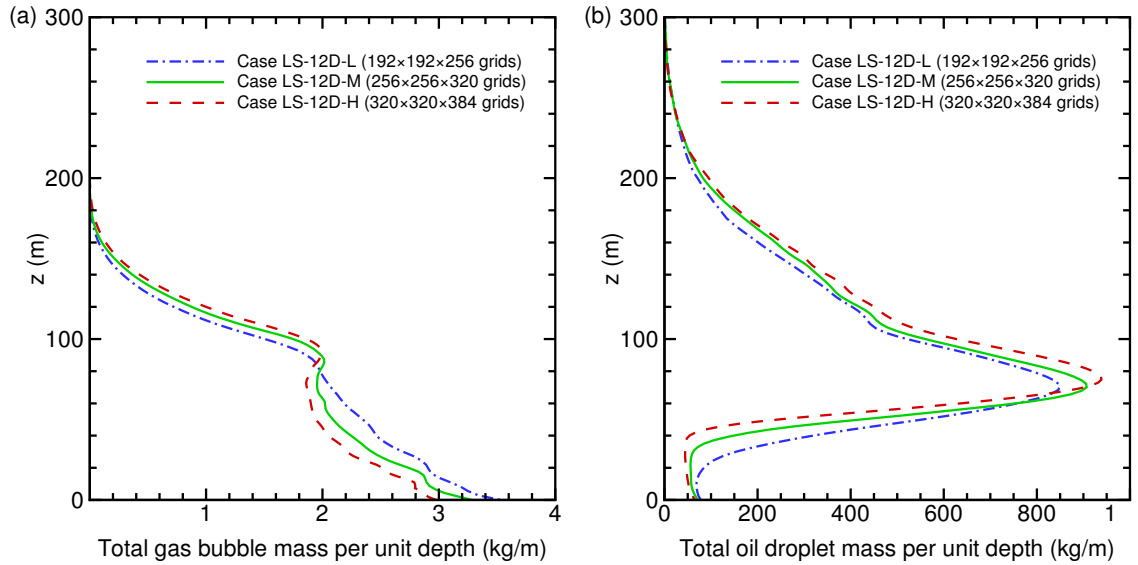


Figure 2.5: Vertical distributions of mass of (a) gas bubbles and (b) oil droplets in the time- and angular-averaged plume obtained from the LES runs with different grid resolutions: case LS-12D-L, case LS-12D-M, and case LS-12D-H.

In Figure 2.3, the gas bubble concentration, vertical velocity of plume flow, and oil droplet concentration of the time- and angular-averaged plume obtained from these three LES cases are shown. Overall, the LES model results exhibit consistent mean plume structures for the three grid resolutions tested here.

Figure 2.4 compares the vertical variations of the bubble diameter along the center line of the time- and angular-averaged plume from the three LES cases. Here the vertical variation of bubble diameter along the center line of the time- and angular-averaged plume obtained from the LES runs with different grid resolutions: case LS-12D-L ($192 \times 192 \times 256$ grid points), case LS-12D-M ($256 \times 256 \times 320$ grid points), and case LS-12D-H ($320 \times 320 \times 384$ grid points).

Figure 2.5 shows the vertical distributions of total masses of gas bubbles and oil droplets per unit depth in the time- and angular-averaged plume obtained from the LES runs with different grid resolutions: case LS-12D-L ($192 \times 192 \times 256$ grid points), case LS-12D-M ($256 \times 256 \times 320$ grid points), and case LS-12D-H ($320 \times 320 \times 384$ grid points). The LES model obtains consistent trends for the center-line bubble diameter as well as the vertical distributions of bubble/droplet masses with the three different grid resolutions. Cases LS-12D-M and LS-12D-H are found to agree fairly well considering the overall complexity of the plume physics and the LES model, which suggests that the medium grid resolution (i.e. with $256 \times 256 \times 320$ grid points) is sufficient for accurately modeling the gas bubble dissolution and capturing its effect on the plume dynamics. Therefore, for other simulation cases reported in this paper (see Table 2.1), the medium grid resolution instead of the high grid resolution is used for the sake of limiting the overall computational cost associated with conducting the simulations and data analyses.

2.4 Effects of gas dissolution and initial bubble size on plume dynamics

The test case with linear seawater stratification discussed in section 2.3 shows that the new LES gas dissolution model developed in the current study can capture the essential dynamics of the multiphase hydrocarbon plume in the deep-water environment. In this section, the LES model is applied to study the effects of gas dissolution and initial bubble size on the nearfield plume dynamics. Similar to the test case in section 2.3, a domain of $(L_x, L_y, L_z) = (700, 700, 700)$ m was used for all the LES cases reported in this section. $N_x \times N_y \times N_z = 256 \times 256 \times 320$ grid points were used for the spatial discretization and the time step was set to be 0.1 s.

Note that in order to match the parameters used in the integral model, the test case reported in section 2.3 uses the same idealized linear seawater stratification considered by [106]. For the LES cases reported in this section, more realistic seawater CDT profiles based on the field data from the Gulf of Mexico R/V Brooks McCall at Station B54 ($28^\circ 43.945'N$, $88^\circ 22.607'W$; 30 May 2010) is used. In particular, the density stratification has a quadratic profile of [82]

$$\rho_w(z) = 1027.77 - 4.60434 \times 10^{-7} \times (z + 800)^2, \quad (2.32)$$

where the vertical coordinate z has the origin at the 700m depth just as in the test case shown in section 2.3. In the simulation, Eq. (2.32) was used to initialize the seawater density. During the simulation, the seawater density field varies dynamically in time and space according to Eqs. (4.26) and (4.25) for modeling the effect of stratification on the

plume dynamics. The temperature profile used in the calculation of the gas dissolution rate (see sections 2.2.1 and 2.2.2) were prescribed based on

$$T(z) = 396.2216 \times (700 - z)^{-0.6205} + 273.15, \quad (2.33)$$

which can be obtained by fitting the temperature data from the R/V Brooks McCall at Station B54 between the 100m and 1546m depth. Note that using the prescribed temperature profile in Eq.(2.33) instead of the instantaneous local temperature from the LES allows us to perform the calculation of gas compressibility factor Z once at the beginning of the simulation instead of performing the calculation at each time step. For the results reported in this section, this simplification only causes error in the estimated gas dissolution rate for less than $\sim 1\%$ for the reported cases, but can significantly reduce the computational cost.

To further explore the effects of gas bubble dissolution on the nearfield plume dynamics, four different initial bubble diameters were considered, including $d_{e,0} = 3$ mm, 6 mm, 12 mm and 18 mm, which are referred to as the cases QS-3D, QS-6D, QS-12D, and QS-18D, respectively. For each initial bubble diameter, an additional reference case without considering gas dissolution was simulated for comparison purpose. These four reference cases are referred to as the cases QS-3N, QS-6N, QS-12N, and QS-18N, respectively. Table 2.1 summarizes the eight simulation cases considered in this section. In these eight cases, other simulations parameters (such as the simulation domain size, the source release rates of gas bubbles, oil droplets, and dye) were set to be identical to the test cases reported in section 2.3.

Figure 2.6 shows the instantaneous flow and scalar fields contours on the (x, z) -plane

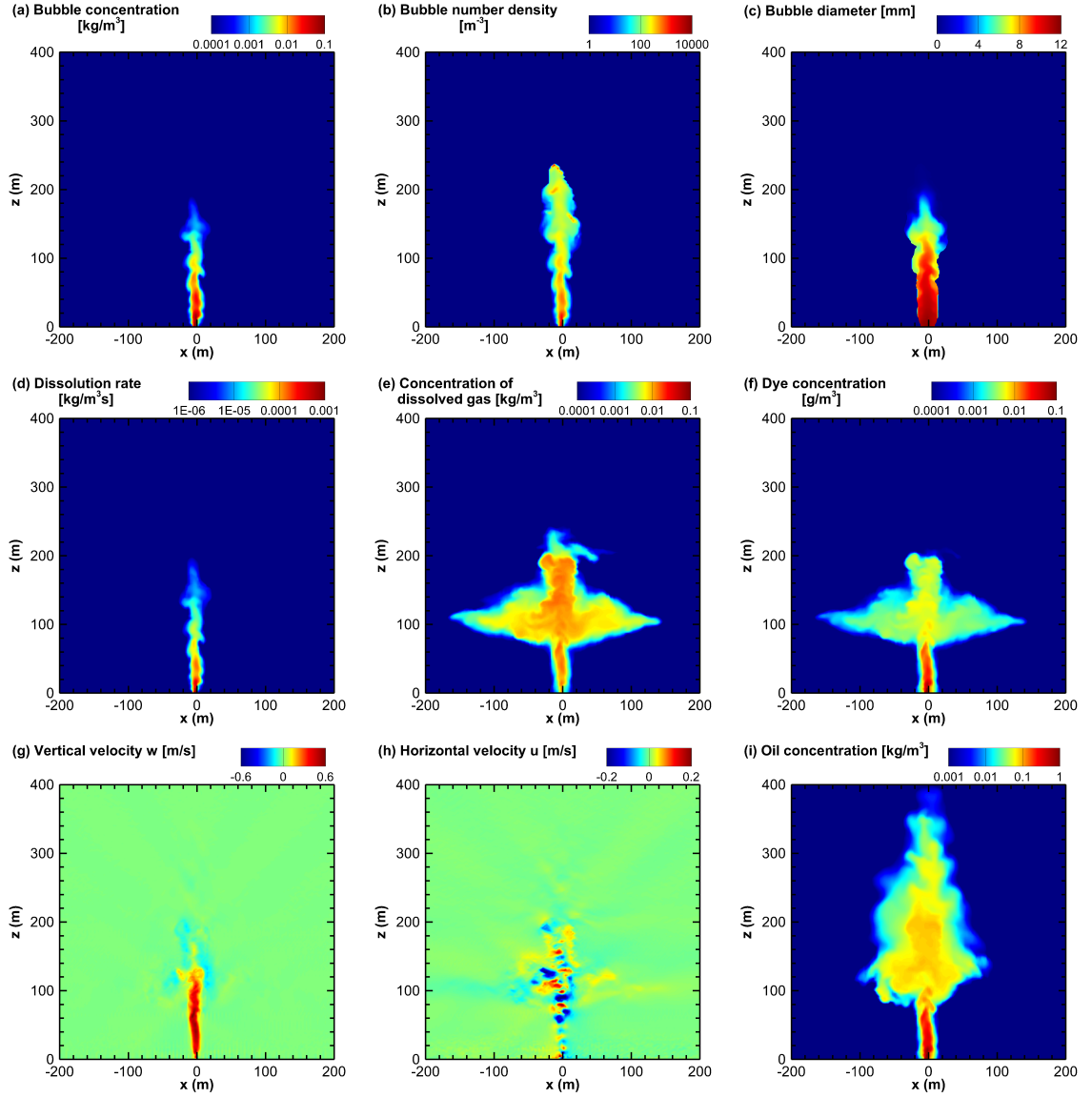


Figure 2.6: Instantaneous plume flow and scalar fields for case QS-12D obtained from the LES. Here the contours show the instantaneous flow and scalar fields on the (x, z) -plane across the center line of the plume at $t = 8000$ s.

across the center line of the plume at $t = 8000$ s: (a) bubble mass concentration (in kg/m^3); (b) bubble number density (in m^{-3}); (c) bubble diameter (in mm); (d) bubble mass dissolution rate (in $\text{kg/m}^3\text{s}$); (e) mass concentration of dissolved gas in the water (in kg/m^3); (f) dye concentration (in g/m^3); (g) vertical velocity of plume flow (in m/s); (h) horizontal velocity of plume flow (in m/s); (i) oil droplets mass concentration (in kg/m^3). Note that case QS-12D has a weaker density stratification near the source (due to the quadratic density profile) than that in case LS-12D-M, while other simulation parameters are identical between the two cases. Consequently, the basic structures of the instantaneous plume appear to be similar between the two cases, but the peel and trap heights as well as the maximum elevation of the gas bubbles in case QS-12D are higher than the corresponding ones in the test case LS-12D-M.

Figure 2.7 compares some of the instantaneous plume features (i.e. the mass concentrations of the bubbles, dye and oil droplets) between case QS-12N (without gas dissolution) and case QS-12D (with gas dissolution). In Figure 2.7, Panels (a) and (b) show the bubble mass concentration $\tilde{C}_b$ (in kg/m^3); (c) and (d) show the dye concentration $\tilde{C}_{dye}$ (in g/m^3); (e) and (f) show the oil droplet mass concentration $\tilde{C}_d$ (in kg/m^3). The contours on the (x, z) -plane across the centre of the plume are shown. Without considering the gas dissolution effect, the simulation results from case QS-12N show that the gas bubbles rise continuously towards the ocean surface, with the local gas concentration diluted due to the turbulent entrainment as well as the horizontal motions in the peeling region at around $z = 300$ m (Figure 2.7a). The persistence of the bubble buoyancy without the gas dissolution effect also causes the plume flow motion to be strong, resulting in strong turbulent mixing between the rising inner plume and the falling outer plume as well as the ambient

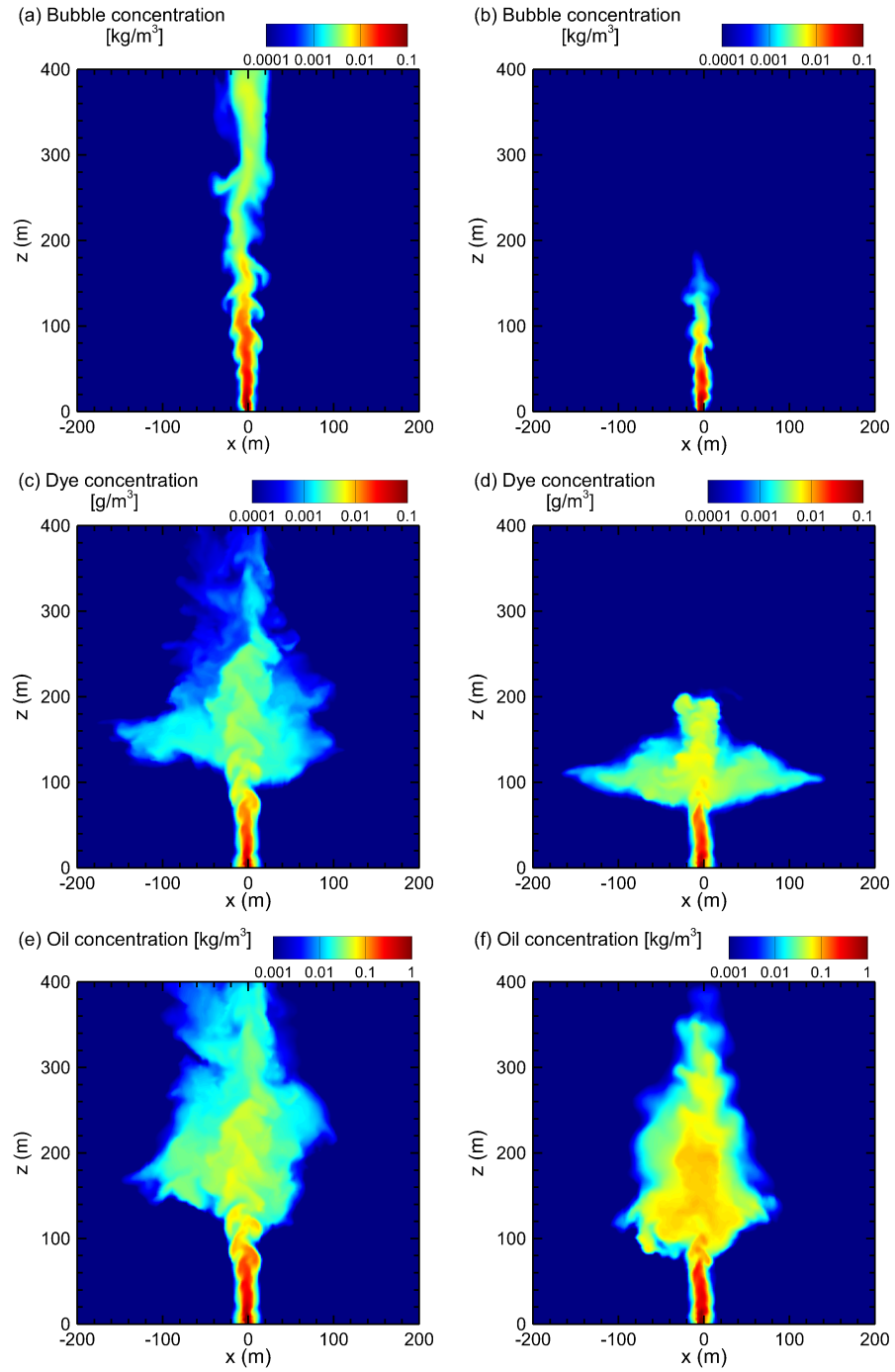


Figure 2.7: Comparison of the instantaneous plume features between case QS-12N(a, c, e) and case QS-12D (b, d, f). Here the contours on the (x, z) -plane across the centre of the plume are shown.

environment as shown by the diluted dye and oil concentrations in $100\text{ m} < z < 400\text{ m}$ (Figures 2.7c and 2.7e). In contrast, the gas dissolution effect considered in case QS-12D causes the gas bubbles to be fully dissolved below $z = 200\text{ m}$ (Figure 2.7b), resulting in a distinct maximum elevation of the dye at around $z = 200\text{ m}$ when the entrained seawater peels from the plume and falls down along the outer plume after the plume loses all the driving force from the bubble buoyancy (Figure 2.7d). Above the peel height (around $z = 200\text{ m}$), in case QS-12D the vertical velocity of the plume fluid has vanished (Figure 2.6g) and the oil droplets continue to rise due to their own buoyancy (Figure 2.7f).

To make more quantitative comparison among different simulation cases with and without gas dissolution, time- and angular-average is performed to obtain the mean plume structure within $0 \leq z \leq 400\text{ m}$. In particular, 400 three-dimensional instantaneous snapshots of the plume (sampled between $t = 4000\text{ s}$ and 20000 s with a constant time interval of 40 s) are used as the samples for time average for each simulation case, and each time-averaged field is further averaged in the angular direction considering the axisymmetry of the mean plume structure [97]. Note that for computing the mean oil concentration field, only the 100 snapshots from $t = 16000\text{ s}$ to 20000 s are used for time average. This is because the oil droplets continue to rise after the bubbles are fully dissolved, causing the oil concentration field to take longer time to reach the statistically steady state within the sampling region (i.e. $0 \leq z \leq 400\text{ m}$).

Figure 2.8 shows the averaged gas mass dissolution rate α for the four cases with the gas dissolution effect modeled. Varying the initial bubble diameter induces two main effects. First, the bubbles with smaller initial diameter have smaller rise velocities and take longer time to rise through the same vertical distance than the larger bubbles. Second,

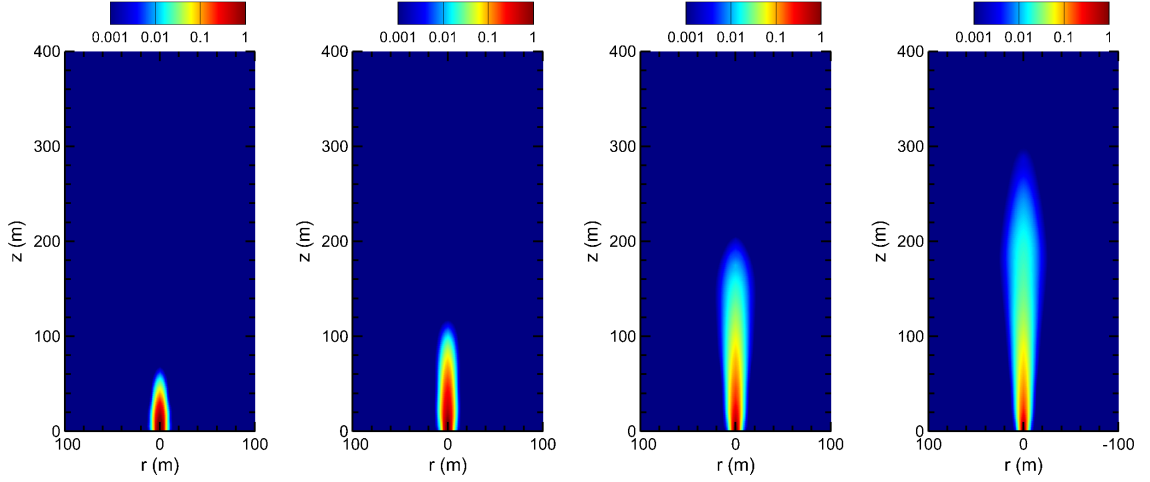


Figure 2.8: Angular- and time-averaged bubble gas mass dissolution rate α (in $\text{kg/m}^3\text{s}$): (a) case QS-3D; (b) case QS-6D; (c) case QS-12D; (d) case QS-18D.

smaller bubbles have higher surface area to volume ratio than larger bubbles. Therefore, with the same gas release rate, a case with a smaller bubble diameter would have a larger total effective bubble surface area than a case with larger bubbles, allowing for more efficient mass transfer through the bubble surfaces. As a result, the gas dissolution rate α is significantly high near the source for case QS-3D, and becomes smaller as the initial bubble diameter increases to allow the bubbles survive over longer travel distance (Figure 2.8).

Figure 2.9 shows contours of the time- and angular-averaged bubble mass concentrations, in which the results for the cases with and without gas dissolution for the same initial bubble diameter are plotted side by side in each figure panel. The subfigures in the Figure 2.9 are, (a) cases Qs-3N (left half) and QS-3D (right half); (b) cases QS-6N (left half) and QS-6D (right half); (c) cases QS-12D (left half) and QS-12D (right half); (d) cases QS-18N (left half) and QS-18D (right half). Without considering the gas bubble dissolution, all the four simulation cases (i.e. QS-3N, QS-6N, QS-12N and QS-18N)

with different initial bubble diameters show similar structure for the mean bubble mass concentration (Figure 2.9): the bubble column extends continuously upward, and the local bubble mass concentration gradually decreases with height when the bubble column width expands due to the turbulent mixing and the radial flow motions associated with the peeling process. When the gas dissolution effect is considered in the LES, the height of the bubble column exhibits strong dependence on the initial bubble diameter due to the different gas dissolution rates shown in Figure 2.8. In particular, for cases QS-3D, QS-6D, QS-12D and QS-18D, the corresponding height of the mean bubble column (based on the averaged bubble mass concentration) increases monotonically as around 50 m, 100 m, 190 m and 280 m, respectively. Note that here the height of the bubble column is estimated based on the bubble mass concentration due to its significance on determining the bubble-induced buoyancy. As shown later in Figure 2.14(a), the individual gas bubbles can survive up to a higher elevation, where the bubbles have been dissolved to become too small to have noticeable effect on the plume dynamics (also see Figures 2.6a and 2.6b).

A more quantitative comparison of the mean gas bubble field between the cases with and without gas dissolution is shown in Figure 2.10, which shows the vertical distributions of the total gas bubble mass per unit depth obtained by horizontally averaging the mean bubble mass concentrations shown in Figure 2.9. With the gas dissolution effect considered, a plume with a smaller initial bubble diameter exhibits more rapid decay of the total bubble mass per depth in comparison to a plume with a larger initial bubble diameter. In contrast, the simulation results show an opposite trend if the gas dissolution is not considered, with the plumes of smaller bubbles exhibiting higher total bubble mass per depth than those with larger bubbles due to the accumulation of smaller bubbles with smaller rise velocity.

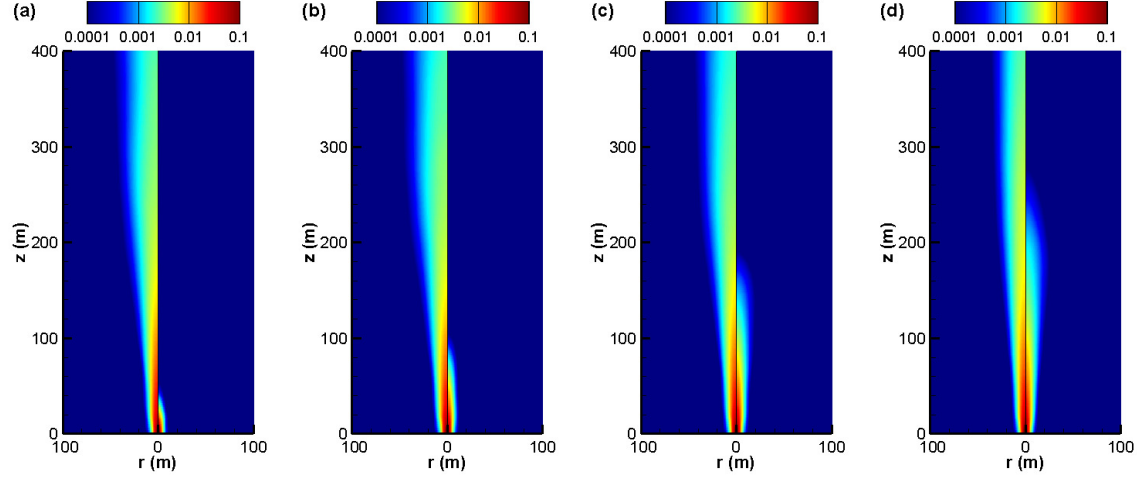


Figure 2.9: Time- and angular-averaged bubble mass concentration C_b (in kg/m^3): (a) cases QS-3N (L) and QS-3D (R); (b) cases QS-6N (L) and QS-6D (R); (c) cases QS-12D (L) and QS-12D (R); (d) cases QS-18N (L) and QS-18D (R).

This opposite trend for the four cases without gas dissolution is also not exactly monotonic (see cases QS-3N and QS-6N). Overall, the omission of the gas dissolution effect in the simulation result in unphysical concentration of gas bubbles continuously through the depth of the simulation domain.

Associated with the change of the bubble mass concentration, the peel height where the entrained seawater reaches the maximum elevation also varies significantly according to the initial bubble diameter. This can be seen from the contours of the mean vertical velocity of the plume shown in Figure 2.11.

In Figure 2.11, The time- and angular-averaged vertical velocity w (in m/s) are shown: (a) cases QS-3N (left half) and QS-3D (right half); (b) cases QS-6N (left half) and QS-6D (right half); (c) cases QS-12D (left half) and QS-12D (right half); (d) cases QS-18N (left half) and QS-18D (right half). The solid black lines indicate the contour lines of

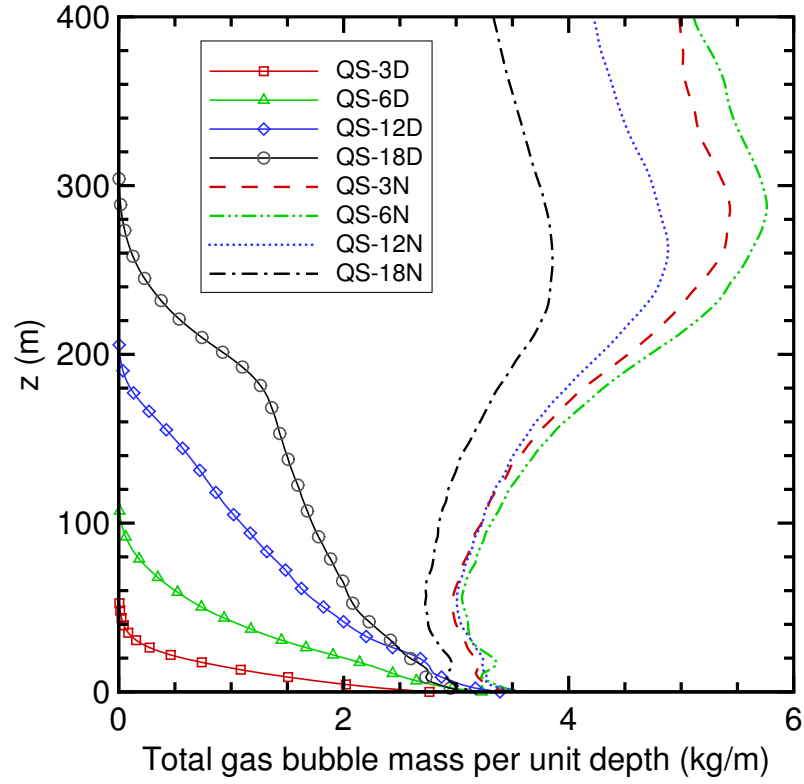


Figure 2.10: Vertical distribution of total gas bubble mass for the time- and angular-averaged plumes shown in Figure 2.9.

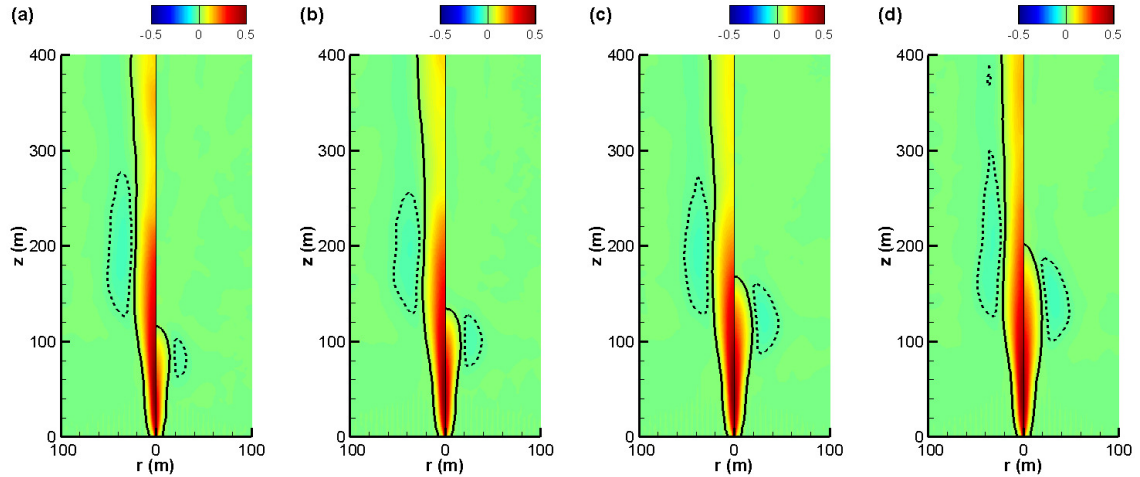


Figure 2.11: Time- and angular-averaged vertical velocity w (in m/s). The solid black lines indicate the contour lines of $w = 0.02 m/s$ and the dashed black lines indicate the contour lines of $w = -0.02 m/s$.

$w = 0.02$ m/s and the dashed black lines indicate the contour lines of $w = -0.02$ m/s.

For case QS-3D, although the bubble mass concentration reduces to a negligible level above $z \approx 50$ m (Figure 2.9a), the plume flow has gained sufficient upward momentum and continues to rise to around $z \approx 120$ m (Figure 2.11a). At this maximum elevation, the entrained seawater with higher density than the local ambient seawater falls down along the outer plume around the inner plume, as indicated by the negative contours of the mean vertical velocity in Figure 2.11(a). Similar situation occurs in case QS-6D, for which the mean plume flow can reach around $z \approx 140$ m (Figure 2.11b) while the bubbles get dissolved to a negligible mass concentration level at a lower elevation of $z \approx 100$ m (Figure 2.9b). For case QS-12D, the maximum elevation of the inner plume flow (i.e. the peel height) is at around $z \approx 170$ m (Figure 2.11c), which is slightly below the height of $z \approx 190$ m where the bubbles get fully dissolved (Figure 2.9c). For case QS-18D, although the relatively low gas bubble dissolution rate allows the bubble column to reach around $z \approx 290$ m (Figure 2.9d), the continuous lifting of higher density seawater entrained from lower elevation as well as the reduction of bubble buoyancy due to gas dissolution cause the plume flow to slow down and peel at around $z \approx 200$ m (Figure 2.11d). As the initial bubble diameter increases, the four cases with gas dissolution effect exhibit an increase of intensity for the peeling process, as indicated by the increase of the outer plume size (see the negative vertical velocity contours in Figure 2.11). For all the four initial bubble diameters, the LES runs with the gas bubble dissolution effect considered show a significantly lower peel height than the corresponding LES runs without considering gas dissolution (i.e. the right half versus the left half in each panel of Figure 2.11).

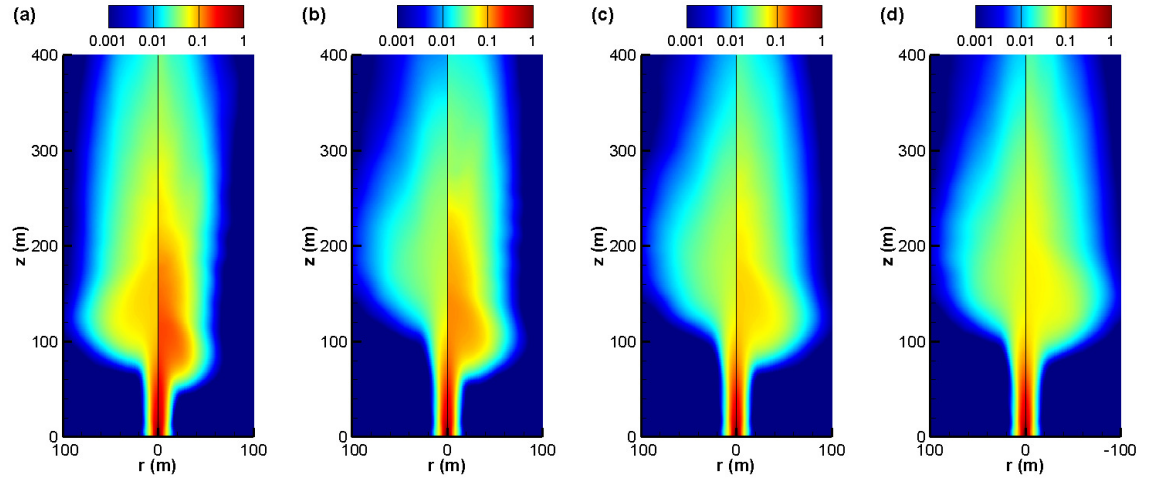


Figure 2.12: Time- and angular-averaged oil concentration $\tilde{C}_d$ (in kg/m^3): (a) cases Qs-3N (L) and QS-3D (R); (b) cases QS-6N (L) and QS-6D (R); (c) cases QS-12D (L) and QS-12D (R); (d) cases QS-18N (L) and QS-18D (R).

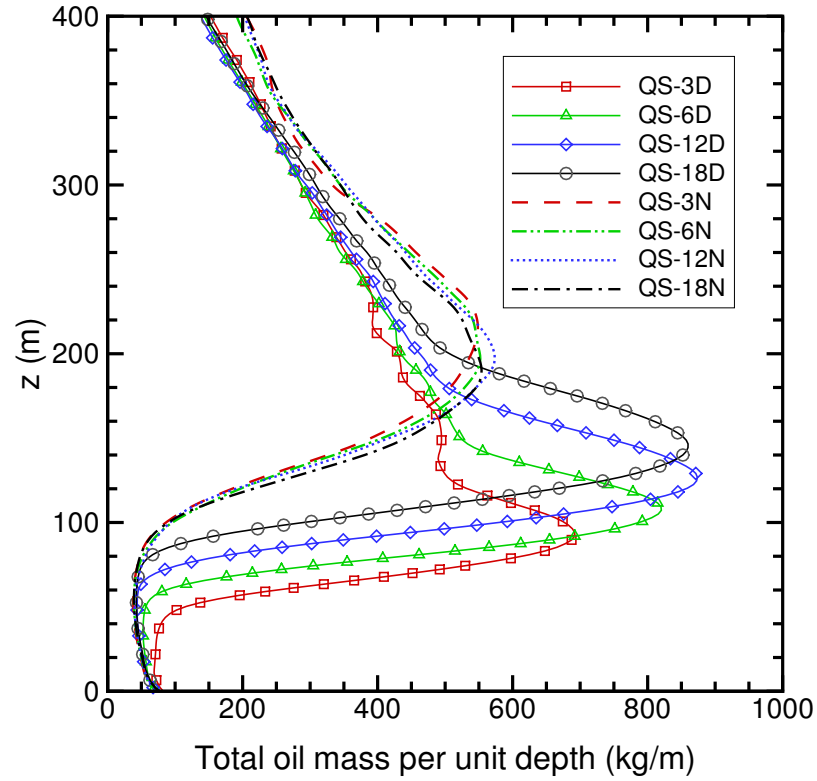


Figure 2.13: Vertical distribution of total oil droplet mass for the time- and angular-averaged plumes shown in Figure 2.12.

Being affected by the dynamics of the plume, the concentration of the oil droplets also shows strong dependence on the initial bubble diameter (Figure 2.12). Figure 2.12 shows the time- and angular-averaged oil concentration $\tilde{C}_d$ (in kg/m^3): (a) cases Qs-3N (left half) and QS-3D (right half); (b) cases QS-6N (left half) and QS-6D (right half); (c) cases QS-12D (left half) and QS-12D (right half); (d) cases QS-18N (left half) and QS-18D (right half). The oil droplets experience lateral dispersion away from the inner plume due to the turbulent mixing between the countercurrent inner and outer plumes as well as the lateral flow motions of the peeling process (see Figures 2.6g and 2.6i). In the four cases with gas bubble dissolution modeled, the oil droplets eventually escape from the inner and outer plumes and continue to rise by their own buoyancy, without further experiencing significant lateral dispersion above the peel height. As shown in Figure 2.12, for the four simulation cases with gas dissolution effect, the oil concentrations are more diluted and laterally spread in the cases with larger initial bubble size. For example, in case QS-3D (Figure 2.12a) the upward plume flow is weak and has limited vertical extension due to the rapid dissolution of the small gas bubbles, which results in weak turbulent entrainment and peeling process for lateral oil dispersion. In case QS-18D (Figure 2.12d) the large bubbles induce strong inner/outer plumes and peeling process to help disperse the oil droplets laterally away from the inner plume and dilute the oil concentration. In contrast, when the gas dissolution effect is not considered, the simulation results for all the four initial bubble diameters show significantly more dilution of the oil concentration compared to the corresponding simulation cases with the gas dissolution effect considered. The overall oil transport process is dominated by the effect of the continuously rising bubble column without the proper gas dissolution effect being included.

For a more quantitative comparison of the plumes of 0.5 mm oil droplets, the mean oil droplet mass concentrations of the 8 cases shown in Figure 2.12 are integrated horizontally to obtain the vertical distributions of the total oil droplet mass per unit depth. Figure 2.13 compares results for the cases with and without the gas bubble dissolution. For each vertical profile of the oil droplet mass distribution, there exists a distinct peak corresponding to the height of the intrusion layer. If the gas dissolution effect is included, the intrusion layer shift upwards as the initial bubble diameter increases because of the higher maximum elevation that the gas bubble column that the reach before full dissolution. Specifically, the oil intrusion layer is located at $z \approx 94$ m for case QS-3D, at $z \approx 107$ m for case QS-6D, at $z \approx 127$ m for case QS-12D, and at $z \approx 147$ m for case QS-18D. The omission of the gas dissolution effect in the simulation causes consistent overestimation of the oil plume intrusion layer for the plumes with all the four different initial bubble diameters, i.e. $z \approx 214$ m for case QS-3N, $z \approx 197$ m for case QS-6N, $z \approx 197$ m for case QS-12N, and $z \approx 190$ m for case QS-18N. Overall, the relative error is in the range of 30%–127%, with larger relative error for the cases with smaller initial bubble diameter.

Several mean plume properties can also be calculated based on the smooth flow and scalar quantity fields of the time- and angular-averaged plume to show the vertical variation of the mean plume characteristics under the influence of gas bubble dissolution. Figure 2.14(a) shows the vertical variation of the mean bubble diameter (normalized by the corresponding initial bubble diameter). Consistent with the time- and angular-averaged gas bubble dissolution rate (Figure 2.8), the cases with smaller initial bubble diameters show more rapid decrease of the mean bubble diameter with height than the cases with larger initial bubble diameters.

The reduction of the bubble size causes the bubble-induced buoyancy flux in the inner plume to reduce continuously as the plume rises. The mean buoyancy flux of the gas bubbles can be calculated as

$$B_g = \int_0^{b_i} \left(\frac{\rho_0}{\rho_b} - 1 \right) \langle \tilde{C}_b \rangle \langle \tilde{w} \rangle g 2\pi r dr. \quad (2.34)$$

Figure 2.14(b) shows the vertical variation of the bubble-induced buoyancy flux B_g in the inner plume. For all the simulation cases, near the source of release the magnitude of B_g increases with height due to the initial acceleration of the vertical plume velocity $\langle \tilde{w} \rangle$ and the accumulated bubble concentration $\langle \tilde{C}_b \rangle$. As the elevation further increases, for the cases with bubble gas dissolution considered, B_g decreases rapidly as the bubbles get dissolved. For cases QS-3D and QS-6D, B_g reduces to a negligible level at around $z = 50\text{m}$ and 100m , respectively. These heights are consistent with the maximum heights of the mean bubble mass concentration contours shown in Figures 2.9(a) and 2.9(b). For cases QS-12D and QS-18D, B_g reduces to zero at around $z = 170\text{m}$ and 200m , respectively, where the corresponding bubble concentration $\langle \tilde{C}_b \rangle$ is still significant but the plume vertical velocity $\langle \tilde{w} \rangle$ has reduced to zero and the peeling process occurs. Comparison among the four cases with gas dissolution effect shows that the magnitude of B_g increases monotonically as the initial bubble diameter increases due to the effect of the monotonic decrease of gas bubble dissolution rate α shown in Figure 2.8.

The response of the plume flow to the variation of bubble buoyancy and seawater strat-

ification can be seen from Figure 2.14(c) based on the mean momentum flux,

$$M = \int_0^{b_i} \langle \tilde{\rho} \rangle \langle \tilde{w} \rangle^2 2\pi r dr. \quad (2.35)$$

For the four cases with gas dissolution effect, several characteristic quantities of the plume momentum flux (including the magnitude, the peak height, and the height where the flux reduces to zero) increase monotonically as the initial bubble diameter increases due to the increase of the bubble buoyancy that drives the plume motion. For the four cases with the gas dissolution effect considered, Figure 2.14 shows that the mean plume peel height (where M reduces to zero) is at $z \approx 115$ m for case QS-3D, at $z \approx 135$ m for case QS-6D, at $z \approx 165$ m for case QS-12D, and at $z \approx 200$ m for case QS-18D. In contrast, the omission of the gas bubble dissolution effect results in a consistent overestimation of the mean plume peel height (at $z \in (250, 300)$ m where M reaches a local minimum) for the four cases without considering the gas bubble dissolution, i.e. at $z \approx 289$ m for case QS-3N, at $z \approx 285$ m for case QS-6N, at $z \approx 260$ m for case QS-12N, and at $z \approx 284$ m for case QS-18N. Overall, the relative error for the estimated mean plume peel height due to the omission of the gas bubble dissolution effect is in the range of 42%–151% for the reported cases, with larger relative error for cases with smaller initial bubble diameter.

The above results illustrate that the current LES plume gas dissolution model can capture the key effects of the gas dissolution on the dynamics and structures of the plume. In contrast, if the gas bubble dissolution effect is not included in the model, the bubble diameter expands with height simply due to the reduction of the hydrostatic pressure in the seawater (Figure 2.14a). The persistence of the bubble-induced buoyancy as the plume

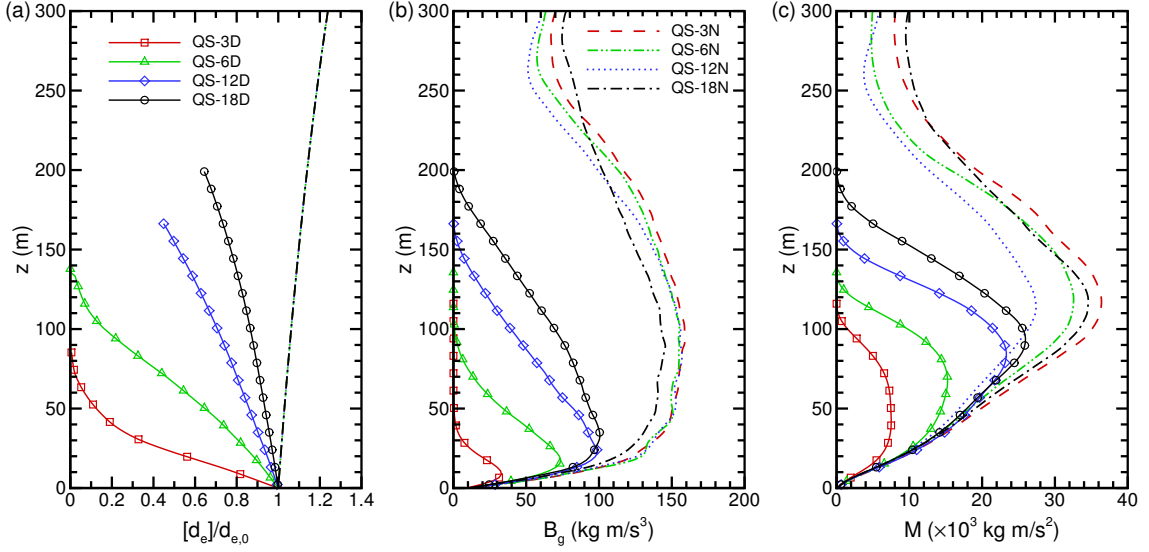


Figure 2.14: Averaged inner plume statistics: (a) mean bubble diameter (normalized by the initial bubble diameter); (b) bubble-induced buoyancy flux; (c) momentum flux of inner plume carrier flow.

risers (Figure 2.14b) results in over-prediction of the plume momentum flux for all the four initial bubble diameters considered in this study (Figure 2.14c), causing inaccurate prediction of the plume peel height and other key plume characteristics as shown in Figure 2.7 and Figures 2.9–2.12.

2.5 Summary

In the case of a subsea blowout event, the dynamics of the nearfield plume is highly affected by the buoyancy provided by the gas bubbles. In the deep-water environment, the gas in the bubbles dissolves continuously into the surrounding seawater, causing the plume to lose its driving force during the rising process. Thus it is crucial to account for the effect of gas bubble dissolution in order to model the dynamics and structure of the nearfield plume properly. In this study, an Eulerian–Eulerian LES modeling strategy has

been developed to model the effect of gas dissolution on the dynamics of the multiphase nearfield plume. In particular, the model parameterizes the local gas dissolution rate within each computational cell based on the instantaneous local Eulerian gas mass concentration and bubble number density functions obtained from the LES. The modeled gas dissolution rate is then included in the transport equation of the gas mass concentration to account for the loss of bubble mass due to the dissolution of gas into the surrounding seawater. This Eulerian–Eulerian LES modeling strategy provides a cost-efficient approach to incorporate the important gas dissolution effect into the simulation of field-scale plumes consisting of a large number of dispersed gas bubbles.

In this chapter, the LES model is applied to simulate the multiphase hydrocarbon plume released from the 700m depth driven by methane bubbles, with four different initial bubble diameters being considered under identical volumetric release rate. Due to the increase of the total surface area to volume ratio as the initial bubble diameter is reduced, the cases with smaller initial bubble diameters experience faster gas dissolution than those cases with larger initial diameters. The new LES model is found to be able to successfully model the bubble dissolution and capture its effect on the plume dynamics. The LES results show that several key physical quantities of the plume, such as the maximum height of the bubble column, the peel height of the plume entrained fluid, as well as the magnitudes of the plume buoyancy and momentum fluxes, all increase monotonically as the initial bubble diameter increases for the cases considered in this study. In contrast, a set of reference LES runs without considering the gas dissolution effect fail to capture the proper trend for the variations in the structure of the plume with different initial bubble diameters, indicating the importance of properly including the gas dissolution effect for an accurate prediction

of the nearfield plume dynamics in subsea blowouts.

Chapter 3

LARGE-EDDY SIMULATION FOR MULTI-COMPONENT GAS BUBBLE DISSOLUTION

3.1 Introduction

The multiphase hydrocarbon plume released from a deep-sea oil spill usually contains a large number of natural gas bubbles that provide the buoyancy force to raise the plume. Natural gas consists of various alkane compounds that can experience considerable dissolution in seawater in the deep-sea environment. This gas dissolution effect causes the reduction of the total buoyancy force as the plume rises, strongly affecting the structure and dynamics of the hydrocarbon plume in the region near the release source.

The previous chapter model the methane bubble dissolution effect (single component) in deep water condition under an Eulerian-Eulerian LES framework [63]. The methane bubble and oil droplet mixture are released at the bottom center of a 700m cubic domain. Three different domain resolutions are tested and we found the medium resolution {256, 256, 320} has a great balance between accuracy and economy. The model can successfully simulate bubble dissolution and capture the effect on plume dynamics.

In this study, the LES model with gas dissolution was extended to multi-component gas bubbles under the same framework. The current model record the Eulerian mass concentration of different gas bubble components and the number density simultaneously to calculate the cell-averaged equivalent bubble diameter. Then the corresponding gas dissolution rate for each component and the terminal velocity for the cell-averaged bubble are modeled based on the bubble diameter and the gas component ratio in the bubble. The bubble dissolution rate of each component is then added back to the transport equations of the bubble mass concentration. The cell-averaged bubble model assumes that the bubbles in a computational cell have the same size, shape, and gas composition, and the variation inside a cell is neglected. The bubble dissolution model focuses on the interaction between different components and can capture the difference in dissolution behavior among the components. To test the multi-component dissolution model, a series of experiments are implemented. The cases including the first one, two, and three major components of natural gas with the same volumetric release rate are compared to show the difference of taking more components into the model. Furthermore, two horizontal crossflow cases are conducted (with one and three components of gas bubble release at the same volumetric rate) to show the different distribution of the concentration of dissolved gas which reveals the improvement of the multi-component gas dissolution model. Systematic data analysis is carried out, and the statistics of plumes under different simulated conditions are compared in this study.

The paper is organized as follows. Section 4.2 provides the method of modeling the multi-component gas bubble dissolution effect in the Eulerian-Eulerian LES model. Section 3.3 shows the results of the test cases and compares the model with different initial gas bubbles components. Section 3.4 compares the result of cases with a uniform horizontal

crossflow. Finally, conclusions are presented in section 4.4.

3.2 Numerical Method

3.2.1 Multi-component gas dissolution rate for a single bubble

For a multi-component gas bubble rising and dissolving in deep water, the different gas components have different dissolution rates. The dissolution rate of each component is related to the surface area of the bubble, the total gas pressure inside the bubble, the molar fraction of the gas component inside the bubble, and the concentration of the dissolved gas in the surrounding water outside the bubble. Considering the high pressure environment in deep water, we model the non-ideal gas behavior of a multi-component gas bubble using the Peng–Robinson model [64, 73, 106]. For one mole of the gas mixture, the Peng–Robinson equation of state is written as [64]

$$p_b = \frac{RT}{V_m - b} - \frac{a}{V_m(V_m + b) + b(V_m - b)}. \quad (3.1)$$

Here, p_b is the total pressure inside the gas bubble, which is assumed to be the same as the pressure of the surrounding seawater by neglecting the effect of surface tension; R is the ideal gas constant; T is the temperature of the gas inside the bubble, which is assumed to be the same as the ambient seawater; V_m is the molar volume of the gas mixture in the bubble; a and b are the mixture coefficients, where a is the attraction factor and b is the van der Waals covolume. The detailed equations for determining these model coefficients are given in Section 3.2.2.

For a single bubble with the total number of moles of gases, n_b , the Peng–Robinson equation of state can be written as

$$p_b V_b = Z n_b R T, \quad (3.2)$$

where V_b is the total volume of a single bubble, Z is the compressibility factor (see Section 3.2.2), and

$$n_b = \sum_i n_{g,i}, \quad (3.3)$$

with $n_{g,i}$ being the number of moles of the i -th gas component in the bubble.

In order to determine the local value of $n_{g,i}$ in real time during the simulation, we adopt the method of [63] originally developed for modeling the dissolution of bubbles with a single gas component, and expand it to the application multi-component gas bubble dissolution. In particular, the bubble number density and the mass concentration for each bubble gas component are computed simultaneously in the LES (details are given in Section 4.2.4). For simplicity, we consider the average bubble size and gas dissolution for all the bubbles within the same local computational cell and neglect the subgrid-scale variations of the bubble size and gas dissolution rate. Then the number of moles of the i -th gas component in a single bubble can be modeled as

$$n_{g,i} = \frac{C_{g,i}}{N_b M_{g,i}}, \quad (3.4)$$

where $C_{g,i}$ is the mass concentration of the i -th gas component in bubbles in the local LES computational cell, N_b is the number density of bubbles in the local LES computational

cell, and $M_{g,i}$ is the molar weight of the i -th gas component.

After we have the single bubble volume V_b from the equation of state, the corresponding equivalent bubble diameter is calculated based on

$$d_e = \sqrt[3]{\frac{6V_b}{\pi}} = \sqrt[3]{\frac{6Zn_bRT}{\pi p_b}}, \quad (3.5)$$

and the density of the multi-component gas in the bubble is given by

$$\rho_b = \frac{\sum_i (n_{g,i} M_{g,i})}{V_b} = \frac{p_b \sum_i C_{g,i}}{ZRT \sum_i (C_{g,i} / M_{g,i})}. \quad (3.6)$$

Once the bubble diameter d_e and gas density ρ_b are obtained, the gas mass transfer coefficient K_i for each gas component and the bubble slip velocity w_r can be modeled based on empirical models, for which the details are given in Chapter 2.2.1 and B, respectively.

The dissolution rate for the i -th gas component in a single bubble, $\alpha_{g,i}$, is modeled as [106]

$$\alpha_{g,i} = A_b K_i (C_{s,i} - C_{dis,i}), \quad (3.7)$$

where $A_b = \pi d_e^2$ is the equivalent surface area of a single bubble, and the parameters with the subscript i are for the i -th gas components. In particular, K_i is the gas mass transfer coefficient from the bubble to the ambient seawater, $C_{s,i}$ is the solubility of the gas in the seawater, and $C_{dis,i}$ is the mass concentration of the dissolved gas in the ambient seawater. In the current model, $C_{dis,i}$ is also simulated by LES (see Section 4.2.4 for details). The gas

solubility is modeled as [47, 52, 106]

$$C_{s,i} = \frac{f_i^g}{K_{H,i}^{pc}} \exp\left(-\frac{p_b V_{m,i}^L}{RT}\right) \cdot \left(\frac{\rho_w}{M_w} M_{g,i}\right), \quad (3.8)$$

where ρ_w is the density of pure water, M_w is the molecular weight of water, and the parameters with the subscript i are for the i -th gas component. In particular, f_i^g is the fugacity, $K_{H,i}^{pc}$ is Henry's law volatility constant, and $V_{m,i}^L$ is the partial molar volume for the i -th gas component in solvent water.

The gas fugacity is modeled based on [64]

$$f_i^g = \chi_i p_b \exp\left[\frac{b_i}{b}(Z-1) - \ln(Z-B) - \frac{A}{2\sqrt{2}B}\left(\frac{2\sum_j \chi_j a_{ij}}{a} - \frac{b_i}{b}\right) \ln\left(\frac{Z+2.414B}{Z-0.414B}\right)\right], \quad (3.9)$$

where χ_i is the mole fraction of the i -th gas component, a , a_{ij} , b and b_i are the parameters for the Peng-Robinson equation of state (see Eqs. 3.17, 3.18, 3.19 and 3.22), and the parameters A and B are given by

$$A = \frac{ap_b}{R^2 T^2} \quad (3.10)$$

and

$$B = \frac{bp_b}{RT}. \quad (3.11)$$

The Henry's law solubility constant $K_{H,i}^{pc}$ is dependent on the temperature T and is

Table 3.1: List of gas properties for the three gas components considered in the present study. The empirical values for the Henry's law solubility H_i^{cp} and its temperature dependence at the standard temperature $T^\ominus = 298.15$ K are from [69].

Component	Index i	$H_i^{cp}(\text{at } T^\ominus)$ $\left(\frac{\text{mol}}{\text{m}^3 \text{ Pa}}\right)$	$\left[\frac{d(\ln H_i^{cp})}{d(1/T)}\right]_{T=T^\ominus}$ (K)
Methane (CH_4)	1	1.4×10^{-5}	1600
Ethane (C_2H_6)	2	1.9×10^{-5}	2400
Propane (C_3H_8)	3	1.5×10^{-5}	2700

modeled based on [69],

$$K_{H,i}^{pc} = \frac{1}{H_i^{cp}(T^\ominus)} \exp \left\{ \left[\frac{d(\ln H_i^{cp})}{d(1/T)} \right]_{T=T^\ominus} \left(\frac{1}{T^\ominus} - \frac{1}{T} \right) \right\}, \quad (3.12)$$

where H_i^{cp} is the Henry's law solubility constant for the i -th gas component and $T^\ominus = 298.15$ K is the standard temperature. The empirical values for H_i^{cp} and $d(\ln H_i^{cp})/d(1/T)$ at $T = T^\ominus$ are listed in Table 3.1. The same method to modeling Henry's law solubility has also been used in the integral plume model of [39].

3.2.2 Peng–Robinson equation of state for non-ideal multi-component gas

The Peng–Robinson equation of state (3.1) for multi-component gas can be rewritten in the polynomial form as [64]

$$Z^3 - (1 - B)Z^2 + (A - 2B^2 - 3B^3) - (AB - B^2 - B^3) = 0, \quad (3.13)$$

where

$$A = \frac{ap_b}{R^2T^2}, \quad (3.14)$$

$$B = \frac{bp_b}{RT}, \quad (3.15)$$

and

$$Z = \frac{p_b V_m}{RT}. \quad (3.16)$$

The attraction parameter of one mole mixed gas, a , and the van der Waals covolume of the gas mixture, b , are defined as [64]:

$$a = \sum_i \sum_j \chi_i \chi_j a_{ij}, \quad (3.17)$$

$$a_{ij} = (1 - \delta_{ij}) a_i^{1/2} a_j^{1/2}, \quad (3.18)$$

and

$$b = \sum_i \chi_i b_i, \quad (3.19)$$

where

$$\chi_i = \frac{C_{g,i}}{\sum_i C_{g,i}}, \quad (3.20)$$

is the mole fraction of the i -th gas component, δ_{ij} is the binary interaction coefficient between gas components i and j , a_i is the attraction parameter for the i -th gas component,

$$a_i = 0.45724 \frac{R^2 T_{c,i}^2}{P_{c,i}} \beta_i(T_{r,i}, \omega_i), \quad (3.21)$$

and b_i is the van der Waals covolume for the i -th gas component,

$$b_i = 0.07780 \frac{RT_{c,i}}{P_{c,i}}. \quad (3.22)$$

In Eqs. (3.21) and (3.22), $T_{c,i}$ is the gas temperature at the critical point, $P_{c,i}$ is the gas pressure at the critical point, ω_i is the acentric factor, and $\beta_i(T_{r,i}, \omega_i)$ is a dimensionless scaling factor,

$$\beta_i^{1/2} = 1 + \kappa(\omega_i) \left(1 - T_{r,i}^{1/2}\right), \quad (3.23)$$

where $T_{r,i} = T/T_{c,i}$ and

$$\kappa(\omega_i) = 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2. \quad (3.24)$$

By solving the polynomial equation (3.13), the compressibility factor Z is obtained. Based on the computed values of Z and n_b , the equivalent bubble diameter d_e is calculated based on Eq. (3.5), which is used for parameterizing the gas mass transfer coefficient K_i and bubble slip velocity w_r (see details in sections 3.2.3 and Appendix B, respectively).

3.2.3 Mass transfer coefficient for multi-component gas dissolution

For the i -th gas component in the bubble, the mass transfer coefficient K_i from the interior of the bubble to the surrounding seawater can be parameterized based on the effective spherical diameter of the bubble, d_e [103, 106].

In particular, if the bubble diameter is in the range of $d_e < 4 \times 10^{-4}$ m, the corresponding

gas mass transfer coefficient K_i is parameterized as [36, 61, 70, 103]

$$\frac{K_i}{D_i/d_e} = 0.552 \text{Re}_b^{1/2} \text{Sc}_i^{1/3}, \quad (3.25)$$

where D_i is the molecular diffusivity of the i -th gas component in the seawater (in m^2/s), $\text{Sc}_i = \mu/(\rho_0 D_i)$ is the Schmidt number, μ is the dynamic viscosity of seawater (in $\text{kg}/(\text{m s})$), ρ_0 is the reference density of seawater (in kg/m^3), $\text{Re}_b = \rho_0 w_r d_e / \mu$ is the particle Reynolds number of the bubble, and w_r is the slip velocity (in m/s) of the gas bubble relative to the surrounding seawater (which also depends on d_e ; see the parameterizations in Appendix B).

If the bubble diameter is in the range of $4 \times 10^{-4} \text{ m} < d_e < 5 \times 10^{-3} \text{ m}$, the corresponding gas mass transfer coefficients is parameterized as [88, 103]

$$\frac{K_i}{(D_i w_r / d_e)^{1/2}} = \frac{2}{\sqrt{\pi}} \left[\left(1 - \frac{2.89}{\sqrt{\text{Re}_b}} \right) f_R \right]^{1/2}, \quad (3.26)$$

where f_R is the surface-flow retardation factor given by [88]

$$\log_{10} f_R = 0.5 \left\{ \tanh \left[3.9 \log_{10} \left(\frac{d_e}{d_0} \right) \right] - 1 \right\}, \quad (3.27)$$

with $d_0 = 8.7 \times 10^{-4} \text{ m}$.

For bubble diameter in the range of $5 \times 10^{-3} \text{ m} < d_e < 1.3 \times 10^{-2} \text{ m}$, the gas mass

transfer coefficient is parameterized as [23, on page 196 underneath equation (7.50)]

$$\frac{K_i}{D_i^{1/2}} = A_0, \quad (3.28)$$

where $A_0 = 6.5 \text{ s}^{-1/2}$.

Finally, for large bubble diameter in the range of $d_e > 1.3 \times 10^{-2} \text{ m}$, the mass transfer coefficient is parameterized as [23, page 214, equation (8.29)],

$$\frac{K_i}{D_i^{1/2}} = \frac{B_0}{d_e^{1/4}}, \quad (3.29)$$

where $B_0 = 2.19 \text{ m}^{1/4} \text{ s}^{-1/2}$ (converted from the original equation in [23] in which d_e was in cm).

3.2.4 Large-eddy simulation model of hydrocarbon plume with multi-component gas bubbles

In this study, the carrier flow is model by the filtered Navier-Stokes equations with Cartesian coordinate, where $\mathbf{x} = (x, y, z)$, x and y are the horizontal axis and z is vertical the axis. The corresponding velocity field is $\mathbf{u} = (u, v, w)$. The filtered Navier-Stokes equations are used to simulate the carrier flow movements [97].

$$\nabla \cdot \tilde{\mathbf{u}} = 0 \quad (3.30)$$

and

$$\begin{aligned} \frac{\partial \tilde{\mathbf{u}}}{\partial t} + \tilde{\mathbf{u}} \cdot \nabla \tilde{\mathbf{u}} = & -\frac{1}{\rho_0} \nabla \tilde{P} - \nabla \cdot \boldsymbol{\tau}^d + \left(1 - \frac{\tilde{\rho}}{\rho_0}\right) g \mathbf{e}_z \\ & + \left(1 - \frac{\rho_b}{\rho_0}\right) \frac{\tilde{C}_b}{\rho_b} g \mathbf{e}_z + \left(1 - \frac{\rho_d}{\rho_0}\right) \frac{\tilde{C}_d}{\rho_d} g \mathbf{e}_z. \end{aligned} \quad (3.31)$$

Here, the tilde denotes the variable resolved by the LES computational grid; ρ_0 is the reference seawater density; $\tilde{\rho}$ is the resolved local seawater density; $\boldsymbol{\tau}^d = \boldsymbol{\tau} - [\text{tr}(\boldsymbol{\tau})/3]\mathbf{I}$ is the deviatoric part of the subgrid-scale stress tensor $\boldsymbol{\tau} = (\widetilde{\mathbf{u}\mathbf{u}} - \tilde{\mathbf{u}}\tilde{\mathbf{u}})$, where $\text{tr}(\boldsymbol{\tau})$ is the trace of $\boldsymbol{\tau}$ and $\mathbf{I}$ is the identity tensor; $\tilde{P} = \tilde{p} + \rho_0[\text{tr}(\boldsymbol{\tau})/3 - gz]$ is the modified pressure, where $\tilde{p}$ is the resolved water pressure and g is the gravitational acceleration; $\mathbf{e}_z$ is the unit vector in the vertical direction; ρ_b is the density of gas in bubbles in local LES computational cell; $C_b = \sum_i C_{bi}$ is the sum of mass concentration of gas bubble components; ρ_d is the density of oil droplet; and C_d is the mass concentration of oil droplets. Boussinesq approximation is used for the buoyancy force represents the last three components in Equation 36, the buoyancy force due to water density stratification, gas bubble concentration, and oil droplet concentration [97].

Following the previous study [17, 32, 49, 59, 65, 96, 97], the virtual potential temperature field regulated by a filtered convection-diffusion equation is used to describe the stratification effect in seawater

$$\frac{\partial \tilde{\theta}}{\partial t} + \nabla \cdot (\tilde{\mathbf{u}}\tilde{\theta}) = -\nabla \cdot \boldsymbol{\pi}_\theta, \quad (3.32)$$

and the corresponding ambient seawater density field $\tilde{\rho}$ varies linearly with the potential

temperature θ as

$$\tilde{\rho} = \rho_0[1 - \alpha_t(\tilde{\theta} - \theta_0)], \quad (3.33)$$

where $\pi_\theta = \widetilde{\mathbf{u}\theta} - \tilde{\mathbf{u}}\tilde{\theta}$ is the SGS thermal flux, α_t is the thermal expansion coefficient, and θ_0 is the reference potential temperature corresponding to the reference seawater density ρ_0 .

The development of gas bubbles transported by the carrier flow are modeled as dispersed phase and by continuous Eulerian functions, the bubble concentration functions $C_{bi}(\mathbf{x}, t)$ and the bubble number density function $N_b(\mathbf{x}, t)$. The development of the bubble mass concentration is modeled by a set of filtered transport equations with the bubble dissolution effect term added for each gas component:

$$\frac{\partial \tilde{C}_{bi}}{\partial t} + \nabla \cdot (\tilde{\mathbf{v}}_b \tilde{C}_{bi}) = -\nabla \cdot \pi_{bi} + q_{bi} - \tilde{\alpha}_i, \quad (3.34)$$

where i denotes for different gas component, $\tilde{\mathbf{v}}_b$ is the Lagrangian transport velocity of bubbles, $\pi_b = \widetilde{\mathbf{u}C_{bi}} - \tilde{\mathbf{u}}\tilde{C}_{bi}$ is the SGS flux of bubble mass concentration of gas component i , $q_{bi} = \gamma_i \rho_{b,0} V_{b,0} q_n$ is the volumetric source term for the release of gas bubble mass, γ_i is the gas mass release ratio of component i at the source, $\rho_{b,0}$ is the gas bubble density in the bubbles at the release source, $V_{b,0}$ is the initial volume of a single bubble at the release source, q_n is the source term representing the number of released bubbles from a subsea blowout, $\tilde{\alpha}_i = \tilde{N}_b \tilde{\alpha}_{bi}$ is the cell-averaged local gas mass dissolution rate (per unit volume) resolved by the LES model.

Similar to the bubble mass concentration, the development of the bubble number den-

sity is modeled by a filtered transport equation

$$\frac{\partial \tilde{N}_b}{\partial t} + \nabla \cdot (\tilde{\mathbf{v}}_b \tilde{N}_b) = -\nabla \cdot \boldsymbol{\pi}_n + q_n, \quad (3.35)$$

where $\boldsymbol{\pi}_n = \widetilde{\mathbf{u}N_b} - \tilde{\mathbf{u}}\tilde{N}_b$ is the SGS flux of bubble number density due to SGS turbulent flow effects. In Eq. (4.28), the effects of bubble breakup and coalescence are neglected for the sake of model simplicity.

The bubble transport velocity $\tilde{\mathbf{v}}_b$ is modeled as:

$$\tilde{\mathbf{v}}_b = \tilde{\mathbf{u}} + w_{r,b} \mathbf{e}_z + \frac{w_{r,b}}{g} \frac{D\tilde{\mathbf{u}}}{Dt}, \quad (3.36)$$

where $w_{r,b}$ is the rise velocity of bubbles relative to the surrounding carrier flow caused by the bubble buoyancy (see Appendix B for the parameterizations of $w_{r,b}$), and $D\tilde{\mathbf{u}}/Dt = \partial\tilde{\mathbf{u}}/\partial t + \tilde{\mathbf{u}} \cdot \nabla \tilde{\mathbf{u}}$ is the material derivative (or Lagrangian acceleration) of the carrier flow velocity.

Based on the quantity of gas mass concentration C_{bi} and number density N_b , applying Eq. (3.7) to obtain the gas dissolution rate per single bubble $\tilde{\alpha}_{bi}$, the cell averaged dissolution rate $\tilde{\alpha}_i$ is given by

$$\tilde{\alpha}_i = \tilde{N}_b \tilde{\alpha}_{bi} = \tilde{N}_b \tilde{A}_b \tilde{K}_i \left(\tilde{C}_{si} - \widetilde{C_{disi}} \right). \quad (3.37)$$

For the concentration of dissolved gas component i in the ambient seawater, the function

$\widetilde{C}_{disi}$ is modeled as

$$\frac{\partial \widetilde{C}_{disi}}{\partial t} + \nabla \cdot (\widetilde{\mathbf{u}} \widetilde{C}_{disi}) = -\nabla \cdot \boldsymbol{\pi}_{disi} + \widetilde{\alpha}_i, \quad (3.38)$$

where $\boldsymbol{\pi}_{disi} = \widetilde{\mathbf{u}} \widetilde{C}_{disi} - \widetilde{\mathbf{u}} \widetilde{C}_{disi}$ is the SGS flux of mass concentration for the dissolved gas. Different from $\widetilde{N}_b$ and $\widetilde{C}_{bi}$, the dissolved gas concentration $\widetilde{C}_{disi}$ is carried as a passive scalar dependent on the carrier flow velocity $\widetilde{\mathbf{u}}$.

Besides the gas bubbles, the plume also contains the oil droplets that spill at the same position and supply buoyancy and affect the development of the plume. The transport of oil droplets is modeled by the filtered transport equation

$$\frac{\partial \widetilde{C}_{oil}}{\partial t} + \nabla \cdot (\widetilde{\mathbf{v}}_{oil} \widetilde{C}_{oil}) = -\nabla \cdot \boldsymbol{\pi}_{oil} + q_{oil}, \quad (3.39)$$

where q_{oil} is a source term for the oil droplet release, $\boldsymbol{\pi}_{oil} = (\widetilde{\mathbf{u}} \widetilde{C}_{oil} - \widetilde{\mathbf{u}} \widetilde{C}_{oil})$ is the SGS flux of oil mass concentration, and $\widetilde{\mathbf{v}}_{oil}$ is the transport velocity of oil droplets (with non-negligible buoyancy effect) [16, 21, 96],

$$\widetilde{\mathbf{v}}_{oil} = \widetilde{\mathbf{u}} + w_{r,oil} \mathbf{e}_z + \frac{w_{r,oil}}{g} \frac{D\widetilde{\mathbf{u}}}{Dt}. \quad (3.40)$$

The oil droplet rise velocity due to buoyancy is modeled as [22, 89, 97]

$$w_{r,d} = \begin{cases} w_{r,oil}^S & \text{Re}_{oil} < 0.2, \\ w_{r,oil}^S (1 + 0.15 \text{Re}_{oil}^{0.687})^{-1}, & 0.2 < \text{Re}_{oil} < 750, \end{cases} \quad (3.41)$$

where $w_{r,oil}^S$ is the oil droplet rise velocity given by Stokes' law as

$$w_{r,oil}^S = \frac{(1 - \rho_{oil}/\rho_0)gd_{oil}^2}{18\nu}, \quad (3.42)$$

ρ_{oil} is the oil density, d_{oil} is the equivalent diameter of the oil droplet, ν is the kinematic viscosity of water, and $Re_{oil} = w_{r,oil}d_{oil}/\nu$ is the oil droplet Reynolds number.

Additionally, the LES model simulates the transport of dye tracers to observe the impacts of plume dynamics and crossflow on passive materials transportation. The development of the dye mass concentration field $\tilde{C}_{dye}$ is used to model passive tracer transport, which is controlled by the filtered transport equation

$$\frac{\partial \tilde{C}_{dye}}{\partial t} + \nabla \cdot (\tilde{\mathbf{u}} \tilde{C}_{dye}) = -\nabla \cdot \boldsymbol{\pi}_{dye} + q_{dye}, \quad (3.43)$$

where q_{dye} is a source term for the dye release and $\boldsymbol{\pi}_{dye} = (\widetilde{\mathbf{u}C_{dye}} - \tilde{\mathbf{u}}\tilde{C}_{dye})$ is the SGS dye concentration flux.

The LES governing equations are closed by parametrizing the SGS terms with appropriate turbulence closures using the Lilly-Smagorinsky eddy-viscosity type model [55, 76]. $\tau^d = -2\nu_\tau \tilde{\mathbf{S}}$, where $\tilde{\mathbf{S}} = [\nabla \tilde{\mathbf{u}} + (\nabla \tilde{\mathbf{u}})^T]/2$ is the resolved strain rate tensor, $\nu_\tau = (c_s \Delta)^2 |\tilde{\mathbf{S}}|$ is the modeled SGS eddy viscosity, c_s is the Smagorinsky model coefficient, and Δ is the LES grid (filter) scale. The value of c_s is determined dynamically during the simulation using the Lagrangian-averaged scale-dependent dynamic SGS model [8]. The SGS fluxes of the scalar quantities are then parametrized as $\boldsymbol{\pi}_\theta = -(\nu_\tau/\text{Pr}_\tau)\nabla \tilde{\theta}$, $\boldsymbol{\pi}_n = -(\nu_\tau/\text{Sc}_\tau)\nabla \tilde{N}_b$, $\boldsymbol{\pi}_b = -(\nu_\tau/\text{Sc}_\tau)\nabla \tilde{C}_b$, $\boldsymbol{\pi}_{dis} = -(\nu_\tau/\text{Sc}_\tau)\nabla \tilde{C}_{dis}$ and $\boldsymbol{\pi}_{dye} = -(\nu_\tau/\text{Sc}_\tau)\nabla \tilde{C}_{dye}$, with a con-

Table 3.2: List of gas properties for the three gas components studied in this paper [12, 67].

Component	Index i	$M_{g,i}$ (g/mol)	$V_{m,i}^L$ (cm ³ /mol)	$T_{c,i}$ (K)	$P_{c,i}$ (bar)	ω_i
Methane (CH ₄)	1	16.043	35.6	190.4	46.0	0.011
Ethane (C ₂ H ₆)	2	30.070	53.0	305.4	48.8	0.099
Propane (C ₃ H ₈)	3	44.094	76.8	369.8	42.5	0.153

stant SGS Prandtl number $Pr_\tau = 0.4$ and SGS Schmidt number $Sc_\tau = 0.4$ [1, 3, 14, 50, 57, 60, 63, 85, 97].

3.3 Gas Bubble Dissolution with Considering Three Major Components

3.3.1 Problem Setup

The single-component gas bubble dissolution model was reported in our previous study [63]. In this study, we focus on the multi-component gas dissolution model. The test cases are set up to compare the multi-component model with the single component model.

For the multi-component model, we considered three major gas components, i.e., methane, ethane, and propane, which contributed to 96.1% of the total mass of the released natural gas in the case of *Deepwater Horizon* oil spill accident [66]. The corresponding parameters for the methane, ethane, and propane used in the current LES model are listed in Table 3.2 [67].

In this test cases, The domain size are $L_x = 700\text{m}$, $L_y = 700\text{m}$, $L_z = 700\text{m}$ with the grid resolution of $\{256, 256, 320\}$. The gas and oil rource released at the bottom center of the domain $\{350\text{m}, 350\text{m}, 700\text{m}\}$. This resolution is verified for single component gas dissolution case in paper [63] and we keep the same in this study. The time resolution is

0.1s. The source released at the simulation starts.

The ambient seawater is linearly stratified by the temperature. The temperature is set as:

$$T(z) = T_b + \gamma z, \quad 0 \leq z \leq L_z, \quad (3.44)$$

where $\gamma = 0.02 \text{ K m}^{-1}$ is the vertical temperature gradient coefficient, $T_b = 284.15 \text{ K}$ is the ambient water temperature at the bottom of the domain (at $z = 0\text{m}$), and $L_z = 700\text{m}$ is the domain height. The background salinity is set to be a constant 0.35%. Same with the [63, 97], the no-slip condition is used at the bottom boundary, the free-slip condition is used at the top boundary, and the periodic boundary conditions are used in the horizontal directions associated with the pseudo-spectral method.

For a plume in no-crossflow condition, the plume characteristics are affected by the buoyancy frequency $N = \sqrt{-g/\rho_r(\partial\rho_a/\partial z)}$, oil/gas bubble rise velocity w_r , source buoyancy flux $B_0 = Q_0(\rho_a - \rho_0)/\rho_r$, where ρ_r is the reference seawater density, ρ_a ambient seawater density, ρ_0 is the density of the initial oil/gas mixture, and Q_0 is the volume flow rate of the initial oil/gas mixture [82]. For the mixture of oil and gas, the $B_0 = B_{gas} + B_{oil}$.

Table 3.3 listed the parameters used in the 1-component and 3-component cases. Here the dimensionless bubble rise velocity parameter $W_N = w_r/(B_0 N)^{1/4}$ are matched among cases with different gas component to keep the characteristic of the plume same [79, 80].

The gas mass release rate is adjusted to keep the gas mole release rate the same. For single-component case, the mass release rate for gas is 2.22kg/s, the gas is 100% methane CH_4 . For three-component case, the mass release rate for gas is 2.78kg/s, the gas consist of 76.64% methane CH_4 and 13.14% ethane C_2H_6 and 10.22% propane C_3H_8 . The bubbles

Table 3.3: List of gas properties for the three gas components studied in this paper [69].

Case	1 component	3 component
$\rho_{gas} [kg/m^3]$	57.9223	71.6093
$W_r [m/s]$	0.2369	0.2353
$B_{gas} [m^4/s^3]$	0.378907	0.368288
$Q_0 [m^3/s]$	0.0383885	0.0389380
$Q_{src} [kg/s]$	2.223547	2.788320
$T=284.15 \text{ K}$		

have a uniform shape and size at the release point. The equivalent initial diameter is 12mm. The oil release rate for all the cases is 16.4312kg/s with a constant density 893kg/m³ and uniform diameter of 5mm. The dye release rate is 1g/s. The dye has the same density as the ambient water and has no buoyancy and dynamic effect in the field. It behaves as a passive transport scalar field and can represent tiny particles.

The general process of plume development can be divided into three steps. In the first step, the gas bubbles and the oil droplets release from the sea bed and supply a strong buoyancy force which lifts the ambient seawater to form an upward plume. In this step, the gas bubbles supply the main buoyancy force and have a larger slip velocity than the oil droplets. The strong buoyancy force counterworks with the background stratification, and the plume gets upward acceleration. In meantime, the gas bubbles have the maximum dissolution rate and the bubble diameter keeps decreasing. In the second step, the bubbles gradually dissolve and disappeared, the density stratification makes the plume decelerate. In the meantime, the oil droplets keep rising with their own buoyancy and separate from the plume. In the last step, the entrained water starts falling down around the center plume due to its heavier density, and finally to the trapping height and forms a disc-shaped trapping layer.

Figure 3.1 shows the snapshot of the instantaneous center plane of the simulation domain of the three-component gas bubble case at $t = 8000s$. The plane is the x-z plane and in the center of the y-axis across the source point. The mass concentration of different component in the gas bubble is captured by the LES simulation and show in figure 3.1 (a), (b), (c). The mass concentration is cell-averaged with all components sharing the same bubble size and number density. As the different components share the same number density, they have the same outline of distribution. The methane has a higher concentration at origin than the other two components in total since the mass release ratio of methane is much higher. With the bubble rising to a higher elevation, the different components dissolve into the ambient water. For methane, the gas phase disappear at the depth of 200m Figure 3.1(a). For ethane, the gas disappear at the depth of 160m Figure 3.1(b). For propane, the gas disappear at the depth of 220m Figure 3.1(c).

The three components have different dissolution rates 3.1 (d), (e), (f). After the gas components dissolve from the bubble into the ambient water, the dissolved gas can still continuously affect the gas bubble by reducing the dissolution rate. However, the transport behavior of the dissolved gas is a passive scalar and will not change the water density and fluid dynamics. Figure 3.1 (g), (h), (i) show the distribution of the dissolved components. The dissolved methane has the largest mass concentration due to the large release rate (3.1(g)). Propane has a relatively low dissolution ratio compared with methane and ethane, and can survive longer in the bubble. As the 3.1(h) show, the dissolved propane can rise up to 280m, whereas the dissolved methane and ethane are remaining below 250m. The dissolved gas phase indicates that in the early stage of the plume development, the water is entrained mainly by the buoyancy from the component of methane, while in the later stage,

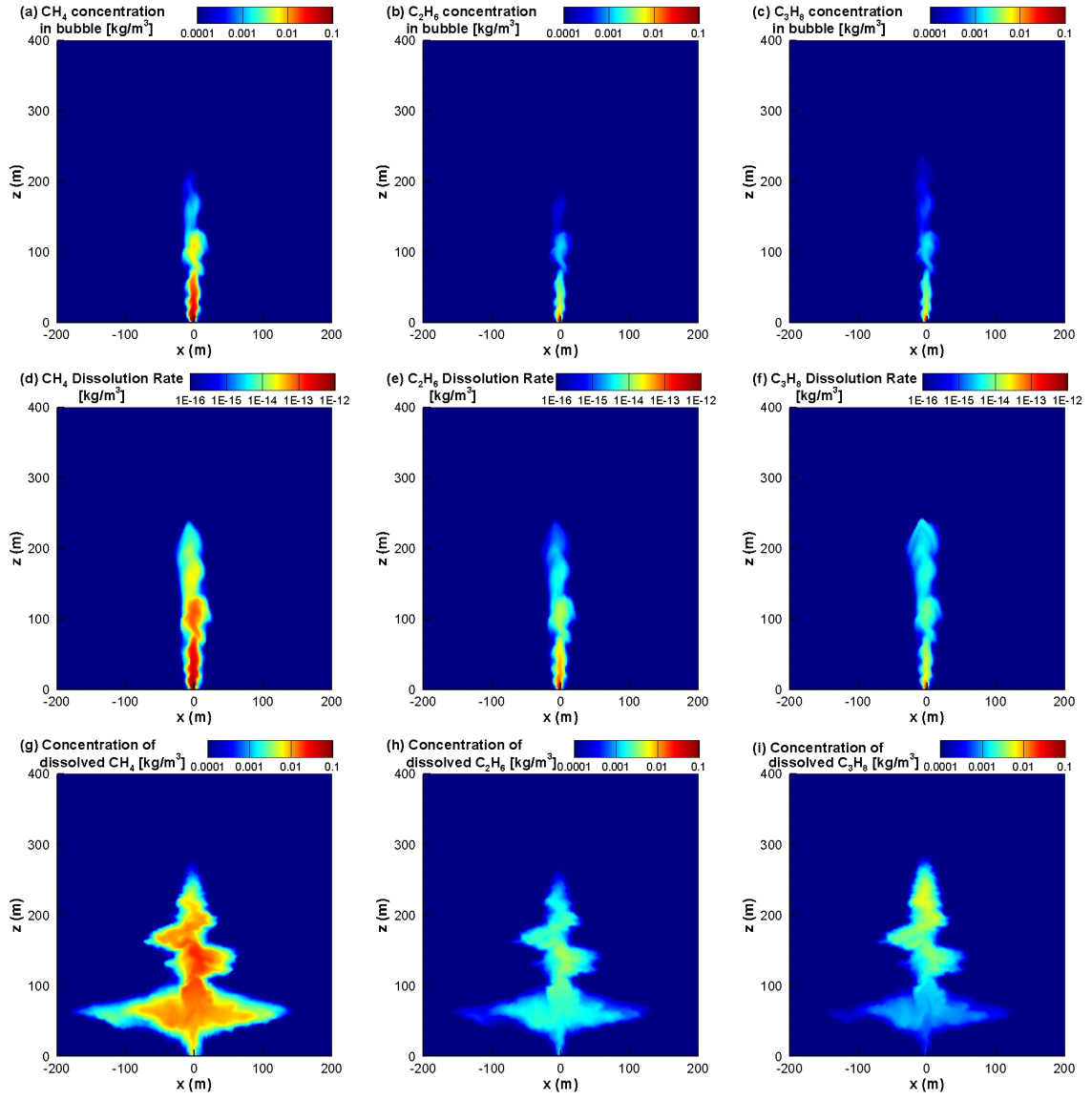


Figure 3.1: Instantaneous plume flow and scalar fields for case LS-3D-0cross obtained from the LES.

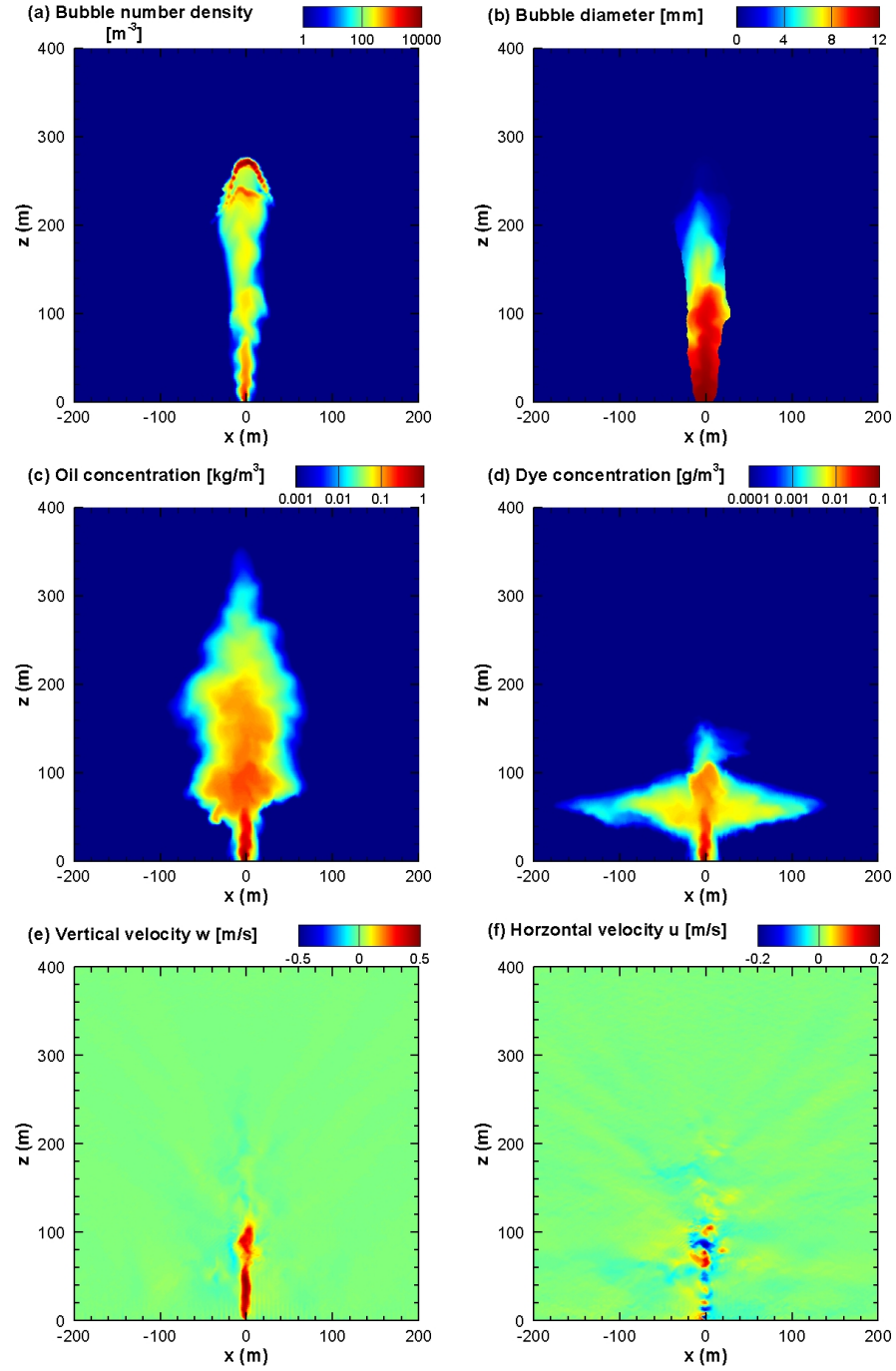


Figure 3.2: Instantaneous plume flow and scalar fields for case LS-3D-0cross obtained from the LES. Here the contours show the (x, z) -plane across the center of the plume.

the buoyancy from the gas bubble is mainly supplied by the propane component.

Figure 3.2 shows the instantaneous plume flow and scalar fields for case LS-3D-0cross obtained from the LES. The contours on the (x, z) -plane across the center of the plume are shown: (a) bubble number density (in m^{-3}); (b) bubble diameter (in mm); (c) oil droplets mass concentration (in kg/m^3); (d) dye concentration (in g/m^3); (e) vertical velocity of plume flow (in m/s); (f) horizontal velocity of plume flow (in m/s).

The corresponding bubble size reduced while rising and dissolving showing in Figure 3.2(b). As the bubble diameter reduces to 0 at 280m, all the three components inside the bubbles get fully dissolved. After this, the large oil droplets keep rising with their own buoyancy Figure 3.2(c). The dye with no buoyancy and terminal velocity behave as a passive scalar that will go downward outside the inner plume and form an intrusion layer Figure 3.2(d). The intrusion layer depth is 60m in this case.

Figure 3.3 compares the instantaneous distribution of the methane in gas bubbles (a, b), the dye concentration (c, d) and oil concentration (e, f) of the one-component case and three-component case. After the ethane and propane add to the system, the total gas bubble dissolution rate is reduced and the bubbles survive to a higher elevation Figure 3.3(c)-(f). At the same time, the plume higher buoyancy force and mix effect during the whole dissolution process. This cause the oil droplet and dye distributed in a larger range Figure 3.3(c)-(f).

To statistically study the difference of add single-component and multi-component gas model, four cases (1-component dissolution, 3-component dissolution, 1-component non-dissolution, 3-component non-dissolution) are compared. Figure 3.4 shows the methane concentration in gas bubble (a-b), oil droplet concentration (c-d), and dye concentration

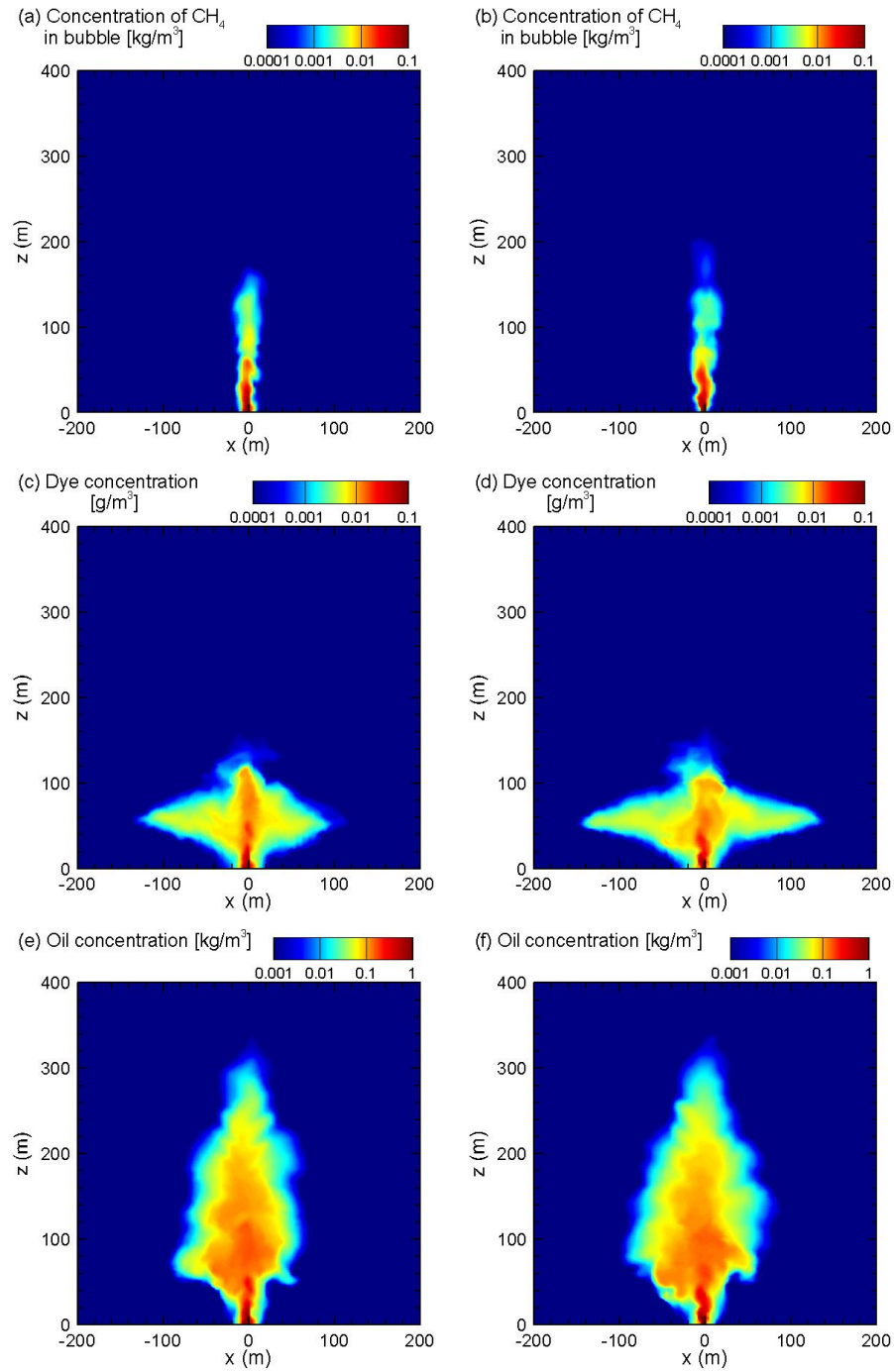


Figure 3.3: Comparison of the instantaneous plume features between 1-component case and (a, c, e) and 3-component case (b, d, f). Here the contours show the (x, z) -plane across the center of the plume.

(e-f) of the time and angular-averaged plume obtained from these four LES cases, in which (a) cases 1N (left half) and 3N (right half), (b) cases 1D (left half) and 3D (right half), (c) cases 1N (left half) and 3N (right half), (d) cases 1D (left half) and 3D (right half), (e) cases 1N (left half) and 3N (right half), (f) cases 1D (left half) and 3D (right half). After the single-component case becomes the three-component case, the non-dissolution cases have no obvious difference in the distribution of methane mass concentration, oil concentration, and dye concentration due to the same buoyancy flux at the release point. For the cases with dissolution, the average peeling height of the methane and dye is 10–20 meters higher than the single component case due to the relatively low dissolution rate.

Time-averaged bubble mass, oil mass, methane, and dye per depth are compared in Figure 3.6. The initial gas bubbles release rate of the four cases is adjusted to have the same buoyancy flux according to [82], the total oil mass per unit depth and total dye mass per unit depth are almost the same at each depth between 1C-D and 3C-D cases, and 1C-N and 3C-N cases Figure 3.6(b)(d). Due to the different initial composition of gas components, the total gas bubble mass per unit depth at the bottom is 3.6 kg/m for the 1C-D and 1C-N cases, while is 4.4 kg/m for the 3C-D and 3C-N cases Figure 3.6(a). For the methane mass in the bubble per unit depth, the single-component cases have 0.4 kg/m less than the three-component cases at the release depth Figure 3.6(c). These cases show a consistency of the plume characters.

Figure 3.5 shows the component ratio change inside the bubbles. As the bubbles rise from the sea bottom, the methane and ethane dissolve more quickly than the propane, the propane will be the main component of the gas bubble after the bubbles reach 250m from the source.

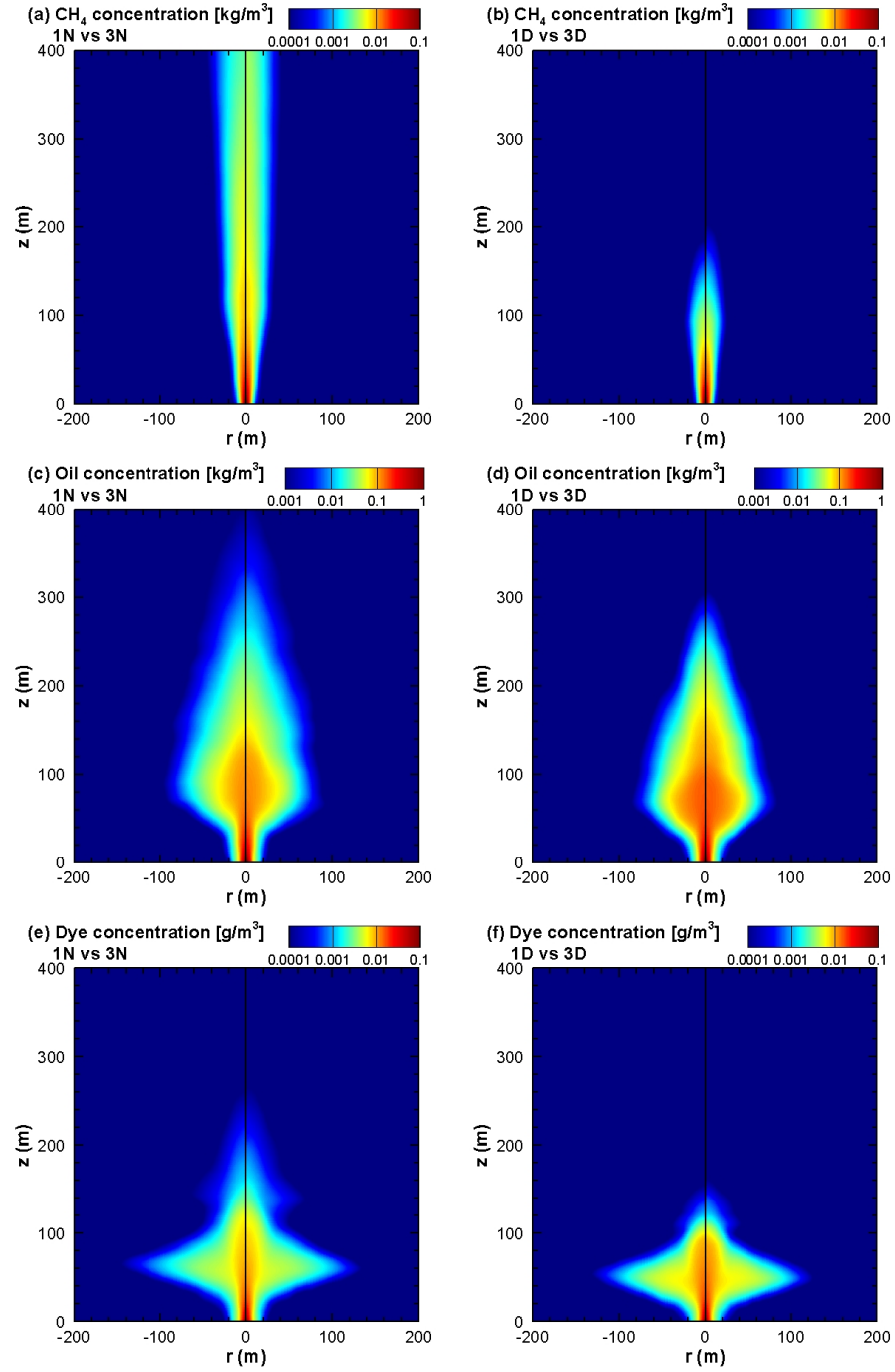


Figure 3.4: Comparison of time and angular-averaged concentration of methane in bubble((a-b) in kg/m^3), concentration of oil droplets ((c-d) in kg/m^3), and dye concentration ((e-f) in g/m^3) from LES runs.

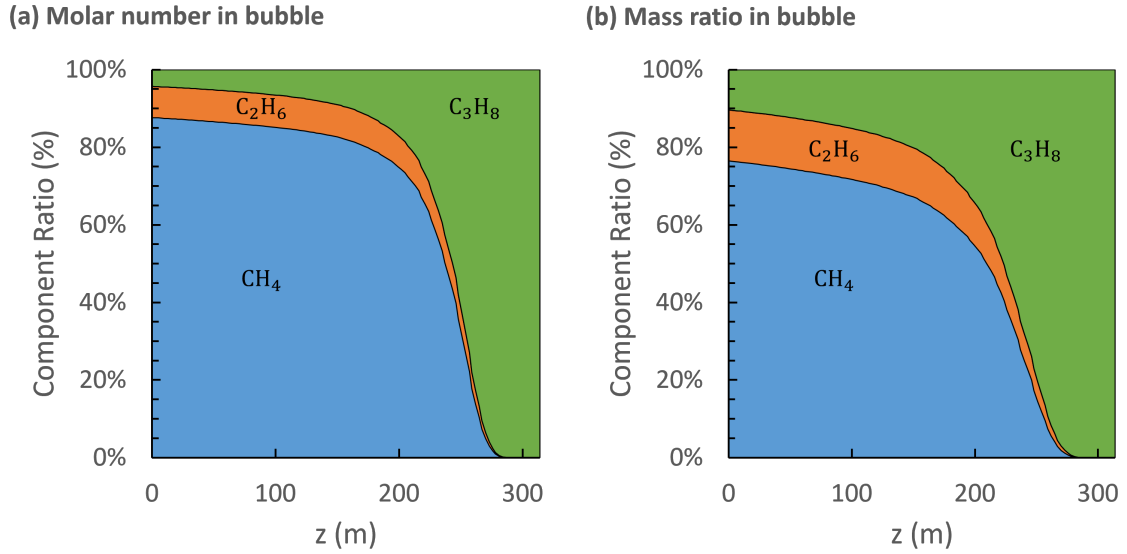


Figure 3.5: (a) Molar mass component ratio and (b) mass component ratio in gas bubble.

Comparing the 1-component case and 3-component case without horizontal crossflow, the result shows the plume with the same density stratification and same initial buoyancy flux will drive and form the same structure of the plume, and the corresponding oil droplet and dye will have the same distribution. This tells us that even with the first major component, the gas bubble dissolution model with a single component will catch the main information of the evolution of plume structure, and the oil and dye transportation and obtain a relatively precise result compared with the multi-component gas model. This is valuable for validation and prediction in an accident that requires a quick response. However, the dissolved natural gases may have a short-term effect on water quality, including changes in dissolved oxygen levels, which can be detrimental to plants and wildlife [94, 102]. The detailed distribution and afterward evolution of each dissolved component can only be captured with the multi-component dissolution model. Each gas component is separated by the ocean density stratification after dissolving. The layer separation of dissolved gas is

more clearly shown under a horizontal crossflow condition in Section 3.4.

3.4 Three-Component Gas Bubble Dissolution with Crossflow

Crossflow is common in the deep ocean and may further complicate the dynamics of the bubble-driven multiphase plume [28, 82, 90, 99]. Due to the differing vertical velocities of the bubble plume and entrained water stream in the multiphase plume, a strong crossflow may cause them to rapidly split at the separation height h_s above the plume source. When the crossflow is weak, the bubbles and entrained water flow in the plume cannot be separated directly by the crossflow before the multiphase plume reaches the peel height [19], resulting in an inclined rising/falling double plume structure with increased complexity in the plume dynamics due to the crossflow [78]. The simulations focus on situations with relatively little crossflow, with the goal of simulating the distribution and destiny of dissolved gases, as well as the complex dynamics of the plume when it is impacted by both stratification and crossflow. The crossflow velocities is set to be 0.04m/s.

The current LES employs a pseudospectral approach based on the Fourier series transformation, which often needs periodic boundary conditions in the horizontal directions. The fringe zone approach [6, 20, 71] is used in this work to allow the application of inflow/outflow conditions in the streamwise direction when simulating a plume interacting with a crossflow. A fringe zone of limited streamwise thickness close to the simulation domain's outflow border is utilized to drive the velocity field back to its value at the inflow boundary, allowing the periodic pseudospectral flow solver to simulate nonperiodic flow. The horizontal domain dimensions for the simulated instances with crossflow are

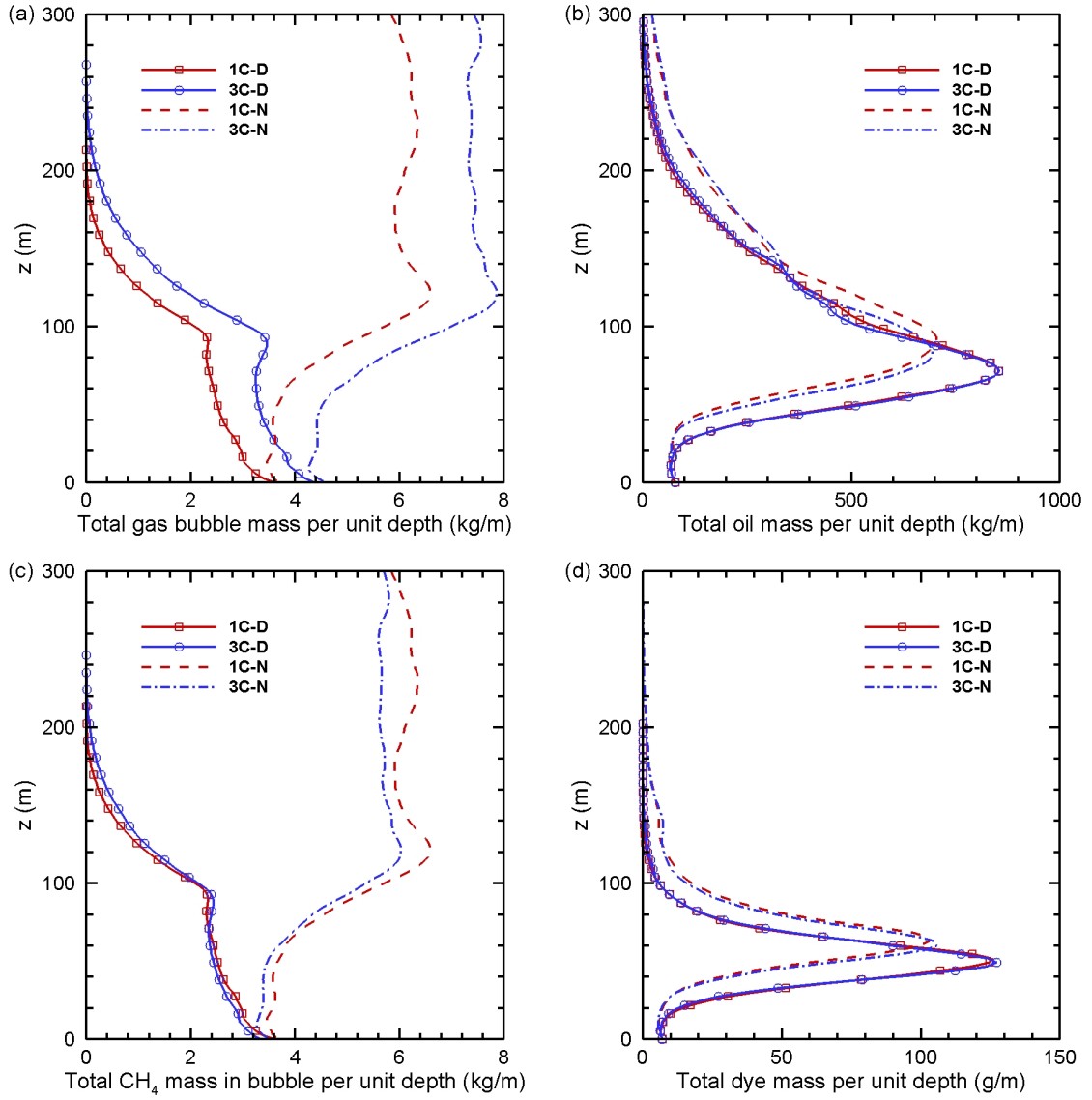


Figure 3.6: Comparison of time-averaged concentration per depth. Panels (a) total gas mass in bubble per depth (in kg/m^3); (b) oil mass per depth (in kg/m^3); (c) methane mass in gas bubble per depth (in kg/m^3); (d) dye mass per depth (in g/m^3).

set to $L_x = 640$ m and $L_y = 640$ m for the x- and y-directions, respectively. $(N_x, N_y, N_z) = (320, 256, 289)$ grid points are used to discretize the simulation domain, with equal grid spacing in each direction. A uniform streamwise velocity U_c is imposed in the x-direction at the inflow boundary 200 m upstream from the bubble source. The last 80 meters of the streamwise domain are designated as the fringe zone for the purpose of enforcing the outflow condition. The simulations with horizontal crossflow use the grid resolution of $(\Delta x, \Delta y, \Delta z) = (2.5, 2.5, 2.1875)$ m.

Figure 3.7 shows the instantaneous plume of the reference case LS-3D-4cross. In Figure 3.7, panels (a-c) shows the concentration of each component (methane, ethane, propane) in bubble (in kg/m^3), (d-f) shows the dissolved gas concentration of each component (methane, ethane, propane) in water (in kg/m^3), (g) shows the corresponding bubble number density (in $1/\text{m}^3$), (h-i) shows fluid vertical and horizontal velocity (in m/s). Due to the turbulence impact of the plume flow and the unsteadiness of the peeling process, the instantaneous plume field displays significant variations in velocities and scalar concentrations. The rising plume of bubbles is tilted towards the positive x-direction, and the gas concentration fields Figure 3.7 (a-c) are no longer axisymmetric about the centerline of the ascending plume. The horizontal peeling flow and subsequent falling plume have a tilt towards the downstream direction of the crossflow, resulting in the intrusion layer forming exclusively in the positive x-direction and the intrusion layer forming in the upstream direction is entirely suppressed Figure 3.7 (d-f). Because the crossflow tilts the gas/oil plume enough away from being vertical, the detrained water creates a strong downward plume at about $(x, z) = (30, 70)$ m, which falls on the downstream side of the rising plume Figure 3.7(h).

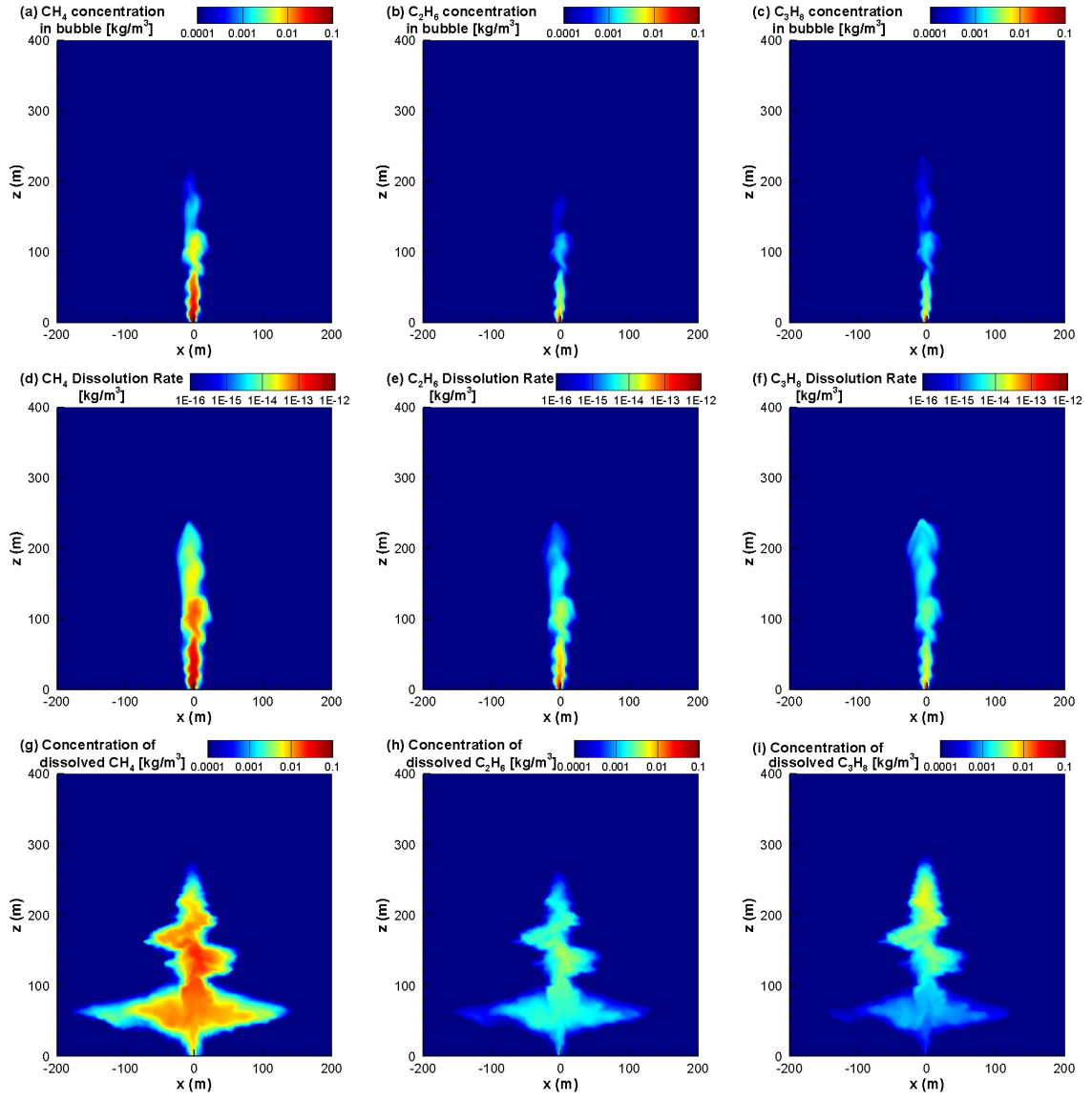


Figure 3.7: Instantaneous plume flow and scalar fields on the (x,z) -plane across the source location for case LS-3D-4cross obtained from the LES.

Figure 3.8 shows the time-averaged plume flow and scalar fields on the (x,z)-plane across the source location for case LS-3D-4cross obtained from the LES. Panels (a-c) shows the concentration of each component (methane, ethane, propane) in bubble (in kg/m^3); (d-f) shows the dissolved gas concentration of each component (methane, ethane, propane) in water (in kg/m^3); (g) shows the corresponding bubble number density (in $1/\text{m}^3$); (h-i) shows fluid vertical and horizontal velocity (in m/s).

In Figure 3.8, the mean plume field is calculated using a temporal average, which demonstrates the influence of crossflow on the averaged plume structure and material movement. The gas and oil were discharged at $t = 0$ s for the crossflow case, and simulations were run until the plume flow and scalar concentration fields achieved a statistically stable state. Then, from $t = 10,000$ to $20,000$ s, instantaneous snapshots of the whole three-dimensional simulation domain were captured, with a constant time interval of the 40s between each sample. In the crossflow case, temporal averaging was performed using a total of 250 instantaneous snapshots of the whole simulation domain. The dashed lines in Figure 3.8(a-c) are calculated using the maximum elevation of the 1 percent threshold contour line of the highest time-averaged gas concentration in the bubbles. Most gas components will dissolve in the dashed outlines. For the methane and ethane components, the highest points of the outlines reach 130m and 135m, while the propane reaches 185m. The propane in the gas bubble dissolves slower and much longer in the gas phase which mainly drives the second peeling event.

The distribution of the dissolved gas concentration in water shows that a primary peeling event occurs at $z = 110$ m, causing most of the initially entrained water to detrain from the rising plume and fall to the neutral buoyancy level to form the thin intrusion layer at $z =$

70 m Figure 3.8(d-f). The remaining undissolved part of the gas bubbles then escape from the first peeling process and continue to climb higher. Then the bubble plume repeats the water entrainment/peel process in the region of $z = 110\text{m}$ to 180m , forming a secondary intrusion layer at $z = 120\text{ m}$ and up. Half of the maximum elevation of the greatest time-averaged dissolved gas concentration in water contour lines in the bubbles was used to construct the dashed lines in Figure 3.8(d-f). The dashed line shows the final destination of the main part of the dissolved gas. For the methane and ethane components, more than half of them will dissolve and stay in the first trap height of 70m . The propane will get higher and mainly stay in the range of $z = 130\text{m}$ to 240m .

Two major peeling events are captured from the averaged fluid vertical velocity field Figure 3.8(h) at 110 m and 180 m as the solid line shows (The solid and dashed lines are the threshold of 0.03 m/s and -0.03 m/s). The dashed line outlines the downward plume in the downstream direction, which push the detrained water to the positive x -direction and form three intrusion layers at $z = 70\text{m}$, 140m , and 190m Figure 3.8(i). Above the 200m , the gas bubbles separate with the plume and become tiny. The tiny bubbles rise with a small slip velocity and accumulated in the range of $z = 200$ to 300m . All the bubbles get fully dissolved below 300m Figure 3.8(g).

Figure 3.9 shows the dissolved gas concentration on the averaged center plane at the downstream line $x = 200\text{ m}$. Here the line is 200 m far enough from the source and not dynamically affected by the plume. The dissolved gas component concentrations reflect the final distribution of each component on different layers. The dissolved component concentrations are normalized by their release mass ratios to avoid the difference in the initial release rate. Three main peaks are found in the line chart at depths of 70 m , 140m ,

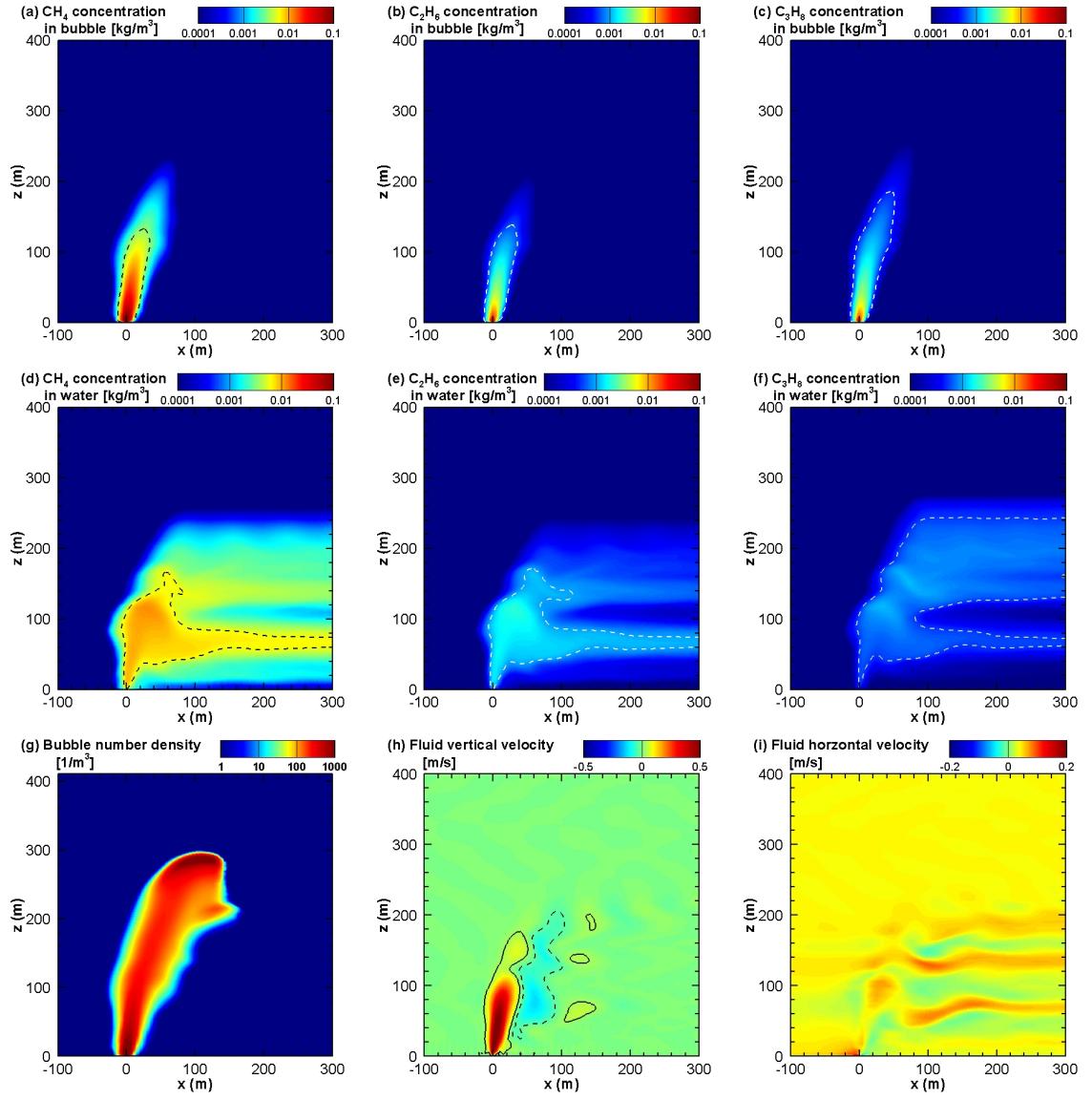


Figure 3.8: Time-averaged plume flow and scalar fields on the (x,z) -plane across the source location for case LS-3D-4cross obtained from the LES.

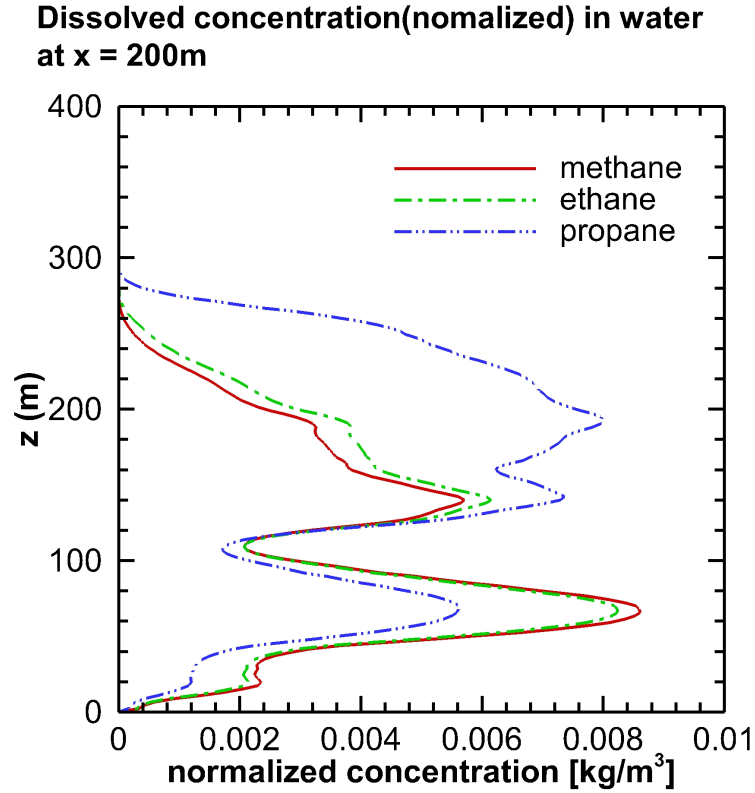


Figure 3.9: Dissolved concentration for case LS-3D-4cross at downward x = 200m.

and 190 m. For the methane and ethane, the highest peak appears at 70m, more than half of the component will finally spread in the first intrusion layer. For the propane, The highest peaks appear at 140m and 190m. The main part of the propane will stay at the second and third intrusion layers. The heavier molecules in the gas bubble will distribute at higher elevations eventually.

3.5 Summary

In deep-sea oil spill accidents, oil and natural gas are released from the seabed and form an upward hydrocarbon plume driven by the buoyancy force. When the gas bubbles and oil droplets rise, the gas will dissolve into the ambient seawater very quickly. The plume will

then lose the driving force and the oil and gas will stay in the ocean and become pollutants. The different gas components in the bubble have different dissolution rate and their synergy effect will influence the plume shape and the pollutant distribution.

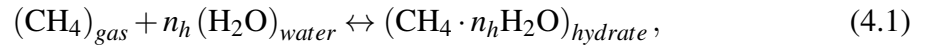
In this chapter, a fast Eulerian large-eddy simulation model is developed to simulate hydrocarbon plumes from the seabed under the influence of multi-component gas bubble dissolution and the crossflow effect. In the simulation, 1-component and 3-component nature gas bubble cases are constructed and show the relationship of the single- and multi-component bubble dissolution model, the gas and oil released from 700m depth and compare with and without a crossflow of 0.04m/s. The result shows the contribution of different gas components to the plume dynamics is highly correlated with the remaining ratio and the relative dissolution rate. A crossflow case clearly shows the distribution of layers separated by dissolved gas components and oil composition via both the instantaneous plume fields and the statistical analysis of time-averaged plume properties.

Chapter 4

LES HYDROCARBON PLUME WITH HYDRATE FORMATION AND DECOMPOSITION IN DEEP OCEAN SPILL

4.1 Introduction

In deep-water conditions, where the gas bubbles are released below the hydrate thermodynamic equilibrium depth, the gases are likely to form 'gas hydrates' with the ambient water under high pressure and low temperature circumstances [101]. The gas hydrate formation and decomposition are a pair of the reversible physical process in which the water molecules form cage-like structures to lock in gas molecules [74, 75]. For methane, the reaction can be described as [107]:



in which n_h is 5.75 for methane. The density of the methane hydrate is $900 [\text{kg}/\text{m}^3]$. The buoyancy force will bring these hydrate particles upward to the low pressure regions above

the hydrate equilibrium depth. The hydrate particles will then decompose into free gas and quickly dissolved into the ambient seawater [101].

Thermodynamics and kinetics studies on gas hydrate reveal the conditions of hydrate formation and the rate of formation and decomposition [42, 73]. The hydrate growth model was developed from experiments [29, 30, 56, 91] and applied to hydrate plugging problems [26, 44]. The hydrate formation model was also applied to deep-water blowouts combined with the plume model [5, 86, 87]. The hydrate clathrate was assumed to form and cover the outside of the gas bubble and the thermal dynamics should be considered [41, 101].

In this study, the method considering the kinetics, mass transfer, and heat transfer [29, 101] was used to build the single bubble formation dynamics model. The single bubble formation model was then coupled with our LES model [63] to simulate the hydrate plume. The single bubble model considers a single gas bubble in infinite water, the hydrate shell grows on the out surface of the gas bubble below the hydrate equilibrium depth, and the gas bubble was considered as an equivalent spherical bubble. Figure 4.1 shows the schematic of hydrate coated bubble with a uniform hydrate shell and ideally spherical bubble shape. The r_b is the inner radius of the gas bubble, the r_h is the outer radius of the hydrate shell. Inside the gas bubble, $r < r_b$ is pure methane (CH_4) in the gas phase; the hydrate shell $r_b \leq r < r_h$ is composed of methane clathrate ($\text{CH}_4 \cdot 5.75\text{H}_2\text{O}$); outside the hydrate shell is the ambient seawater. During the hydrate formation process, the hydrate nucleation process is neglected due to the shortness of the nuclear time [7, 9, 56].

When the hydrate coated gas bubbles/hydrate particles travel above the hydrate equilibrium depth, the hydrate clathrate starts to decompose. The kinetics of hydrate decomposition for the single bubble model was built with the method of Kim [46, 101], and the

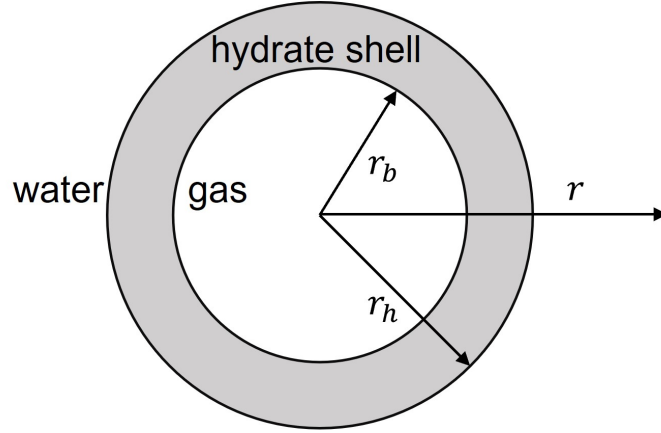


Figure 4.1: Schematic of hydrate coated bubble with uniform hydrate shell on the outside of a equivalent spherical bubble. The r_b is the inner radius of the gas bubble, the r_h is the outer radius of the hydrate shell.

decomposed free gas was considered as the dissolved gas.

The current chapter is organized as follows. The detailed formulations for hydrate formation/decomposition simulation of a single bubble in the deep ocean and the formulas are shown in section 4.2. Section 4.3, gives the setup condition and the results for the LES simulation cases with the gas bubble hydrate effect. Summary is given in section 4.4.

4.2 Numerical Method

4.2.1 Hydrate formation of gas bubble

For a single gas bubble under hydrate conditions, the gas consumption rate is [29, 101, 107]:

$$\frac{dn}{dt} = K_f A (f_{dis} - f_{eq}), \quad (4.2)$$

where f_{dis} is the fugacity [MPa] of dissolved gas and f_{eq} is the fugacity of gas at the three-phase equilibrium condition.

Table 4.1: Kinetic parameter (K_f) for methane hydrate formation [29].

Temperature [K]	$K_f \times 10^5$ [mol/m ² s · MPa]
274	0.65
276	0.55
279	0.57
282	0.58

The three-phase (L_W-H-V) equilibrium pressure under the given temperature is calculated using a cubic polynomial function fitted from the result of the CSMHYD program [18, 74]:

$$p_{eq} = 3.74949295 \times T^3 - 3146.01672 \times T^2 + 880424.908 \times T - 82174990.6, \quad (4.3)$$

With the equilibrium pressure, the equilibrium gas fugacity is modeled based on [64]:

$$f^g = p_b \exp \left[Z - 1 - \ln(Z - B) - \frac{A}{2\sqrt{2}B} \ln \left(\frac{Z + 2.414B}{Z - 0.414B} \right) \right], \quad (4.4)$$

in which A and B are the model coefficients involved in calculating the compressibility factor Z (see Eqs. (A.9) and (A.10) in Appendix A for more details). Note that Eq. (4.4) is valid for bubbles with a single gas component. If a bubble contains multiple gas components, a variant of Eq. (4.4) needs to be used to calculate the fugacity coefficient for each gas component (see Eq. (19) in [64]).

The fugacity of dissolved gas can be calculated by:

$$f = H \frac{C_i}{C_{w0} + C_i} \approx H \frac{C_i}{C_{w0}}, \quad (4.5)$$

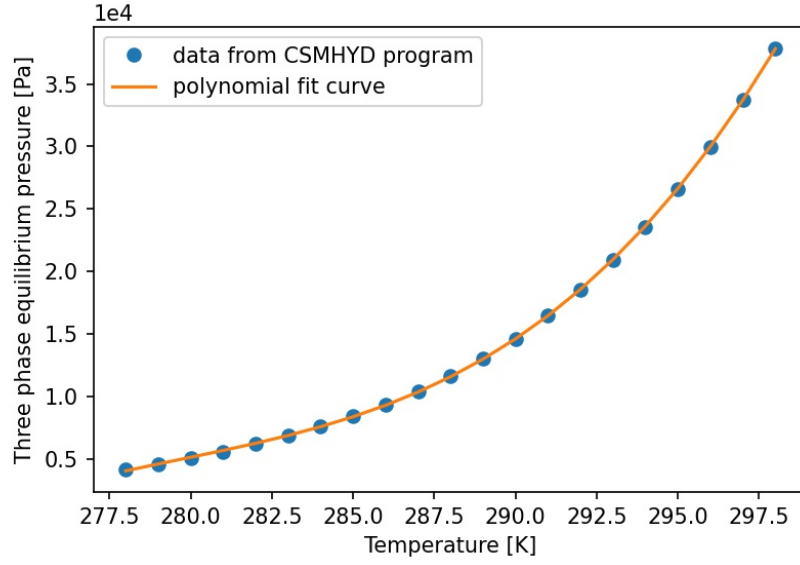


Figure 4.2: The three-phase (L_W-H-V) equilibrium pressure v.s. temperature. The data points are from the result of CSMHYD program, and the orange curve is the fitted cubic polynomial function.

where H is Henry's constant [MPa], which is a function of temperature [18, 48]:

$$-\ln H = \frac{H_{KW}^{(0)}}{R} + \frac{H_{KW}^{(1)}}{RT} + \frac{H_{KW}^{(2)}}{R} \ln T + \frac{H_{KW}^{(3)} T}{R}, \quad (4.6)$$

where the parameters in the equation are $H_{KW}^{(0)} = -365.183$, $H_{KW}^{(1)} = 18106.7$, $H_{KW}^{(2)} = 49.7554$, $H_{KW}^{(3)} = -0.000285$. Here the H is in [atm] and $R = 1.9858775$ [cal/K/mol].

C is the quantity of gas in the gas phase per unit volume of the hydrate shell, [mol/m³]; C_i is the value at the hydrate-water interface, and C_{w0} is the initial number of modes of water per unit volume of the water phase.

The mass transfer rates can be modeled by the diffusion equations:

$$\frac{d}{dr} \left(r^2 \frac{dC}{dr} \right) = 0, r_b \leq r \leq r_h, \quad (4.7)$$

$$C(r_b) = C_0, \quad (4.8)$$

$$C(r_h) = C_i, \quad (4.9)$$

and

$$-D_g 4\pi r_h^2 \psi_s \left. \frac{dC}{dr} \right|_{r=r_h} = \frac{dn}{dt}, \quad (4.10)$$

where $D_g = 1.0 \times 10^{-6}$ is the effective diffusion coefficient [m^2/s], $C_0 = P_\infty/ZRT$, P_∞ is the hydrostatic pressure of surrounding water, ψ is chosen to match experimental results.

The heat transfer is described by:

$$\frac{d}{dr} \left(r^2 \frac{dT}{dr} \right) = 0, r \geq r_h, \quad (4.11)$$

$$T(r_h) = T_i, \quad (4.12)$$

and

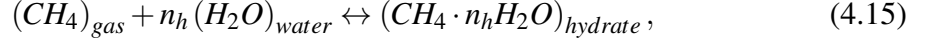
$$-K_w 4\pi r_h^2 \psi_s \left. \frac{dT}{dr} \right|_{r=r_h} = \lambda \frac{dn}{dt}, \quad (4.13)$$

where T_i is the temperature at the hydrate-water interface [K], $K_w = 0.5626$ [$\text{W}/\text{m} \cdot \text{K}$] is the thermal conductivity of water, $\lambda = 62800$ [J/mol] is the latent heat of hydrate formation [44, 107]. The volume of the hydrate shell is given by:

$$V_h = \frac{4}{3}\pi (r_h^3 - r_b^3). \quad (4.14)$$

The relation between the moles of gas consumption and the hydrate shell volume can be

calculated through:



where $n_h \approx 5.75$ for methane, density of hydrate ρ_h is 900 kg/m^3 . When the number of moles of gas consumption is calculated, the mass and volume of the hydrate shell can be obtained.

We apply the Peng-Robinson equation of state to determine how the bubble's size varies overtime throughout the rise [64]

$$\frac{4}{3} \pi r_b^3 P_\infty = n Z R T_\infty. \quad (4.16)$$

Solving the mass transfer equations and heat transfer equations, we get:

$$C_i = \frac{D_g r_b C_0 C_{w0} + K_f \psi_r f_{eq} (r_h - r_b) r_h C_{w0}}{D_g r_b C_{w0} + K_f \psi_r H (r_h - r_b) r_h} \quad (4.17)$$

and

$$T_i = \frac{\lambda K_f \psi_r r_h (H C_i - f_{eq} C_{w0})}{K_w C_{w0}} + T_\infty, \quad (4.18)$$

where $r_b = \left(\frac{3nZRT_\infty}{4\pi} \right)^{1/3}$, $C_0 = \frac{P_\infty}{ZRT}$, $C_{w0} = 5.55 [\text{mol/m}^3]$ is the initial number of moles of water per unit volume of water phase, $K_f = 0.57 \times 10^{-11} [\text{mol gas/m}^2 \text{Pa s}]$ is the intrinsic formation rate constant, $\psi_r = 1$ [44, 107] is the surface roughness factor, f_{eq} is the fugacity of gas at three-phase equilibrium condition.

At the initial moment, the thickness of the hydrate shell is 0, $r_h = r_b$, $T_i(t = 0) = T_\infty$,

we can calculate C_i and T_i , then the C_i and T_i is used to calculate $\frac{dn}{dt}$. The $\frac{dn}{dt}$ will used to update the r_b and r_h in the next time step.

4.2.2 Decomposition rate of hydrate particles

For a single Hydrate particle under dehydrate conditions, the gas decomposition rate is:

$$-\frac{dn}{dt} = K_d A_p (f_{eq} - f_g^v), \quad (4.19)$$

where $A_p = 4\pi r_h^2 \psi_h$ is the surface area of a hydrate coated particle, ψ_h is the shape factor, K_d is the decomposition factor:

$$K_d = K_d^0 \exp(-\Delta E / RT_i) \quad (4.20)$$

where T_i is the particle surface temperature [K], K_d^0 and ΔE for methane were given in [46]:

$$\ln K_d^0 = 29.4 \pm 1.9 [s^{-1}] \quad (4.21)$$

and

$$\frac{\Delta E}{R} = 9400 \pm 545 [K^{-1}]. \quad (4.22)$$

Here, $A_p = 4\pi r_h^2 \psi_h$ is the surface area of a particle, ψ_h is a shape factor, K_d is the decomposition rate [mol gas/m²MPa · s], $R = 8.31 \left[\frac{J}{mol \cdot K} \right]$ is the molar gas constant.

4.2.3 Gas dissolution

In this chapter, the gas dissolution effect is excluded during the hydrate formation process. When gas bubbles/hydrate particles move above the hydrate equilibrium depth, the hydrate clathrate decomposes into free gas and water, the free gas dissolves into the ambient seawater at the same time. The hydrate decomposition rate is relatively very slow compared with the gas dissolution rate, the free gas from the decomposition is considered to be fully dissolved into the ambient seawater.

4.2.4 Large-eddy simulation model of deep-water hydrocarbon plume

In this study, the carrier flow is modeled by the filtered Navier-Stokes equations with Cartesian coordinate, where $\mathbf{x} = (x, y, z)$, x and y are the horizontal axis and z is vertical the axis. The corresponding velocity field is $\mathbf{u} = (u, v, w)$. The filtered Navier-Stokes equations are used to simulate the carrier flow movements [97].

$$\nabla \cdot \tilde{\mathbf{u}} = 0 \quad (4.23)$$

and

$$\begin{aligned} \frac{\partial \tilde{\mathbf{u}}}{\partial t} + \tilde{\mathbf{u}} \cdot \nabla \tilde{\mathbf{u}} = & -\frac{1}{\rho_0} \nabla \tilde{P} - \nabla \cdot \boldsymbol{\tau}^d + \left(1 - \frac{\tilde{\rho}}{\rho_0}\right) g \mathbf{e}_z + \left(1 - \frac{\rho_h}{\rho_0}\right) \frac{\tilde{C}_h}{\rho_h} g \mathbf{e}_z + \\ & \left(1 - \frac{\rho_b}{\rho_0}\right) \frac{\tilde{C}_b}{\rho_b} g \mathbf{e}_z + \left(1 - \frac{\rho_d}{\rho_0}\right) \frac{\tilde{C}_d}{\rho_d} g \mathbf{e}_z. \end{aligned} \quad (4.24)$$

Here, the tilde denotes the variable resolved by the LES computational grid; ρ_0 is the reference seawater density; $\tilde{\rho}$ is the resolved local seawater density; $\boldsymbol{\tau}^d = \boldsymbol{\tau} - [\text{tr}(\boldsymbol{\tau})/3]\mathbf{I}$ is the

deviatoric part of the subgrid-scale stress tensor $\tau = (\widetilde{\mathbf{u}\mathbf{u}} - \widetilde{\mathbf{u}}\widetilde{\mathbf{u}})$, where $\text{tr}(\tau)$ is the trace of τ and $\mathbf{I}$ is the identity tensor; $\widetilde{P} = \widetilde{p} + \rho_0[\text{tr}(\tau)/3 - gz]$ is the modified pressure, where $\widetilde{p}$ is the resolved water pressure and g is the gravitational acceleration; $\mathbf{e}_z$ is the unit vector in the vertical direction; ρ_b is the density of gas in bubbles in local LES computational cell; C_h is the mass concentration of hydrate shell; C_b is the mass concentration of gas phase; ρ_d is the density of oil droplet; and C_d is the mass concentration of oil droplets. Boussinesq approximation is used for the buoyancy force represents the last three components in Equation 36, the buoyancy force due to water density stratification, gas bubble concentration, and oil droplet concentration [97].

Following the previous studies [17, 32, 49, 59, 65, 96, 97], this work describes the stratification effect in seawater in terms of the virtual temperature field governed by a filtered convection-diffusion equation:

$$\frac{\partial \widetilde{\theta}}{\partial t} + \nabla \cdot (\widetilde{\mathbf{u}}\widetilde{\theta}) = -\nabla \cdot \pi_\theta, \quad (4.25)$$

and a linear relationship between potential temperature and corresponding seawater density is described as:

$$\widetilde{\rho} = \rho_0[1 - \alpha_t(\widetilde{\theta} - \theta_0)], \quad (4.26)$$

where $\pi_\theta = \widetilde{\mathbf{u}\theta} - \widetilde{\mathbf{u}}\widetilde{\theta}$ is the SGS thermal flux, α_t is the thermal expansion coefficient, and θ_0 is the reference potential temperature corresponding to the reference seawater density ρ_0 . These gas bubbles are treated as dispersed phase and continuous Eulerian functions, namely the bubble concentration functions $C_b(\mathbf{x}, t)$ and a bubble number density function

$N_b(\mathbf{x}, t)$ respectively. A set of filtered transport equations with the bubble dissolution effect term included for each gas component is used to predict the bubble mass concentration:

$$\frac{\partial \tilde{C}_b}{\partial t} + \nabla \cdot (\tilde{\mathbf{v}}_b \tilde{C}_b) = -\nabla \cdot \boldsymbol{\pi}_b + q_b + \frac{dn}{dt} - \tilde{\alpha}_b, \quad (4.27)$$

where $\tilde{\mathbf{v}}_b$ is the Lagrangian transport velocity of bubbles, $\boldsymbol{\pi}_b = \widetilde{\mathbf{u}C_b} - \tilde{\mathbf{u}}\tilde{C}_b$ is the SGS flux of bubble mass concentration, $q_b = \rho_{b,0}V_{b,0}q_n$ is the volumetric source term for the release of gas bubble mass, $\rho_{b,0}$ is the gas bubble density in the bubbles at the release source, $V_{b,0}$ is the initial volume of a single bubble at the release source, q_n is the source term representing the number of released bubbles from a subsea blowout, $\left(\frac{dn}{dt}\right) = \tilde{N}_b \left(\frac{dn}{dt}\right)_b$ is the cell-averaged local gas mass consumption from hydrate (per unit volume) resolved by the LES model, $\tilde{\alpha} = \tilde{N}_b \tilde{\alpha}_b$ is the cell-averaged local gas mass dissolution rate (per unit volume) resolved by the LES model.

A filtered transport equation is used to predict the growth of the bubble number density, Similar to the bubble mass concentration:

$$\frac{\partial \tilde{N}_b}{\partial t} + \nabla \cdot (\tilde{\mathbf{v}}_b \tilde{N}_b) = -\nabla \cdot \boldsymbol{\pi}_n + q_n, \quad (4.28)$$

where $\boldsymbol{\pi}_n = \widetilde{\mathbf{u}N_b} - \tilde{\mathbf{u}}\tilde{N}_b$ is the SGS flux of bubble number density due to SGS turbulent flow effects. In Eq. (4.28), For the purpose of the model's simplicity, bubble breakage and coalescence are ignored.

The bubble transport velocity $\tilde{\mathbf{v}}_b$ is modeled as:

$$\tilde{\mathbf{v}}_b = \tilde{\mathbf{u}} + w_{r,b} \mathbf{e}_z + \frac{w_{r,b}}{g} \frac{D\tilde{\mathbf{u}}}{Dt}, \quad (4.29)$$

where $w_{r,b}$ is the rise velocity of bubbles relative to the surrounding carrier flow caused by the bubble buoyancy (see B for the parameterizations of $w_{r,b}$), and $D\tilde{\mathbf{u}}/Dt = \partial\tilde{\mathbf{u}}/\partial t + \tilde{\mathbf{u}} \cdot \nabla \tilde{\mathbf{u}}$ is the material derivative (or Lagrangian acceleration) of the carrier flow velocity.

Based on the quantity of gas mass concentration C_b and number density N_b , applying Eq. (3.7) to obtain the gas dissolution rate per single bubble $\tilde{\alpha}_b$, the cell averaged dissolution rate $\tilde{\alpha}$ is given by

$$\tilde{\alpha} = \tilde{N}_b \tilde{\alpha}_b = \tilde{N}_b \tilde{A}_b \tilde{K} \left(\tilde{C}_s - \tilde{C}_{dis} \right). \quad (4.30)$$

For the concentration of dissolved gas in the ambient seawater, the function $\tilde{C}_{dis}$ is modeled as

$$\frac{\partial \tilde{C}_{dis}}{\partial t} + \nabla \cdot \left(\tilde{\mathbf{u}} \tilde{C}_{dis} \right) = -\nabla \cdot \boldsymbol{\pi}_{dis} + \tilde{\alpha}, \quad (4.31)$$

where $\boldsymbol{\pi}_{dis} = \widetilde{\mathbf{u} C_{dis}} - \tilde{\mathbf{u}} \tilde{C}_{dis}$ is the SGS flux of mass concentration for the dissolved gas. Different from $\tilde{N}_b$ and $\tilde{C}_b$, the dissolved gas concentration $\tilde{C}_{dis}$ is carried as a passive scalar dependent on the carrier flow velocity $\tilde{\mathbf{u}}$.

Other than gas bubbles, there are also oil droplets that spill in a similar location and provide the plume with buoyancy. When it comes to modeling oil droplet travel, the filtered transport equation comes in handy,

$$\frac{\partial \tilde{C}_{oil}}{\partial t} + \nabla \cdot (\tilde{\mathbf{v}}_{oil} \tilde{C}_{oil}) = -\nabla \cdot \boldsymbol{\pi}_{oil} + q_{oil}, \quad (4.32)$$

where q_{oil} is a source term for the oil droplet release, $\pi_{oil} = (\widetilde{\mathbf{u}C_{oil}} - \widetilde{\mathbf{u}}\widetilde{C_{oil}})$ is the SGS flux of oil mass concentration, and $\widetilde{\mathbf{v}}_{oil}$ is the transport velocity of oil droplets (with non-negligible buoyancy effect) [16, 21, 96],

$$\widetilde{\mathbf{v}}_{oil} = \widetilde{\mathbf{u}} + w_{r,oil}\mathbf{e}_z + \frac{w_{r,oil}}{g} \frac{D\widetilde{\mathbf{u}}}{Dt}. \quad (4.33)$$

The oil droplet rise velocity due to buoyancy is modeled as [22, 89, 97]

$$w_{r,d} = \begin{cases} w_{r,oil}^S & \text{Re}_{oil} < 0.2, \\ w_{r,oil}^S (1 + 0.15\text{Re}_{oil}^{0.687})^{-1}, & 0.2 < \text{Re}_{oil} < 750, \end{cases} \quad (4.34)$$

where $w_{r,oil}^S$ is the oil droplet rise velocity given by Stokes' law as

$$w_{r,oil}^S = \frac{(1 - \rho_{oil}/\rho_0)gd_{oil}^2}{18\nu}, \quad (4.35)$$

where ρ_{oil} is the oil density, d_{oil} is the equivalent diameter of the oil droplet, ν is the kinematic viscosity of water, and $\text{Re}_{oil} = w_{r,oil}d_{oil}/\nu$ is the oil droplet Reynolds number.

The LES governing equations are closed by parametrizing the SGS terms with appropriate turbulence closures using the Lilly-Smagorinsky eddy-viscosity type model [55, 76]. $\tau^d = -2\nu_\tau\widetilde{\mathbf{S}}$, where $\widetilde{\mathbf{S}} = [\nabla\widetilde{\mathbf{u}} + (\nabla\widetilde{\mathbf{u}})^T]/2$ is the resolved strain rate tensor, $\nu_\tau = (c_s\Delta)^2|\widetilde{\mathbf{S}}|$ is the modeled SGS eddy viscosity, c_s is the Smagorinsky model coefficient, and Δ is the LES grid (filter) scale. The value of c_s is determined dynamically during the simulation using the Lagrangian-averaged scale-dependent dynamic SGS model [8]. The SGS fluxes of the scalar quantities are then parametrized as $\pi_\theta = -(\nu_\tau/\text{Pr}_\tau)\nabla\widetilde{\theta}$, $\pi_n = -(\nu_\tau/\text{Sc}_\tau)\nabla\widetilde{N}_b$,

$\pi_b = -(\nu_\tau/\text{Sc}_\tau)\nabla\tilde{C}_b$, $\pi_{dis} = -(\nu_\tau/\text{Sc}_\tau)\nabla\tilde{C}_{dis}$ and $\pi_{dye} = -(\nu_\tau/\text{Sc}_\tau)\nabla\tilde{C}_{dye}$, with a constant SGS Prandtl number $\text{Pr}_\tau = 0.4$ and SGS Schmidt number $\text{Sc}_\tau = 0.4$ [1, 3, 14, 50, 57, 60, 63, 85, 97].

4.3 Gas Bubble Hydration Effect

4.3.1 Problem Setup

In our earlier research, we studied the gas bubble dissolution effect in the deep ocean hydrocarbon plume simulation [63]. In this study, we gas bubble hydrate effect is added to the model and combined with the dissolution effect. The test cases only including the hydrate formation/decomposition effect are set up to compare with the results in [101] paper and validate the hydrate modeling.

In the test cases, The domain size are $L_x = 450\text{m}$ (from -225m to 225m), $L_y = 450\text{m}$ (from -225m to 225m), $L_z = 1000\text{m}$ (from -1000m to 0m). Two test cases with different source release locations were studied, including a case released at the point $\{225\text{m}, 225\text{m}, -1000\text{m}\}$ of the domain and another case release at $\{225\text{m}, 225\text{m}, -630\text{m}\}$. Three test runs with different grid numbers for the spatial discretization were considered for each case, including a coarse-grid case with $N_x \times N_y \times N_z = 128 \times 128 \times 320$ points, a medium-grid case with $160 \times 160 \times 384$ points, and a fine-grid case with $192 \times 192 \times 448$ points. The simulation time steps used for these LES runs with different grid resolutions were $\Delta t = 0.1\text{ s}$. The source released at the simulation starts. The domain aspect ratio of $0.45: 0.45: 1$ offers enough horizontal room for the horizontal intrusion layers from the plume to expand.

In the test cases, the ambient seawater is linearly stratified by the temperature with a

two-slope linear function [101]. The temperature is set as:

$$\begin{aligned} T(z) = & T_1 + \gamma_1 z, \quad -1000\text{m} \leq z \leq -400\text{m}, \\ & T_2 + \gamma_2 z, \quad -400 < z \leq 0\text{m}, \end{aligned} \quad (4.36)$$

where $\gamma_1 = 0.00833 \text{ K m}^{-1}$, $\gamma_2 = 0.0375 \text{ K m}^{-1}$ are the vertical temperature gradient coefficients, $T_1 = 278.15 \text{ K}$, $T_2 = 260.65 \text{ K}$ are the ambient water temperature at the reference depths (at $z = -1000\text{m}$). The background salinity is set to be a constant 0.35%. Same with the [63, 97], the no-slip condition is used at the bottom boundary, the free-slip condition is used at the top boundary, and the periodic boundary conditions is used in the horizontal directions associated with the pseudo-spectral method.

The gas mass release rate is $Q_v^0 = 3.2752 \text{ normal m}^3/\text{s}$ (i.e. defined under normal condition at the sea level) [101]. The corresponding mass release rate of methane is $Q_c = 2.32 \text{ kg/s}$ (at $z = 0\text{m}$ and $z = 370\text{m}$). The bubbles have uniform shape and size at the release points. The equivalent initial diameter is 12mm. The oil release rate for all the cases is 16.4312 kg/s with a constant density 893 kg/m^3 and uniform diameter of 12mm. The dye release rate is 1 g/s . The dye has the same density as the ambient water and has no buoyancy and dynamic effect in the field. It behaves as passive transport scalar and can represent tiny particles.

The general process of plume development can be divided into three steps. In the first step, the gas bubbles and the oil droplets release from the sea bed and supply a strong buoyancy force which lifts the ambient seawater to form an upward plume. In this step, the gas bubbles supply the main buoyancy force and have a larger slip velocity than the

oil droplets. The strong buoyancy force counterworks with the background stratification, and the plume gets upward acceleration. In meantime, the gas bubbles have the maximum dissolution rate and the bubble diameter keeps decreasing. In the second step, the bubbles gradually dissolve and disappeared, the density stratification makes the plume decelerate. In the meantime, the oil droplets keep rising with their buoyancy and separate from the plume. In the last step, the entrained water starts falling around the center plume due to its heavier density, and finally to the trapping height and forms a disc-shaped trapping layer.

4.3.2 Simulation Results

The gas bubble hydrate formation model coupled with the basic turbulent flow and scalar transport solver utilized in the current LES model has been validated against the integral plume model [101].

Here, Figure 4.3 shows the vertical variation of gas bubble inner diameter(left) and hydrate shell thickness (right) of the time- and angular-averaged inner plume obtained from the LES runs with different grid resolutions of the -630m released case and the -1000m released case. In the figure, the low resolution ($128 \times 128 \times 320$ grid points) cases are in blue dash-dotted lines, the medium resolution ($160 \times 160 \times 384$ grid points) cases are in green solid lines, and the high resolution ($192 \times 192 \times 448$ grid points) are in red dashed lines. All the lines with marks (blue square, green triangle, red diamond, black cross) on them are the -1000m cases. The solid black lines on the bubble diameter figure are the predictions from Yapa, Zheng, and Chen (2001) [101].

In Figure 4.3 (left), the variation of inner plume gas bubble diameter with height was compared. The bubble diameter is estimated by the same method in Chapter 2. The pre-

dictions from the integral model of Yapa, Zheng, and Chen (2001) [101] are included. In Yapa, Zheng, and Chen (2001), two different integral model cases are simulated, including a case with a gas release depth of -630m, and another case with a gas release depth of -1000m. For comparison, the LES runs were performed accordingly by matching the physical parameters as well as the gas hydrate setting. In all the cases, the hydrate equilibrium depth is at -570m and the gas dissolution effect is excluded from the comparison. Above the hydrate equilibrium depth, the gas bubbles which do not have enough time to fully form hydrate will increase the bubble diameter with height due to the reduction of the ambient hydrostatic pressure in the 630m released cases. For the -1000m released case, the gas bubble diameter monotonically decreases with height. The gas bubbles fully become hydrate clathrate and the bubble diameters get to zero in the first 100m after release. The bubble hydrate LES model shows good agreement with the integral model of Yapa, Zheng, and Chen (2001) [101] for modeling the gas bubble size variation due to gas hydrate formation and change in hydrostatic pressure.

In Figure 4.3 (right), the variation of hydrate shell thickness along the centerline of the time and the angular-averaged plume was compared for -630m released cases and -1000m released cases. For the -630m released cases, the hydrate shell increase with height under the hydrate equilibrium depth due to hydrate formation and decreases above hydrate equilibrium depth due to hydrate decomposition. For the -1000m released cases, the hydrate shell thickness increase with height until the gas bubble fully become hydrate at -920m, then the gas bubbles become hydrate particles and the particle radius keeps the same until they arrive at the hydrate equilibrium depth, after that the hydrate particles start to decomposition and dissolve into the ambient water, therefore, the particle radius starts to gradually

decrease.

To test the grid resolution convergence of the hydrate formation LES model, here the simulation results from the low-resolution cases ($128 \times 128 \times 320$ grid points), medium resolution cases ($160 \times 160 \times 384$ grid points), and high-resolution cases ($192 \times 192 \times 448$ grid points) are compared. Figure 4.3 compares the bubble diameter, and the hydrate shell thickness for -1000m released cases and -630m released cases. The LES model obtains consistent trends for the inner plume bubble diameter as well as the center-line hydrate shell thickness with the three different grid resolutions. Medium resolution and high-resolution cases are found to agree very well, which suggests the medium grid resolution is sufficient for accurately modeling the gas bubble hydrate formation and decomposition effect.

Figure 4.4 shows a representative snapshot of the plume structure of the -630m-released case at $t = 10000$ s, in which the contours of several key physical quantities obtained from the LES are shown on the (x, z) -plane across the plume center line. The sub-figures show: (a) bubble number density (in m^{-3}); (b) bubble mass concentration (in kg/m^3); (c) hydrate shell mass concentration (in kg/m^3); (d) vertical velocity of plume flow (in m/s); (e) mass concentration of dissolved gas in the water (in kg/m^3); (f) hydrate formation rate (in $\text{kg}/\text{m}^3\text{s}$); (g) oil droplets mass concentration (in kg/m^3); (h) dye concentration (in g/m^3); (i) hydrate decomposition rate (in $\text{kg}/\text{m}^3\text{s}$).

The LES model obtains the instantaneous number density N_b (Figure 4.4(a)) and bubble mass concentration C_b (Figure 4.4(b)) by solving their transport equations, based on which the local cell-averaged bubble diameter and hydrate formation rate (Figure 4.4(f)) are modeled. The hydrate formation only happens under the hydrate equilibrium depth (-570m) as shown in (Figure 4.4(f)). The methane gas in the bubbles becomes hydrate shells (Figure

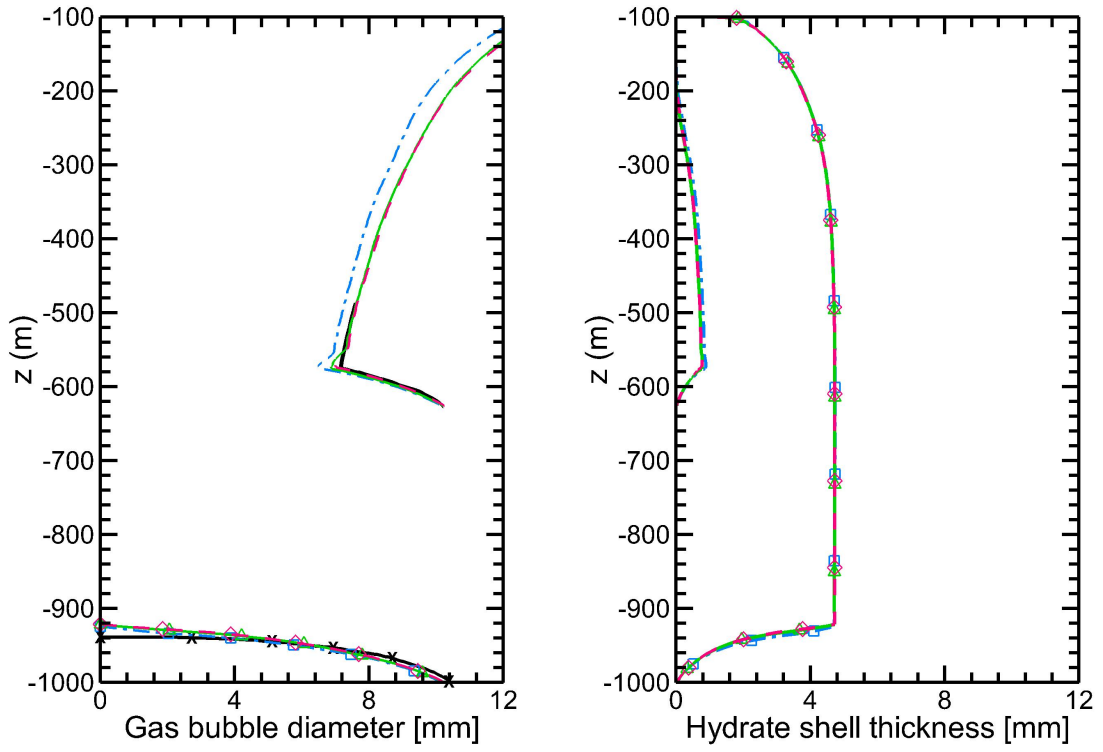


Figure 4.3: Vertical variation of gas bubble inner diameter(left) and hydrate shell thickness (right) of the time- and angular-averaged inner plume obtained from the LES runs with different grid resolutions.

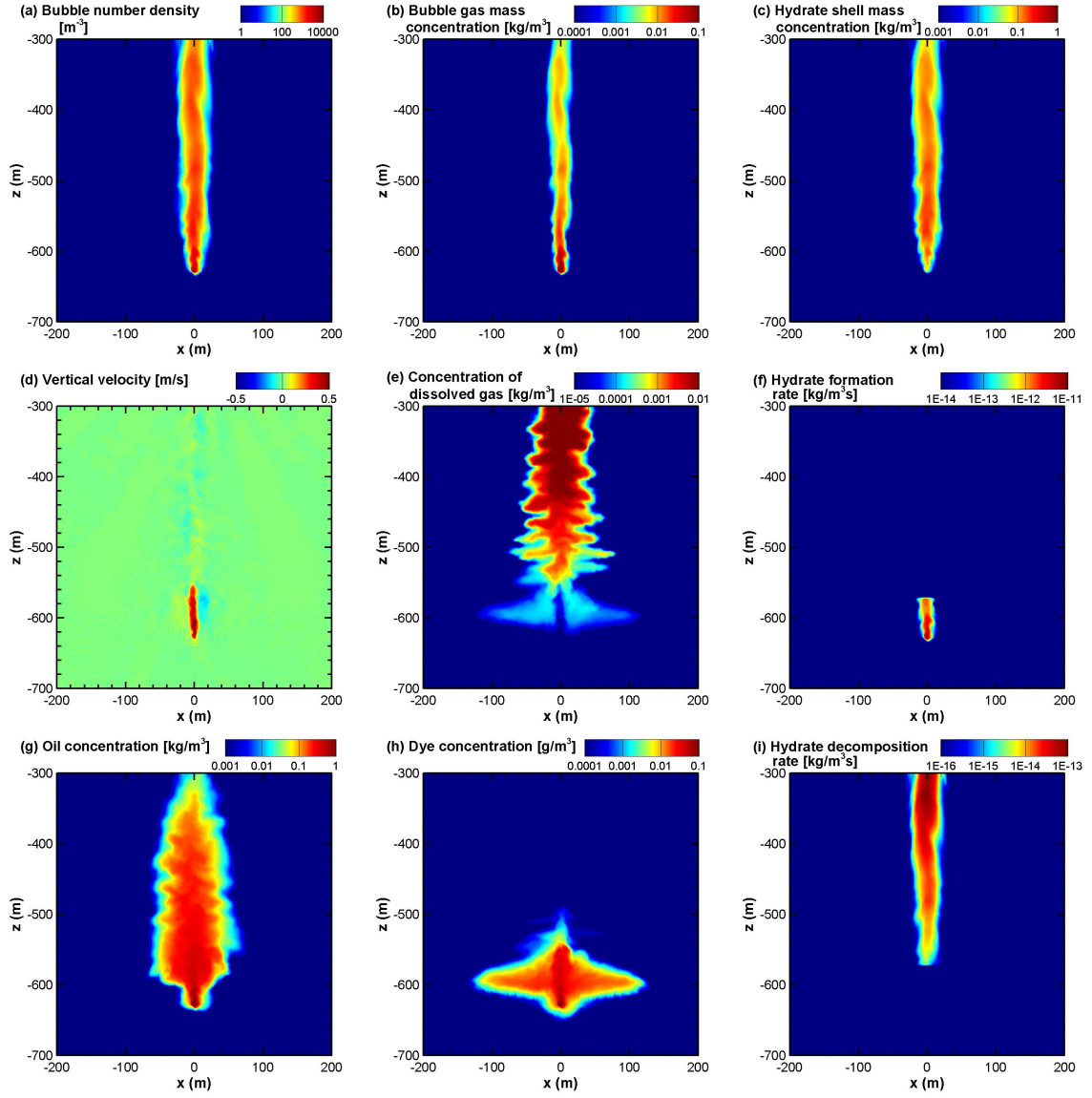


Figure 4.4: Instantaneous plume flow and scalar fields for 630m release case obtained from the LES at $t = 10,000$ s. Here the contours show the (x, z) -plane across the center of the plume field.

4.4(c)) and cover the bubble at the modeled instantaneous hydrate formation rate, causing the bubble diameter to reduce with the height from the source.

Above the equilibrium depth, the hydrate-coated gas bubbles start the hydrate decomposition process. The LES model obtains the instantaneous number density N_b (Figure 4.4(a)) and hydrate shell mass concentration (Figure 4.4(c)) by solving their transport equations, based on which the local cell-averaged bubble diameter, hydrate shell thickness, and hydrate decomposition rate (Figure 4.4(i)) are modeled. The hydrate shells (Figure 4.4(c)) become dissolved gas concentration (Figure 4.4(e)) in the ambient water at the modeled instantaneous hydrate decomposition rate (Figure 4.4(i)), and the inner gas bubble will not dissolve due to the case setting, causing the bubble diameter to increase with height and the hydrate shell thickness decrease with the height from the equilibrium depth.

The plume dynamics can be seen from the contours of the vertical velocity w (Figure 4.4(d)). The plume is released with zero initial velocity right at the source but quickly reaches a noticeable vertical velocity due to the bubble-induced buoyancy. During the strong peeling process, the dissolved methane (Figure 4.4(e)) and dye (Figure 4.4(h)) are carried by the detrained seawater to fall together along the downward outer plume and then transported horizontally to form an intrusion layer at around $z = -600\text{m}$ where the detrained seawater reaches the new equilibrium height in density. Note that the dye concentration is negligible above $z = -500\text{ m}$, indicating that most of the seawater entrained and carried by the plume from lower elevation near the source gets detrained from the rising plume at the peel height at $z = -550\text{ m}$. This is consistent with the large peeling fraction in deep-sea blowout conditions reported in Socolofsky et al. (2011) [82]. The oil droplets with 0.5mm diameter (Figure 4.4(g)) initially rise upwards along the narrow inner plume together with

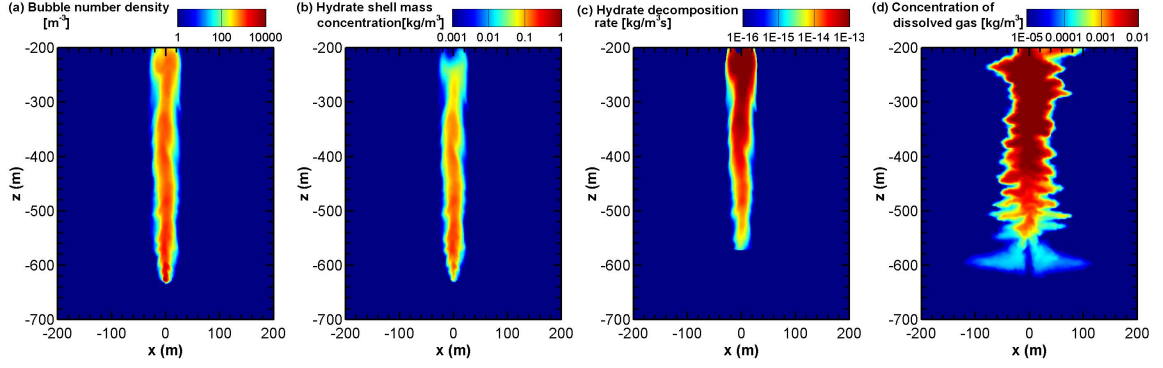


Figure 4.5: Instantaneous plume flow and scalar fields for -630m release case obtained from the LES (from release source to the ocean mixed depth). The contours show the (x, z) -plane across the center of the plume.

the bubbles and entrained seawater. At the peel height, the oil column expands horizontally due to the horizontal velocity associated with the peeling process. Additional entrainment of the oil droplet from the inner plume also occurs below the primary peel height (at $z = -550$ m) due to the turbulence in the shear layer between the inner and outer plumes. The combined effect of the peeling and turbulent entrainment processes results in a noticeable expansion of the oil column starting from $z = -580$ m. Different from passive scalars, the oil droplets have small but non-negligible rise velocity relative to the surrounding seawater flow. As a result, the oil droplets can escape from the falling outer plume and continue to rise slowly by their buoyancy even after all the gas bubbles are fully dissolved.

Figure 4.5 is a selected scalar fields of Figure 4.4 with larger depth range from -700m to the mix-layer depth. Here the contours on the (x, z) -plane across the center of the plume are shown: (a) bubble number density (in m^{-3}); (b) hydrate shell mass concentration (in kg/m^3); (c) hydrate decomposition rate (in $\text{kg}/\text{m}^3\text{s}$); (d) mass concentration of dissolved gas in the water (in kg/m^3).

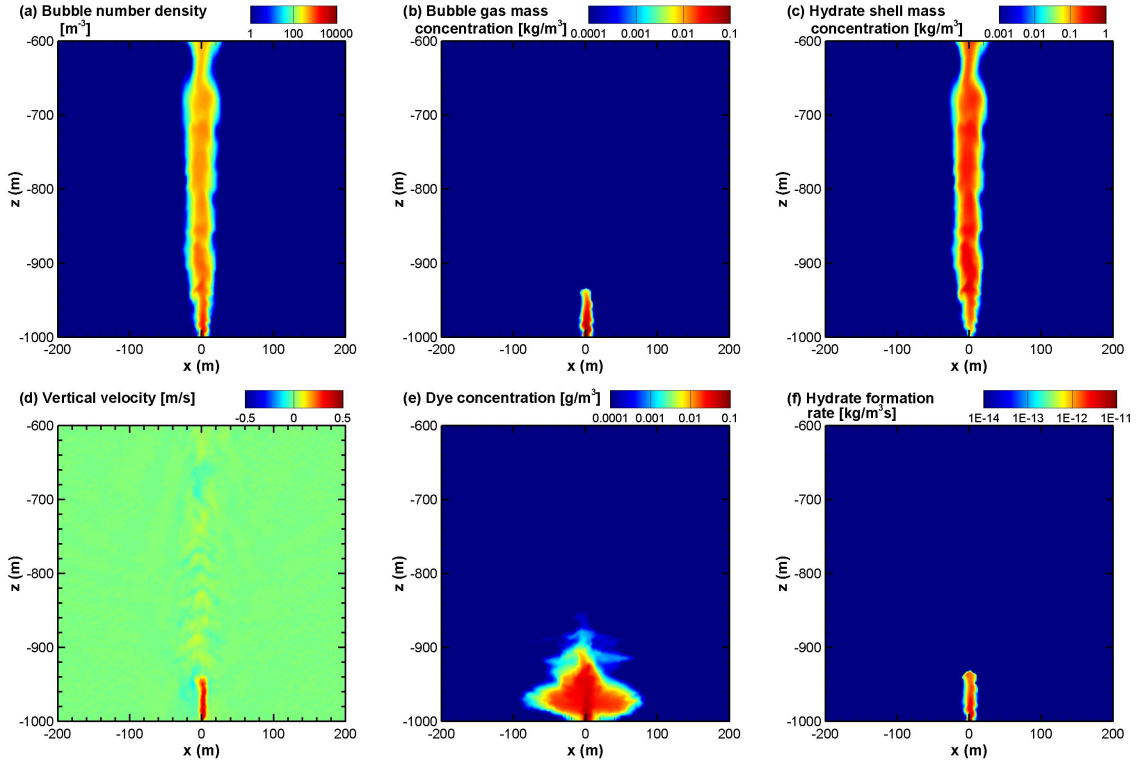


Figure 4.6: Instantaneous plume flow and scalar fields for 1000m release case obtained from the LES at $t = 10,000$ s. Here the contours show the (x, z) -plane across the center of the plume field.

Figure 4.6 shows the instantaneous flow and scalar fields of the medium resolution case released from -1000m on the (x, z) -plane across the center line of the plume at $t = 10,000$ s. The sub-figures show: (a) bubble number density (in m^{-3}); (b) bubble mass concentration (in kg/m^3); (c) hydrate shell mass concentration (in kg/m^3); (d) vertical velocity of plume flow (in m/s); (e) dye concentration (in g/m^3); (f) hydrate formation rate (in $\text{kg}/\text{m}^3\text{s}$).

In 1000m released case, the gas bubbles fully become hydrate particles after moving upward 70m from the release point (Figure 4.6 (b) 4.6 (f)). Then the hydrate particles keep moving upward due to their buoyancy force until they reach the hydrate equilibrium depth (-570 m). During this process, the hydrate particles will not dissolve and the particle radius

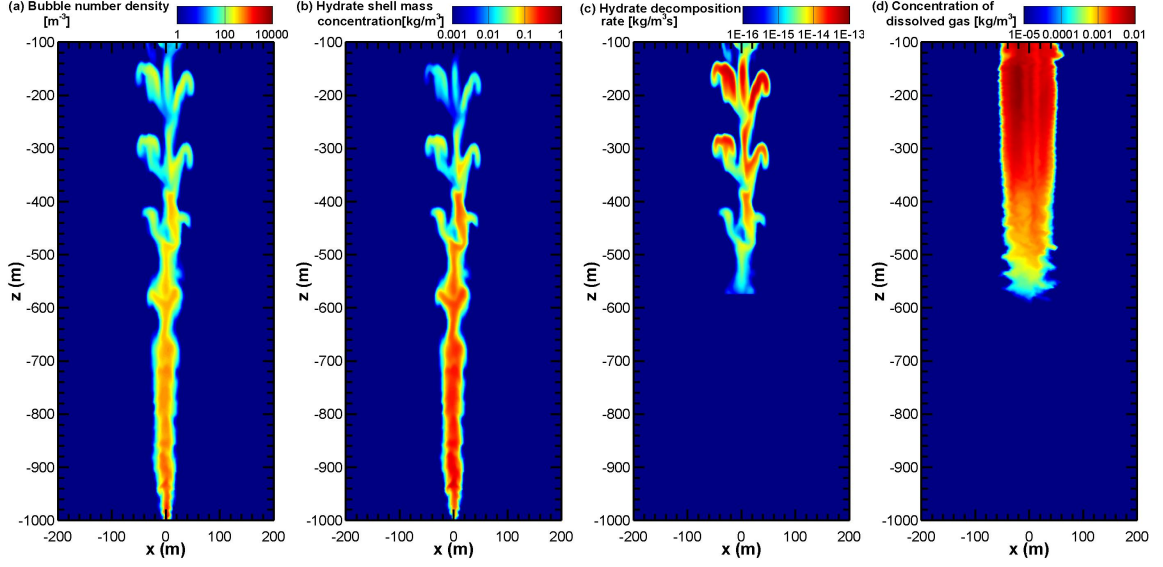


Figure 4.7: Instantaneous plume flow and scalar fields for 1000m release case obtained from the LES (from release source to the ocean mix-layer depth). The contours show the (x, z) -plane across the center of the plume.

will keep the same (Figure 4.3 (right)).

Figure 4.7 is a selected scalar fields of Figure 4.4 with larger depth range from -1000m to the mix-layer depth. Here the contours on the (x, z) -plane across the center of the plume are shown: (a) bubble number density (in m^{-3}); (b) hydrate shell mass concentration (in kg/m^3); (c) hydrate decomposition rate (in $\text{kg}/\text{m}^3\text{s}$); (d) mass concentration of dissolved gas in the water (in kg/m^3).

Figure 4.8 shows the flow and scalar fields of the time- and angular-averaged plume obtained from the medium resolution case released from -630m. The sub-figures show: (a) bubble mass concentration (in kg/m^3); (b) hydrate shell mass concentration (in kg/m^3); (c) mass concentration of dissolved gas in the water (in kg/m^3); (d) vertical velocity of plume flow (in m/s); (e) oil droplets mass concentration (in kg/m^3); (f) dye concentration (in g/m^3).

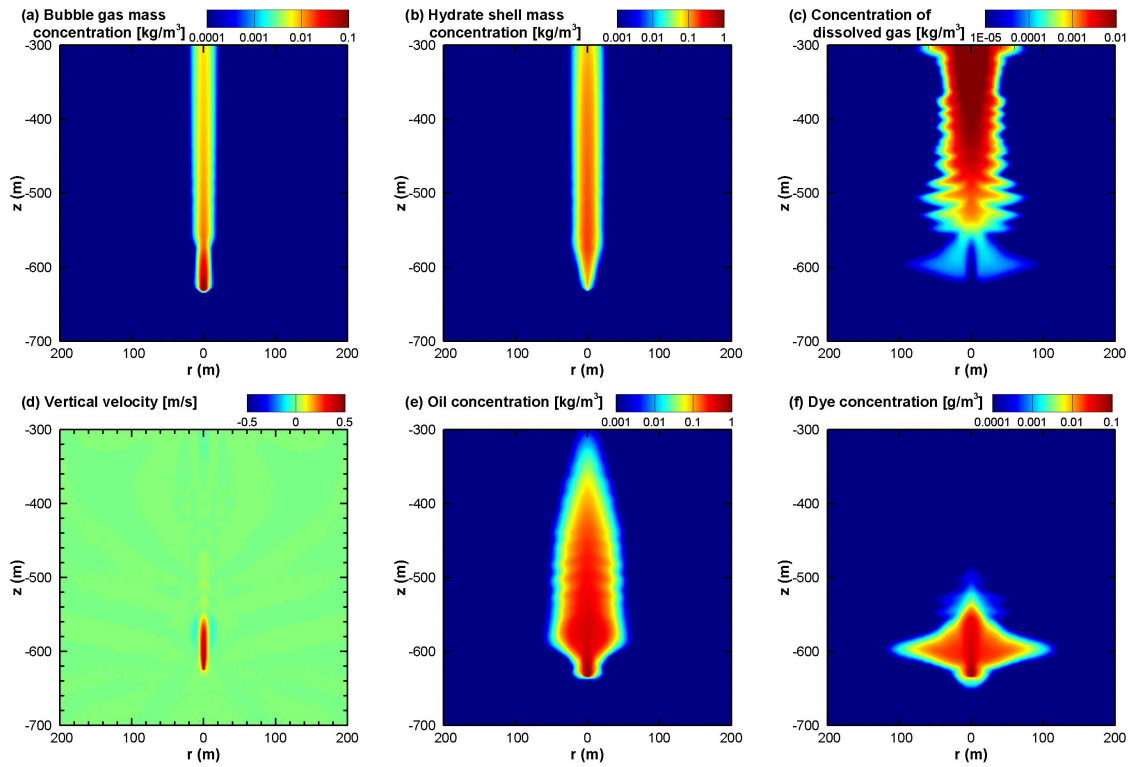


Figure 4.8: Time- and angular-averaged plume flow and scalar fields for 630m release case obtained from the LES. The contours show on the (x, r) -plane across the center of the plume.

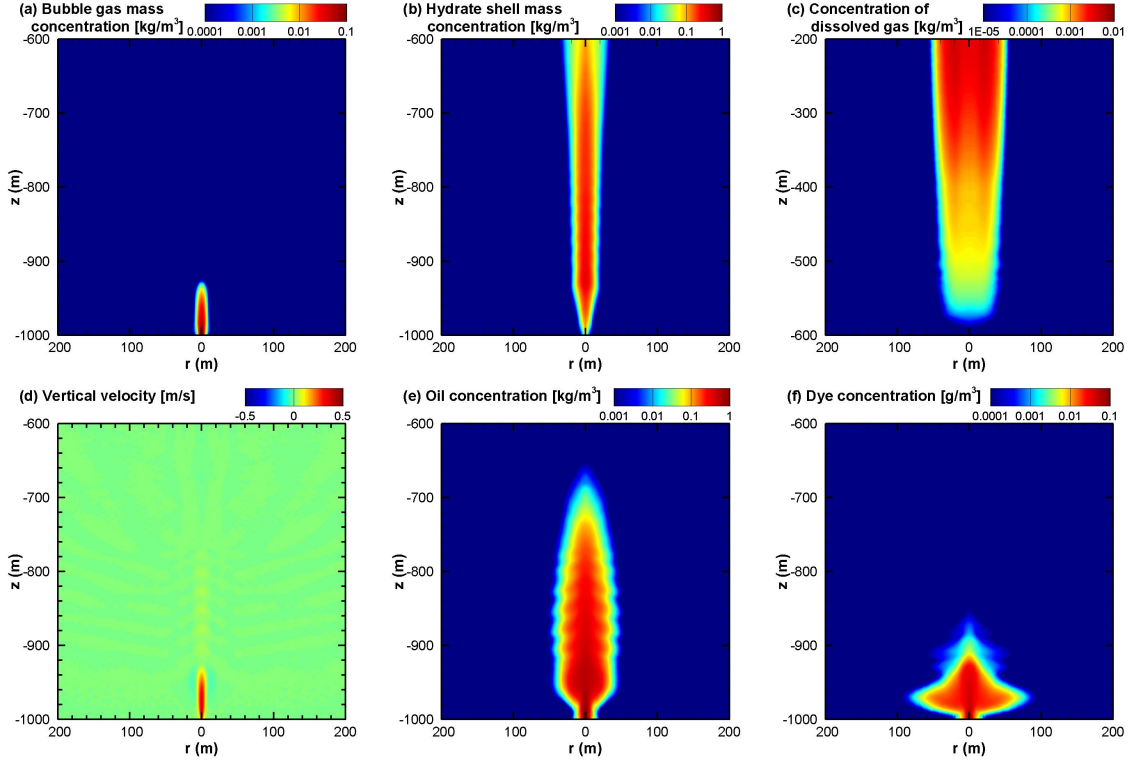


Figure 4.9: Time- and angular-averaged plume flow and scalar fields for 1000m release case obtained from the LES. The contours show on the (x, r) -plane across the center of the plume.

Figure 4.9 shows the flow and scalar fields of the time- and angular-averaged plume obtained from the medium resolution case released from -1000m. The sub-figures show: (a) bubble mass concentration (in kg/m^3); (b) hydrate shell mass concentration (in kg/m^3); (c) mass concentration of dissolved gas in the water (in kg/m^3); (d) vertical velocity of plume flow (in m/s); (e) oil droplets mass concentration (in kg/m^3); (f) dye concentration (in g/m^3).

Overall, the time-averaged figures clearly show the peeling and trapping event. The oil distributions and plume vertical velocity show some similarity on the plume structure (Figure 4.8(d) 4.9(d)) (Figure 4.8(e) 4.9(e)), while the dissolved gas and dye concentration

show the -630m released case has larger distribution range due to the lower hydrostatic pressure and larger buoyancy flux than the -1000m released case (Figure 4.8(c) 4.9(c)) (Figure 4.8(f) 4.9(f)).

4.4 Summary

This research developed an LES model with gas bubble hydrate formation and decomposition in deep ocean conditions. The gas bubble cases with hydrate effect are constructed and show the relationship between different release depth (-630m and -1000m) conditions. The influence of the hydrate formation/decomposition effect on plume dynamics and material transport is investigated via both the instantaneous plume fields and the statistical analysis of time-averaged plume properties.

Chapter 5

CONCLUSIONS AND FUTURE WORK

5.1 Conclusions

In deep-water horizon, the bubble-induced buoyancy plume interacted with the background stratification. During this process, the main upward driving force comes from the gas bubbles and the dissolution and hydrate formation/decomposition of the gas bubbles play an important role. The strong dissolution and hydrate formation effect make the bubble anti-expand from the hydro-pressure drop and finally fully dissolved and lose the buoyancy force. The dissolution and hydrate formation/decomposition effect has significantly changed plume structure and the fate of oil droplets. Because of the gas bubble dissolution and hydrate formation/decomposition, the plume forms a peeling and trapping event, this will trap the small oil droplets in the deep ocean and make the large oil droplets rise more slowly and higher concentrated.

In this study, we first investigate the dissolution effect compared with the non-dissolution case. Without dissolution effect, the gas bubbles expand and rise up to the ocean surface. While considering the dissolution of gas, the bubble will quickly dissolve and disappear, and the plume will lose the upward driving force. Thus, the plume has a much less mixing

effect with the bubble dissolution and the background stratification.

Our study also compared different initial bubble sizes. The result shows the small bubbles dissolve more quickly because of the larger relative surface area of the bubbles and the smaller terminal velocity. The quickly dissolved smaller bubbles are fully dissolved under the first peeling height, and the mixing effect of the inner and outer plume is smaller. In contrast, the larger bubbles survive longer in the water and break the first peeling height. This will potentially cause the second peeling event. The larger bubbles also bring larger buoyancy flux and make the fluid has a larger vertical momentum flux. In consequence, the inner and outer plume obtained a stronger mixing effect, which makes the dispersed oil droplets and other particles horizontally expand to a larger range.

This research also developed an LES model with multi-component gas dissolution in deep ocean conditions. 1-component and 3-component nature gas bubble cases are constructed and show the relationship of the single- and multi-component bubble dissolution model. The influence of a weak crossflow on plume dynamics and material transport is investigated via both the instantaneous plume fields and the statistical analysis of time-averaged plume properties.

For bubble release deeper than the gas hydrate equilibrium depth, the hydrating effect will form hydrate clathrate shells with the ambient water outside the gas bubble. The LES model also studied the hydrate formation and decomposition effect under this condition.

5.2 Future Work

The current model has a gas bubble dissolution module and a gas bubble hydrate formation and decomposition module. The gas dissolution and hydration effect would happen simultaneously in some specific ocean conditions. In the future, the model can add the two main effects together and study their synthetic effect.

The current model for hydrate formation and decomposition has many assumptions for simplification, including the uniform hydrate shell assumption. However, the real situation is the hydrate can not always wrap the gas bubble perfectly. We can model this by adding an effective coverage rate in the future when more data from the experiments are available.

We can also use realistic stratification and crossflow conditions to set up the simulation and compare it with the existing field experiment results and the results from integral models[19, 45].

All of the simulation cases in this dissertation release the gas bubble with the same equivalent bubble diameter and the bubbles have a single size that is tracked in each computational cell, while in a real situation, the bubble size at the source is not uniform. We can simulate this by adding multiple diameter bubbles. By tracking multi-bins of bubble sizes in a computational cell, and calculating their transformation probability, we can even simulate the bubble break up and coalescence effect under the current LES framework [1]. The different size bubbles are released and tracked separately and accumulate the buoyancy effect together to the fluid field. This would multiply the computation cost and may have some interesting effects.

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APPENDIX A

PENG–ROBINSON EQUATION OF STATE FOR NON-IDEAL SINGLE COMPONENT GAS

Following [73] and [106], under the deep-water environment the gas in the bubbles is assumed to behave as non-ideal gas. The state of the non-ideal gas can be modeled using the Peng–Robinson equation [64],

$$p_b = \frac{RT}{V_m - b} - \frac{a}{V_m(V_m + b) + b(V_m - b)}, \quad (\text{A.1})$$

where V_m is the gas molar volume, and a and b are model coefficients. For bubbles with a single gas component, a and b can be modeled as

$$a(T) = a(T_c) \beta(T_r, \omega), \quad (\text{A.2})$$

$$b(T) = b(T_c). \quad (\text{A.3})$$

where, T is the temperature, T_c is the critical temperature,

$$a(T_c) = 0.45724 \frac{R^2 T_c^2}{P_c^2}, \quad (\text{A.4})$$

$$b(T_c) = 0.07780 \frac{RT_c}{P_c}, \quad (\text{A.5})$$

and P_c is the critical pressure. In case if the state of bubbles with multiple gas components is to be modeled, the calculations of a and b need to be modified by including the gas mixture parameters for different gas components [64].

In Eq. (A.2), $\beta(T_r, \omega)$ is a dimensionless function of the reduced temperature T_r and acentric factor ω [64, 77],

$$\beta^{1/2} = 1 + \kappa(\omega) \left(1 - T_r^{1/2}\right), \quad (\text{A.6})$$

where $T_r = 0.7$ and

$$\kappa(\omega) = 0.37464 + 1.54226\omega - 0.26992\omega^2. \quad (\text{A.7})$$

In this study, we consider the dissolution of methane bubbles, for which the corresponding values of the above modeling parameters are $T_c = 190.4 \text{ K}$, $P_c = 4.6 \times 10^6 \text{ Pa}$, and $\omega = 0.011$ [67].

Equation (A.1) can be rewritten in polynomial form as [64]

$$Z^3 - (1 - B)Z^2 + (A - 2B^2 - 3B^2) - (AB - B^2 - B^3) = 0, \quad (\text{A.8})$$

where

$$A = \frac{ap_b}{R^2T^2}, \quad (\text{A.9})$$

$$B = \frac{bp_b}{RT}, \quad (\text{A.10})$$

$$Z = \frac{p_b V_m}{RT}. \quad (\text{A.11})$$

By solving Eq. (A.8), the compressibility factor Z can be obtained and used in the model equations (3.6), (2.3) and (2.4).

APPENDIX B

TERMINAL VELOCITY OF A SINGLE BUBBLE

Following the modeling approach in [105] and [103], in the current study the bubble rise velocity w_r relative to the surrounding fluid flow is modeled based on the equivalent spherical diameter d_e using the parameterizations from [23]. In particular, for the small spherical bubbles with $d_e \leq 1$ mm [105], the rise velocity is parameterized based on the particle Reynolds number $\text{Re}_b = \rho w_r d_e / \mu$, where ρ and μ are the density and dynamic viscosity of the water, respectively. By reversing the definition of Reynolds number, one obtains [105]

$$w_r = \frac{\text{Re}_b \mu}{\rho d_e}, \quad (\text{B.1})$$

in which Re_b can be parameterized in explicit function form as [23]

$$\left\{ \begin{array}{ll} \text{Re}_b = N_D/24 - 1.7569 \times 10^{-4} N_D^2 \\ \quad + 6.9252 \times 10^{-7} N_D^3 \\ \quad - 2.3027 \times 10^{-10} N_D^4, & \text{if } N_D \leq 73, \\ \log_{10} \text{Re}_b = -1.7095 + 1.33438W - 0.11591W^2, & \text{if } 72 < N_D \leq 580, \\ \log_{10} \text{Re}_b = -1.81391 + 1.34671W - 0.12427W^2 \\ \quad + 0.006344W^3, & \text{if } 580 < N_D \leq 1.55 \times 10^7, \end{array} \right. \quad (\text{B.2})$$

where $N_D = 4\rho(\rho - \rho_b)gd_e^3/3\mu^2$ and $W = \log_{10} N_D$.

As the bubble diameter increases, the bubble shape becomes the ellipsoidal shape for the intermediate size regime and the spherical-cap shape for the large size regime, with the two regimes separated by a critical bubble diameter d_{cr} [23, 105]. For the ellipsoidal bubbles with $1 \text{ mm} < d_e \leq d_{cr}$, the bubble rise velocity is modeled as [23]

$$w_r = \frac{\mu}{\rho d_e} M^{-0.149} (J - 0.857), \quad (\text{B.3})$$

where $M = g\mu^4(\rho - \rho_b)/\rho^2\sigma^3$ is the Morton number, and J is a general correlation,

$$J = \begin{cases} 0.94h^{0.757}, & \text{if } 2 < h \leq 59.3, \\ 3.42h^{0.411}, & \text{if } h > 59.3. \end{cases} \quad (\text{B.4})$$

Here, h is given by

$$h = \frac{4}{3} Eo M^{-0.149} \left(\frac{\mu}{\mu_*} \right)^{-0.14}, \quad (\text{B.5})$$

where $\mu_* = 9 \times 10^{-4} \text{ kg/(ms)}$ is a reference dynamic viscosity of water [38]. For the spherical-cap shape bubbles with $d_e > d_{cr}$, the rise velocity is modeled as [23],

$$w_r = 0.711 \sqrt{gd_e(\rho - \rho_b)/\rho}. \quad (\text{B.6})$$

The critical diameter d_{cr} that separates the ellipsoidal and spherical-cap shape regimes of the bubble rise velocity parameterization may be determined based on the criterion $Eo = 40$ [23, 105]. [105] pointed out that this approach would result in the parameterization of w_r

being discontinuous near d_{cr} . They proposed to determine d_{cr} by finding the intersection of the two lines that represent Eqs. (B.3) and (B.6), which has also been used by [103]. Applying the approach of [105] to the plume conditions considered in the current study yields a critical bubble diameter of about $d_{cr} = 10\text{mm}$, which is used for determining the applicable regimes of Eqs. (B.3) and (B.6).

APPENDIX C

SUMMARY OF THE LES MODEL'S SOLUTION PROCESS AND NUMERICAL SCHEMES

The current LES modeling framework involves a number of equations describing the motions of the plume flow as well as the transport of scalar quantities. This appendix highlights the process for solving the LES model's equations. Details of the model equations can be found in section 2.2.

The solution process for advancing the plume flow and scalar fields forward for one time step in the LES model is summarized as follows:

- (a) At the beginning of each time step, the cell-averaged number of moles of gas per bubble, n_b , is computed based on Eq. (2.2) using the bubble mass concentration $\tilde{C}_b$ and number density $\tilde{N}_b$ available at the current time step. The three Boussinesq buoyancy terms in Eq. (4.25) are also calculated based on the corresponding scalar values at the current time step.
- (b) The equivalent diameter d_e for the cell-averaged bubble size is calculated using Eq. (2.4) based on n_b obtained from Step (a).
- (c) The corresponding gas mass transfer coefficient K is calculated using Eqs. (3.25), (3.26), (3.28) and (3.29) for different bubble diameter regimes.

- (d) The cell-averaged value of the single bubble dissolution rate α_b is modeled based on Eqs. (3.7)–(3.12), and the bubble mass dissolution rate per volume for a local LES cell, $\tilde{\alpha}$, is calculated based on Eq. (4.30).
- (e) The gas-related transport equations (4.28), (4.27) and (4.31) are integrated in time based on the modeled gas dissolution rate $\tilde{\alpha}$, with the bubble rise velocity in Eq. (4.29) being parameterized based on the equivalent bubble diameter d_e using Eqs. (B.1), (B.3) and (B.6) given in Appendix B. The bubble number density $\tilde{N}_b$ and mass concentration $\tilde{C}_b$ as well as the dissolved gas mass concentration $\tilde{C}_{dis}$ are updated to a new time step.
- (f) The LES scalar transport equations (4.25), (3.43) and (4.32) are integrated in time and the corresponding scalar fields $\tilde{\theta}$, $\tilde{\rho}$, $\tilde{C}_{dye}$ and $\tilde{C}_d$ are updated to a new time step.
- (g) The LES carrier flow equations (4.23) and (4.25) are advanced in time with the Boussinesq buoyancy terms calculated in Step (a), and the carrier flow velocity $\tilde{\mathbf{u}}$ is updated to the new time step.

The solution process summarized above is repeated in every time step to advance the entire plume simulation forward in time. The current LES model uses a hybrid scheme for simulating the flow and scalar field evolutions. For the flow field, Eqs. (4.23)–(4.25) are discretized by the pseudo-spectral method in the horizontal directions on collocated grids and the second-order central finite difference method in the vertical direction on staggered grids [2]. The velocity field is advanced in time by a fractional-step method, including a velocity prediction step that integrates Eq. (4.25) by the second-order Adams–Bashforth scheme, and a pressure correction step by constructing and solving a pressure Poisson

equation based on the divergence-free constraint Eq. (4.23) to project the predicted velocity field onto the divergence-free space. Equation (4.25) is also integrated in time by the second-order Adams–Bashforth scheme. The transport equations (4.28), (4.27), (4.31)–(4.32) for the spatially nonhomogeneous concentration fields are discretized by a finite-volume method, which uses the carrier flow velocity field interpolated from the pseudo-spectral/finite-difference flow solver’s computational grids to the finite-volume grids using a constrained interpolation scheme that conserves the velocity divergence-free condition [13]. The LES solver for these transport equations uses a bounded third-order upwind scheme for the advection term [37] and advances the concentration fields in time using the second-order Adams–Bashforth scheme [13].