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Endothermic and exothermic chemically reacting plumes

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We develop a model for a turbulent plume in an unbounded ambient that takes into account a general exothermic or endothermic chemical reaction. These reactions can have an important effect on the plume dynamics since the entrainment rate, which scales with the vertical velocity, will be a function of the heat release or absorption. Specifically, we examine a second-order non-reversible reaction, where one species is present in the plume from a pure source and the other is in the environment. For uniform ambient density and species fields the reaction has an important effect on the deviation from pure plume behaviour as defined by the source parameter Γ. In the case of an exothermic reaction the density difference between the plume and the reference density increases and the plume is 'lazy', whereas for an endothermic reaction this difference decreases and the plume is more jet-like. Furthermore, for chemical and density-stratified environments, the reaction will have an important effect on the buoyancy flux because the entrainment rate will not necessarily decrease with distance from the source, as in traditional models. As a result, the maximum rise height of the plume for exothermic reactions may actually decrease with reaction rate if this occurs in a region of high ambient density. In addition, we investigate non-Boussinesq effects, which are important when the heat of reaction is large enough.

1. Introduction

Convection induced by chemical reactions is an important process in many industrial and environmental settings. For example, a plume will develop above a pool fire if the vaporization rate is large enough (Tieszen 2001). The plume forms with two distinct stages. In the first stage a reacting plume rises above the fuel source in which hot buoyant fuel mixes with entrained ambient air. The highly exothermic reaction increases the buoyancy of the plume until the initial plume species is completely consumed. In the second stage, from this height up, the plume behaves as a non-Boussinesq plume without reaction and with a virtual origin correction. Many industrial chemicals are pyrophoric materials and undergo a reaction with air or water vapour at normal ambient condition. An accidental release of such a buoyant chemical in an occupied space is potentially very hazardous. In the aqueous phase, there are many acid–base reactions, such as the neutralization reaction between sodium hydroxide and hydrochloric acid, which can be exothermic (Patnaik 1999).

A similar process occurs in relation to evaporative cooling which has been used for years in cooling towers to cool circulated water (Fisenko, Brin & Petruchik 2004) and in air-conditioning systems in hot dry climates. The fundamental fluid-dynamical aspect of this problem is the presence of a distribution of water droplets with variable size and concentration within a turbulent plume. As the plume entrains ambient fluid, the water droplets will evaporate (provided the air is sufficiently dry) in order to maintain the equilibrium vapour concentration. Latent heat will be absorbed, thus increasing the density of the gaseous phase. This will couple to the plume dynamics through the buoyancy force.

The plume theory developed by Morton, Taylor & Turner (1956, henceforth MTT56) relies on an entrainment assumption that scales the rate at which turbulent eddies are engulfed into the plume with the centreline velocity. This assumption leads to a simple set of equations describing the flux of volume, momentum and buoyancy. The Boussinesq approximation is often used, but is not always appropriate. A rational derivation of the non-Boussinesq plume equations was given by Rooney & Linden (1996). In all plume models the buoyancy flux is a function of ambient stratification and the plume will keep rising in an unstratified or weakly stratified ambient, although in a stratified ambient the plume will reach a maximum height (Caulfield & Woods 1998).

Chemistry was added to the original plume model of MTT56 by Conroy, Llewellyn Smith & Caulfield (2005, henceforth CLSC) for a passive chemical reaction that decouples from the plume dynamics. The species concentrations in the plume are treated in the same fashion as the dynamic fluxes, starting from the conservation of species. CLSC considered the ventilated filling box problem and compared experiment to theory, finding good agreement. However, in cases where the reaction is strongly exothermic or endothermic, this model is inadequate since the buoyancy flux must be modified to account for the heat absorption or release due to reaction.

Plumes with volumetric heating supplied by a line source of heat were investigated experimentally and theoretically by Bhat & Narashima (1996). This model was extended by Hunt & Kaye (2005) to analyse the plume-like or jet-like nature of plumes with an internal buoyancy flux gain represented as a constant source of heat. However, these studies were not concerned with exothermic or endothermic reactions between the source fluid and the ambient.

In this paper we generalize previous work on turbulent plumes to include a general reaction mechanism with a non-negligible heat of reaction. The buoyancy flux is a function of the addition or removal of heat by the chemical reaction. Hence it can be a non-uniform function of height and is coupled to the entrainment rate. Since many reactions have a large chemical heat release we consider both non-Boussinesq plumes and Boussinesq plumes. We limit ourselves to pure plume source conditions, following MTT56, Rooney & Linden (1996), Caulfield & Woods (1998) and others, although a forced plume can be investigated in a similar fashion.

The paper is organized as follows. In § 2, we formulate the energy equation in terms of density, taking into account the heat of reaction. The reaction mechanism is expressed in general terms but we limit ourselves subsequently to a second-order non-reversible reaction for comparison with CLSC, and also to perfect gases. In § 3 we develop the plume model following MTT56 for a Boussinesq plume, which is valid for sufficiently small heats of reaction. We examine the deviation from pure plume behaviour with uniform ambient density and species stratification and investigate the maximum rise height in ambient chemical stratifications with power law behaviour. In § 4 we extend the analysis to non-Boussinesq plumes. Finally we conclude in § 5.

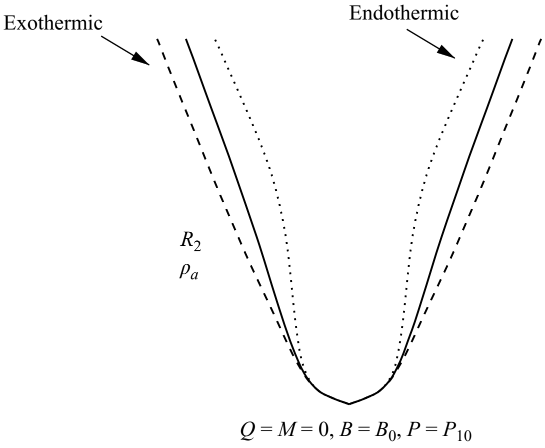

FIGURE 1. Pure plume entering an infinite ambient with concentration R_2 of species 2 from a source with concentration P_{10} of species 1.

2. Model description

2.1. *Governing equations*

We consider a body of fluid rising in an infinite medium due to the action of buoyancy forces with a sufficiently large velocity so that diffusion of momentum, energy and species is negligible. An exothermic or endothermic chemical reaction is allowed to occur within the body, thus increasing or decreasing the buoyancy force acting on the plume fluid. Figure 1 shows the configuration. We allow for compressibility effects, and the shape of the plume is modified by the reaction. In general an unsteady, reacting high-Reynolds-number three-dimensional flow with negligible diffusion is governed by the equations (Williams 1985)

$$\frac{\mathrm{D}\rho}{\mathrm{D}t} + \rho\nabla\cdot\boldsymbol{v} = 0, \tag{2.1a}$$

$$\rho\frac{\mathrm{D}\boldsymbol{v}}{\mathrm{D}t} = \nabla p + \rho\boldsymbol{g}, \tag{2.1b}$$

$$\rho\frac{\mathrm{D}e}{\mathrm{D}t} = -p\nabla\cdot\boldsymbol{v}, \tag{2.1c}$$

$$\rho\frac{\mathrm{D}Y_i}{\mathrm{D}t} = \omega_i. \tag{2.1d}$$

Here ρ is the density, $\boldsymbol{v}$ is the bulk fluid velocity, p is the pressure, $\boldsymbol{g}$ is the acceleration of gravity downwards, e is the internal energy, $Y_i = \rho_i/\rho$ is the mass fraction of species i and ω_i is the reaction rate which will be specified in §2.2. We define the enthalpy $h = e + p/\rho$ to be an average enthalpy of the mixture with

$$h = \sum_{i=1}^{N} h_i Y_i \quad \text{and} \quad h_i = h_i^o + \int_{T_0}^{T} C_{p,i}\,\mathrm{d}T,$$

where h_i^o is the standard enthalpy at the standard temperature, T_0, and $C_{p,i}$ is the specific heat of species i.

We seek an alternative form to equation (2.1*c*) that describes the change in density of a material particle due to reaction effects. In general the change in internal energy of a fluid particle is governed by the first and second laws of thermodynamics as follows:

$$\mathrm{d}e = T\,\mathrm{d}s - p\,\mathrm{d}(1/\rho) + \sum_{i=1}^{N}(\mu_i/W_i)\,\mathrm{d}Y_i, \tag{2.2}$$

where s is the entropy, μ_i is the chemical potential and W_i is the molecular weight of species i. Substituting this relationship and (2.1*a*) into (2.1*c*) yields

$$\frac{\mathrm{D}s}{\mathrm{D}t} = -\frac{1}{T}\sum_{i=1}^{N}\frac{\mu_i}{W_i}\frac{\mathrm{D}Y_i}{\mathrm{D}t}, \tag{2.3}$$

which expresses the rate of production of entropy by the irreversible chemical reaction.

On substituting this equation into the mathematical identity

$$\frac{\mathrm{D}\rho}{\mathrm{D}t} = \left(\frac{\partial\rho}{\partial p}\right)_{s,Y_i}\frac{\mathrm{D}p}{\mathrm{D}t} + \left(\frac{\partial\rho}{\partial s}\right)_{p,Y_i}\frac{\mathrm{D}s}{\mathrm{D}t} + \sum_{i=1}^{N}\left(\frac{\partial\rho}{\partial Y_i}\right)_{s,p,Y_j(i\neq j)}\frac{\mathrm{D}Y_i}{\mathrm{D}t}, \tag{2.4}$$

one can show by thermodynamic arguments (cf. e.g. Clarke and McChesney 1964)

$$\frac{\mathrm{D}\rho}{\mathrm{D}t} = \frac{1}{a_f^2}\frac{\mathrm{D}p}{\mathrm{D}t} + \rho\sum_{i=1}^{N}\left[\frac{\beta}{C_p}\left(\frac{\partial h}{\partial Y_i}\right)_{p,T,Y_{j(i\neq j)}} - \rho\left(\frac{\partial\rho^{-1}}{\partial Y_i}\right)_{p,T,Y_{j(i\neq j)}}\right]\frac{\mathrm{D}Y_i}{\mathrm{D}t} \tag{2.5}$$

where a_f is the frozen speed of sound defined by $a_f^2 = (\partial p/\partial\rho)_{s,Y_i}$, $\beta = \rho(\partial\rho^{-1}/\partial T)_{p,Y_i}$ is the frozen volumetric thermal expansion coefficient and $C_p = (\partial h/\partial T)_{p,Y_i}$ is the frozen specific heat at constant pressure.

For a perfect gas with equation of state $p = \rho RT\sum_{i=1}^{N} Y_i/W_i = \rho RT\bar{Y}$, evaluating the derivatives gives

$$\frac{\mathrm{D}\rho}{\mathrm{D}t} = \frac{1}{a_f^2}\frac{\mathrm{D}p}{\mathrm{D}t} + \frac{\beta}{C_p}\sum_{i=1}^{N}h_i\omega_i - \frac{1}{\bar{Y}}\sum_{i=1}^{N}\frac{\omega_i}{W_i} = \frac{1}{a_f^2}\frac{\mathrm{D}p}{\mathrm{D}t} + \rho\sigma. \tag{2.6}$$

This equation represents the change in density due to pressure, chemical energy released or absorbed by reactions and changes in mixture concentrations. The latter two changes are grouped into σ. In general the first term can be neglected for fluid velocities that are small compared to the speed of sound, and we do so here.

For steady flow with no swirl, i.e. $\boldsymbol{v} = (u, 0, w)$ in cylindrical coordinates (r, θ, z), the equations underlying plume dynamics can be written in almost-conservative form as

$$\frac{1}{r}\frac{\partial}{\partial r}(ru\rho) + \frac{\partial}{\partial z}(w\rho) = 0, \tag{2.7a}$$

$$\frac{1}{r}\frac{\partial}{\partial r}(ruw\rho) + \frac{\partial}{\partial z}(w^2\rho) = g(\rho_a - \rho), \tag{2.7b}$$

$$u\frac{\partial\rho}{\partial r} + w\frac{\partial\rho}{\partial z} = \rho\sigma, \tag{2.7c}$$

$$\frac{1}{r}\frac{\partial}{\partial r}(ru\rho Y_i) + \frac{\partial}{\partial z}(w\rho Y_i) = \omega_i \tag{2.7d}$$

for mass, vertical momentum, energy and species respectively, using (2.6). We have assumed the plume to be thin so that $\partial_r p \ll \partial_z p$, in which case the pressure may be shown to be hydrostatic: $\mathrm{d}p/\mathrm{d}z = -\rho_a g$, where $\rho_a(z)$ is the ambient fluid density

(Rooney & Linden 1996). The additional term in (2.7*c*) is due to fluid expansion or compression via reaction, while the additional term in (2.7*d*) is due to reaction.

For Boussinesq plumes, the equations simplify to

$$\frac{1}{r}\frac{\partial}{\partial r}(ru) + \frac{\partial w}{\partial z} = 0, \tag{2.8a}$$

$$\frac{1}{r}\frac{\partial}{\partial r}(ruw) + \frac{\partial w^2}{\partial z} = \frac{g}{\rho_0}(\rho_a - \rho), \tag{2.8b}$$

$$u\frac{\partial \rho}{\partial r} + w\frac{\partial \rho}{\partial z} = \rho_0 \sigma, \tag{2.8c}$$

$$\frac{1}{r}\frac{\partial}{\partial r}(ruY_i) + \frac{\partial}{\partial z}(wY_i) = \frac{\omega_i}{\rho_0}, \tag{2.8d}$$

where ρ_0 is a reference density. Here the mass fractions are given by $Y_i = \rho_i/\rho_0$. The flow is incompressible, but density can change due to the reactions. If $\sigma \ll 1$, the right-hand side of (2.8*c*) vanishes and we recover the equations of CLSC.

2.2. *Chemical reaction mechanism*

In general we can represent the chemical reaction mechanism as (Williams 1985)

$$\omega_i = W_i \sum_{k=1}^{n} (\nu''_{i,k} - \nu'_{i,k}) K_k \prod_{j=1}^{N} c_j^{\nu'_{j,k}}, \tag{2.9}$$

where $c_j = Y_j \rho / W_j$ is the molar concentration of species j, K_k is the rate constant (in general a function of temperature) of the kth reaction, $\nu'_{i,k}$ is the stoichiometric coefficient of reactants and $\nu''_{i,k}$ is the stoichiometric coefficient of products. Conservation of mass at the molecular level implies that $\sum_i \omega_i = 0$, which can also be written as a constraint on the W_i, $\nu''_{i,k}$ and $\nu'_{i,k}$.

In this paper we will only consider second-order reactions of the form $c_1 + c_2 \rightarrow c_3$, although other forms are possible. Therefore

$$\omega_i = \pm W_i K c_1 c_2 = \pm \frac{K W_i \rho^2}{W_1 W_2} Y_1 Y_2, \tag{2.10}$$

where the sign is negative for ω_1 and ω_2, and positive for ω_3. Note that $W_1 + W_2 = W_3$.

In the case of the perfect gas we have the following expression:

$$\rho\sigma = \left[\frac{\beta}{C_p}(-h_1 W_1 - h_2 W_2 + h_3 W_3) + \frac{1}{\bar{Y}}\right] \frac{K\rho^2}{W_1 W_2} Y_1 Y_2 = \Omega \rho^2 Y_1 Y_2, \tag{2.11}$$

which defines Ω. The term in parentheses is just the heat of reaction ΔH_r, which is positive for an endothermic reaction. The $\bar{Y}$ term is present for the second-order reaction considered here, but in general is multiplied by a numerical factor which can be zero.

In the Boussinesq case, ρ in (2.10) is to be replaced by ρ_0, and all quantities in (2.11) are to be evaluated using the reference value ρ_0 for ρ. While Ω is in general a function of temperature (through K and h_i) and of pressure (since by the perfect gas law T is a function of ρ, p and Y_j), we ignore these considerations here and take Ω and K to be constant. This is because the pressure dependence, which enters via the hydrostatic relation, is very weak unless the plume extends very high, while the temperature dependence is negligible unless the reaction is very exothermic or endothermic. In the non-Boussinesq case the change in density will be significant, but we can ignore the thermal dependence of the properties provided the coefficient of thermal expansion, β, is sufficiently large.

3. Boussinesq plume

3.1. *Plume equations*

We consider an isolated source of buoyancy released into an infinite environment. Following MTT56 we define the plume volume flux πQ, momentum flux πM, buoyancy flux πB and species flux πP_i as follows:

$$\pi Q(z) = 2\pi \int_0^\infty rw \, \mathrm{d}r = \pi \bar{w} b^2, \tag{3.1a}$$

$$\pi M(z) = 2\pi \int_0^\infty rw^2 \, \mathrm{d}r = \pi \bar{w}^2 b^2, \tag{3.1b}$$

$$\pi B(z) = 2\pi \int_0^\infty rwg \frac{\rho_a - \rho}{\rho_0} \, \mathrm{d}r = \pi g \frac{\rho_a - \bar{\rho}}{\rho_0} \bar{w} b^2 = \pi g' \bar{w} b^2, \tag{3.1c}$$

$$\pi P_i(z) = 2\pi \int_0^\infty Y_i rw \, \mathrm{d}r = \pi \bar{Y}_i \bar{w} b^2. \tag{3.1d}$$

We take top hat profiles for quantities in the plume so that the integrals extend to b, the plume width, and quantities with overbars are functions of z only. Here g' is the reduced gravity of the plume relative to the local ambient fluid.

The plume equations for volume and momentum flux are as in MTT56:

$$\frac{\mathrm{d}Q}{\mathrm{d}z} = 2\alpha M^{1/2}, \qquad \frac{\mathrm{d}M}{\mathrm{d}z} = \frac{BQ}{M}. \tag{3.2}$$

Note that $b^2 = Q^2/M$, $\bar{w} = M/Q$ and α is the entrainment constant. The buoyancy flux is found by differentiating (3.1c) with respect to height and using (2.8a) and (2.8c), yielding

$$\frac{\rho_0}{2g}\frac{\mathrm{d}B}{\mathrm{d}z} = \int_0^\infty rw \frac{\mathrm{d}\rho_a}{\mathrm{d}z} \, \mathrm{d}r - \int_0^\infty \rho_0 \sigma r \, \mathrm{d}r + \int_0^\infty ru(\rho - \rho_a)_r \, \mathrm{d}r - \int_0^\infty (\rho_a - \rho)(ru)_r \, \mathrm{d}r. \tag{3.3}$$

The last two terms integrate to zero and we find

$$\frac{\mathrm{d}B}{\mathrm{d}z} = -N^2 Q - g\sigma \frac{Q^2}{M}, \tag{3.4}$$

where $N^2 = -(g/\rho_0)\mathrm{d}\rho_a/\mathrm{d}z$. The first term represents the decrease in buoyancy flux by entrainment and the second represents its increase by an exothermic reaction or decrease by an endothermic reaction and changes in average molecular weights. Integrating (2.8d) across the plume gives

$$\frac{\mathrm{d}P_i}{\mathrm{d}z} = 2\alpha R_i M^{1/2} + \frac{\omega_i}{\rho_0}\frac{Q^2}{M}, \tag{3.5}$$

where R_i is the mass fraction of species i in the ambient. The first term represents the increase in species flux by entrainment, whereas the second term represents a decrease (for reactants) or increase (for products) by chemical reaction. By using top hat profiles we are taking the plume to be a well-mixed reactor, as is commonly used for combustion studies (Williams 1985). This is possible provided the time scale for reaction is slower than the turbulent mixing by small-scale motions. Following

Komori *et al.* (1990) we require the Damköhler number $Da=(\nu/\epsilon)^{1/2}K(c_1c_2)^{1/2}$ to be small, where ν is the kinematic viscosity and ϵ is the viscous dissipation.

To compute the right-hand sides of these equations for our case, we express concentrations in terms of fluxes through the plumes using $P_i = Q\bar{Y}_i$. Then, replacing Y_i by $\bar{Y}_i$ so as to work with plume variables, as in the derivation of the equation for $\mathrm{d}M/\mathrm{d}z$ above, we have

$$\frac{\omega_i}{\rho_0}\frac{Q^2}{M} = \pm\frac{KW_i\rho_0}{W_1W_2}\frac{P_1P_2}{M} = \psi_i\frac{P_1P_2}{M}, \tag{3.6}$$

and similarly

$$g\sigma\frac{Q^2}{M} = g\Omega\rho_0Y_1Y_2\frac{Q^2}{M} = g\rho_0\Omega\frac{P_1P_2}{M} = \kappa\frac{P_1P_2}{M}, \tag{3.7}$$

where

$$\kappa = g\psi_3\left[\frac{\beta\Delta H_r}{W_3C_p} + \frac{Q}{\bar{P}}\right] = g\psi_3(\hat{H}_r + Q/\bar{P}) \tag{3.8}$$

and $\bar{P}=\sum_{i=1}^{3}W_3P_i/W_i$. Now the terms within the brackets are non-dimensional (denoted by hats) and express the density change by heat released/absorbed and change in mixture fraction respectively. Here ψ_3 is the reaction rate corresponding to species 3 and has been chosen because it is positive.

At the plume source we will only consider a pure plume as in Morton *et al.* (1956) and Caulfield & Woods (1998) so that $Q(z_s)=M(z_s)=0$ and $B(z_s)=B_0$. In addition we will only consider a single species at the source so that $P_1(z_s)=P_{10}$, $P_2(z_s)=0$ and $P_3(z_s)=0$. Therefore species 2 only enters the plume through entrainment and species 3 enters the plume through reaction only.

3.2. *Ambient conditions*

In order to examine the importance of non-uniform stratification and how the properties of the plume depend on the coupling between species and density entrainment, we extend the results of Caulfield & Woods (1998) to the case with reaction. We define static ambient profiles of power law form ($\beta \geqslant 0$):

$$\rho_a = \rho_0\,(z/z_s)^{\beta}, \qquad N^2 = N_s^2\,(z/z_s)^{\beta-1}, \qquad R_2 = R_{20}(z/z_s)^{\gamma}, \tag{3.9}$$

where z_s is the height of the source, N_s^2 is a reference buoyancy frequency and R_{20} is the concentration of species 2 at the source. In order to focus on the effects of chemistry in a simple yet informative way, we will not examine the effects of other species in the ambient, so we take $R_1(z)=0$, $R_2(z_s)=R_{20}$ and $R_3(z)=0$.

3.3. *Non-dimensionalization*

For pure plumes it is common to scale the governing equations with the buoyancy flux and an imposed length scale, except with unbounded plumes in uniform environments, where a length scale does not exist and a similarity solution is possible. For a plume in a constant-stratification ambient, MTT56 found that the maximum rise height of the plume is determined from

$$H = (2\alpha)^{-1/2}B_0^{1/4}N_s^{-3/4}, \tag{3.10}$$

as a function of source buoyancy flux and buoyancy frequency. We use this to scale N_s^2 and the length in § 3.6. In addition we can form another length scale from the source buoyancy flux and reaction time scale $t_r = W_2\,(K\,\rho_0\,R_{20})^{-1}$:

$$H_c = \frac{B_0^{1/4}}{(W_2 K \rho_0 R_{20})^{3/4}}, \tag{3.11}$$

which is a chemistry length scale that expresses the height over which chemistry is important. This scale must be used in the absence of stratification but either one may be appropriate when chemistry and stratification are of comparable order.

We use these to scale vertical height and the other quantities of interest,

$$z = \hat{z}\ell, \qquad B = \hat{B}B_0, \qquad Q = \hat{Q}(2\alpha)^{4/3}B_0^{1/3}\ell^{5/3}, \tag{3.12}$$

$$M = \hat{M}(2\alpha)^{2/3}B_0^{2/3}\ell^{4/3}, \quad P_i = R_{20}\hat{P}_i(2\alpha)^{4/3}B_0^{1/3}\ell^{5/3}, \tag{3.13}$$

where ℓ is an arbitrary length scale to be defined as either H or H_c later. With this same scaling in mind we scale the reaction rate and enthalpy of reaction as follows:

$$\lambda_i = \psi_i R_{20}(2\alpha)^{2/3}\ell^{4/3}B_0^{-1/3}. \tag{3.14}$$

In addition we scale the density, ambient species concentration and buoyancy frequency with ρ_0, R_{20} and N_s^2, respectively, and the ambient stratification becomes

$$\rho_a = (z/\hat{z}_s)^{\beta}, \quad N^2 = (z/\hat{z}_s)^{\beta-1}, \quad R_2 = (z/\hat{z}_s)^{\gamma}, \tag{3.15}$$

where $\hat{z}_s = z_s/\ell$ is the non-dimensional source position.

In non-dimensional form the plume equations with hats dropped are

$$\frac{\mathrm{d}Q}{\mathrm{d}z} = M^{1/2}, \tag{3.16a}$$

$$\frac{\mathrm{d}M}{\mathrm{d}z} = \frac{BQ}{M}, \tag{3.16b}$$

$$\frac{\mathrm{d}B}{\mathrm{d}z} = -\left(\frac{\ell}{H}\right)^{8/3} N^2 Q - \lambda_3^* \left[H_r + \frac{Q}{R_{20}\bar{P}}\right]\frac{P_1 P_2}{M}, \tag{3.16c}$$

$$\frac{\mathrm{d}P_i}{\mathrm{d}z} = R_i M^{1/2} + \lambda_i \frac{P_1 P_2}{M}, \tag{3.16d}$$

where $\lambda_3^* = g R_{20}(2\alpha)^{4/3}B_0^{-2/3}\ell^{5/3}\lambda_3$ and the boundary conditions are

$$Q = M = P_2 = 0, \quad B = 1, \quad P_1 = \frac{P_{10}}{R_{20}(2\alpha)^{4/3}B_0^{1/3}\ell^{5/3}} = \phi \qquad \text{at } z = z_s \tag{3.17}$$

If we choose the chemistry length scale $\ell = H_c$ then the length scale ratio in (3.16c) can be written as $H_c/H = (2\alpha)^{1/2}N_s^{3/4}/(W_2 K \rho_0 R_{20})$, which expresses the relative importance of stratification to chemical reaction. For large values of this parameter stratification may dominate and we have the model of CLSC, whereas for small values of this parameter chemistry may dominate. In this case we can ignore stratification, provided the heat of reaction is significant, as long as the source concentration P_1 is sufficiently large.

3.4. *No ambient stratification*

For weakly stratified environments with $N^2 \approx 0$ the buoyancy flux is controlled by the chemistry, while the species concentrations when the ambient concentrations are uniform are governed by the entrainment and reaction rates. In this case we use the

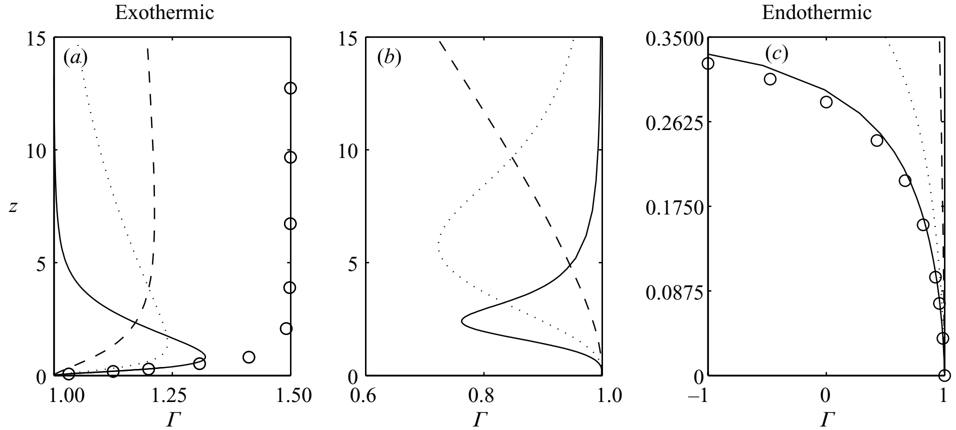

FIGURE 2. Numerical solutions to equations (3.18*a*)–(3.18*b*), showing Γ_b profiles for $H_r=-10$ (*a*), 0 (*b*), 10 (*c*), and $\lambda_3=0.1$ (dashed line), 1 (dotted line), 10 (solid line). The circles represent the profiles of Γ_b corresponding to the exact solution (3.25) in the large reaction rate limit. Here $z_s^{-1}=100$, $\phi=1$, $R_{20}=1$ and $\lambda_3^*=\lambda_3$.

chemistry length scale $\ell=H_c$ and the governing equations reduce to

$$\frac{\mathrm{d}Q}{\mathrm{d}z}=M^{1/2},\qquad \frac{\mathrm{d}M}{\mathrm{d}z}=\frac{BQ}{M},\tag{3.18a}$$

$$\frac{\mathrm{d}B}{\mathrm{d}z}=-\lambda_3^*\left[H_r+\frac{Q}{R_{20}\bar{P}}\right]\frac{P_1P_2}{M},\qquad \frac{\mathrm{d}P_i}{\mathrm{d}z}=R_iM^{1/2}+\lambda_i\frac{P_1P_2}{M},\tag{3.18b}$$

When the reaction rate is small, i.e. $\kappa\approx 0$, and $B=1$, we recover the well-known similarity solution of MTT56:

$$Q=\frac{3}{5}\left(\frac{9}{20}\right)^{1/3}z^{5/3},\quad M=\left(\frac{9}{20}\right)^{2/3}z^{4/3},\tag{3.19}$$

for which the volume flux increases monotonically and the velocity decreases monotonically due to entrainment.

For forced plumes one may define the non-dimensional parameter (see Hunt & Kaye 2005)

$$\Gamma_b=\frac{5Q^2B}{4M^{5/2}},\tag{3.20}$$

which is a function of height. This parameter has been used to indicate whether the plume is forced ($\Gamma_b<1$) and hence jet-like, pure ($\Gamma_b=1$) or lazy ($\Gamma_b>1$). For our model, where the plume is pure at the source, we can use this parameter to determine quantitatively the deviation from pure plume behaviour with chemical reactions.

In figure 2 we plot profiles of Γ_b for different values of H_r and λ_3 in order to discuss three distinct behaviours of the plume. To reduce our parameter space we set $R_{20}=1$ and $\phi=1$. In addition we set $\lambda_3^*=\lambda_3$, since a change in this value would only appear as an effective increase in the heat of reaction. In the first case the reaction is exothermic ($H_r<0$) so the plume density decreases in opposition to the increase in density by entrainment. As fluid is entrained, the reaction plays a more important role and the plume becomes lazy with a deficit of momentum, but if κ or P_1 is too small the effects of reaction never dominate and the solution continues to behave as a pure plume described by equations (3.19). In any case, at large distances from the source

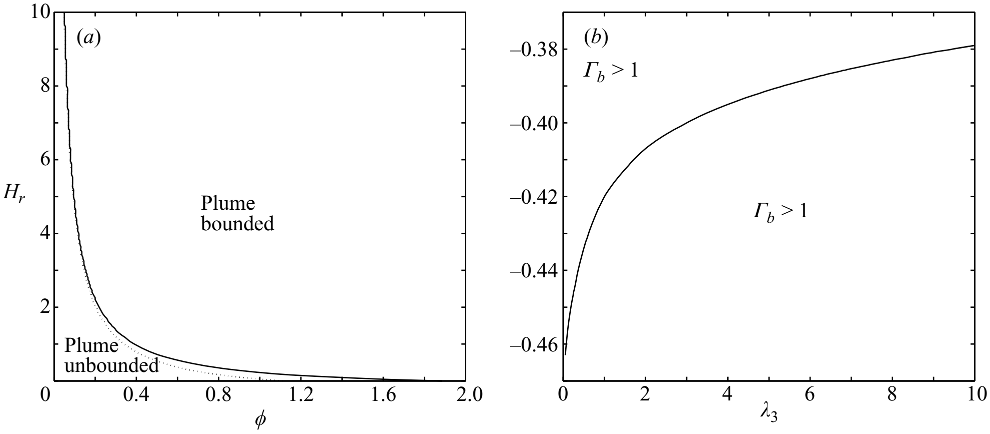

FIGURE 3. (*a*) Variation in the heat of reaction separating bounded and unbounded solutions as a function of the source concentration ϕ for $\lambda_3 = 0.1$ (dotted line) and 10 (solid line). (*b*) Boundary separating lazy and forced plumes as a function of H_r and λ_3 for $\phi = 1$. Here $z_s^{-1} = 100$, $W_1 = W_2 = 1$, $R_{20} = 1$ and $\lambda_3^* = \lambda_3$.

species P_1 will be completely consumed, and we can use the similarity solutions with a virtual origin correction (Caulfield & Woods 1995).

In the second case there is no heat generated or absorbed ($H_r = 0$) but for this reaction the production of species 3 acts to increase the average density of the plume. Since the chemical components have different densities, the buoyancy flux will be a function of the average mixture concentration, $\bar{Y}$, which is coupled to the entrainment and reaction rates. Therefore, the plume will be dominated by momentum with jet-like characteristics ($\Gamma_b < 1$) while there is a sufficient concentration of species 1, but will behave as a pure plume at larger distances from the source, where the reaction is weak. Finally, in the endothermic case we expect similar characteristics, although with an approximately constant κ. Since the heat of reaction is relatively large, the density difference will decrease and the plume will have jet-like characteristics. Ultimately the reaction will absorb a sufficient amount of thermal energy and the density difference will lead to a negatively buoyant plume that will behave as a fountain (Bloomfield & Kerr 2000).

We can quantify the critical conditions for the plume to be bounded or unbounded as a function of the chemically related parameters ϕ, H_r and λ_3. This is shown in figure 3. For relatively small source concentrations and heats of reaction, the chemistry will be unable to decrease the density below the ambient and the plume will be unbounded. For a large source concentration and heat of reaction, the plume will eventually become neutrally buoyant and spread out horizontally. We have quantified the transition zone between lazy and forced plumes in figure 3. Because of the term $Q/\bar{P}$ in (3.8), the heat of reaction and reaction rate must be sufficiently large for an effectively exothermic reaction to exist.

3.5. *Large reaction rate and large heat of reaction*

When the reaction is very fast, i.e. $K \gg 1$, the ambient chemical species 2 in the plume is consumed on a time scale much shorter than the residence time in the plume. As a result the concentration of species 2 in the plume is very small and the vertical gradient in the flux P_2 is approximately zero ($\mathrm{d}P_2/\mathrm{d}z \approx 0$). Then the constancy of P_2 shows that $\lambda_2 P_1 P_2 M^{-1} \approx -M^{1/2}$, where we require $\lambda_2 P_2 = O(1)$ since $\lambda_2 \gg 1$ and

$P_2 \ll 1$. This order relation expresses equality of entrainment and reaction time scales. Therefore, by an infinite reaction we mean that the entrainment rate is balanced by the reaction rate, although we still require Da to be small for the top hat species profiles to apply.

This result may be substituted into the equations for B and P_1 to give

$$\frac{\mathrm{d}Q}{\mathrm{d}z} = M^{1/2}, \qquad \frac{\mathrm{d}M}{\mathrm{d}z} = \frac{BQ}{M}, \tag{3.21}$$

$$\frac{\mathrm{d}B}{\mathrm{d}z} = -M^{1/2}\chi, \qquad \frac{\mathrm{d}P_1}{\mathrm{d}z} = -\frac{\lambda_1}{\lambda_2}M^{1/2}, \tag{3.22}$$

where $\chi = -\lambda_3^* H_r/\lambda_2$ and we have assumed that $Q/\bar{P} \ll H_r$ to obtain an explicit solution. We introduce χ, which represents the heat of reaction, for ease of presentation. It is positive for endothermic reactions and negative for exothermic reactions. Once the source chemical is completely consumed so that $P_1 = 0$, the reaction stops and we have the usual plume equations of MTT56 from that height up. There is a boundary layer in which the buoyancy flux tends to a constant, which we ignore.

The buoyancy and volume flux equations can be combined and integrated to obtain

$$B = 1 - \chi Q, \tag{3.23}$$

where the deviation from pure plume behaviour is explicitly expressed by the exothermic/endothermic term χ. The three equations (3.21) and (3.23) can be combined to form a single equation in terms of volume and momentum fluxes, and integrated to obtain

$$\frac{\mathrm{d}Q}{\mathrm{d}z} = \left(\frac{5\chi}{6}\right)^{1/5} Q^{2/5}(\epsilon - Q)^{1/5}, \tag{3.24}$$

where $\epsilon = 3/2\chi$.

Now (3.24) can be integrated to give

$$\left(\frac{5|\chi|}{6}\right)^{1/5}(z - z_s) = \int_0^Q \frac{q^{-2/5}}{(|\epsilon| \mp q)^{1/5}}\mathrm{d}q = \frac{5}{3}|\epsilon|^{-1/5}Q^{3/5}\ {}_2F_1(1/5, 3/5; 8/5; Q/\epsilon), \tag{3.25}$$

in terms of hypergeometric functions, and where the choice of signs is $-$ for $\chi > 0$ and $+$ for $\chi < 0$. In both cases, we find for small $z - z_s$

$$Q = \left(\frac{3}{5}\right)^{5/3}\left(\frac{5\epsilon\chi}{6}\right)^{1/3}(z - z_s)^{5/3}. \tag{3.26}$$

In the endothermic case with $\chi > 0$, the plume becomes a fountain, provided ϕ is not too small, and terminates at $Q = \epsilon$ with

$$\left(\frac{5\chi}{6}\right)^{1/5}(z_{\max} - z_s) = \frac{5}{3}\epsilon^{2/5}\frac{\Gamma(8/5)\Gamma(4/5)}{\Gamma(7/5)}, \tag{3.27}$$

where Γ is the Gamma function. In the exothermic case, the plume continues to rise and behaves for large z as

$$\left(\frac{5|\chi|}{6}\right)^{1/5}(z - z_s) = \frac{5}{3}Q^{2/5}\frac{\Gamma(8/5)\Gamma(2/5)}{\Gamma(3/5)\Gamma(7/5)}. \tag{3.28}$$

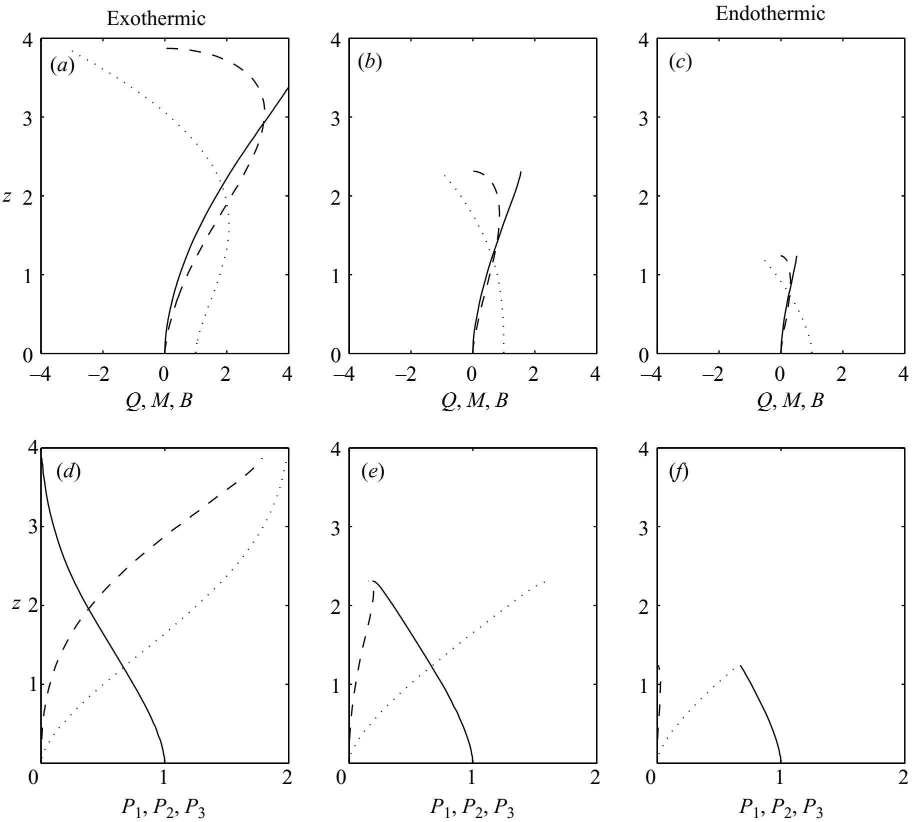

FIGURE 4. Numerical solution to (3.16*a*)–(3.16*d*) showing Q, P_1 (solid); M, P_2 (dashed); B, P_3 (dotted) for $H_r = -2$ (a,d), 0 (b,e) and 2 (c,f). Here $z_s^{-1} = 100$, $\phi = 1$, $W_1 = W_2 = 1$, $R_{20} = 1$, $\lambda_3 = 10$, $\lambda_3^* = \lambda_3$ $\gamma = -0.1$ and $\beta = 1$.

The mass flux hence has a $(z - z_s)^{5/2}$ dependence. Of course, this is a transitory phase until $P_1 = 0$, at which the usual MTT56 solution applies again. This scenario is similar to plumes with decreasing source strengths (Scase, Caulfield & Dalziel 2006), in which there is a narrowing of the plume at some height.

The parameter Γ_b starts at 1 and tends to $-\infty$ as $z \to z_{\max}$ in the endothermic case. It starts at 1 and grows slowly in the exothermic case, before ultimately returning to 1 when the reaction ends. We have plotted the profiles of Γ_b against the numerical solution in figure 2 for $\lambda_3 = 10$. The reduced model yields a good approximation until the concentration of species 1 has diminished to a sufficiently small value so that $\mathrm{d}P_2/\mathrm{d}z \approx 0$ is no longer valid. At this point the reaction no longer dominates the buoyancy flux and the plume transitions to the usual plume model of MTT56 with similarity solutions (3.19).

3.6. *Stratified ambient*

When reaction and stratification are significant ($H \sim H_c$) there is a non-trivial coupling between the change in buoyancy flux by entrainment and reaction. Here we extend the model of Caulfield & Woods (1998) to investigate the effects of reaction, and for that reason we choose the same length scale $\ell = H$. We have solved the governing equations (3.16*a*)–(3.16*d*) numerically and plotted our results in figures 4 and 5. Since we are mainly interested in the effect of chemistry on the maximum rise height, we only vary the chemically related parameters and set the ambient density stratification to be linear, i.e. $\beta = 1$. In addition we fix the chemical concentration ratio $\phi = 1$ in order to reduce our parameter space and concentrate on the effect of λ, H_r and γ.

In figure 4 we have plotted the profiles for a positive, zero and negative heat of reaction H_r to be consistent with the rest of the paper. We have chosen to display a large rate constant, $\lambda_3 = 10$, to elucidate the effects of reaction and a power coefficient $\gamma = -0.1$, which one would likely encounter in industrial settings. The species fluxes in the plume are a function of entrainment and reaction rate, which of course is dependent on the heat of reaction and average mixture density. P_1 has a maximum value at the source and decreases with height by reaction. On the other hand, P_2 has a minimum value at the source and increases by entrainment and decreases by reaction. Similarly, P_3 increases with reaction from zero initially and has the same characteristics as species 1 since $\mathrm{d}P_1/\mathrm{d}z \propto \mathrm{d}P_3/\mathrm{d}z$. The reaction will have the largest contribution to the plume dynamics near the source, since species 1 has a high concentration. Far above this point the source species concentration will be sufficiently small and the plume will be governed by the model of MTT56.

The buoyancy flux is controlled by two processes: entrainment of dense ambient fluid and exothermic or endothermic chemical reactions. In the case of a constant ambient density gradient, the former always acts to decrease the buoyancy flux and ultimately force the plume to become neutrally buoyant and spread out horizontally. For environments with a decreasing stratification in height, the plume will be unbounded, but we will not discuss this case further (Caulfield & Woods 1998). The reaction will cause the buoyancy flux to increase near the source for exothermic reactions but decrease faster for endothermic reactions than from entrainment alone. The momentum flux grows with distance from the source but ultimately becomes zero, which corresponds to the maximum rise height when the plume density is equal to the ambient. For an exothermic (or endothermic) reaction this point will occur at a larger (or smaller) value compared to a plume with no reaction. Finally, the volume flux will always increase with distance from the source, although it will be coupled to the reaction dynamics through the entrainment rate. Since we have assumed the plume fluid to be incompressible, the plume radius cannot expand or contract due to compressibility effects with an exothermic or endothermic reaction, respectively. In § 4 we will allow for compressibility effects, which will appear as a source term on the volume flux equation.

We have plotted the maximum rise height $H_{\max} = z_{\max}/2.57$, which is 1 for the exact solution of Morton *et al.* (1956), for which no reaction is present, in figure 5. The ambient species concentration R_2 is allowed to vary as a power law function, so for $\gamma < 0$ the concentration decreases with height and for $\gamma > 0$ the concentration increases with height. In general, when $\gamma \ll 0$ the ambient species will only exist at levels very close to the source and as a result the plume can only entrain a very small amount of this chemical. This leads to a small amount of reaction and the maximum rise height will be approximately the same at MTT56. When $\gamma \gg 1$ the ambient species concentration is very large above $z = 1$. Since this chemical concentration is also very large here, species 1 gets consumed rapidly in this region regardless of reaction rate and $H_{\max}$ is approximately the same for all rate constants, λ_3. In addition the maximum rise height increases with an exothermic reaction and decreases with an endothermic reaction, as we expect.

For $\gamma > 0.5$, the maximum rise height, $H_{\max}$, is larger in the exothermic case for smaller reaction rate constants. In this region species 2 increases rapidly above

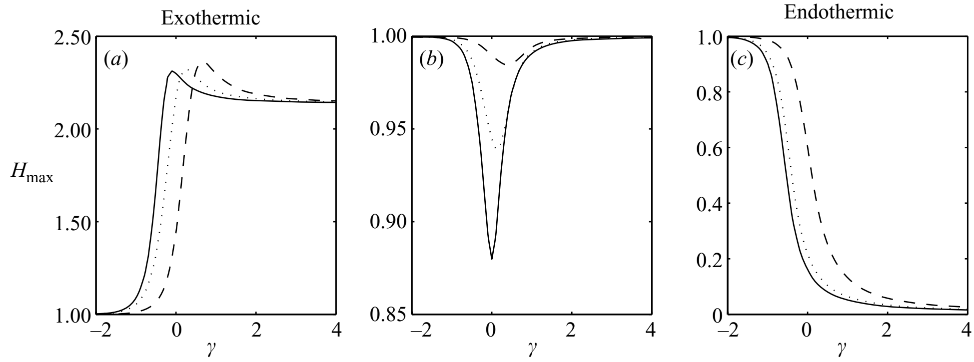

FIGURE 5. Numerical solutions showing the maximum rise height of the plume, $H_{\max}$, for $H_r = -10$ (a), 0 (b), 10 (c) and $\lambda_3 = 0.1$ (dashed line), 1 (dotted line), 10 (solid line). Here $z_s^{-1} = 100$, $\phi = 1$, $W_1 = W_2 = 1$, $R_{20} = 1$, $\lambda_3^* = \lambda_3$ and $\beta = 1$.

$z = 1$ and the plume entrains a large amount of this chemical. Subsequently, the reaction rate is very fast, which acts to increase the buoyancy flux and entrainment rate. Even though the exothermic reaction acts to decrease the plume density, the entrainment rate is large in a region of large density difference, and consequently the plume does not rise as high. In addition, for $\gamma \gg 1$ and $H_r = 0$, the maximum rise height $H_{\max} \approx 1$ and is therefore independent of the chemical reaction. In this case $\lambda_3 Q/\bar{F} \sim (z_s^{-1} z)^{-\gamma} \approx 0$ for $z_s^{-1} z \gg 1$ and $\gamma \gg 1$. Therefore the density is dominated by species 2, which has the same mass fraction as the source fluid, and the production of species 3 by reaction has a negligible effect. As $\gamma \to 0$ the ambient species concentration is approximately uniform, $R_2 \approx 1$ and the maximum rise height has a minimum value in this region. Here the reaction is relatively strong and the production of heavier species 3 leads to an increase in the plume density. Alternatively, for $\gamma \ll 1$ and $H_r = 0$, $R_2 \ll 1$ (except near $z = 0$) and the reaction is weak. Therefore the mixture density is dominated by species 1 and $H_{\max} \approx 1$.

4. Non-Boussinesq plume

4.1. *Plume equations*

When the density difference between plume and ambient becomes large, the Boussinesq assumption breaks down. In this case we need to reformulate the problem without this assumption. We follow Rooney & Linden (1996) and define fluxes with top hat profiles as

$$\pi \rho_0 Q'(z) = 2\pi \int_0^\infty r w \rho \, \mathrm{d}r = \pi \bar{\rho} \bar{w} b^2, \tag{4.1a}$$

$$\pi \rho_0 M'(z) = 2\pi \int_0^\infty \rho r w^2 \, \mathrm{d}r = \pi \bar{\rho} \bar{w}^2 b^2, \tag{4.1b}$$

$$\pi V'(z) = 2\pi \int_0^\infty r w \, \mathrm{d}r = \pi \bar{w} b^2, \tag{4.1c}$$

$$\pi \rho_0 P_i'(z) = 2\pi \int_0^\infty \rho Y_i r w \, \mathrm{d}r = \pi \bar{\rho} \bar{Y}_i \bar{w} b^2 \tag{4.1d}$$

for mass, momentum, volume and species respectively (note the factor of ρ_0 on the left-hand sides). We have used primes to denote non-Boussinesq variables, to distinguish the model from the previous sections. Following the procedure for a Boussinesq plume the appropriate equations can be derived by integrating equations (2.7*a*)–(2.7*d*) across the plume, yielding

$$\frac{\mathrm{d}Q'}{\mathrm{d}z} = 2\alpha\left(\frac{\rho_a}{\rho_0}\right)^{1/2} M'^{1/2}, \tag{4.2a}$$

$$\frac{\mathrm{d}M'}{\mathrm{d}z} = g\left(\frac{\rho_a}{\rho_0} - \frac{Q'}{V'}\right)\frac{Q'V'}{M'}, \tag{4.2b}$$

$$\frac{\mathrm{d}V'}{\mathrm{d}z} = 2\alpha\frac{M'^{1/2}}{(\rho_a/\rho_0)^{1/2}} - \sigma\frac{Q'V'}{M'}, \tag{4.2c}$$

$$\frac{\mathrm{d}P_i'}{\mathrm{d}z} = 2\alpha R_i\left(\frac{\rho_a}{\rho_0}\right)^{1/2} M'^{1/2} + \frac{\omega_i}{\rho_0}\frac{Q'V'}{M'}. \tag{4.2d}$$

With these definitions the density is $\bar{\rho} = \rho_0 Q'/V'$, the velocity is $\bar{w} = M'/Q'$ and the plume radius is $b^2 = Q'V'/M'$. In this analysis we have used the entrainment assumption $u_e = \alpha w(\rho/\rho_a)^{1/2}$, which is consistent with the experimental results of Ricou & Spalding (1961) and has been used by Rooney & Linden (1996) and Woods (1997). To compute the right-hand sides of equations (4.2*c*) and (4.2*d*) we express the concentrations in terms of fluxes using $P_i' = \rho\bar{Y}_i V'/\rho_0$. Then

$$\sigma\frac{Q'V'}{M'} = \Omega\rho^2 Y_1 Y_2\frac{Q'V'}{M'} = \rho_0\Omega\frac{P_1'P_2'}{M'}, \tag{4.3}$$

$$\frac{\omega_i}{\rho_0}\frac{Q'V'}{M'} = \pm\frac{\rho_0 K W_i}{W_1 W_2}\frac{P_1'P_2'}{M'}\frac{Q'}{V'} = \psi_i\frac{P_1'P_2'}{M'}\frac{Q'}{V'}. \tag{4.4}$$

In addition we can define a buoyancy flux as in equation (3.1*c*); this gives

$$B = gV'\left(\frac{\rho_a}{\rho_0} - \frac{Q'}{V'}\right), \tag{4.5}$$

and the momentum flux equation becomes

$$\frac{\mathrm{d}M'}{\mathrm{d}z} = \frac{BQ'}{M'}. \tag{4.6}$$

The governing equation for B is then

$$\frac{\mathrm{d}B}{\mathrm{d}z} = -N^2 V' - \kappa\frac{\rho_a}{\rho_0}\frac{P_1'P_2'}{M'}, \tag{4.7}$$

where

$$\kappa = g\psi_3\left[\frac{\beta\Delta H_r}{W_3 C_p} + \frac{Q'}{\bar{P}'}\right] = g\psi_3(\hat{H}_r + Q/\bar{P}'), \tag{4.8}$$

and $\bar{P}' = \sum_{i=1}^{3} W_3 P_i'/W_i$. Finally, the boundary conditions at the source are

$$Q' = M' = 0, \quad B = B_0, \quad V' = B_0/g, \quad P_2' = P_3' = 0, \quad P_1' = P_{10}' \quad \text{at} \quad z = z_s. \tag{4.9}$$

Note that these equations are formally identical to the Boussinesq equations for a uniform ambient density and negligible reaction rate but differ in general, owing to the factor $(\rho_a/\rho_0)^{1/2}$ and Q'/V' appearing in the equations. One important difference is the extra term on the volume flux equation (4.2c) that allows the plume to expand or contract with an exothermic or endothermic reaction respectively.

Using the scaling of § 3.3 with the density scaled with ρ_0 and V' scaled the same as Q', we can express the plume equations in non-dimensional form with hats dropped as

$$\frac{\mathrm{d}Q'}{\mathrm{d}z} = \rho_a^{1/2} M'^{1/2}, \tag{4.10a}$$

$$\frac{\mathrm{d}M'}{\mathrm{d}z} = \frac{BQ'}{M'}, \tag{4.10b}$$

$$\frac{\mathrm{d}B}{\mathrm{d}z} = -\left(\frac{\ell}{H}\right)^{8/3} N^2 V' - \rho_a \lambda_3^* \left[H_r + \frac{Q}{R_{20}\bar{P}}\right] \frac{P_1' P_2'}{M'}, \tag{4.10c}$$

$$\frac{\mathrm{d}V'}{\mathrm{d}z} = 2\alpha \frac{M'^{1/2}}{\rho_a^{1/2}} - R_{20}\lambda_3 \left[H_r + \frac{Q}{R_{20}\bar{P}}\right] \frac{P_1' P_2'}{M'} \tag{4.10d}$$

$$\frac{\mathrm{d}P_i'}{\mathrm{d}z} = R_i \rho_a^{1/2} M'^{1/2} + \lambda_i \frac{P_1' P_2'}{M'} \frac{Q'}{V'}, \tag{4.10e}$$

and the boundary conditions are

$$Q' = M' = P_2' = 0, \quad B = 1, \quad V' = \eta, \quad P_1' = \phi \quad \text{at} \quad z = z_s, \tag{4.11}$$

where $\eta = g^{-1}(2\alpha)^{-4/3} B_0^{2/3} \ell^{-5/3}$.

We do not pursue the stratified non-Boussinesq case: it is relevant only to situations like volcanic plumes with very hot gases rising high into the stratified atmosphere. In engineering applications with non-Boussinesq plumes, stratification does not play an important role. Of course this case can be investigated as a straightforward combination of § 3.6 and of § 4.1.

4.2. *No ambient stratification*

Following § 3.4, we take $\ell = H_c$ and the equations take on a simpler form when the vertical density and species gradients go to zero. When $H_r + Q/\bar{P}R_{20} \approx 0$ the reaction has a negligible effect on the plume dynamics and we may combine the above equations with $B = 1$ to obtain

$$Q' = \frac{3}{5}\left(\frac{9}{20}\right)^{1/3} z^{5/3}, \quad M' = \left(\frac{9}{20}\right)^{2/3} z^{4/3}. \tag{4.12}$$

These solutions are the analogue of the Boussinesq similarity solutions and may be shown to be equivalent when $\rho = \rho_0$. We should note that $\rho_a = \rho_0$ when the ambient density is uniform. From these solutions we can define a non-dimensional source parameter as (Carlotti & Hunt 2005)

$$\Gamma_{nb} = \frac{5BQ'^2}{4M'^{5/2}}, \tag{4.13}$$

which indicates whether the plume is dominated by buoyancy or momentum.

Following the previous sections we set $\phi = 1$, $R_{20} = 1$, $\eta = 1$ and $\lambda^* = \lambda_3$ in order to reduce our parameter space. Therefore, we focus on the effect of heat of reaction and reaction rate on the plume dynamics and the differences between the Boussinesq and non-Boussinesq formulations. In figure 6 we plot profiles of Γ_b and Γ_{nb} as a function of the reaction rate for a strongly exothermic and endothermic reactions. The two

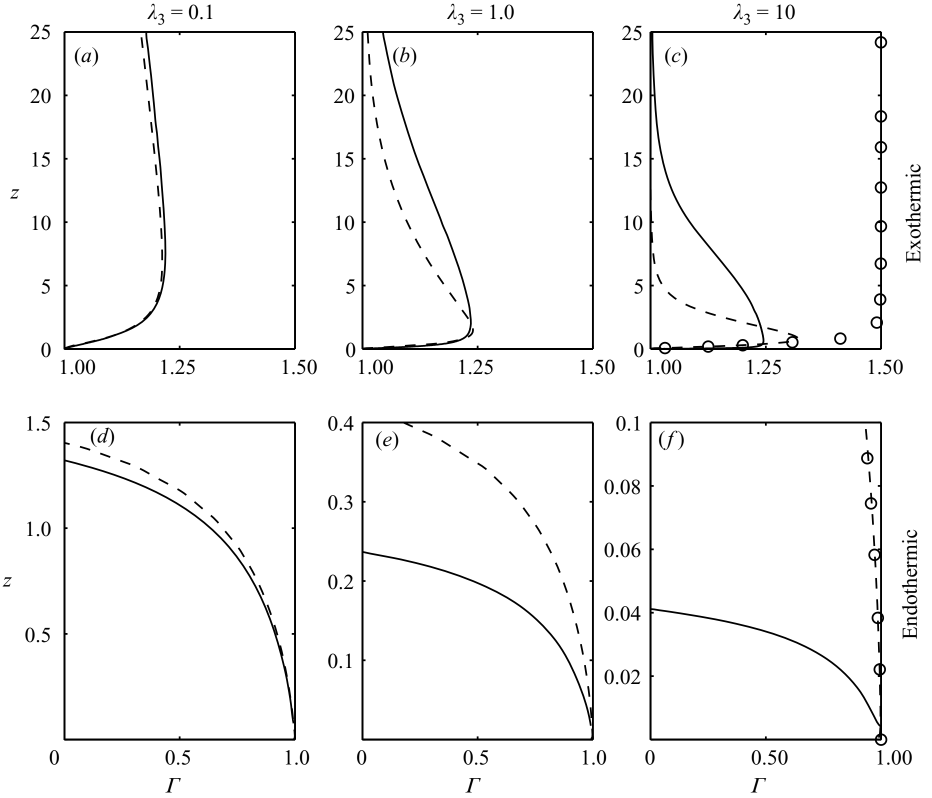

FIGURE 6. Numerical solution to the Boussinesq and non-Boussinesq equations for no ambient stratification showing Γ_b (dashed line) and Γ_{nb} (solid line) corresponding to $\lambda_3 = 0.1$ (*a*, *d*), 1 (*b*, *e*) and 10 (*c*, *f*) and $H_r = -10$ (*a*–*c*) and 10 (*d*–*f*). The circles represent the infinite reaction model. Here $z_s^{-1} = 100$, $\phi = 1$, $W_1 = W_2 = 1$, $\eta = 1$, $R_{20} = 1$ and $\lambda_3^* = \lambda_3$.

models are identical in form except for the factor Q'/V', multiplying the reaction rate in (4.10*e*). This term is always less than one (otherwise we have a fountain) and $\mathrm{d}P_1'/\mathrm{d}z$ is effectively reduced in comparison to the Boussinesq model. The buoyancy flux in the non-Boussinesq case can be shown by comparing (4.10*c*) and (4.10*e*) to scale as $B - 1 \sim H_r\, \rho^{-1}(P_1' - \phi)$. Since $\rho < 1$ near the source (although it approaches 1 for large z), B in the non-Boussinesq formulation is larger for an exothermic reaction and smaller for an endothermic reaction. Therefore, for regions close to the source the non-Boussinesq model behaves more like a plume for the exothermic case ($\Gamma_{nb} > \Gamma_b$) and more like a jet in the endothermic case ($\Gamma_{nb} < \Gamma_b$). Since the buoyancy flux, in the absence of stratification, is controlled by reaction, we expect the vertical gradients of B and P_1 to be similar. Furthermore the source parameters (Γ_b and Γ_{nb}), being functions of P_1, will have the largest variation in regions of strong reaction rate. For this reason $\Gamma_b > \Gamma_{nb}$ for $\lambda \gg 1$ at intermediate heights, where the reaction is stronger in the Boussinesq model and $\Gamma_b < \Gamma_{nb}$ for larger heights, where the reaction rate is slower (due to a small concentration of species 1).

We have plotted the plume radius as a function of height in figure 7 for the Boussinesq and non-Boussinesq formulations. Near the source, the density of the plume is small relative to the ambient and since the mass flux of both formulations are the same, the volume flux for the non-Boussinesq plume is larger (Woods 1997). The

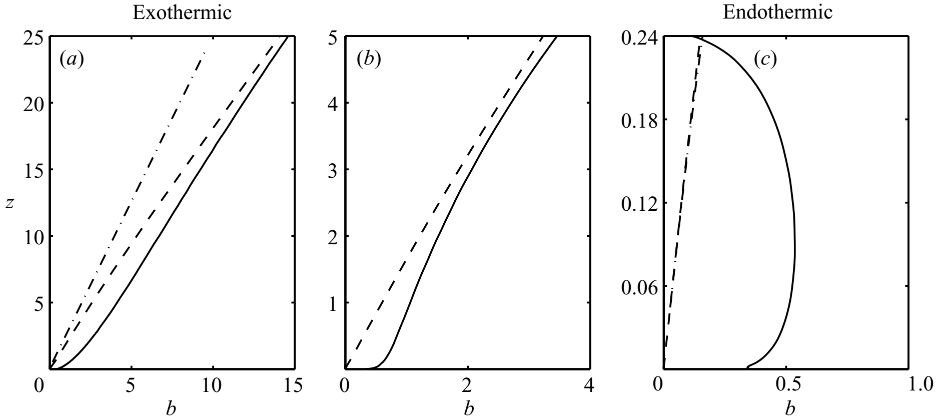

FIGURE 7. Numerical solution to the Boussinesq (dashed line) and non-Boussinesq (solid line) equations for no ambient stratification, showing the plume radius b corresponding to $H_r = -10$ (*a*), 0 (*b*) and 10 (*c*). Here $\lambda_3 = 1$, $z_s^{-1} = 100$, $\phi = 1$, $W_1 = W_2 = 1$, $\eta = 1$, $R_{20} = 1$ and $\lambda *_3 = \lambda_3$. The dot-dashed line is the Boussinesq infinite reaction rate solution.

effect of an exothermic reaction is then to make the expansion larger, since the density difference will have a greater sustained value above the source. At sufficiently large distances above the source, where species 1 is sufficiently consumed, the plume density will approach the ambient density and the volume flux will behave as a Boussinesq plume. In the case of an endothermic reaction the absorption of thermal energy will cause the density of the plume to increase relative to the ambient. For sufficiently large heats of reaction the plume density will be larger than the ambient density and since the mass flux for both formulations is the same, the volume flux will be smaller for the non-Boussinesq formulation. Since the volume flux for the non-Boussinesq formulation experiences a change in volume with reaction, the plume radius will narrow for large endothermic reactions as opposed to the Boussinesq model.

5. Conclusion

We have developed a model for a plume rising into an unbounded ambient with a reaction between the source plume chemical species and the ambient with a non-negligible heat of reaction, in the case of a second-order non-reversible chemical reaction. This model extends the work of CLSC to account for a source term on the buoyancy flux, which is a function of the heat released or absorbed. We first investigate the limiting case of a Boussinesq plume, where density effects are only important on the buoyancy terms. The difference with respect to the original plume equations of MTT56 is an extra term in the buoyancy flux equation, which depends strongly on the species flux equations. In the special case of an unstratified ambient, we can obtain a similarity solution for an infinite reaction rate, which indicates that the volume ($Q \propto z^{5/2}$) and momentum ($M \propto z^3$) flux equations scale on a different length scale to that of a plume without reaction (e.g. $Q \propto z^{5/3}$ and $M \propto z^{4/3}$). Furthermore, we showed that the reaction will cause the plume to be ‘lazy’ for an exothermic reaction and ‘forced’ for an endothermic reaction. In the former case the plume ultimately asymptotes to a pure plume when the sources species is consumed, but in the latter case a fountain may form provided the reaction rate and heat of absorption are sufficiently large.

For a density and chemically stratified ambient we examined the effects of reaction rate and heat of reaction on the maximum rise height of the plume in comparison to the linear density model of MTT56. For an exothermic plume with a large reaction rate the increase in buoyancy will increase the velocity and consequently the entrainment rate near the source. Since the ambient density is larger here (due to the linear density stratification), the decrease in buoyancy flux by entrainment will dominate the increase in buoyancy flux by reaction. We expect this behaviour to exist in general provided the ambient has a stable density gradient. Moreover, for strongly decreasing ambient chemical stratifications the maximum rise height will be the same as for a non-reacting plume, since only a small amount of species 2 can be entrained.

Finally, we have extended our model to a non-Boussinesq plume using an entrainment rate that depends on the ratio of plume to reference density. In this case the two formulations are only comparable when the plume density is similar to the ambient density, which is always true at large heights above the source. Either way, an exothermic reaction will cause the reaction rate to decrease, since it depends on the density, and an endothermic reaction will cause the reaction rate to increase. This will have an important effect on the source parameter Γ_{nb} and plume property profiles since the reaction rate is non-uniformly modified. Furthermore, the plume radius can have very different profiles, owing to the effects of compressibility on the non-Boussinesq formulation. For an exothermic reaction the plume will expand at early times compared to a Boussinesq plume as long as the density change by heat release dominates the decrease in density by entrainment. Alternatively, for an endothermic reaction the plume contracts at early times and may become a fountain for sufficiently large reaction rates and heat absorption.

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REFERENCES

Bhat, G. S. & Narashima, R. 1996 A volumetrically heated jet: large-eddy structure and entrainment characteristics. *J. Fluid Mech.* **325**, 303–330.

Bloomfield, L. & Kerr, R. C. 2000 A theoretical model of a turbulent fountain. *J. Fluid Mech.* **424**, 197–216.

Carlotti, P. & Hunt, G. R. 2005 Analytical solutions for turbulent non-Boussinesq plumes. *J. Fluid Mech.* **538**, 343–359.

Caulfield, C. C. P. & Woods, A. W. 1995 Plumes with nonmonotonic mixing behaviour. *Geophys. Astrophys. Fluid Dyn.* **79**, 173–199.

Caulfield, C. P. & Woods, A. W. 1998 Turbulent gravitational convection from a point source in a non-uniformly stratified environment. *J. Fluid Mech.* **360**, 229–248.

Clarke, J. F. & McChesney, M. 1964 *The Dynamics of Real Gases*. Butterworth.

Conroy, D. T., Llewellyn Smith, S. G. & Caulfield, C. P. 2005 Evolution of a chemically reacting plume in a ventilated room. *J. Fluid Mech.* **537**, 221–253.

Fisenko, S. P., Brin, A. A. & Petruchik, A. I. 2004 Evaporative cooling of water in a mechanical draft cooling tower. *Intl J. Heat Mass Transf.* **47**, 165–177.

Hunt, G. R. & Kaye, N. B. 2005 Lazy plumes. *J. Fluid Mech.* **533**, 329–338.

Komori, S., Hunt, J. C. R., Kanzaki, T. & Murakami, Y. 1990 The effects of turbulent mixing on the correlation between two species and on concentration fluctuations in non-premixed reacting flows. *J. Fluid Mech.* **228**, 629–659.

Morton, B. R., Taylor, G. I. & Turner, J. S. 1956 Turbulent gravitational convection from maintained and instantaneous sources. *Proc. R. Soc. Lond.* A **234**, 1–23.

Patnaik, P. 1999 *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*, 2nd edn. Wiley.

Ricou, F. P. & Spalding, D. B. 1961 Measurements of entrainment by axisymmetrical turbulent jets. *J. Fluid Mech.* **11**, 21–32.

Rooney, G. G. & Linden, P. F. 1996 Similarity considerations for non-Boussinesq plumes in an unstratified environment. *J. Fluid Mech.* **318**, 237–250.

Scase, M. M., Caulfield, C. P. & Dalziel, S. B. 2006 Boussinesq plumes and jets with decreasing source strengths in stratified environments. *J. Fluid Mech.* **563**, 463–472.

Tieszen, S. R. 2001 On the fluid mechanics of fires. *Annu. Rev. Fluid Mech.* **33**, 67–92.

Williams, F. A. 1985 *Combustion Theory*, 2nd edn. Benjamin/Cummings.

Woods, A. W. 1997 A note on non-Boussinesq plumes in an incompressible stratified environment. *J. Fluid Mech.* **345**, 347–356.