Development of a two-dimensional laminar mixing layer at supercritical pressures

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Abstract

Numerical analysis of a shear layer between a cool liquid hydrocarbon and a hotter oxygen gas at supercritical pressures shows that a well-defined phase equilibrium can be established. Variable properties are considered with the product $\rho \mu$ in the gas phase showing a nearly constant result. Sufficiently thick diffusion layers form around the liquid-gas interface for the selected free-stream velocities at a streamwise distance of $x = 1$ cm for different pressures (i.e., 10 - 18 $\mu$m in the liquid phase and 30 - 160 $\mu$m in the gas phase). While molecules are exchanged for both species at all pressures, net mass flux across the interface shifts as pressure is increased. Net vaporization occurs for low pressures while net condensation occurs at higher pressures. For a mixture of $n$-decane and oxygen, the transition occurs around 50 bar. The equilibrium values at the interface quickly reach their asymptotes. For all cases, profiles of diffusing-advection quantities collapse to a similar solution (i.e., function of one independent variable). However, similarity for the normalized results from cases with different boundary conditions is lost when comparing different pressure or temperature cases to each other as the thermodynamics and interface conditions change.

Keywords: laminar mixing layer, phase equilibrium, supercritical pressure, phase change, diffusion layer, similarity

1. Introduction

Modern combustion devices such as liquid fueled rocket engines, diesel engines, and gas turbines operate at high pressures to meet the ever-increasing demand for higher propulsive power and fuel efficiency. The injectors used in these devices are designed to optimize atomization, where liquid droplets form and vaporize into the surrounding gas to allow for the combustion reaction to occur. In some cases, the operating pressure can be larger than the critical pressure of the injected liquid. In this supercritical environment, the thermodynamics and fluid dynamics during injection are modified considerably. Furthermore, a shear layer is formed about the interface between the liquid and the gas during injection before substantial disruption of the liquid stream. Understanding how this shear layer evolves at supercritical pressures is crucial to understanding the initial stages of high-pressure atomization.

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There have been many experimental investigations of supercritical phenomena [1–4], but they are limited by measurement techniques and high costs associated with the extreme environments. Computational modeling allows for more accurate simulation of these environments and complements experimental data.

2. Two-phase laminar mixing layer

2.1. Problem definition

As shown in Figure 1, a liquid of pure species B with velocity $V_B$ is introduced into a gas with a slower velocity $V_A$. Steady state is assumed marching downstream creating a two-dimensional problem. Transverse momentum imbalance at the edges of the developing diffusion layers becomes negligible quickly. Thus, it is reasonable to assume a fixed interface at $y = 0$ m. The liquid temperature remains lower than the gas temperature, within the critical temperature range for the pure liquid species. Pressure is held constant throughout the domain. Supercritical pressures enhance the dissolution of lighter gas species A into the liquid phase through the imposition of thermodynamic phase equilibrium. Thus, a binary mixture exists on either side of the interface as molecules of liquid species B mix with the surrounding gas while gaseous molecules of species A enter the liquid phase. A net condensation or vaporization results about the interface depending on the interface energy balance and pressure regime.

2.2. Laminar flow conditions and instability analysis

A Reynolds number must be chosen such that the resulting flow is laminar and stable. Very little is known about the critical Reynolds numbers at which a two-phase laminar mixing layer becomes unstable. Even less is known about the transition Reynolds number to a turbulent flow. Huang and Ho [5] found that the transition displacement-thickness Reynolds number for a plane mixing layer occurred in the range $114 < Re_\delta < 140$. However, it was noted that the transition was not definite, but rather local Reynolds number dependent. Thus, a boundary layer approximation is assumed to provide some guidance. Tani [6] states that two-dimensional instability oscillations begin to form above a displacement thickness Reynolds number
Taking into account a degree of uncertainty, a Reynolds number with respect to displacement thickness, \( Re_\delta = 100 \) is used in this work.

A streamwise domain length of 1 cm was chosen searching for a self-similar solution to ensure a fully-developed flow. To satisfy this requirement with \( Re_\delta = 100 \), \( \Delta u \) is computed between the free-stream liquid and gas phases using the Reynolds number definition with respect to streamwise distance:

\[
Re_L = \frac{\rho_L \Delta u}{\mu_g}
\]  

(1)

where the density, \( \rho_g \), and the viscosity, \( \mu_g \), are computed from the bulk gas.

Assuming a mean flow velocity, \( u_{\text{mean}} = 10 \text{ m/s} \), \( u_g \) and \( u_l \) are found for each pressure case. Their values are illustrated in Table 1. Viscosity, density, and surface tension computed at the interface are shown in Table 2. More information on how to evaluate these properties is provided in Section 3.2.

| p (bar) | \( u_g \) (m/s) | \( u_l \) (m/s) |
|--------|----------------|----------------|
| 10     | 7.673          | 12.327         |
| 50     | 9.525          | 10.475         |
| 100    | 9.755          | 10.246         |
| 150    | 9.830          | 10.170         |

Table 1: Laminar flow conditions.

| p (bar) | \( \rho_g \) (kg/m\(^3\)) | \( \rho_l \) (kg/m\(^3\)) | \( \mu_g \) (kg m/s) | \( \mu_l \) (kg m/s) | \( \sigma \) (kg/s\(^2\)) |
|--------|-----------------|-----------------|----------------|----------------|----------------|
| 10     | 12.392          | 593.843         | 1.956×10\(^{-5}\) | 1.804×10\(^{-4}\) | 9.728×10\(^{-3}\) |
| 50     | 47.915          | 580.960         | 2.501×10\(^{-5}\) | 1.295×10\(^{-4}\) | 7.218×10\(^{-3}\) |
| 100    | 91.435          | 572.604         | 2.662×10\(^{-5}\) | 9.772×10\(^{-5}\) | 5.109×10\(^{-3}\) |
| 150    | 134.381         | 564.875         | 2.778×10\(^{-5}\) | 7.836×10\(^{-5}\) | 3.499×10\(^{-3}\) |

Table 2: Interface thermodynamic conditions.

Under such flow conditions, it’s important to analyze Kelvin-Helmholtz (KH) hydrodynamic instabilities to determine the potential effects different high-pressure environments have on surface perturbations and confirm the stability of the chosen Reynolds number. KH wave growth is evaluated within the streamwise domain at the interface, where the largest gradients exist. Small perturbations at the liquid-gas interface for liquid sheets flowing parallel to a gas can be analyzed by studying the evolution of the perturbation amplitude [7, 8]. It is given by

\[
\eta(x, t) = \tilde{\eta} e^{\epsilon t} e^{ikx}
\]  

(2)

where \( \eta \) represents the perturbation amplitude as a function of the initial oscillation amplitude, \( \tilde{\eta} \), growth rate, \( \epsilon \), time, \( t \), wave number, \( k = 2\pi/\lambda \), and location, \( x \).

The growth rate parameter, \( \epsilon \), can be expressed as

\[
\epsilon = \epsilon_R + \epsilon_I i
\]  

(3)

where the real part, \( \epsilon_R \), can be analyzed to characterize the stability of a perturbation. \( \epsilon_R < 0 \) is stable and \( \epsilon_R > 0 \) is unstable. A linear analysis of small-amplitude interface perturbations provides an expression for \( \epsilon \)
as a function of the fluid properties without the effects of gravity is found to be \[8\]

\[
\epsilon = -\frac{k(\rho_g u_g + \rho_l u_l)}{\rho_g + \rho_l} - k^2 \frac{\mu_g + \mu_l}{\rho_g + \rho_l} \pm \left[ \frac{\rho_g \rho_l k^2 (u_g - u_l)^2}{(\rho_g + \rho_l)^2} - \frac{\sigma k^3}{\rho_g + \rho_l} + \frac{k^4 (\mu_g + \mu_l)^2}{(\rho_g + \rho_l)^2} + 2ik^3 (\rho_g \mu_l - \rho_l \mu_g)(u_g - u_l) \right]^{1/2}
\]

which includes the streamwise velocity, \(u\), viscosity, \(\mu\), density, \(\rho\), and the surface tension, \(\sigma\). \(u\) is taken in the bulk liquid and gas while \(\mu, \rho\), and \(\sigma\) are obtained at the interface. Viscosity and surface tension calculations at the interface are discussed in Section 3.2. This expression can only roughly represent the problem analyzed in this paper since it only considers normal viscous stress where shear stress and vorticity are ignored.

Figure 2 shows the real part of the growth rate as a function of wavelength for a mean flow velocity \(u_{\text{mean}} = 10\) m/s. Only \(\epsilon_R > 0\) is shown as it represents flow instabilities. Table 3 shows the maximum growth rate with its associated wavelength and characteristic time, \(\tau\), for the four pressure cases. For increasing pressure, there is an increase in the critical wavelength for the instabilities to develop and a decrease in the growth rate. For flow moving at 10 m/s, it takes \(\tau^* = 1\) ms to pass through a 1 cm domain. Thus for \(p = 50, 100,\) and 150 bar, the characteristic time for instabilities to develop is larger than the time it takes
the flow to pass through the domain. Therefore, it will be safe to consider instabilities as negligible before diffusion layers become sufficiently thick to use continuum theory on each side of the phase interface with its discontinuity in density and chemical composition.

However, note the development of instabilities within the domain for the 10 bar pressure case. As previously mentioned, Eq. (4) does not take into account shear-layer effects. Such effects would dampen the perturbations, thus decreasing the growth rate and moving the most unstable waves to longer wavelengths [9–12]. Thus, it is expected that the 10 bar case would also be stable or very slowly growing in amplitude within the analyzed domain.

2.3. Governing equations

For a sufficiently large Reynolds number, the governing equations for a two-dimensional laminar mixing layer follow the boundary-layer approximation [13], where \( \nu \ll u \), partial derivatives in \( x \) are much smaller than partial derivatives in \( y \) and \( \partial p / \partial y \approx 0 \). By assuming constant pressure everywhere, \( \partial p / \partial x \approx \partial p / \partial y \approx 0 \). Under these assumptions, it is unnecessary to include the transverse momentum equation in the problem formulation and the transverse velocity is directly obtained from the continuity equation [14, 15]. Furthermore, the pressure term in the energy equation disappears and viscous dissipation and kinetic energy become negligible for low-Mach number flows at high pressures.

The steady-state, high-pressure, two-phase mixing layer equations in conservative form are the global continuity equation, Eq. (5), the species continuity equation, Eq. (6), the streamwise momentum equation, Eq. (7), and the energy equation, Eq. (8). These equations are valid on each individual phase and take into account spatial variations in density and other fluid properties. Conservation relations must be satisfied across the liquid-gas interface together with thermodynamic phase equilibrium (see Subsection 3.3).

\[
\frac{\partial}{\partial x} (\rho u) + \frac{\partial}{\partial y} (\rho v) = 0 \quad (5)
\]

\[
\frac{\partial}{\partial x} (\rho u Y_i) + \frac{\partial}{\partial y} (\rho v Y_i) + \frac{\partial}{\partial y} (J_y^i) = 0 \quad (6)
\]

\[
\frac{\partial}{\partial x} (\rho u u) + \frac{\partial}{\partial y} (\rho v u) = \frac{\partial}{\partial y} \left( \mu \frac{\partial u}{\partial y} \right) \quad (7)
\]

\[
\frac{\partial}{\partial x} (\rho u h) + \frac{\partial}{\partial y} (\rho v h) + \sum_{i=1}^{N} \frac{\partial}{\partial y} (J_y^i h_i) = \frac{\partial}{\partial y} \left( \lambda \frac{\partial T}{\partial y} \right) \quad (8)
\]

The non-conservative form of the governing equations is used for the numerical discretization of the equations (see Subsection 4.1). Substitution of the global and species continuity equations into the conservative forms yields the non-conservative forms of the species continuity equation, Eq. (9), the stream-wise momentum equation, Eq. (10), and the energy equation, Eq. (11).

\[
\rho u \frac{\partial Y_i}{\partial x} + \rho v \frac{\partial Y_i}{\partial y} + \frac{\partial}{\partial y} (J_y^i) = 0 \quad (9)
\]

\[
\rho u \frac{\partial u}{\partial x} + \rho v \frac{\partial u}{\partial y} = \frac{\partial}{\partial y} \left( \mu \frac{\partial u}{\partial y} \right) \quad (10)
\]

\[
\rho u \frac{\partial h}{\partial x} + \rho v \frac{\partial h}{\partial y} - \rho u \sum_{i=1}^{N} h_i \frac{\partial Y_i}{\partial x} - \rho v \sum_{i=1}^{N} h_i \frac{\partial Y_i}{\partial y} + \sum_{i=1}^{N} J_y^i \frac{\partial h_i}{\partial y} = \frac{\partial}{\partial y} \left( \lambda \frac{\partial T}{\partial y} \right) \quad (11)
\]
3. Thermodynamic Modeling

The governing equations need accurate estimates of the thermodynamic and transport properties in a wide range of thermodynamic states to properly capture physical processes at high pressures. A real-gas equation of state is used to evaluate density, enthalpy and other thermodynamic parameters given a state point in the thermodynamic space (i.e., $p$, $T$ and $Y_i$). Transport properties are obtained from various models and correlations developed for high-pressure environments or high-dense fluids.

3.1. Equation of state

In this work, the Soave-Redlich-Kwong (SRK) cubic equation of state is used [16]. From a computational perspective, a cubic equation of state is more efficient to implement than other more accurate parametric equations of state, while still providing reasonable accuracy in predicting liquid and gas solutions. However, the SRK equation of state density predictions start to deviate from experimental values as fluid density increases (e.g., liquid phase or fluids under high pressures), with errors up to 20% [17, 18]. To improve the accuracy of the equation of state, a volumetric correction is implemented, which recovers the molar volume, $v_c$, at the critical point $T_c$ and $p_c$. This method also increases the accuracy of density predictions for other temperatures and pressures.

The modified SRK equation of state in terms of the compressibility factor, $Z$, becomes

$$Z^3 + (3C - 1)Z^2 + (C(3C - 2) + A - B - B^2)Z + C(C^2 - C + A - B - B^2) - AB = 0$$

with

$$Z = \frac{\bar{v}p}{R_uT}; \quad A = \frac{a(T)p}{R_u^2T^2}; \quad B = \frac{b_p}{R_uT}; \quad C = \frac{c(T)p}{R_uT}$$

Eq. (12) is a cubic equation for $Z$, which can be solved to obtain the molar volume or the density ($\rho = MW/\bar{v}$) of the mixture for a given pressure, temperature and composition. $a(T)$ represents a temperature-dependent cohesive energy parameter, $b$ represents the volumetric parameter and $c(T)$ is a temperature-dependent volume correction. The cohesive parameter is evaluated as

$$a(T) = a_c \alpha(T); \quad a_c = \frac{1}{9(2^{1/3} - 1)} \frac{R_u^2T^2_c}{p_c}$$

$$a(T) = [1 + m(1 - T_r^{0.5})]^2; \quad m = 0.48508 + 1.55171\omega - 0.15613\omega^2$$

where $T_r = T/T_c$ stands for the reduced temperature and the coefficient $m$ is computed according to the modification proposed by Graboski and Daubert [19, 20]. The volumetric parameter and its correction are obtained from

$$b = b_c = \frac{2^{1/3} - 1}{3} \frac{R_uT_c}{p_c}; \quad c(T) = c_c f(T_r); \quad c_c = \bar{v}_c^{SRK} - \bar{v}_c = \left(\frac{1}{3} - Z_c^{exp}\right) \frac{R_uT_c}{p_c}$$

with $Z_c^{exp}$ being the experimental compressibility factor of the critical point and $f(T_r)$ a temperature-dependent function which becomes 1 at the critical point ($T_r = 1$). This function is obtained from Lin et al. [21], given by

$$f(T_r) = \beta + (1 - \beta) \exp(\eta|1 - T_r|)$$
In Eq. (17), $\beta$ and $\eta$ are experimentally fitted parameters for each species. To avoid isotherm crossing near the critical temperature at very high pressures, the volume correction should be temperature-independent if $p > p_c$. Then, Eq. (17) is modified as in [21]

$$f(T_r) = \beta + (1 - \beta) \exp(0.5\eta)$$

For mixtures, quadratic mixing rules are used to follow the original guidelines provided by Soave [16]. Other mixing rules could be implemented, but the analysis of their performance is out of scope of the present work and satisfactory matching with experimental data has been obtained with the present model. Note that for nomenclature convenience, the dependence on temperature for the terms related to $a$ and $c$ is not explicitly written. The mixing rules are

$$a = \sum_{i=1}^{N} \sum_{j=1}^{N} X_i X_j (a_{ij})^{0.5} (1 - k_{ij}) \quad ; \quad b = \sum_{i=1}^{N} X_i b_i \quad ; \quad c = \sum_{i=1}^{N} X_i c_i$$

(19)

Evaluation of other fluid properties needed in the governing equations, such as mixture enthalpy, can be found in Appendix A.

### 3.2. Transport properties

The thermodynamic modeling is coupled with the computation of transport properties via high-pressure correlations that require information of the thermodynamic state of the mixture (i.e., pressure, temperature, composition and density). Viscosity and thermal conductivity are evaluated using the correlations from Chung et al. [22] while surface tension for the instability analysis is obtained from the Macleod-Sugden correlation, as suggested by Poling et al. [23]. The diffusion coefficient is based on the model developed by Leahy-Dios and Firoozabadi [24]. The latter uses the Maxwell-Stefan equations, Eq. (20), to obtain generalized diffusion fluxes for each species in a mixture.

$$\sum_{j \neq i} X_i X_j \left( \frac{J_{i,j}^M}{cX_j} - \frac{J_{j,i}^M}{cX_i} \right) = d_i - \sum_{j \neq i} X_i X_j \left( \frac{D_{i,j}^T}{\rho Y_j} - \frac{D_{j,i}^T}{\rho Y_i} \right) \nabla \ln T$$

(20)

In the present work, thermal diffusion effects are neglected and, for a binary mixture, the Maxwell-Stefan equations are solved and recast in Fickian form in a mass-based frame of reference [24, 25] as

$$J_1^T = -J_2^T = -\rho D_m \nabla Y_1$$

(21)

where

$$D_m = D_{12} \Gamma_{12} \quad ; \quad \Gamma_{12} = 1 + X_1 \left( \frac{\partial \ln \Phi_1}{\partial X_1} \right)_{p,T} - \left( \frac{\partial \ln \Phi_1}{\partial X_2} \right)_{p,T}$$

(22)

with $D_{12}$ computed from [24]. Partial derivatives of the fugacity coefficient based on the SRK equation of state are shown in Appendix B. Therefore, the transverse diffusion mass flux, $J_i^T$, in Eqs. (9) and (11) may be substituted by $J_i^T = -\rho D_m \frac{\partial Y_i}{\partial T}$.

Binary diffusion coefficients are obtained from high-pressure correlations and the thermodynamic factor, $\Gamma$, representing non-idealities in the diffusion process, is included in the diffusion driving force, $d_i$ [15, 24, 26]. The thermodynamic factor tends to 1 for an ideal mixture and it is identical to 1 for a pure substance. However, there is no mathematical restriction for this coefficient and it may become negative for a given composition range at a specified pressure and temperature. As other authors report [27], this situation of negative or reversed diffusion is associated to phase instability of the mixture and should be avoided.
3.3. Interface matching and phase equilibrium

The solution of the governing equations is not continuous across the interface since a jump in fluid and transport properties is present. To relate both liquid and gas phases, mass, momentum and energy conservation relations are imposed. In a frame of reference moving with the interface, the mass flux, Eqs. (23) and (24), and energy flux, Eq. (25), crossing the interface must be continuous (i.e., fluxes normal to the interface). This corresponds to matching the governing equations in the \( y \)-direction for the mixing layer.

The transverse interface velocity, \( V_\Gamma \), is an eigenvalue of the problem that can be determined by the specific boundary conditions (i.e., \( V_\Gamma = 0 \) for a fixed interface).

\[
\dot{\omega} = \rho_g(v_g - V_T) = \rho_l(v_l - V_T) \quad (23)
\]

\[
\rho_g Y_{gi}(v_g - V_T) + J^g_{yi} = \rho_l Y_{li}(v_l - V_T) + J^l_{yi} \quad (24)
\]

\[
\dot{\omega}(h_g - h_l) = \lambda_g \left( \frac{\partial T}{\partial y} \right)_g - \lambda_l \left( \frac{\partial T}{\partial y} \right)_l + \sum_{i=1}^{N} J^g_{yi} h_l - \sum_{i=1}^{N} J^l_{yi} h_l \quad (25)
\]

Rearranging Eq. (23), the normal velocity jump is obtained as

\[
v_g - v_l = \left( \frac{1}{\rho_g} - \frac{1}{\rho_l} \right) \dot{\omega} \quad (26)
\]

The streamwise momentum equation is matched under the following conditions, which state that the tangential component of the fluid velocity at the interface should be continuous (i.e., no-slip condition), Eq. (27), as well as the tangential stress or shear stress at the interface, Eq. (28).

\[
u_g = u_l = U_\Gamma \quad (27)
\]

\[
\mu_g \left( \frac{\partial u}{\partial y} \right)_g = \mu_l \left( \frac{\partial u}{\partial y} \right)_l \quad (28)
\]

Phase-equilibrium relations provide a necessary thermodynamic closure for the interface matching. Phase equilibrium is imposed through an equality in chemical potential for each species on both sides of the interface. This condition can be expressed in terms of an equality in fugacity [16, 23] as

\[
f_{li}(T_l, p_l, X_{li}) = f_{gi}(T_g, p_g, X_{gi}) \quad (29)
\]

where fugacity is a function of temperature, pressure and mixture composition. Under the constant pressure assumption, the interface pressure is continuous (i.e., \( p_l = p_g = p_\Gamma = p_{ch} \)). Eq. (29) can be rewritten in terms of the fugacity coefficient defined as

\[
\Phi_i = \frac{f_i}{p_i} = \frac{f_i}{p X_i} \quad (30)
\]

so for constant pressure across the interface, phase equilibrium is now given by

\[
X_{gi} \Phi_{gi} = X_{gi} \Phi_{gi} \quad (31)
\]

Furthermore, the interface presents a negligible thickness of the order of nanometers [28, 29] and diffusion layers grow fast enough on both sides of the interface [14]. Thus, temperature can be assumed to be the same on both sides of the interface (i.e., \( T_g = T_l = T_\Gamma \)). These assumptions simplify the solution of phase equilibrium and a mixture composition can readily be obtained on each side of the interface.
4. Numerical method

4.1. Discretization of the governing equations

Figure 3: Transverse domain mesh definition.

Eqs. (5), (9), (10), and (11) are discretized using a finite-volume approach [30]. Figure 3 defines the mesh within the transverse domain. An explicit first-order Euler method is used to discretize Eqs. (9), (10), and (11) instead of high order explicit or implicit approaches [15]. The Courant-Friedrichs-Lewy (CFL) conditions are satisfied to ensure numerical stability [15, 31]. Eq. (5) is discretized using an implicit approach to obtain the transverse velocity field from density variations within the domain. The discretized equations are

\[
\frac{(\rho u)^{m+1} - (\rho u)^m}{\Delta x} V_P + [(\rho v)^{m+1} - (\rho v)^{s,m+1}] \Delta x \Delta z = 0
\]  
(32)

\[
(\rho u_P)^m \frac{Y^{m+1} - Y^m}{\Delta x} V_P + (\rho_P v_P)^m [Y^m_{n,j} - Y^m_{s,j}] \Delta x \Delta z + [J^m_{n,j} - J^m_{s,j}] \Delta x \Delta z = 0
\]  
(33)

\[
(\rho_P u_P)^m \frac{h^{m+1} - h^m}{\Delta x} V_P + (\rho_P v_P)^m (h^m_{n} - h^m_{s}) \Delta x \Delta z =
\]
\[
\frac{1}{2} \left[ (\mu_N + \mu_P) \left( \frac{u^m_{n,j} - u^m_{s,j}}{\Delta y} \right) - (\mu_N + \mu_P) \left( \frac{u^m_{n,j} - u^m_{s,j}}{\Delta y} \right) \right] \Delta x \Delta y
\]
(34)

\[
(\rho_P u_P)^m \frac{h^{m+1} - h^m}{\Delta x} V_P + (\rho_P v_P)^m [h^m_{n} - h^m_{s}] \Delta x \Delta z - (\rho_P u_P)^m \sum_{i=1}^{N} b_{P,i}^m \frac{Y^{m+1} - Y^m_{P,i}}{\Delta x} V_P - (\rho_P v_P)^m \sum_{i=1}^{N} b_{P,i}^m [Y^m_{n,j} - Y^m_{s,j}] \Delta x \Delta z
\]
\[
- \left[ \left( \frac{\Lambda}{c_P} \frac{\partial h}{\partial y} \right) + \left( \frac{\Lambda}{c_P} \frac{\partial h}{\partial y} \right) \right] \Delta x \Delta z = 0
\]  
(35)

9
where the subscript \( P \) denotes the center of the cell being computed and \( n \) and \( s \) are the cell face locations directly above and below \( P \) respectively. The superscripts \( m \) and \( m + 1 \) denote the current and next position step. Similarly, the grid parameters \( V_P, \Delta x, \Delta y, \) and \( \Delta z \) represent the cell volume and cell sizes in streamwise, transverse, and spanwise directions respectively. For this 2-D problem, \( V_P = \Delta x \Delta y \Delta z \), where \( \Delta z = 1 \).

The transverse velocity and diffusion mass fluxes are computed on the cell faces, while all other properties are evaluated at the node center. A second-order central-difference scheme was used to compute those variables evaluated at both the cell face and node center. Since transverse velocities are very small in this problem, a central-difference approach does not introduce numerical instabilities and produces similar results as upwind schemes [15]. For example,

\[
v_P = \frac{1}{2} (v_n + v_s) ; \quad Y_{sj} = \frac{1}{2} (Y_{pj} + Y_{sj})
\]

Gradients at the cell faces are computed using a first-order approximation. For instance,

\[
\left( \frac{\partial u}{\partial y} \right)_n = \frac{u_N - u_P}{\Delta y} ; \quad \left( \frac{\partial u}{\partial y} \right)_s = \frac{u_P - u_S}{\Delta y}
\]

However, this scheme cannot be used at the interface as a discontinuity exists. A first-order approximation would produce inaccurate results. A one-sided second-order Taylor series expansion is instead used to correctly evaluate the gradients on both the liquid and gas sides of the interface. Thus, Eqs. (38) and (39) show the corrections to the streamwise velocity gradient calculations at the interface. Similar gradients are used for the other variables.

\[
\left( \frac{\partial u}{\partial y} \right)_g = \frac{u(IT + 1) - u_{int} + \frac{u_{in} - u_{IB}}{\Delta y_{1,2}} (\Delta y_{1,2} + \Delta y_{2,2})^2}{(\Delta y_{1,2} + \Delta y_{2,2} - \frac{1}{\Delta y_{1,2}} (\Delta y_{1,2} + \Delta y_{2,2})^2)}
\]

\[
\left( \frac{\partial u}{\partial y} \right)_l = \frac{u(IB - 1) - u_{int} + \frac{u_{in} - u_{IT}}{\Delta y_{1,2}} (-\Delta y_{1,2} - \Delta y_{2,2})^2}{(-\Delta y_{1,2} - \Delta y_{2,2} + \frac{1}{\Delta y_{1,2}} (-\Delta y_{1,2} - \Delta y_{2,2})^2)}
\]

4.2. Solution algorithm

The governing equations and matching conditions at the interface are solved in a manner similar to the methods used by Poblador-Ibanez and Sirignano [14]. However, Eq. (34) in the current work is solved to obtain the streamwise velocity field at the next streamwise position before Eq. (32) is used to develop the updated transverse velocity profile.

5. Results and discussion

5.1. Diffusion layer evolution

Cold, liquid n-decane and hot, gas oxygen were chosen to analyze the physics within the shear layer. Figure 4 plots the diffusion layer evolution for density and temperature at a constant pressure, \( p = 150 \) bar. Density in the liquid phase continuously decreases with streamwise distance as the diffusion layers grow. Conversely, the density increases in the gas phase. This is expected as the heavier n-decane is vaporizing into the gas phase while the lighter oxygen is condensing into the liquid phase. The temperature increases and decreases with streamwise distance in the liquid phase and gas phase, respectively, because of energy balance and heat conduction.
Figure 4: Streamwise evolution of the density and temperature distributions in the transverse direction for the oxygen/\textit{n}-decane mixture at $p = 150$ bar. The interface is located at $y = 0 \mu m$. (a) liquid density; (b) gas density; (c) liquid temperature; (d) gas temperature.

Figures 5a and 5b show the development of the viscosity profiles as the flow progresses downstream. Interestingly, the liquid-phase viscosity decreases with streamwise distance because the viscosity is dependent on the temperature and density. In the gas phase, temperature sees a rapid decrease as it tends towards the interface. Conversely, density increases rather minimally. Because there is a large drop in temperature across the diffusion layer in the gas phase, it overcomes density variation effects, allowing the viscosity to drop below the bulk gas viscosity. A similar result is not observed in the liquid phase where there is a large drop in density and an increase in temperature from the bulk conditions to the interface. Because the liquid temperature increase is slight, it has little influence on the viscosity profile.

Figures 5c and 5d show the streamwise velocity development. Since the bulk liquid has a significantly larger density than the bulk gas, the diffusion-layer thickness is small. The layer is much thicker on the gas side as it is has a much smaller viscosity making it more readily influenced by the liquid phase. Similarly, a comparison of fully evolved streamwise velocity profiles for varying pressures can be seen from Figure
Figure 5: Streamwise evolution of the viscosity and streamwise velocity distributions in the transverse direction for the oxygen/n-decane mixture at $p = 150$ bar. The interface is located at $y = 0 \, \mu m$. (a) liquid viscosity; (b) gas viscosity; (c) liquid streamwise velocity; (d) gas streamwise velocity.

6. The layer thickness remains consistent over varying pressures in the liquid phase while the thickness progressively increases as pressure decreases in the gas phase. Density decreases as pressure decreases in both phases. Since the mean velocity of the flow remained at 10 m/s and the streamwise Reynolds number was kept constant, the velocity difference must increase for decreasing pressures. Combination of this constraint with the large difference in density between the liquid and gas phases accounts for the diffusion-layer thickness increase in the gas phase.

The interface streamwise velocity also increases as pressure decreases. While this is affected by the velocity difference increase, it is primarily caused by the shear matching at the interface. Viscosity in the gas phase remains remotely constant while the viscosity decreases significantly in the liquid phase. The liquid is faster and more viscous than the gas. Therefore, the interface streamwise velocity must increase towards the bulk liquid streamwise velocity.
Across all pressures, the flow variables at the interface tend toward steady-state values. The effects of increasing pressure on temperature, mixture composition, and mass flux across the interface are shown in Table 4. For pressures above 50 bar, a negative mass flux is observed. This is indicative of net condensation occurring at the interface for these supercritical pressures. The dissolution of O$_2$ in the liquid phase is enhanced by the phase-equilibrium requirements. Net vaporization occurs at the interface for the subcritical 10 bar and supercritical 50 bar pressure cases. Note that the 50 bar pressure case is very close to the transition between overall vaporization and condensation resulting in a near zero mass flux. Interface temperature is heavily influenced by the bulk liquid. As pressure increases, the interface temperature’s dependence on the bulk liquid temperature strengthens considerably.

Figure 7 plots the transverse velocity and mole fractions of n-decane profiles at a streamwise distance $x = 0.01$ m for varying pressures. The diffusion layer thickness ranges from 10 - 18 $\mu$m in the liquid phase and 30 - 160 $\mu$m in the gas phase. A considerably thick diffusion layer (i.e., $y = 160$ $\mu$m) occurs in the gas phase at 10 bar. This is caused by net vaporization of dense n-decane molecules into the less dense oxygen gas. Similarly, the thickest diffusion layer in the liquid phase (i.e., $y = 18$ $\mu$m) occurs at 150 bar due to the enhanced dissolution of oxygen. The same conclusion cannot be reached for the streamwise velocity distributions in Figure 6. Because of substantially higher densities in the liquid phase, the thickness is much smaller for all pressure cases. However, at 10 bar, the largest layers are witnessed on both sides of the interface.

### Table 4: Interface mean-steady temperature, mole fraction of n-decane in the liquid phase, mole fraction of n-decane in the gas phase, and mass flux for all pressure cases at streamwise distance $x = 0.01$ m.

| $p$ (bar) | $T$ (K) | $X_{C_{10}H_{22},l}$ | $X_{C_{10}H_{22},g}$ | $\dot{\omega}$ (kg m$^{-2}$ s$^{-1}$) |
|-----------|---------|----------------------|----------------------|----------------------------------|
| 10        | 451.153 | 0.974                | 0.127                | 0.0665                           |
| 50        | 457.119 | 0.865                | 0.0405               | 0.00144                          |
| 100       | 460.708 | 0.745                | 0.0318               | -0.0590                          |
| 150       | 463.382 | 0.640                | 0.0317               | -0.117                           |
Figure 7: Comparison of the transverse velocity and mole fraction distributions in the transverse direction for the oxygen/n-decane mixture at $p = 150 \text{ bar}$ and streamwise distance 1 cm ($Re = 10,000$). (a) liquid transverse velocity; (b) gas transverse velocity; (c) $n$-decane mole fraction in the liquid phase; (d) $n$-decane mole fraction in the gas phase.

While Table 4 and Figure 7 show a shift from vaporization to condensation as pressure is increased, the hotter gas still conducts heat to the colder liquid. However, the influence of energy transport by mass diffusion reverses the energy flux across the interface. That is, at high pressures both vaporization and condensation can provide the proper energy balance [32].

5.2. Similarity

A potential similar solution can be seen from Figures 4 - 7. The existence of such a solution is important as it collapses the profiles onto each other effectively removing dependence on the transient variable and creating dependence on a single similarity variable. In such a situation, the system of PDEs can be reduced to a system ODEs that is much easier to solve. Here, a rough estimate is made concerning similarity. The
similarity variable is defined as
\[ \eta = \frac{\sqrt{u_\infty} \int_0^y \rho dy'}{\sqrt{\hat{\rho} \mu} \int_0^x dx'} \] (40)

\[
\begin{array}{cccccc}
\text{10 bar} & 50 \text{ bar} & 100 \text{ bar} & 150 \text{ bar} \\
(\rho\mu)_l \text{ Difference (\%)} & 11.961 & 58.968 & 98.154 & 124.305 \\
(\rho\mu)_g \text{ Difference (\%)} & 6.644 & 5.945 & 7.311 & 9.036 \\
\end{array}
\]

Table 5: \( \rho\mu \) product variation with transverse distance from ambience to interface at \( x = 1 \text{ cm} \) in the liquid and gas phases.

Eq. (40) contains a density weighted transverse distance divided by the square root of the streamwise distance. This definition also requires that the product of density and viscosity be roughly constant. Table 5 shows \( \rho\mu \) variation at all pressures. While the variation trends towards small as pressure decreases, the validity of this similarity analysis is more convincing for the gas phase as the difference is under 10\% for all pressures whereas the liquid phase has a much larger difference in \( \rho\mu \) for higher pressures.

Figure 8 plots the similarity profile development for temperature and density at \( p = 150 \text{ bar} \). Variables are normalized with respect to the interface as
\[ \phi_{\text{normalized}}(y) = \frac{\phi(y) - \phi_f}{\phi_f - \phi_\Gamma} \] (41)

where \( \phi \) represents an arbitrary flow variable. For very early streamwise locations, there is a large deviation from the rest of the profiles. This is more embellished in the liquid phase. Early on, the diffusion layers are influenced by a transient effect causing a loss of similarity from the rest of the locations.

To check similarity of the transverse velocity, a transformation must first be made. Defining \( f \) as a function of the stream function \( \psi \):
\[ f(\xi, \eta) = \frac{\psi}{\sqrt{2u_\infty} \xi} \] (42)

and
\[ \frac{\partial f}{\partial \eta} = \frac{u}{u_\infty} \] (43)

Integrating Eq. (43) and using Eq. (42), the stream function can be obtained in terms of \( \eta \) as
\[ \psi = \sqrt{2u_\infty} \xi \int_0^\eta \frac{\mu(\eta')}{u_\infty} d\eta' \] (44)

where
\[ \xi = \int_0^x \rho(x')\mu(x')dx' \] (45)

Differentiating Eq. (45) with respect to the streamwise distance, \( x \), it yields
\[ -\frac{\partial \psi}{\partial x} = \frac{\sqrt{2u_\infty}}{2} \frac{\sqrt{\int_0^x \rho(x')\mu(x')dx'}}{\rho(x)\mu(x)} \int_0^\eta \frac{\mu(\eta')}{u_\infty} d\eta' \frac{\rho(\eta')}{\rho(x)} = \rho \hat{v} \] (46)
where the transformed transverse velocity, $\hat{v}$, can be extracted.

Eq. (46) can be used to obtain the transformed transverse velocity profile. Figure 9 plots the normalized streamwise velocity and transformed transverse velocity profiles against $\eta$. After any initial transient effects, both velocity profiles appear to reach a similar solution very quickly in the development of the mixing layer, similar to the temperature and density profiles. Notably, the transformed transverse velocity similarity profiles are nearly linear besides a slight bend for small $\eta$'s in the gas phase.

Across different pressure cases, it is expected that the similarity weakens as the thermodynamics change. Figure 10 plots the similarity profiles of temperature and streamwise velocity for different pressure cases. As the interface temperature in the liquid phase is strongly related to the bulk liquid temperature, there is still reasonable similarity for temperature between the different pressures. This is not the case for the streamwise velocity. As prior stated, the diffusion layer evolution and thickness are dependent on the density, viscosity, and streamwise velocity difference between the two phases. All of these parameters change as pressure.
Figure 9: Evolution of the streamwise and transformed transverse velocity distributions in the transverse direction against the similarity variable, $\eta$ for the oxygen/n-decane mixture at $p = 150$ bar. (a) streamwise velocity in the liquid phase near the interface; (b) streamwise velocity in the gas phase near the interface; (c) transformed transverse velocity in the liquid phase near the interface; (d) transformed transverse velocity in the gas phase near the interface.

changes and hence, the streamwise velocity profiles will also vary.

A similar conclusion can be made for varying temperature cases. This can be seen in Figure 11. Changing the bulk temperature conditions for both the liquid and gas phase affects the thermodynamics and thus, near perfect similarity is lost. However, the streamwise velocity profiles are only weakly dependent on the temperature. Thus, the velocity profiles retain similarity at 150 bar, even when the mean temperature and temperature range change considerably.

6. Summary and conclusions

The variable-density, multicomponent laminar boundary-layer equations coupled with a real-fluid thermodynamic model were used to analyze the resulting shear layer between a cold liquid and hot gas. A
Figure 10: Comparison of the temperature and streamwise velocity distributions in the transverse direction against the similarity variable, $\eta$ for the oxygen/n-decane mixture at $p = 10, 50, 100, \text{ and } 150$ bar and streamwise position $x = 1$ cm. (a) normalized temperature in the liquid phase near the interface; (b) normalized streamwise velocity in the liquid phase near the interface.

Figure 11: Comparison of the temperature and streamwise velocity distributions in the transverse direction against the similarity variable, $\eta$ for the oxygen/n-decane mixture at $p = 150$ bar and streamwise position $x = 1$ cm. (a) normalized temperature in the liquid phase near the interface; (b) normalized streamwise velocity in the liquid phase near the interface.

Kelvin-Helmholtz instability analysis was performed to ensure slow deformation of the interface between oxygen gas and n-decane liquid. A transverse momentum comparison showed that setting a fixed interface at $y = 0$ m is reasonable. Thick diffusion layers form around the liquid-gas interface at $x = 1$ cm downstream for different pressures (i.e., 10 - 18 $\mu$m in the liquid phase and 30 - 160 $\mu$m in the gas phase). It was found that the diffusion layer thickness increased in the liquid phase and decreased in the gas phase as pressure increased. While gaseous oxygen dissolves and liquid n-decane mixes with the gas vaporizes at all pressures, a transition from net vaporization to condensation of the liquid phase occurred around 50 bar.

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post-processing, an average value of $\rho \mu$ is used to examine the similarity of the solution (i.e., the asymptotic behavior as a function of one new spatial variable). The profiles collapse, which suggests that a similar solution exists for both phases. However, the $\rho \mu = \text{constant}$ assumption is more accurate in the gas phase making the existence of similarity more convincing. When pressure or temperature is varied, similarity is lost as the thermodynamics change the interface properties and the diffusion layer evolution. However, the interface temperature is strongly dependent on the bulk liquid phase temperature allowing for close similarity for various gas temperatures.

Conflict of interest

The authors declared that there is no conflict of interest.
Appendix A. Evaluation of enthalpies, internal energy, entropy, fugacity coefficient, and specific heat

Expressions for enthalpy, Eq. (A.1), internal energy, Eq. (A.2), entropy, Eq. (A.3), and fugacity coefficient, Eq. (A.4), are derived from fundamental thermodynamic principles, where deviations from the ideal gas state (denoted by *) are introduced by means of a departure function [23].

\[ h = h^*(T) + \frac{1}{MW} \left[ R_a T (Z - 1) + R_a T \int_0^\infty \left( T \left( \frac{\partial Z}{\partial T} \right)_{\bar{v}, X_i} \right) \frac{d\bar{v}}{\bar{v}} \right] \quad (A.1) \]

\[ e = e^*(T) + \frac{R_a T}{MW} \int_0^\infty \left( T \left( \frac{\partial Z}{\partial T} \right)_{\bar{v}, X_i} \right) \frac{d\bar{v}}{\bar{v}} \quad (A.2) \]

\[ s = s^*(T, p_0) + \frac{1}{MW} \left[ -R_a \ln \left( \frac{p}{p_0} \right) - R_a \sum_{i=1}^N X_i \ln (X_i) \right] + \frac{1}{MW} \left[ \ln (\Phi_i) - \ln (\Phi_i^*) \right] \quad (A.3) \]

Note that Eq. (A.3) also includes terms to account for deviations from the reference pressure of the ideal gas mixture entropy and the entropy of mixing caused by the irreversible mixing process between different species [33–35]. Combining the previous expressions with the modified SRK equation of state, we obtain

\[ h = h^*(T) + \frac{1}{MW} \left[ R_a T (Z - 1) + \frac{T (\partial a/\partial T)_{\bar{v}, X_i} - a}{b} \ln \left( 1 + \frac{B}{Z + C} \right) + R_a T^2 \left( \frac{\partial c}{\partial T} \right)_{\bar{v}, X_i} \right] \quad (A.5) \]

\[ e = e^*(T) + \frac{1}{MW} \left[ \frac{T (\partial a/\partial T)_{\bar{v}, X_i} - a}{b} \ln \left( 1 + \frac{B}{Z + C} \right) + R_a T^2 \left( \frac{\partial c}{\partial T} \right)_{\bar{v}, X_i} \right] \quad (A.6) \]

\[ s = s^*(T, p_0) + \frac{1}{MW} \left[ -R_a \ln \left( \frac{p}{p_0} \right) - R_a \sum_{i=1}^N X_i \ln (X_i) \right] + \frac{1}{MW} \left[ \ln (\Phi_i) - \ln (\Phi_i^*) \right] \quad (A.7) \]

\[ \ln (\Phi_i) = \frac{Z + C - 1}{B/a} \frac{\partial b}{\partial X_i} - \frac{C}{c/a} \frac{\partial c}{\partial X_i} - \ln (Z + C - B) - A \left( \frac{1}{B/a} \frac{\partial a}{\partial X_i} - \frac{1}{b/a} \frac{\partial b}{\partial X_i} \right) \ln \left( 1 + \frac{B}{Z + C} \right) \quad (A.8) \]

Furthermore, expressions for the specific heat at constant pressure and partial enthalpy of species \( i \) in a mixture are needed. They are obtained by applying the respective thermodynamic definitions. The specific heat at constant pressure becomes

\[ c_p = c_p^* (T) + \frac{1}{MW} \left[ \frac{T}{b} \left( \frac{\partial^2 a}{\partial T^2} \right)_{p, X_i} \ln \left( 1 + \frac{B}{Z + C} \right) - R_a \right] + \frac{1}{MW} \left[ \left( \frac{a}{\bar{v} + c + b} \right) \left( \frac{\partial^2 \bar{v}}{\partial T^2} \right)_{p, X_i} + \left( \frac{\partial c}{\partial T} \right)_{p, X_i} \right] \quad (A.9) \]
and the partial molar enthalpy is

\[ \bar{h}_i = \left( \frac{\partial \bar{h}}{\partial X_i} \right)_{p,T,X_j} = \bar{h}_i'(T) + p \left( \frac{\partial \bar{v}}{\partial X_i} \right)_{p,T,X_j} - R_a T + \frac{a A_1}{\bar{v} + c + b} \left[ A_2 - \frac{1}{\bar{v} + c} \left( \frac{\partial \bar{v}}{\partial X_i} \right)_{p,T,X_j} + \left( \frac{\partial c}{\partial X_i} \right)_{p,T,X_j} \right] + \frac{1}{b} \left( T \left( \frac{\partial^2 a}{\partial X_i \partial T} \right)_{p,T,X_j} \right) - \left( \frac{\partial a}{\partial X_i} \right)_{p,T,X_j} - a A_1 A_2 \ln \left( \frac{\bar{v} + c + b}{\bar{v}} \right) \]

\[ + R_a T^2 \left( \frac{Z}{\bar{v}} \right) \left( \frac{\partial^2 c}{\partial X_i \partial T} \right)_{p,T,X_j} \]  \hspace{1cm} (A.10)

where \( A_1 \) and \( A_2 \) are defined as:

\[ A_1 \equiv \frac{T}{a} \left( \frac{\partial a}{\partial T} \right)_{v,X_i} - 1 \]  \hspace{1cm} ;  \hspace{1cm} \[ A_2 \equiv \frac{1}{b} \left( \frac{\partial b}{\partial X_i} \right)_{v,X_i} \]  \hspace{1cm} (A.11)

Once the partial molar enthalpy is known, the partial specific enthalpy needed in Eq. (11) is obtained as

\[ h_i = \frac{\bar{h}_i}{MW_i} \]

All partial derivatives involved in the previous expressions can be found in Appendix B. Ideal-gas enthalpy, internal energy, entropy and specific heat at constant pressure are obtained from the correlations by Passut and Danner [36] and ideal gas mixing rules as

\[ h^*(T) = \sum_{i=1}^{N} Y_i h^*_i(T) \]  \hspace{1cm} ;  \hspace{1cm} \[ e^*(T) = h^*(T) - p/\rho^* \]  \hspace{1cm} (A.12)

\[ s^*(T, p_0) = \sum_{i=1}^{N} Y_i s^*_i(T, p_0) \]  \hspace{1cm} ;  \hspace{1cm} \[ c^*_{p_i}(T) = \sum_{i=1}^{N} Y_i c^*_{p_i}(T) \]  \hspace{1cm} (A.13)

with

\[ h^*_i(T) = \hat{A} + \hat{B} T + \hat{C} T^2 + \hat{D} T^3 + \hat{E} T^4 + \hat{F} T^5 \]  \hspace{1cm} (A.14)

\[ s^*_i(T, p_0) = \hat{B} \ln T + 2 \hat{C} T + \frac{3}{2} \hat{D} T^2 + \frac{4}{3} \hat{E} T^3 + \frac{5}{4} \hat{F} T^4 + \hat{G} \]  \hspace{1cm} (A.15)

\[ c^*_{p_i}(T) = \hat{B} + 2 \hat{C} T + 3 \hat{D} T^2 + 4 \hat{E} T^3 + 5 \hat{F} T^4 \]  \hspace{1cm} (A.16)

where \( \rho^* \) is the ideal gas density evaluated using the ideal gas law, \( p_0 \) is the reference pressure for entropy calculations set at 1 atm and \( \hat{A} - \hat{G} \) are correlation constants given in [36].
Appendix B. Thermodynamic derivatives based on the SRK equation of state

Appendix B.1. “a” derivatives

\[
\left( \frac{\partial a}{\partial X_i} \right)_{p,T,X_{jm}} = 2 \sum_{j=1}^{N} X_j (a_i a_j) \alpha a_j \left( 1 - k_{ij} \right) \tag{B.1}
\]

\[
\left( \frac{\partial^2 a}{\partial X_i \partial X_j} \right)_{p,T} = 2 (a_i a_j) \alpha a_j \left( 1 - k_{ij} \right) \tag{B.2}
\]

\[
\left( \frac{\partial a}{\partial T} \right)_{p,X_{jm}} = \sum_{j=1}^{N} X_j \left( \frac{a_i}{a_j} \right) \frac{0.5}{\alpha a_j} \left( \frac{da_j}{dT} \right) + \left( \frac{a_j}{a_i} \right) \frac{0.5}{\alpha a_i} \left( \frac{da_i}{dT} \right) \left( 1 - k_{ij} \right) \tag{B.3}
\]

\[
\left( \frac{\partial^2 a}{\partial T^2} \right)_{p,X_{jm}} = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} X_i X_j \left( \frac{a_i}{a_j} \right) \frac{0.5}{\alpha a_j} \left( \frac{da_j}{dT} \right)^2 + \left( \frac{a_j}{a_i} \right) \frac{0.5}{\alpha a_i} \left( \frac{da_i}{dT} \right)^2 \left( 1 - k_{ij} \right) \tag{B.4}
\]

\[
\frac{d a_i}{d T} = a_i \frac{d a_i}{d T} = \frac{a_i}{\alpha_i} \frac{d a_i}{d T} \tag{B.5}
\]

\[
\frac{d^2 a_i}{d T^2} = a_i \frac{d^2 a_i}{d T^2} = a_i \frac{d^2 a_i}{d T^2} \tag{B.6}
\]

\[
\frac{d^2 a_i}{d T^2} = \frac{1}{2} \left( \frac{1}{\alpha_i} \frac{d a_i}{d T} \right)^2 - \frac{1}{T} \frac{d a_i}{d T} \tag{B.7}
\]

Appendix B.2. “b” derivatives

\[
\left( \frac{\partial b}{\partial X_i} \right)_{p,T,X_{jm}} = b_i \tag{B.8}
\]

Appendix B.3. “c” derivatives

\[
\left( \frac{\partial c}{\partial X_i} \right)_{p,T,X_{jm}} = c_i \tag{B.9}
\]

\[
\left( \frac{\partial^2 c}{\partial X_i \partial T} \right)_{p,T,X_{jm}} = \left( \frac{\partial c_i}{\partial T} \right)_{p,X} = \frac{c_i}{T_{ci}} f'(T_{ci}) \tag{B.10}
\]

\[
\left( \frac{\partial c}{\partial T} \right)_{p,X_{jm}} = \sum_{i=1}^{N} X_i \left( \frac{\partial c_i}{\partial T} \right)_{p,X} = \sum_{i=1}^{N} X_i \frac{c_i}{T_{ci}} f'(T_{ci}) \tag{B.11}
\]

\[
\left( \frac{\partial^2 c}{\partial T^2} \right)_{p,X} = \sum_{i=1}^{N} X_i \left( \frac{\partial^2 c_i}{\partial T^2} \right)_{p,X} = \sum_{i=1}^{N} X_i \frac{c_i}{T_{ci}^2} f''(T_{ci}) \tag{B.12}
\]

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Appendix B.4. “ψ” derivatives

\[
\left( \frac{\partial \tilde{\psi}}{\partial X_j} \right)_{p,T,X_{in}} = \frac{R_g T}{p} \left( Z + C - \frac{C}{c} \frac{\partial c}{\partial X_j} \right)_p \left( Z + C - \frac{C}{c} \frac{\partial c}{\partial X_j} \right)_{p,T,X_{in}} + \frac{R_g T}{p} \left( \frac{(B - Z - C)[\frac{1}{a} \frac{\partial a}{\partial X_j} + 2A]}{3Z^2 + 2(3C - 1)Z + 3C^2 - 2C + A - B - B^2} \right) \]

\[
\frac{R_g T}{p} \left( \frac{(Z + C + 2B[Z + C] + A)[\frac{b}{b} \frac{\partial b}{\partial X_j} - B]}{3Z^2 + 2(3C - 1)Z + 3C^2 - 2C + A - B - B^2} \right) \]

\[
\left( \frac{\partial \tilde{\psi}}{\partial T} \right)_{p,X_i} = \frac{R_g T}{p} \left( \frac{Z + C}{T} \right) \left( \frac{Z + C - B + 2b}{3Z^2 + 2(3C - 1)Z + 3C^2 - 2C + A - B - B^2} \right) \]

Appendix B.5. “Φ” derivatives

\[
\left( \frac{\partial \ln(\Phi_j)}{\partial X_j} \right)_{p,T,X_{in}} = \frac{B}{Z + C - B} \frac{1}{b^2} \frac{\partial b}{\partial X_j} - \frac{Z + C - 1}{b^2} \frac{\partial b}{\partial X_i} + \frac{C}{b} \frac{\partial c}{\partial X_i} + 1 \]

\[
+ \frac{A}{Z + C + B} \frac{1}{b^2} \frac{\partial b}{\partial X_j} - \frac{Z + C - B}{b^2} \frac{\partial b}{\partial X_i} \cdot \frac{a}{b} \frac{\partial a}{\partial X_j} \]

\[
+ \frac{A}{B} \left( \frac{1}{ab} \frac{\partial a}{\partial X_j} + \frac{1}{ab} \frac{\partial a}{\partial X_i} \right) \ln \left( 1 + \frac{B}{Z + C} \right) \]

\[
\left( \frac{\partial \ln(\Phi_j)}{\partial X_j} \right) = \frac{1}{T} \left( Z + C - B \right) \frac{\partial b}{\partial X_j} + \left( \frac{C}{b} \frac{\partial c}{\partial X_j} \right) \]

\[
+ \frac{A}{B} \left( \frac{1}{ab} \frac{\partial a}{\partial X_i} - \frac{1}{b} \frac{\partial b}{\partial X_j} \right) \frac{1}{T} \frac{\partial c}{\partial X_j} + \frac{\partial \tilde{\psi}}{\partial X_j} \]

\[
\frac{\partial \ln(\Phi_j)}{\partial T} \right)_{p,X_i} = \left( \frac{Z + C + B}{T} \right) \frac{\partial b}{\partial X_i} - \left( \frac{C}{b} \frac{\partial c}{\partial X_i} \right) \]

\[
+ \frac{A}{B} \left( \frac{1}{T} \frac{1}{\partial X_j} - \frac{1}{T} \frac{1}{\partial X_j} \right) \frac{1}{T} \frac{\partial c}{\partial T} + \frac{\partial \tilde{\psi}}{\partial T} \]

\[
+ \left( \frac{1}{b} \frac{\partial b}{\partial X_i} - \frac{1}{Z + C + B} \right) \frac{\partial \tilde{\psi}}{\partial T} + \frac{\partial \psi}{\partial T} \]

\[
+ \left( \frac{1}{b} \frac{\partial b}{\partial X_i} - \frac{1}{Z + C + B} \right) \frac{\partial \tilde{\psi}}{\partial T} + \frac{\partial \psi}{\partial T} \]
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