Journal Pre-proof

Turbulent chemical-species mixing in the Venus lower atmosphere at different altitudes: A Direct Numerical Simulation study relevant to understanding species spatial distribution

Stefano Morellina, Josette Bellan

PII: S0019-1035(21)00342-0
DOI: <https://doi.org/10.1016/j.icarus.2021.114686>
Reference: YICAR 114686

To appear in: *Icarus*

Received date : 26 October 2020
Revised date : 23 August 2021
Accepted date : 25 August 2021

Please cite this article as: S. Morellina and J. Bellan, Turbulent chemical-species mixing in the Venus lower atmosphere at different altitudes: A Direct Numerical Simulation study relevant to understanding species spatial distribution. *Icarus* (2021), doi: <https://doi.org/10.1016/j.icarus.2021.114686>.

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2021 Elsevier Inc. All rights reserved.

Turbulent chemical-species mixing in the Venus lower atmosphere at different altitudes: a Direct Numerical Simulation study relevant to understanding species spatial distribution

Stefano Morellina^a, Josette Bellan^{a,b,*},

^a*Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109, USA*

^b*Department of Mechanical and Civil Engineering, California Institute of Technology, Pasadena, CA 91125, USA*

Abstract

To evaluate a recent hypothesis of species stratification in the Venus lower atmosphere, a time-dependent, three-dimensional model is proposed for studying turbulent mixing of many species in the Venus lower atmosphere. This model is based on fundamental physics embedding non-equilibrium thermodynamics, the Onsager classical relationship between fluxes and forces, high-pressure transport property calculation and a real-gas equation of state. The conservation equations are self-contained, with no need for coefficients based on parametrizations to match Venus observations. The rationale for solving these equations in relatively small spatial domains at different altitudes in the Venus lower atmosphere is presented. The equations are solved in a temporal mixing layer configuration that is eminently suited to investigate turbulent mixing between two streams of different composition. The adopted simulation method is Direct Numerical Simulation (DNS). A substantial database of DNS realizations is generated for mixtures of two and seven species, with different levels of initial stratification, and at the realistic conditions of pressures and temperatures in the Venus lower atmosphere at three altitudes. High density-gradient magnitude regions (HDGM) are shown to form under initial high stratification conditions, with larger gradient values obtained at low altitudes where supercritical conditions occur. Independent of the altitude lower than 50 km, under low stratification conditions, mixing produces a more uniform spatial distribution of the density than at higher initial stratification. Under low initial stratification conditions, the influence of the minor species on the global behavior of the flow seems to be negligible. At high initial stratification conditions, differences in diffusion of various species play an important role in determining the mixture characteristics. The hypothesis of chemical species separation is discussed in the light of the present results which do not support the existence of stable species separation in the lower Venus atmosphere, independent of the number of species or the altitude.

Key words: Venus lower atmosphere turbulent species mixing at several altitudes

1 Introduction

Recent progress in the investigation of the Venus lower atmosphere (e.g. Johnson and de Oliveira, 2019, Jacobson et al., 2017, Morellina et al., 2020) reveals increasingly detailed information regarding the global thermodynamic and dynamic conditions up to approximately 50 km of altitude. The knowledge of the chemical composition, as provided by species mass fraction provided within a range of values for each species (Jacobson et al., 2017, Johnson and de Oliveira, 2019), together with the information regarding the temperature, T , and pressure, p , allowed the computation of a multitude of other characteristics of the Venus lower atmosphere (Morellina et al., 2020). For example, transport properties such as chemical mixture viscosity, μ , and thermal conductivity, λ , were calculated according to high-pressure (high- p) models (Reid et al., 1987). The μ knowledge in conjunction with density, ρ , computed from the Peng-Robinson real-gas equation of state (EoS), together with information on wind speeds at the planet's surface permitted the calculation of the Reynolds number, Re , value for several possible characteristic length scales. Independent of the selected length scale over three orders of magnitude, the Reynolds number was found to be in the fully turbulent regime at all altitudes up to 50 km and to be a non-monotonic function of altitude, H , having a maximum at $H \simeq 25$ km. The EoS was also utilized to construct the thermodynamic phase diagram, and it was shown unequivocally that the lower atmosphere is in the single-phase regime at the particular composition (Jacobson et al., 2017), p and T . Calculations of the speed of sound employing the EoS, combined with the knowledge of the wind speed revealed that the Mach number is subsonic and an increasing function of H .

Despite this progress, many questions remain, particularly with respect to detailed aspects of the Venus lower atmosphere. For example, while it has been proposed that species separation occurs (Lebonnois and Schubert, 2017) as noted by Limaye et al. (2018), experimental studies meant to probe this assumption remain inconclusive (Lebonnois et al., 2020). At least one modeling and numerical study (Cordier et al., 2019) concludes that molecular diffusion is very inefficient so that it could not be responsible for the hypothesized separation of N_2 and CO_2 , and that phase separation is also very unlikely, a conclusion in concert with more recent findings (Morellina et al., 2020). However,

* Corresponding author. Tel: (818) 354-6959, Fax: (818) 393-6682.

Email address: Josette.Bellan@jpl.nasa.gov (Josette Bellan).

the study of Cordier et al. (2019) exclusively utilized thermodynamics and molecular dynamics, and thus one may question these conclusions given that thermodynamics is inappropriate for computing gradients which are the indicators of species distribution, and therefore of potential separation, and that molecular dynamics relies on the knowledge of a molecular potential, and this potential must be appropriate for high-pressure (high- p) situations, as is for example the ReaxFF potential (van Duin et al., 2001). It was unclear whether the potential used by Cordier et al. (2019) was high- p appropriate. The accurate prediction of gradients necessitates the solution of time-dependent three-dimensional (3D) fluid dynamic equations combined with an appropriate EoS and with thermodynamic-appropriate models for computing transport properties. So far, no mathematical formulation has been proposed that has the ability, now or in the future, to evaluate the stratification hypothesis through these types of simulations. Proposing such a formulation will not only answer this pending question but will ultimately have the ability to study the Venus Planetary Boundary layer (PBL), the super-rotation and to develop estimates of the torque exerted on the planet by the atmosphere; in turn, such estimates can be compared with changes in the length of the day and thereby determine the moment of inertia of the planet.

Compared to the study of Morellina et al. (2020), the present investigation is an additional step towards developing a formulation for the description of the entire Venus lower atmosphere that will be time-dependent, 3D and not rely on parametrizations from Venus atmosphere observations. Bierson and Zhang (2020) conclusively show that no parametrization is reliable for explaining the variations of all species in the Venus atmosphere. Thus, although it is typical to use parametrized models (e.g. Lebonnois et al., 2018), Bierson and Zhang (2020) make it clear that the parametrization avenue leads to a dead end. Instead, the present formulation is based on fundamental high-pressure physics of turbulent species-mixing. The rationale for choosing the mathematical formulation of Direct Numerical Simulation (DNS) is described in Section 2. A condensed explanation of the governing equations is presented in Section 3 and the details of the mathematical formulation are relegated to Appendices A - C. The numerical method is described in Section 4 and the physical configuration, initial and boundary conditions are stated in Section 5. The results are described in Section 6. The importance of the findings in the context of the Venus lower atmosphere is discussed in Section 7. Finally, a summary and conclusions are offered in Section 8.

2 Rationale for the selected mathematical formulation

According to Morellina et al. (2020), single-phase and high-turbulence prevail in the Venus lower atmosphere. To model this atmosphere, there are three

choices of fluid dynamic computations, as follows (Zhiyin, 2015): (i) Direct Numerical Simulation (DNS) in which all continuum-level flow scales overwhelmingly responsible for dissipation are computed, (ii) Large Eddy Simulation (LES) in which the large scales are computed and the small scales are modeled using functional relationships multiplied by coefficients which can be computed temporally and spatially during the computation using the LES solution (Germano et al., 1991), avoiding calibration with previously obtained information, and (iii) Reynolds Averaged Navier-Stokes (RANS) in which the solution represents an ensemble average over solutions obtained with initial and/or boundary conditions having small deviations from reference values and terms of the original Navier-Stokes equations are each replaced by a semi-empirical model which does not discriminate between the characteristics of the corresponding phenomenon at large or small scales. Thus, each of the RANS, LES and DNS methods has its drawbacks, and the present notion is to select that which will most enhance the current Venus lower atmosphere understanding.

RANS is clearly not a good choice for exploring fundamental science, but it is usually helpful for industrial applications. LES is attractive, however, models for small scales (SGS models) are necessary and these models are thermodynamic-regime dependent (Selle et al., 2007); these SGS models are not parametrizations, i.e. ‘tuning’ and case-by-case adjustments if the dynamic SGS methodology of Germano et al. (1991) is used. For example, additional SGS models may be required to appropriately represent high- p flows such as the Venus lower atmosphere (Selle et al., 2007; Taşkinoglu and Bellan, 2010; Taşkinoglu and Bellan, 2011; Gnanaskandan and Bellan, 2020). The inherent need for SGS models means that species mixing may not be directly computed at the scale at which it occurs, but rather modeled. Additionally, a SGS model must be included to account for the interaction of the flow with the Venus-planet surface. Indeed, to account for surface-flow interaction and bypass resolving the computationally intensive region near the surface (where viscosity is important and fluctuation scales become increasingly small), fluid dynamics uses ‘wall’ boundary conditions that relate surface boundary conditions to points in the fluid away from the surface. The first ‘law of the wall’ was published by von Karman (1930) and stated that past the viscous and buffer regions in the boundary layer, the average velocity of a turbulent flow follows a logarithmic behavior dependent on the perpendicular distance to the surface. This law may be, however, dependent on the thermodynamic regime and on the chemical composition of the fluid, and no equivalent to the mentioned logarithmic relationship has been explored for high- p conditions for multi-species flows. Only recently, pioneering fluid/wall interaction studies have been conducted for high- p single species flows (Ma et al., 2018; Kawai, 2019), however, these are not sufficient to provide wall models for multi-species situations where molecular species-mixing might modify the flow field. In DNS one must resolve all scales overwhelmingly responsible for dissipation, and cur-

rently DNS can only be performed for incipient turbulence, that is, for flows having turbulence characteristics but not having a Reynolds number as large as in the fully turbulent regime.

When considering the form of the momentum equation, in principle, the Coriolis force must be included. Whether the Coriolis force plays a role in situation depends on the Rossby number, $Ro = \mathcal{U}/\mathcal{L}f$, where $\mathcal{U}$ and $\mathcal{L}$ are, respectively, the characteristic velocity and the length scales of the phenomenon as related to global rotational features and $f = 2\Omega \sin(\phi)$ is the Coriolis frequency, Ω is the angular frequency of planetary rotation and ϕ the latitude. When the Rossby number is large, the Coriolis force is negligible and the momentum balance occurs between pressure and centrifugal forces – the cyclostrophic balance; on the contrary, when the Rossby number is small, the centrifugal force is negligible and the momentum balance occurs between Coriolis and pressure forces – the geostrophic balance (Holton, 2004). Since Venus has a very small sidereal rotational period, revolving on itself 243 times slower than Earth, the resulting Rossby number is large, meaning that the inertial force overcomes the Coriolis force. For that reason the circulation in Venus’s troposphere follows the cyclostrophic flow (Svedhem et al., 2007; Limaye et al., 2018), where the Coriolis force is neglected.

Gravity is another force to envisage for inclusion in the momentum equation. Whether gravity is important depends on the value of the Froude number, $Fr = U/\sqrt{gl}$, where g is the gravity acceleration on the planet ($8.87 \text{ [m/s}^2\text{]}$ on Venus), with U and l being, respectively, a characteristic velocity and a length scale of the phenomenon as related to the local velocity. If the Froude number is very large, then gravity effects on the flow are negligible when compared to the inertial term; on the contrary, if the Froude number is small, then gravity plays a significant role and should be included in the model. It will be shown in Section 5 that flows in large computational domains ($l \gtrsim O(10^3) \text{ m}$) exhibit large gravitational effects whereas flows in small computational domains are impervious to such effects. In situations where gravitational effects are important, the interaction of the flow with the Venus surface becomes one of the crucial aspects of the physics; such boundary conditions necessarily play a major role in recovering the phenomenon of super-rotation in the simulations. According to the discussions above, the current absence of applicable wall model makes it impossible to conduct high-fidelity simulations of large domains adjacent to the Venus surface.

Thus, as of now, conducting LES for large domains of the Venus atmosphere encounters at least two major challenges: (1) Wall-type boundary conditions derived for high- p multi-species situations do not exist. In the only turbulence-resolving 3D study of the lower atmosphere of Venus, using atmospheric- p wall boundary conditions, Yamamoto (2011) performed Wall-modeled LES by adapting a Weather Research and Forecasting (WRF) model to Venus condi-

tions, resolving scales $\sim 10^2$ m in a domain which extended 4 km above the surface, with meridional/zonal extents up to 16 km. However, since the WRF was designed for Earth conditions, the different physics of the lower Venus atmosphere where the thermochemistry effects of the supercritical pressure may be important, were most likely not accurately represented in that study; indeed, supercritical conditions could have a profound effect on atmospheric stability. The Yamamoto (2011) results showed that microscale dynamics control the thermal structures near the surface of Venus, with significant differences in the eddy diffusivity arising due to the near surface turbulence, thus demonstrating that the surface layer dynamics must be resolved correctly for an accurate representation of the entire Venus lower atmosphere. Of note is that the Yamamoto (2011) study did not resolve the layer closest to the surface and instead assumed Monin-Obukhov (MO) similarity holding near the surface. The applicability of MO theory to the surface layer of the Venus atmosphere has not been verified and, even if applicable, the relevant stability functions needed to perform the simulation are unknown. In addition, MO theory requires knowledge of heat flux at the surface, that is unavailable, and thus an arbitrary heat flux was applied in the Yamamoto (2011) study. The heat flux, divided by the product of atmospheric density and specific heat at constant pressure, ranged from 0 to 0.256 (K m/s), compared to 0.24 (K m/s) used for simulation of Earth's convection boundary layer (Yamamoto, 2011). Thus, it is questionable whether the information currently available allows accurate LES of the Venus lower atmosphere. (2) Because LES originated in Earth atmospheric science, SGS models have been developed to only address the SGS viscous stresses. However, more recently it has been shown that for high- p flows there are other SGS models that must be considered (Selle et al., 2007; Taşkınoglu and Bellan, 2010; Taşkınoglu and Bellan, 2011; Gnanaskandan and Bellan, 2020). For studying a flow where the fluid is composed of many species, there is no definitive guidance (Borghesi and Bellan, 2015) as to the additional SGS models that may be required to portray the SGS species fluxes for multi-species mixtures.

Given this status-quo, it is clear that there is insufficient information for conducting LES representative of large domains in the Venus lower atmosphere. Even if that information were available, species mixing cannot be directly computed in LES at the scale at which it occurs, but is rather mathematically described at small scales by SGS models. If the purpose is to elucidate species mixing, LES is thus not a direct methodology to study it. Thus, it is clear that currently it is not possible to directly resolve both gravity effects and small-scale mixing in the same simulation. The study of Lebonnois and Schubert (2017) used thermodynamics and a specified turbulent mixing coefficient parametrized from a Global Circulation Model that according to Bierson and Zhang (2020) cannot be considered a valid strategy. The present study can be considered to a certain extent as a counterpart to that of Lebonnois and Schubert (2017): mixing among species is here accurately computed in do-

205 mains in which gravity is shown to be relatively unimportant. The simulations
 206 are performed at a relatively modest Reynolds number (Re) in the turbulent
 207 regime and thus its findings will be considerably amplified at the much larger
 208 Re value prevailing on Venus (Morellina et al., 2020).

209 According to Moin and Mahesh (1998), DNS represents a virtual experiment,
 210 reproducing the physical aspects in the most accurate way, thus enabling the
 211 study of poorly understood phenomena and even the discovery of new physics.
 212 The present idea is to use this beneficial aspect of DNS to explore the influence
 213 of realistic thermodynamic conditions on the mixing of species present in the
 214 Venus lower atmosphere. That is, by conducting DNS the present intention
 215 is not to simulate an actual situation but rather to understand small-scale
 216 turbulent mixing on Venus at different altitudes and use this understanding
 217 to discuss the hypothesis of species separation. Further discussion on the ra-
 218 tionale underlying the choice of DNS is presented in Section 5.

219 **3 Condensed description of the underlying physics and features of** 220 **the governing equations**

221 The presently adopted physical model, of which that of Gnanaskandan and
 222 Bellan (2018) is a subset, relies on the most fundamental formulation of fluid
 223 mechanics combined with transport phenomena models and thermodynamics.
 224 The conservation equations are based upon the Keizer (1987) fluctuation-
 225 dissipation theory which is combined with Onsager’s reciprocal relations (On-
 226 sager, 1931) connecting flows and forces; the combined theory has the distinct
 227 advantage of formally accounting for systems which are not in thermodynamic
 228 equilibrium. This formalism therefore leads to the most general fluid equations
 229 – valid for any (p, T, Y_α) with Y_α being the mass fraction of species $\alpha \in [1, N]$
 230 and N being the total number of chemical species – where the heat flux, $\mathbf{q}$,
 231 and the partial molar fluxes for each species α , $\mathbf{J}_\alpha$, contain contributions pro-
 232 portional to ∇T , ∇p and all ∇Y_β , $\beta \in [1, N]$. Each of these contributions has
 233 the mathematical form of a diffusion-matrix multiplied by the respective gra-
 234 dient. The term proportional to ∇p is called the barodiffusion term. In $\mathbf{J}_\alpha$,
 235 the term proportional to ∇T is called the Soret term; in $\mathbf{q}$, the contribution of
 236 ∇Y_β , $\beta \in [1, N]$ occurs as a summation of terms each proportional to a ∇Y_β ,
 237 $\beta \in [1, N]$ and is called the Dufour term, which is one of the manifestations
 238 of enthalpy transport by the species-mass fluxes. Thermal conduction is also
 239 included in $\mathbf{q}$.

240 The Onsager reciprocal relations state that both matrices of ‘phenomenologi-
 241 cal coefficients’, i.e. for all $\mathbf{J}_\alpha$ and for $\mathbf{q}$, are symmetric. These positive semi-
 242 definite coefficients are called ‘phenomenological’ because the Onsager theory
 243 does not provide the information to compute them; instead, other topics of

physics, that are related to collisional processes among molecules, must be invoked to consistently compute these coefficients. Inspection of the expression for $\mathbf{J}_\alpha$ and $\mathbf{q}$ reveals that there are four significant transport collisional-process properties – viscosity, thermal conductivity, mass diffusivity and thermal diffusion. An example of how these mass diffusion and thermal diffusion factor coefficients can be computed at high- p conditions is provided in Harstad and Bellan (2004a); this validated formulation (Castiglioni and Bellan, 2018) is adopted in the present model. Methods to compute viscosity and thermal conductivity for mixtures of species at high p are available in Reid et al. (1987).

The final equations, which are provided in detail in Appendix A, consist of the differential conservation equations for mass, momentum, species partial density and total energy, combined with a real-gas EoS. The differential conservation equations are essentially the Navier-Stokes equations complemented by the species partial-density conservation equations and a total energy conservation equation; more details are found elsewhere (Masi et al., 2013, Bellan, 2017a). The details of the calculation of the four transport coefficients is provided in Appendix B and the specifics regarding the calculation of EoS coefficients are presented in Appendix C.

Examination of the ensemble of equations communicates several important aspects of the model. The calculation of the diffusion coefficients requires input from thermodynamics in the form of the mass-diffusion factors for the mass-diffusion coefficients, and of the species partial molar volume for the barodiffusion coefficient. The significance of this feature is that specific details related to the EoS appear in the conservation equations. Since momentum transport influences ∇T , ∇p and ∇Y_α all of which appear in the species and energy conservation equations, this means that thermodynamics, transport properties and dynamics are all intertwined facets. The strong coupling among these three facets determines the physics of the situation, unlike in atmospheric- p flows for which this coupling is weak. The fact that real-gas EoSs are strongly non-linear means that small changes in one thermodynamic variable may result in large changes in other thermodynamic variables. The physics of high- p multi-species flows is dominated by these aspects of strong coupling and strong non-linearity (Bellan, 2020).

4 Numerical method

The differential equations are numerically solved using a fourth-order explicit Runge-Kutta time integration and a sixth-order compact scheme spatial discretization (Lele, 1992). Time stability is achieved by filtering spurious information from the conservative variables using the eighth-order compact filter

described in Gaitonde and Visbal (1998). The filter order is sufficiently large to ensure that the filter only acts on the shortest wavelengths resolved on the grid, without affecting the physical content of the data. The code is parallelized using three-dimensional domain decomposition and message passing. The tridiagonal solvers for the compact derivative scheme and the compact filter are efficiently parallelized using the method of Muller and Scheerer (1991).

The grid spacing is uniform in the three directions x_1, x_2, x_3 , i.e. $\Delta x = \Delta y = \Delta z$, and the choice of the grid spacing ensures resolution of the smallest scales relevant to dissipation. Typically, the choice of the grid spacing and its scaling with Re can be predicted from consideration of the integral scale and the Kolmogorov length scale, leading to the grid spacing growing as a power law of Re for fully turbulent flows. For turbulent transitional flows (i.e. flows with turbulent characteristics but that are not fully turbulent) the same scaling does not necessarily hold, and a certain degree of experimentation is necessary to find an appropriate grid. For high- p flows, the thermodynamic scales may be smaller than the dynamic scales (Masi et al., 2013) and this aspect requires attention when considering grid resolution. Therefore, several tests have been performed with grid refinement, and since all realizations were conducted with the same initial Re value, and the final grid retained showed excellent resolution. The grid spacing used for the DNS realizations is listed in the caption of Table 4. Proof of excellent resolution is provided in Section 6.1.

The domain length, L_i , in each direction is the same for all simulations. Given the choice of the streamwise domain length L_1 and the grid points $N_1 \times N_2 \times N_3$, the grid spacing is $\Delta x = \Delta y = \Delta z = L_1/N_1$, the cross-stream domain length is $L_2 = \Delta y \times N_2$, and the spanwise domain length is $L_3 = \Delta z \times N_3$.

5 Configuration, boundary conditions and initial conditions

A temporal mixing layer, as shown in Fig. 1, has been chosen as the configuration of the study because it ideally portrays the mixing between two streams which may have different chemical composition. The boundary conditions are periodic in the streamwise (x_1) and spanwise (x_3) directions and non-reflecting in the cross-stream (x_2) direction (Okong'o and Bellan, 2002). The choice of the temporal mixing layer with periodic streamwise and spanwise conditions and non-reflecting cross-stream boundary conditions is eminently well suited to a study in small domains, in that there are no solid boundaries and the fluid flow proceeds with no material impediments; it is as if an observer were watching a fluid parcel moving and evolving on its trajectory.

The initial mean flow is prescribed in the form of error functions according

Fig. 1. Configuration of the temporal mixing layer. The initial conditions for upper stream and lower stream for the DNS realizations are summarized in Tables 1 and 3.

to Masi et al. (2013), and an analytical perturbation also derived in Masi et al. (2013) is superimposed on the mean flow in the streamwise and spanwise directions so as to hasten the flow transition to turbulence characteristics (see Appendix B in Masi et al., 2013). The L_1 and L_3 domain lengths are chosen so as to accommodate four vortices associated with the wavelengths λ_1 and λ_3 of perturbations $\lambda_1/\delta_{\omega,0} = 7.29$ and $\lambda_3 = 0.6 \lambda_1$ as in Moser and Rogers (1991). The amplitudes of the initial perturbations are $F_{3D} = 0.08$ and $F_{2D} = 0.05$, selected according to criteria established in the past (see Moser and Rogers, 1991; Moser and Rogers, 1993; Okong'o and Bellan, 2004; Appendix B in Masi et al., 2013). In each simulation, pressure and temperature initial conditions are the same for upper and lower streams, and portray the values of these quantities on Venus at the selected nominal H , as shown in Table 1. The

Conditions			Cases
H [km]	p [atm]	T [K]	
0.4	90	732	$2lsH0.4, 2hsH0.4, 7lsH0.4, 7hsH0.4$
10	45	652	$2lsH10, 2hsH10, 7lsH10, 7hsH10$
50	1	348	$2lsH50, 2hsH50, 7lsH50, 7hsH50$

Table 1

Free-stream p and T conditions for the DNS realizations at different H values. Each case is denoted by an acronym of the type $NsHy$, where the number of species is $N = 2$ or $N = 7$, ' s ' is the species stratification (ls denotes low stratification, and hs labels high stratification), and ' y ' is the value of H in km.

initial value of Re , Re_0 , is computed as

$$Re_0 \equiv \frac{0.5(\rho_U + \rho_L)\Delta U_0 \delta_{\omega,0}}{\mu_R} \quad \text{with} \quad \delta_{\omega,0} = \frac{\Delta U_0}{\left. \frac{\partial \langle U_0 \rangle}{\partial x_2} \right|_{\max}} \quad (1)$$

where $\langle \rangle$ symbolizes averages over homogeneous (x_1, x_3) planes. Subscripts U and L denote upper and lower stream, respectively. Here, $\delta_{\omega,0}$ is the initial vor-

336 ticity thickness, ρ_U and ρ_L are mixture initial densities, $\Delta U_0 = U_U - U_L$ is the
 337 initial free-stream velocity difference across the layer and μ_R is a reference vis-
 338 cosity. A physical value of the initial mixture viscosity $\mu_{ph,0}$ is computed based
 339 on the physical initial species viscosities, then a reference value μ_R is obtained
 340 from the chosen value of Re_0 , and finally a factor $\mathcal{F} \equiv \mu_R/\mu_{ph,0}$ is defined. All
 341 transport properties computed during the simulation are then scaled by $\mathcal{F}$, a
 342 procedure which allows the computation of accurate dimensionless numbers,
 343 which according to Batchelor (1999) define the character of the solution. The
 344 value of $\mathcal{F}$ was computed at the initial time, for the initial constant p_0 and T_0 ,
 345 using a mixture composed of either 2 or 7 species, each species being averaged
 346 over the entire domain. In this manner, a unique $\mathcal{F}$ value is employed in the
 347 computational domain. The value of ΔU_0 is calculated from a specified value
 348 of the convective Mach number, Ma_c , through the expressions

$$U_U = 2Ma_c a_U \left[1 + \left(\frac{a_U}{a_L} \right) \sqrt{\frac{\rho_U}{\rho_L}} \right]^{-1}, \quad U_L = -\sqrt{\frac{\rho_U}{\rho_L}} U_U, \quad (2)$$

349 where a is the speed of sound computed from the EoS as shown in Miller
 350 et al. (2001) (see Eqs. (2.14) - (2.16)). The convective Mach number, first
 351 defined in the experimental study of Papamoshou and Roshko (1988), is set
 352 to $Ma_c = 0.4$ for all simulations and is interpreted as the Mach number of
 353 the parcel of fluid represented by the entire mixing layer moving with the
 354 characteristic convective velocity ΔU_0 . Indeed, the goal of the specification of
 355 U_U, U_L and Ma_c is to keep the initial vortices, and the ultimate formed vortex
 356 (see below), inside the mixing layer, that is, within the field of observation;
 357 details are provided in Okong'o et al. (2002) and in Appendix B of Masi et al.
 358 (2013). The situation is similar to that of a fixed observer looking at a parcel of
 359 fluid (here the entire mixing layer domain) moving as an entity at $Ma_c = 0.4$;
 360 this is a classical Lagrangian representation in fluid dynamics. The value of a_c
 361 is computed from the initial thermodynamic conditions. Ma_c is different from
 362 the local Ma in the flow that depends on the local a computed at the local
 363 thermodynamic conditions and on the local velocity. Since ρ_L, a_L, ρ_U and a_U
 364 change with the thermodynamic conditions according to H , Eqs. 2 show that
 365 the initial dynamic conditions are different according to H .

366 Two constraints are used to select the domain size in the cross-stream di-
 367 rection, L_2 : avoid (1) numerical boundary interference with the ultimately
 368 developed mixing layer at all times of the simulation, and (2) gravity effects,
 369 and therefore obtain a Froude number that is large for the selected value
 370 of L_2 . Table 2 shows the Froude number value for several values of L_2 . The
 371 Froude number is computed using the characteristic velocity ΔU_0 calculated
 372 as an average over all simulations; upon knowing L_2 , the corresponding $\delta_{\omega,0}$
 373 is computed using Eq. (1). Clearly, for $L_2 = 0.22$ m, the Froude number is
 374 sufficiently large so that gravity effects can be neglected. Thus, the effect of
 375 buoyancy is here neglected and any possible density stratification can only

L_2 [m]	0.22	1.11	11.1	111	1110	11100
$\delta_{\omega,0}$ [m]	0.00686	0.0343	0.343	3.43	34.3	343
Froude number	1289	577	182	58	18	6

Table 2

Magnitude of the Froude number as function of the computational domain size in the cross-stream direction, L_2 , and the initial vorticity thickness, $\delta_{\omega,0}$.

be due to turbulence and diffusion phenomena. Our approach is strengthened by the findings of Kit et al., 2017 who interpreted recent observations of the Earth nocturnal atmospheric boundary layer and found unusual turbulence at intermediate scales between inertial and dissipative, and who questioned whether the observed effects fit into the notion that either viscous effects or buoyancy effects modify the local energy cascade via non-local effects; thus, it appears that the dissipation at the smallest scales is not affected by buoyancy effects. The domain lengths are $L_1 = 0.2\text{ m}$, $L_2 = 0.22\text{ m}$, $L_3 = 0.12\text{ m}$ for all simulations.

A set of twelve DNS realizations is generated, allowing the study of the mixing process under several different free-stream values of p , T , N and upper and lower streams chemical composition typical of the Venus lower atmosphere. Given the current uncertainty regarding the species distribution as a function of H , both low stratification (ls) and high stratification (hs) realizations are generated, representing nominal compositions which are sometimes extreme cases of what might be expected in the Venus lower atmosphere. Each DNS realization is identified by a notation of the type $NsHy$, where $N = 2$ or $N = 7$, ' s ' is the species stratification (ls or hs), and ' y ' is the value of H in km. Table 3 lists the various species considered and their corresponding mole fractions, X_α , in both the lower stream and the upper stream; the values of Y_α listed in Table 3 are computed from those of X_α . All cases in the same Case bin of Table 3 have the same free-stream composition. This approach allows understanding whether different assumptions on the chemical composition of the mixture produce variations in the mixing process and, in that case, the sensitivity of such variations to these assumptions. For the $7lsHy$ cases, the composition was selected according to the information provided in Jacobson et al. (2017). For the $7hsHy$ cases, the composition was arbitrarily chosen for illustrative purposes.

Other details on the DNS realizations and the numerical resolution are provided in Table 4.

Case	Stream	CO ₂	N ₂	SO ₂	H ₂ O	H ₂ S	HCl	HF
2lsH50	$Y_{\alpha,U}$	9.6693×10^{-1}	3.407×10^{-2}	0	0	0	0	0
2lsH10	$Y_{\alpha,L}$	9.8879×10^{-1}	1.121×10^{-2}	0	0	0	0	0
2lsH0.4	$X_{\alpha,U}$	9.4750×10^{-1}	5.250×10^{-2}	0	0	0	0	0
	$X_{\alpha,L}$	9.8250×10^{-1}	1.750×10^{-2}	0	0	0	0	0
7lsH50	$Y_{\alpha,U}$	9.6580×10^{-1}	3.407×10^{-2}	1.1×10^{-4}	1.9×10^{-5}	3.6×10^{-6}	7.6×10^{-7}	3.5×10^{-9}
7lsH10	$Y_{\alpha,L}$	9.8846×10^{-1}	1.121×10^{-2}	3.3×10^{-4}	6×10^{-6}	1.2×10^{-6}	2.5×10^{-7}	1.1×10^{-9}
7lsH0.4	$X_{\alpha,U}$	9.4737×10^{-1}	5.251×10^{-2}	7.4×10^{-5}	4.6×10^{-5}	4.6×10^{-6}	8×10^{-7}	7.6×10^{-9}
	$X_{\alpha,L}$	9.8226×10^{-1}	1.750×10^{-2}	2.25×10^{-4}	1.5×10^{-5}	1.6×10^{-6}	3×10^{-7}	2.4×10^{-9}
2hsH50	$Y_{\alpha,U}$	0	1	0	0	0	0	0
2hsH10	$Y_{\alpha,L}$	1	0	0	0	0	0	0
2hsH0.4	$X_{\alpha,U}$	0	1	0	0	0	0	0
	$X_{\alpha,L}$	1	0	0	0	0	0	0
7hsH50	$Y_{\alpha,U}$	0	9.200×10^{-1}	0	3.00×10^{-2}	2.00×10^{-2}	2.00×10^{-2}	10^{-2}
7hsH10	$Y_{\alpha,L}$	9.300×10^{-1}	10^{-2}	6.00×10^{-2}	0	0	0	0
7hsH0.4	$X_{\alpha,U}$	0	9.087×10^{-1}	0	4.61×10^{-2}	1.62×10^{-2}	1.52×10^{-2}	1.38×10^{-2}
	$X_{\alpha,L}$	9.423×10^{-1}	1.590×10^{-2}	4.18×10^{-2}	0	0	0	0

Table 3

Initial mass fraction, Y_a , computed from initially specified mole fraction, X_a , in the mixing layer for all DNS realizations. These values serve as initial conditions for the conservation equations. The lower stratification cases are listed in the upper part of the table; the higher stratification cases are listed in the lower part of the table.

6 Results

A non-dimensional time is defined, $t^* = t\Delta U_0/\delta_{\omega,0}$, and all simulations are pursued until a transitional time, denoted t_{tr}^* , is reached at which the one-dimensional fluctuation-based energy spectra (see Section 6.1) become smooth. This smoothness indicates that the memory of the initial flow specification has been lost (except for the peak corresponding to the perturbation frequency) and that the flow has reached turbulent characteristics. Since it has been determined in Morellina et al. (2020) that the Venus lower atmosphere is turbulent, almost all the analysis is conducted at t_{tr}^* . In Section 6.1, proof is provided that the flow at t_{tr}^* has indeed turbulent characteristics and it is shown that the numerical resolution conforms to the DNS requirements, thereby producing corresponding DNS-information when analyzed. The time evolution of global quantities characterizing the mixing layer is also discussed in Section 6.1, in particular showing the development of the turbulent small scales and of the flow morphology consistent with turbulent features. Then, the global time-wise evolution of the flow is examined in Section 6.2. Subsequently, the formation of High Density Gradient Magnitude (HDGM) regions is analyzed in Section 6.3, followed by a discussion in Section 6.4 on the T distribution in the mixing layer. Species mixing, which is the ultimate topic of this study, is investigated in Section 6.5. To further understand how molecular and turbulent transport interact to produce the species distribution, an analysis is performed in Section 6.6 leading to information about “effective transport” which is defined as molecular transport modulated by turbulence.

Case	$\mathcal{F}$	p_0 [atm]	$\frac{\rho_L}{\rho_U}$	$\Delta\rho$ $\left[\frac{kg}{m^3}\right]$	$\frac{ \rho U _L}{ \rho U _U}$	$Re_{m,tr}$
<i>2lsH50</i>	138	1	1.0131	0.02	1.0065	2227
<i>2lsH10</i>	2570	45	1.0141	0.51	1.0070	2220
<i>2lsH0.4</i>	4365	90	1.0145	0.93	1.0072	2221
<i>7lsH50</i>	138	1	1.0132	0.02	1.0066	2227
<i>7lsH10</i>	2571	45	1.0142	0.52	1.0071	2220
<i>7lsH0.4</i>	4365	90	1.0146	0.94	1.0073	2221
<i>2hsH50</i>	122	1	1.5761	0.57	1.2554	2207
<i>2hsH10</i>	2416	45	1.6083	14.06	1.2681	2224
<i>2hsH0.4</i>	4155	90	1.6221	25.15	1.2736	2217
<i>7hsH50</i>	126	1	1.6165	0.60	1.2714	2231
<i>7hsH10</i>	2463	45	1.6471	14.80	1.2833	2228
<i>7hsH0.4</i>	4230	90	1.6598	26.43	1.2883	2218

Table 4

List of the Direct Numerical Simulation realizations. In all simulations, $Re_0 = 1000$ and grid was $N_1 \times N_2 \times N_3 = 660 \times 732 \times 396$. Information regarding the initial temperature values and the initial upper stream and lower stream compositions are provided in Tables 1 and 3, respectively. The subscript *tr* denotes the transitional time. $t_{tr}^* = 85$ for all simulations.

6.1 Verification of the flow turbulent characteristics and evidence of DNS resolution

As a test of simulation-data validity for studying the Venus atmosphere, a verification is needed that the database represents a flow with turbulent characteristics. Computationally achieving such characteristics is not trivial in that (i) there must be a proliferation of turbulent small scales and the flow morphology must be representative of the stretching and twisting characteristic of turbulence, (ii) the resolution should indicate that the smallest scales overwhelmingly responsible for dissipation, i.e. capturing the majority of the real dissipation at the smallest scales, are computed in a manner such that

there is no accumulation of energy at the smallest resolved scales, and (iii) the spectra based on fluctuations of dynamic and thermodynamic quantities must be smooth, epitomizing the transport of energy between scales, as it is typical of turbulence.

Since in DNS all the length scales associated with the overwhelming amount of dissipation must be solved (Moin and Mahesh, 1998), Δx must be sufficiently fine to capture the appropriate length scales associated with dynamic, thermal diffusion and mass diffusion processes. In a turbulent flow, the length scales associated with the dynamic fluctuations extend over a wide range, with the smallest dynamic scales related to the turbulent kinetic energy dissipation $\langle \varepsilon \rangle \equiv \langle \sigma'_{ij} \partial u'_i / \partial x_j \rangle$, where $(\cdot)'$, denotes fluctuations from the average. The order of magnitude of the smallest dynamic scales is classically provided by the Kolmogorov length scale, defined as

$$\eta_K = \left(\frac{\langle \mu \rangle^3}{\langle \rho \rangle^2 \langle \varepsilon \rangle} \right)^{1/4}. \quad (3)$$

The scrutiny of η_K must be complemented by the mixing scale and/or by the thermal scale if the Schmidt number, Sc (which indicates the mixing scale), and/or if the Prandtl number, Pr (which indicates the thermal scale), are larger than unity. For atmospheric- p flows Pr has characteristic values ~ 0.7 (Rapp, 2017); under the assumption of mass and heat transfer similarity, $Sc \simeq Pr$. The smallest mixing scale is called the Batchelor scale, η_B , related to η_K by $\eta_B = \eta_K Sc^{-0.5}$, but it is classically defined only for a two-species mixture. However, the thermal scale $\eta_\theta = \eta_K Pr^{-0.5}$ (Goto and Kida, 1999) is defined for a mixture of an indefinite number of species, and is thus adopted here to indicate the quality of the resolution; it is noted that if $Pr > 1$ the smallest thermal scale is smaller than the smallest dynamic scale, thus becoming the limiting factor for selecting the grid resolution. Therefore, all spectra, i.e. not only those associated with velocity fluctuations, are of interest in considering resolution.

In Fig. 2 the cross-stream resolution of the dynamic and thermal scales at t_{tr}^* are represented for all the DNS realizations; as is evident, $\Delta x / \eta_K|_{max} < 1.3$ and $\Delta x / \eta_\theta|_{max} < 1.1$, showing the excellent spatial resolution. The achievement of turbulence transition is demonstrated in Fig. 3, where the one-dimensional fluctuation-based energy spectra versus the wavenumber k are illustrated at t_{tr}^* in both streamwise and spanwise directions for the dynamic and thermodynamic variables and for all the simulations. The spectra exhibit the smooth aspect (except for the forcing frequency) characteristic of turbulence. The absence of energy accumulation in the smallest scales (i.e. as indicated by the monotonic decay of the spectra at the higher wavenumbers) reinforces the proof of the excellent resolution also shown in Fig. 2. This preliminary analysis indicates that at t_{tr}^* the flow has turbulent characteristics, as indeed it

Fig. 2. Ratio of the grid spacing to characteristic scales of the flow at t_{tr}^* showing the cross-stream resolution of the (a) dynamic scales and (b) thermal scales of the DNS realizations.

should, and that the quality of the database is excellent because it captures the overwhelming amount of dissipation since there is no accumulation of energy at the smallest scales. This database is thus pertinent to represent the turbulent mixing of chemical species in the Venus lower atmosphere.

6.2 Global features of the flow time-wise evolution

To understand the timeline of the flow development, and thus of its turbulent features, it is useful to examine the momentum thickness

$$\delta_m = \frac{\int_{x_{2,\min}}^{x_{2,\max}} [\langle \rho u_1 \rangle_{x_{2,\max}} - \langle \rho u_1 \rangle] [\langle \rho u_1 \rangle - \langle \rho u_1 \rangle_{x_{2,\min}}] dx_2}{(\langle \rho u_1 \rangle_{x_{2,\max}} - \langle \rho u_1 \rangle_{x_{2,\min}})^2} \quad (4)$$

which is the typical quantity used to describe the growth of a mixing layer; $x_{2,\min} = -0.5L_2$, $x_{2,\max} = 0.5L_2$. By definition, the momentum-thickness-based Reynolds number is $Re_m = Re_0 \delta_m / \delta_{\omega,0}$, making Re_m a global diagnostic of turbulent enhancement during the mixing layer temporal evolution, as shown by the temporal variation of $\delta_m / \delta_{\omega,0}$ in Fig. 4. Examination of animations representing the layer evolution reveal the initial-perturbation-enhanced double pairing of the initial four vortices into an ultimate vortex in which small scales proliferate; $t^* = 25$ approximately corresponds to the first vortex pairing and the second vortex pairing occurs in the vicinity of $t^* = 45 - 50$. Table 4 indicates that all realizations reach transition to turbulence at $t_{tr}^* = 85$ and $Re_{m,tr} \simeq 2200$ following indications from previous studies (Masi et al., 2013) that both t_{tr}^* and $Re_{m,tr}$ are primarily functions of Re_0 .

To understand the formation of small scales leading to the layer growth as portrayed in Fig. 4, two quantities are examined: the domain-averaged (sym-

Fig. 3. One-dimensional spectra at t_{tr}^* for several simulations: streamwise spectra of (a) u_1 , (b) u_2 , (c) u_3 , (g) T , (h) Y_{CO_2} ; spanwise spectra of (d) u_1 , (e) u_2 , (f) u_3 , (i) T , (j) Y_{CO_2} . The units of the wavenumber k are m^{-1} . For $E(k)$ in (a, b, c, d, e, f) the units are m^3s^{-2} . For $E(k)$ in (g, i) the units are K^2m . For $E(k)$ in (h, j) the units are m .

bol $\langle\langle\omega_3^+\rangle\rangle$ positive spanwise vorticity $\langle\langle\omega_3^+\rangle\rangle$ which is a diagnostic for small scale formation since $\langle\langle\omega_3\rangle\rangle$ is initially negative, and the domain-averaged enstrophy $\langle\langle\omega_i\omega_i\rangle\rangle$ which provides an indication of the flow morphology through the twisting and stretching mechanisms in turbulent flows; ω_i is the i -th component of the vorticity vector $\boldsymbol{\omega} = \nabla \times \mathbf{u}$ where $\mathbf{u}$ is the velocity vector. The temporal evolution of these non-dimensionalized quantities, $\langle\langle\omega_3^+\rangle\rangle \delta_{\omega,0}/\Delta U_0$ and $\langle\langle\omega_i\omega_i\rangle\rangle (\delta_{\omega,0}/\Delta U_0)^2$, is illustrated in Fig. 5. At $t^* = 0$, $\langle\langle\omega_3^+\rangle\rangle$ and $\langle\langle\omega_i\omega_i\rangle\rangle$ are null indicating that there are no small scales and there is no tur-

Fig. 4. Time-wise evolution of the normalised momentum thickness $\delta_m / \delta_{\omega,0}$.

507 bulent morphology. $\langle\langle\omega_3^+\rangle\rangle$ starts increasing only mid-way through the first
 508 vortex pairing but subdued turbulent morphological features appear earlier
 509 than small scales, as shown by the quick and sustained increase in $\langle\langle\omega_i\omega_i\rangle\rangle$
 510 while $\langle\langle\omega_3^+\rangle\rangle$ is still null. This indicates that in this initial stage it is the
 511 change in flow morphology which induces the small-scales formation rather
 512 than vice-versa. At approximately $t^* = 25$, a small kink in both $\langle\langle\omega_3^+\rangle\rangle$ and
 513 $\langle\langle\omega_i\omega_i\rangle\rangle$ profiles indicate the end of the first pairing and the increase in both
 514 quantities proceeds at a very slightly reduced rate. The $\langle\langle\omega_3^+\rangle\rangle$ growth ex-
 515 hibits a maximum at $t^* \approx 40$, then displays an approximate plateau for the
 516 *hs* cases; in contrast, the *ls* cases achieve a maximum after the plateau, at
 517 $t^* \approx 60$. Compared to $\langle\langle\omega_3^+\rangle\rangle$, all simulations reach a maximum $\langle\langle\omega_i\omega_i\rangle\rangle$
 518 near $t^* \approx 45$. Thus, as the layer reaches the last vortex pairing, *hs* layers
 519 display a lower vorticity content than *ls* layers, this being due to the larger
 520 ρ_L/ρ_U as it is more difficult to entrain denser fluid (see concurring information
 521 in Almagro et al., 2017 and Pantano and Sarkar, 2002) and their morpholog-
 522 ical complexity decays faster due to larger values of $|\nabla\rho|$ (see Section 6.3)
 523 which induce increased dissipation. Independent of the stratification, $\langle\langle\omega_i\omega_i\rangle\rangle$
 524 begins to decay before $\langle\langle\omega_3^+\rangle\rangle$, showing that the breakdown of the turbulent
 525 flow morphology can no longer sustain the formation of small scales. Thus,
 526 the flow development is consistent with the physics of turbulence, as expected
 527 in the Venus lower atmosphere.

528 6.3 Density gradients

529 One of the foremost characteristics experimentally observed during the mixing
 530 of fluids at high p is the occurrence of HDGM regions (Oswald and Schik,
 531 1999; Oswald et al., 1999; Polikhov and Segal, 2007). These HDGM regions

Fig. 5. Time-wise evolution of integral quantities: (a) normalised positive spanwise vorticity $\langle\langle\omega_3^+\rangle\rangle\delta_{\omega,0}/\Delta U_0$, (b) normalised enstrophy $\langle\langle\omega_i\omega_i\rangle\rangle(\delta_{\omega,0}/\Delta U_0)^2$. Legend as in figure 4.

occur due to the reduced molecular diffusion and reduced effective diffusion occurring under high- p conditions, as explained in Masi et al. (2013). Movie visualizations of $|\nabla\rho|$ show that these HDGM features appear practically as soon as the computation is initiated and persist during the entire simulation. These features are not stationary and instead change continuously with t in the (x_1, x_2, x_3) directions as the composition and dynamics change at all locations in the flow. The present flow visualizations are entirely consistent with those of previous such simulations conducted in a different context (e.g. Okong'o et al., 2002; Masi et al., 2013) and supported by observations (Oschwald and Schik, 1999; Oschwald et al., 1999; Polikhov and Segal, 2007). That is, even if the initial species distribution is entirely stratified as in cases *2hsH50*, *2hsH10* and *2hsH0.4*, representing a species-separation condition, turbulence in conjunction with molecular mixing will induce, in time, lack of separation at these small scales.

The range of $|\nabla\rho|$ values in the present DNS is documented in Figs. 6 and 7. In Fig. 6, the spatial distribution of $|\nabla\rho|$ in the $x_3/L_3 = 0.5$ plane is displayed in logarithmic scale $\log_{10}|\nabla\rho|$ at t_{tr}^* for the seven-species simulations at different H and stratification level. The visualizations show that the species stratification level influences the morphology of the HDGM regions, leading to formation of HDGM loci at the upper and lower mixing layer boundaries in high stratification conditions, and to a more uniform density distribution in low stratification conditions. The magnitude of the density gradients increases with increasing p and T values for both *ls* and *hs* cases, i.e. decreasing with increasing altitude. The same conclusions about the influence of p , T and stratification level can be observed in Fig. 7, where the probability density functions (p.d.f.s) of $|\nabla\rho|$ at t_{tr}^* are represented for the entire set of simulations; there are as many as seven orders of magnitude between the most probable and least probable values, this range being a manifestation of the complexity evident

Fig. 6. Spatial distribution of $|\nabla\rho|$ in the $x_3/L_3 = 0.5$ plane using logarithmic scale $\log_{10} |\nabla\rho|$ at t_{tr}^* for (a) $7lsH50$, (b) $7hsH50$, (c) $7lsH10$, (d) $7hsH10$, (e) $7lsH0.4$, (f) $7hsH0.4$.

in Fig. 6. The p.d.f.s with the larger $|\nabla\rho|$ range are those corresponding to the larger ρ_L/ρ_U values. The influence of the number of species on $|\nabla\rho|$ seems to be negligible, although larger $|\nabla\rho|$ values are reached in the *hs* 7-species cases compared to the corresponding 2-species cases, primarily due to smaller ρ_L/ρ_U values of the latter. For larger domains than those considered here, gravity will play a role in exerting a downward force on the entire flow; the situation is conceptually reminiscent of the Earth below the homopause (situated at approximately 100 km) in which all major Earth species experience small-scale (i.e. local) gradients but are considered well-mixed at the scale below the homopause compared to the molar-mass-dependent exponential decay computed from hydrostatic equilibrium that prevails at altitudes higher than the homopause. The atmosphere below the homopause is controlled by winds representing flows which can attain large Re values, whereas above it, gravity segregates the species according to the molar mass and this latter process is governed by pure molecular diffusion. For higher Venus altitudes, 65–80 and 75–90 km, Ando et al. 2015, found a stable gravity-induced stratification, similar to the situation on Earth. The Venus gravity is similar to that on Earth

Fig. 7. Probability density function of $|\nabla\rho|$ (in kg/m^4) at t_{tr}^* .

(8.87 m^2/s versus 9.81 m^2/s), and thus the influence of Fr is approximately similar at same domain size; small-scale species mixing is a well-known feature at all altitudes below the homopause. On Venus, the denser lower atmosphere compared to Earth induces both a larger gravitational force (ρg) and larger Re values (due to ρ). The present simulations do not consider the counteracting effects of gravity and small-scale mixing, but instead provide a glimpse into the small-scale mixing on Venus, similar to the situation on Earth. Thus, the present results, although not definitive for the entire Venus lower atmosphere, can plausibly conceptually compare the lowest 50 km on Venus altitude to those of the lowest 100 km on Earth.

6.4 Temperature distribution

The intertwining of dynamics and thermodynamics in high- p flows, as discussed in Section 3, makes it of interest to examine the T spatial distribution in the mixing layers as a function of H . For the 7-species set of simulations, the spatial distribution of T in the $x_3/L_3 = 0.5$ plane at t_{tr}^* is illustrated in Figs. 8a - 8f, where the legends necessarily show different range of temperatures according to the value of H . To compare the thermal effects for various simulations, a non-dimensional temperature is defined,

$$\theta = \frac{T - T_{ref}}{T_{ref}} \quad (5)$$

with $T_{ref} = T_L = T_U$ according to Table 1. The local distribution of θ for the 7-species simulations above is displayed in Figs. 9a - 9f. Both Figs. 8 and

Fig. 8. Spatial distribution of T in the $x_3/L_3 = 0.5$ plane at t_{tr}^* for (a) $7lsH0.4$, (b) $7lsH10$, (c) $7lsH50$, (d) $7hsH0.4$, (e) $7hsH10$, (f) $7hsH50$. Units are K .

Fig. 9. Spatial distribution of the non-dimensional temperature, θ , in the $x_3/L_3 = 0.5$ plane at t_{tr}^* for (a) $7lsH0.4$, (b) $7lsH10$, (c) $7lsH50$, (d) $7hsH0.4$, (e) $7hsH10$, (f) $7hsH50$.

9 show that starting from the same T value, mixing under higher stratification levels leads to larger T values, suggesting enhanced dissipation effects stemming from the species mass fraction gradients (the Dufour effect). The p and T conditions at different H seem to slightly influence the complexity of the T spatial distribution at t_{tr}^* , and higher values of θ are achieved in mixing at higher altitudes. The conclusion is that species gradients do influence the T spatial distribution in ways that have not been envisaged so far when

interpreting Venus observational data (Lebonnois and Schubert, 2017), and future studies should devote more attention to this coupling, particularly to the Dufour effect discussed in Section 3.

6.5 Species mixing

The study of species mixing, or lack thereof, is the ultimate goal of this study. To analyze the degree of species mixing and be able to compare simulations with different initial mass fractions in the upper stream and lower streams, a normalized mass fraction variable

$$\Xi_{\alpha} = \frac{Y_{\alpha} - Y_{\alpha,ref}^{\min}}{Y_{\alpha,ref}^{\max} - Y_{\alpha,ref}^{\min}} \quad (6)$$

is introduced where $Y_{\alpha,ref}^{\max} = \max(Y_{\alpha,U}, Y_{\alpha,L})$ and $Y_{\alpha,ref}^{\min} = \min(Y_{\alpha,U}, Y_{\alpha,L})$. Therefore, $\Xi_{\alpha} = 0$ and $\Xi_{\alpha} = 1$ represent the initial species mass fraction of the upper and lower streams or vice-versa, depending on the free-stream location of the species.

The first category of cases examined is that of the two species CO_2 and N_2 in an initially completely stratified situation at the 3 altitudes of 0.4 km, 10 km and 50 km, representing an extreme situation compared with the species-separation hypothesis of Lebonnois and Schubert (2017). Illustrated in Fig. 10 are visualizations of the distributions of Ξ_{CO_2} , both for the 2-species low-stratification and 2-species high-stratification cases, corresponding to the species-separation hypothesis, akin to the proposal of Lebonnois and Schubert, 2017. All visualizations are illustrated in the $x_3/L_3 = 0.5$ plane at t_{tr}^* ; since the mixtures are binary, Ξ_{N_2} is the complement of Ξ_{CO_2} . The qualitative physical picture is similar for the *hs* cases compared to the *ls* cases, except that the *ls* cases exhibit thicker intense mixing regions adjacent to the lower stream. There seems to be no remarkable influence of H conditions on the global morphology of the Ξ_{α} 's. The inference from the study of Ξ_{α} is that for a given number of species, here 2, the coupling of turbulent convection and molecular mixing proceeds qualitatively in a similar way whether the composition was initially completely stratified or unstratified; in both cases, the species become spatially distributed over the entire domain, although this distribution is not uniform. That is, even if the species were entirely stratified at an observed time, small-scale mixing resulting from the combined effects of molecular diffusion and turbulence will disturb this stratification unless the gravity effect overwhelms these effects.

To examine how the above inference might vary according to the number of species, the potential differences in the Ξ_{α} distributions between the *2hs* and

Fig. 10. Spatial distribution of Ξ_{CO_2} in the $x_3/L_3 = 0.5$ plane at t_{tr}^* for (a) $2lsH0.4$, (b) $2lsH10$, (c) $2lsH50$, (d) $2hsH0.4$, (e) $2hsH10$, (f) $2hsH50$.

639 $7hs$ cases were assessed. For brevity, only the Ξ_α distribution at t_{tr}^* is portrayed
 640 in the $x_3/L_3 = 0.5$ plane for each species in Fig. 11 for case $7hsH0.4$, but
 641 a comparison was made among $7lsH0.4$, $7hsH0.4$ and $7hsH50$ cases. This
 642 comparison reveals that the increased stratification results in a more non-
 643 uniform spatial distribution, but this non-uniformity is reduced as H increases.
 644 The presence of the minor species does not influence remarkably the Ξ_{CO_2} and
 645 Ξ_{N_2} spatial distributions during ls mixing. However, during hs mixing there
 646 are differences in the spatial distributions according to H . For the smaller H
 647 (i.e. higher p and T) one observes larger differences in the spatial distributions
 648 of Ξ_{CO_2} and Ξ_{N_2} between $2hs$ and $7hs$ cases, with formation of sharper spikes
 649 penetrating the free streams in the 7-species cases.

650 Final attention is given to uphill diffusion, which is a phenomenon first ex-
 651 perimentally observed by Duncan and Toor (1962). During uphill diffusion, a
 652 species may separate from the remaining mixture and form regions of very high
 653 concentration and regions of very small concentration even if that species was
 654 initially uniformly distributed over the entire spatial domain. Unlike counter-
 655 gradient diffusion defined for turbulent flows, uphill diffusion can occur in
 656 laminar flows and in situations where there is only diffusion and no convec-
 657 tion (Duncan and Toor, 1962). Uphill diffusion occurs when a species diffuses
 658 against its gradient and the phenomenon stems from the tight coupling of the
 659 flux of that species to the flux of other species in the mixture (see Masi et
 660 al., 2013); usually, species of small concentration experience uphill diffusion
 661 because their fluxes is strongly coupled to that/those of species having high
 662 concentration. No uphill diffusion can occur in a two-species mixture (Tay-
 663 lor and Krishna, 1993); the physical explanation is that in the binary-species

Fig. 11. Spatial distribution of normalized mass fractions in the $x_3/L_3 = 0.5$ plane at t_{tr}^* for $7shH0.4$. (a) Ξ_{CO_2} , (b) Ξ_{N_2} , (c) Ξ_{SO_2} , (d) Ξ_{H_2O} , (e) Ξ_{H_2S} , (f) Ξ_{HCl} , (g) Ξ_{HF} .

case all the coefficients of the diffusion matrix are positive definite, whereas uphill diffusion can only occur for a species when its effective diffusivity is negative (see Masi et al., 2013). Essentially, for multi-species mixtures, uphill diffusion is another mechanism for species separation (Masi et al., 2013). For simulations to reproduce uphill diffusion experimental data, it is required to include a physically accurate model of multi-species molecular diffusion in the conservation equations (Castiglioni and Bellan, 2018). The manifestation of uphill diffusion is through values $\Xi_\alpha < 0$ and $\Xi_\alpha > 1$, meaning that at some locations the mass fraction is smaller than the initial minimum in the field, and at other locations it is larger than the initial prescribed maximum in the

field, none of which can occur during regular diffusion. In the present 7-species simulations, no uphill diffusion is observed, thus eliminating this phenomenon as a potential cause for species separation.

6.6 Effect of the interaction between molecular transport and turbulent transport on species diffusion

To understand how molecular scales interact with the turbulent scales to produce the species distribution discussed in Section 6.5, the methodology of Masi et al. (2013) is adopted wherein the complex functional form of Eq. A.6 for the species diffusive fluxes is expressed as a function of single effective diffusion coefficient, $D_{\alpha,eff}$, for each species α . Then, Eq. A.4 is rewritten as

$$\frac{\partial(\rho Y_\alpha)}{\partial t} + \frac{\partial(\rho u_j Y_\alpha)}{\partial x_j} = \frac{\partial}{\partial x_j} \left(\rho D_{\alpha,eff} \frac{\partial Y_\alpha}{\partial x_j} \right), \quad (7)$$

where

$$D_{\alpha,eff} \equiv Y_\alpha \frac{D_{T,\alpha}}{T} \frac{\delta T}{\delta Y_\alpha} + Y_\alpha \frac{D_{p,\alpha}}{p} \frac{\delta p}{\delta Y_\alpha} + \sum_{\beta=1}^{N-1} \mathfrak{D}_{\alpha\beta} \frac{\delta Y_\beta}{\delta Y_\alpha} \quad (8)$$

and δ signifies functional derivatives. Equation 8 is only used for analyzing the database (i.e. it is not employed the simulations) and is only relevant to flows with turbulent characteristics because in these flows the dependent variables are functionally related. Masi et al. (2013) showed that the functional derivatives can be very accurately modeled using uniquely the DNS solution (see Appendix D and Masi et al., 2013 for details of the functional derivative models); the larger are the fluxes, the more accurately this model holds. Essentially, these functional derivatives embed the turbulence effects specific to the particular flow and the model for them is entirely parameter-free and is computed from the three-dimensional solution at the time of interest. Therefore, $D_{\alpha,eff}$ can be considered as a molecular diffusion coefficient modulated by turbulence effects and it thus inherently represents the interaction between molecular transport and turbulent transport. Each $D_{\alpha,eff}$ is used to define a species effective Schmidt number

$$Sc_{\alpha,eff} \equiv \frac{\mu}{\rho D_{\alpha,eff}}. \quad (9)$$

Figure 12a illustrates the p.d.f.s of $D_{\alpha,eff}$ over the mixing layer for case *7hsH0.4* at t_{tr}^* ; only results for six independent $D_{\alpha,eff}$ are shown, as the seventh coefficient is related to the others by the constraint that all diffusion fluxes must add to zero. The first observation is that the value of $D_{\alpha,eff}$ is $O(10^{-6})$ m²/s,

703 which is intermediary between gases and liquids, consistent with what can be
 704 expected of supercritical fluids; this $D_{\alpha,eff}$ order of magnitude thereby qual-
 705 itatively validates the model for the functional derivatives. The p.d.f.s can
 706 be categorized into three groups according to the $D_{\alpha,eff}$ at which the respec-
 707 tive p.d.f. peaks. For each species, the molar mass and the kinetic diameter
 708 are relevant quantities influencing diffusion. The kinetic diameter is related
 709 to the mean free path (the square of the kinetic diameter is inversely propor-
 710 tional to the mean free path) and is a measure indicating the likelihood that
 711 a molecule will collide with another molecule; it is basically related to the size
 712 of the sphere of influence around a molecule in which scattering events may
 713 occur. Small kinetic diameters are related to large mean free paths, leading
 714 to large diffusion coefficients. However, the effect of turbulence modifies the
 715 molecular processes. Indeed, simulation results reveal that turbulence inter-
 716 venes to somewhat modify the expectations from simple molecular diffusion
 717 theory, as evident in Fig. 12. The smallest $D_{\alpha,eff}$ at which the p.d.f. peaks is for
 718 SO_2 (molar mass 64.1 kg/kmol, kinetic diameter 360×10^{-12} m). The second
 719 group is that of H_2S , HCL and CO_2 (molar masses 34.1, 36.5 and 44 kg/kmol,
 720 respectively; kinetic diameters 360×10^{-12} , 320×10^{-12} and 330×10^{-12} m, re-
 721 spectively); these p.d.f.s are narrower than that of SO_2 , and therefore their
 722 peak, which occurs at larger values than for SO_2 , is more statistically sig-
 723 nificant. The third group is that of HF and H_2O (molar masses 20 and 18
 724 kg/kmol, respectively; kinetic diameter of HF is unavailable including on the
 725 NIST WebBook; kinetic diameter of H_2O is 265×10^{-12} m); these p.d.f.s peak
 726 at larger $D_{\alpha,eff}$ values than those in the second group, the p.d.f.s are wider
 727 than those for all other species and therefore their peak is less statistically sig-
 728 nificant. It is clear that the three groups are partitioned according to the molar
 729 mass of the species in the group, but within each group the kinetic diameter
 730 as well as turbulent effects combine to produce specific results not predictable
 731 from diffusion theory alone. That is, the partition in three groups shows that
 732 generally heavier species have peak $D_{\alpha,eff}$ smaller than those of lighter species,
 733 the molecules being typically less mobile; at same kinetic diameter, SO_2 which
 734 is heavier than H_2S , has a smaller most probable $D_{\alpha,eff}$. Within the second
 735 group, however, the smallest $D_{\alpha,eff}$ at which a peak occurs is for the lightest
 736 species and with the largest kinetic diameter, this being clearly the direct in-
 737 fluence of turbulence which modifies molecular transport. The corresponding
 738 effective $\text{Sc}_{\alpha,eff}$ p.d.f.s are depicted in Fig. 12b and show the opposite ordering
 739 compared to $D_{\alpha,eff}$, as expected. The peak values range from 0.65 to 1, this
 740 being a typical range for supercritical fluids at high temperature that are not
 741 too far in thermodynamic compressibility from perfect gases (Morellina et al.,
 742 2020).

743 Finally, the effect of altitude, initial stratification and number of species on
 744 $D_{\text{CO}_2,eff}$ are presented in Fig. 13 as p.d.f.s over the mixing layer at t_{tr}^* , showing
 745 a wide range of $D_{\text{CO}_2,eff}$ values. Altitude dominates the values of $D_{\text{CO}_2,eff}$. For
 746 $H = 0.4$ km, the values are consistent with the range expected for supercritical

Fig. 12. Probability density functions over the entire three-dimensional mixing layer for case 7hsH0.4 at t_{tr}^* . (a) $D_{\alpha, eff}$ ($10^{-7} m^2 s^{-1}$, not $\mathcal{F}$ scaled), (b) $Sc_{\alpha, eff}$.

fluids whereas for $H = 50$ km the values are consistent with those known for perfect gases. At each altitude, the width of the p.d.f.s is governed by the initial stratification and modulated by the number of species, both of which influence turbulence. For larger initial stratification, species mass fraction gradients are larger, the p.d.f.s are narrower and thus the most expected value of $D_{CO_2, eff}$ is more significant. Increasing the number of species adds spatial scales, as evident from Fig. 7 and these additional scales interact with the turbulence scales, but their effect on the $D_{CO_2, eff}$ p.d.f. appears subdued.

6.7 Dissipation at different altitudes

The importance of the dissipation in the Venus atmosphere was highlighted by Izakov, 2010 who investigated turbulence in the troposphere of Venus due to buoyancy waves, which originate when the wind flows along the planetary surface following its relief. However, in Izakov, 2010 only the dissipation due to turbulence, i.e. momentum dissipation, has been addressed. When turbulence is intertwined with heat and species-mass transfer, as it is in the present case, examination of turbulence alone provides an incomplete view of the dissipation. Instead, the focus is here on the total dissipation which led to heating and the temperature increase discussed in Section 6.4, meaning that all processes of dissipation must be investigated: turbulence, the species mixing discussed in Sections 6.5 and 6.6, and heat transfer.

The dissipation is classically defined to be the rate of irreversible entropy production (e.g., De Groot and Mazur, 1984), namely, the source term of the entropy equation. From the entropy conservation equation, a generalized form of the dissipation g , has been derived by Masi et al., 2013. The dissipation has three origins, representing respectively viscous, thermal and species-mass

Fig. 13. Probability density function of $D_{CO_2,eff}$ ($10^{-7}m^2s^{-1}$, not $\mathcal{F}$ scaled) computed over the entire three-dimensional mixing layer at t_{tr}^* for different simulations.

772 contributions, g_{visc} , g_{temp} and g_{mass}

$$g = \underbrace{\frac{\mu}{T} \left(2S_{ij}S_{ij} - \frac{2}{3}S_{kk}S_{ll} \right)}_{g_{visc}} + \underbrace{\lambda \frac{1}{T^2} \frac{\partial T}{\partial x_j} \frac{\partial T}{\partial x_j}}_{g_{temp}} + \underbrace{\frac{1}{2} \sum_{\beta=1}^N \sum_{\alpha=1}^N \frac{R_u}{(-\mathbb{D}_{\alpha\beta})} \frac{\rho}{m_\alpha Y_\beta} \Pi_{\alpha\beta j} \Pi_{\alpha\beta j}}_{g_{mass}} \quad (10)$$

773 where $(-\mathbb{D}_{\alpha\beta}m)/(Y_\alpha m_\beta)$ is a symmetric positive semi-definite matrix (Gio-
774 vangigli et al., 2011, Keizer, 1987) and

$$\begin{aligned} \Pi_{\alpha\beta j} = & -X_\beta \mathbb{D}_{\alpha\beta} \left[\left(\frac{m_\alpha}{m} \bar{\alpha}_{T,\beta}^b - \frac{m_\beta}{m} \bar{\alpha}_{T,\alpha}^b \right) \frac{1}{T} \frac{\partial T}{\partial x_j} + \frac{m_\alpha m_\beta}{m R_u T} \left(\frac{v_\alpha}{m_\alpha} - \frac{v_\beta}{m_\beta} \right) \frac{\partial p}{\partial x_j} \right] \\ & - \sum_{\gamma=1}^{N-1} \left(\frac{m_\beta}{m_\gamma} \mathbb{D}_{\beta\alpha} \alpha_{D\alpha\gamma} - \frac{m_\alpha}{m_\gamma} \mathbb{D}_{\alpha\beta} \alpha_{D\beta\gamma} \right) \left[\frac{\partial Y_\gamma}{\partial x_j} - Y_\gamma \sum_{\delta=1}^{N-1} \left(\frac{m}{m_\delta} - \frac{m}{m_N} \right) \frac{\partial Y_\delta}{\partial x_j} \right] \end{aligned} \quad (11)$$

775 with $\Pi_{\alpha\alpha j} = 0$, $\Pi_{\alpha\beta j} = -\Pi_{\beta\alpha j}$. Thus, g_{visc} is due to momentum dissipation
776 through the action of viscosity, g_{temp} is due to heat dissipation through the
777 action of thermal conductivity, and g_{mass} is due to dissipation of species partial
778 densities through the action of mass diffusion.

Fig. 14. Planar averages in (x_1, x_3) planes of the three terms of dissipation, (a) g_{visc} , (b) g_{temp} , (c) g_{mass} , and (d) g at t_{tr}^* . Units are $W(m^3K)^{-1}$.

Planar averages in (x_1, x_3) planes of the three contributions to dissipation are depicted in Fig. 14 for the DNS realizations at t_{tr}^* . The general observation is that g increases with decreasing altitude and with increasing stratification. The number of species has almost no impact on g . For the *ls* cases the viscous dissipation accounts almost for the total of the dissipation since species mixing is subdued. In contrast, for the *hs* cases the viscous term is only approximately 20% of the total dissipation, and the remaining 80% is due to the species-mass diffusion term. The higher total amount of dissipation explains to a substantial extent the higher temperature reached in the *hs* cases (see figure 8), as the dissipation is converted into heat. It is for these *hs* cases that the contribution of the species-mass diffusion is considerable.

A comparison of the values from Fig. 14 with those of figure 6 from Izakov, 2010 is not meaningful since the scales of the phenomena for which those values were found are at least two orders of magnitude larger than those considered here; the Izakov, 2010 results are for a scale characterizing the transition from turbulence-dominated to buoyancy-dominated dynamics, whereas the present scale is that of molecular and turbulent mixing. Another study which considered the dissipation is that of Kit et al., 2017. In that investiga-

tion, observational data from turbulence spectra was used to deduce aspects of the turbulent kinetic energy (TKE) dissipation rate. The TKE dissipation rate and the irreversible entropy production are different quantities which are only indirectly related. The TKE dissipation rate is proportional to molecular viscosity and its computation requires the knowledge of the spatial variation (i.e. gradients) of the velocity fluctuations (Wang et al., 2021) which can only be computed once an averaging process is defined; if the averaging process is different in two physical situations, it is clear that there is little hope that the results could be compared. The TKE is indirectly related to the turbulence energy spectra, which are computed from products of velocity fluctuations as the spectra are agnostic to the spatial gradients of the fluctuations; the wavenumber range of the spectra is directly related to the value of the viscosity (at same value of length scale, density and velocity, a smaller dynamic viscosity will imply a larger range of wavenumbers) and the shape of the spectra versus the wavenumber is related to the characteristics of the energy transfer between scales but not to spatial gradients of velocity fluctuations. Kit et al., 2017 identified “bumps at scales intermediate to inertial and dissipation subranges, resembling a bottleneck phenomenon” and also stated that these “may not convincingly fit into the framework of previous bottleneck-effect theories that allude to either viscous effects or buoyancy effects modifying the local energy cascade via non-local effects.” because “humps did not consistently appear near the Taylor microscale or the buoyancy scale.” However, existing turbulence theory indicates that pile up of energy in the spectra may be indicative of new physics preventing this energy cascade, as discussed by Alexakis and Biferale (2018). Perhaps consideration of the total dissipation as defined in Eq. (10) would have clarified the physical origin of those bottlenecks.

7 Implications for species potential separation in the Venus lower atmosphere

In general, it is considered that the atmospheres of solid-surface planets, other than Earth (for which the atmosphere has been studied in detail for decades), are too complex to lend themselves to fundamental modeling; these atmospheres interact at one end with the planet surface and at the other end are influenced by the effects from the stars around which they revolve. This hesitation to utilize fundamental models for exotic atmospheres is considerably stronger for Venus which has an atmosphere defying in complexity that of other planets or space bodies. Remote or on-the-ground observations of the Venus atmosphere have led to some established facts, but also to controversy in explaining data which seem inconsistent, as discussed in Section 1. In a previous study (Morellina et al., 2020), it was shown how existing Venus information can be used in conjunction with models to develop an enhanced and

quantitative understanding of the global characteristics of the Venus lower atmosphere. The aspects addressed in Morellina et al. (2020) were the turbulence level as measured by the Reynolds number, the value of the Mach number and of the Prandtl number, all as functions of altitude. Thermodynamic phase calculations showed that the Venus lower atmosphere is in the single-phase regime.

The present study goes farther. Using as a starting point the conclusions of Morellina et al. (2020) and a fundamental model of transient and three-dimensional high- p multi-species mixing, simulations were performed in small atmospheric domains of the Venus lower atmosphere to determine the flow features as a function of altitude. While only a simulation of the full atmosphere can conclusively determine whether or not there is a hypothesized species stratification (Lebonnois and Schubert, 2017), in particular by including gravity effects, the present results indicate that species gradients exist at all studied altitudes, and that they become reduced with altitude implying a more uniform composition at higher altitudes. According to fundamental physics, species gradients also affect the heat flux through the Dufour effect and thus influence the temperature distribution. That is, in the absence of gravity, even when initiating calculations with complete stratification for a mixture composition of CO_2 and N_2 , or when the fluid composition contains these two species mixed with several other trace species, the prevailing turbulent flow distributes the species everywhere in the domain and no separation of species occurs for CO_2 and N_2 . This result is not entirely surprising because although molecular mass diffusion and effective mass diffusion are reduced at high p compared to atmospheric p (Masi et al., 2013), the turbulent flow stirs the species and convects them in the entire flow. The identified gradients are the result of two processes: turbulent processes which stir the flow and tend to make it more uniform, and diffusion processes which occur at scales smaller than turbulence and may or may not have a homogenizing tendency, as discussed above. An initial stratification leads to eventual larger gradients, but never to CO_2/N_2 species separation. For a seven species composition including CO_2 and N_2 , uphill diffusion has also been ruled out as a potential phenomenon for the separation of the major species. The deviation from this physical picture once gravity effects are included, remains to be studied and this study will require simulations of the entire Venus lower atmosphere. However, because according to Morellina et al. (2020) the Reynolds number in the Venus lower atmosphere is at least 10^6 , simulations having the accuracy of the present DNS are not possible for a domain as large as the entire Venus lower atmosphere; such simulations would necessarily rely on LES in which the small-scale effects are modeled, so that the accuracy of those calculations could not match that of the present DNS, which has been though only conducted in small domains. Future results from LES await the emergence of wall models, as discussed in Section 2, but it will be of interest to find out whether, with well-tested SGS models, such results will support the same conclusion as reached in the present

study.

8 Summary and conclusions

To investigate species mixing in the Venus lower atmosphere, a validated state-of-the-art high-pressure conservation-equations model in conjunction with state-of-the-art transport properties and a well-established real-gas equation of state have been used to perform three-dimensional time-dependent Direct Numerical Simulations (DNSs). Considering that there is currently uncertainty regarding the chemical species present at different altitudes, simulations were performed at each altitude for both a low-stratification and a high-stratification case, using species identified in previous publications as existing in the Venus lower atmosphere. The simulations were performed in small domains travelling as an entity at a specified Mach number, as explained in Section 5; in these small domains, gravity effects were shown to be small. A set of twelve DNS realizations has been created using realistic values of pressures and temperatures at those altitudes, with each simulation being pursued to a time at which the flow shows turbulent characteristics. The results from these DNS reveal the detailed flow and thermodynamic features at three different altitudes within the Venus lower atmosphere. One of the most prominent features of these flows is the existence of high density-gradient magnitude (HDGM) regions. The density gradients are larger with decreasing altitude and increasing initial stratification. The influence of the minor species on the global behavior of the flow is negligible at low stratification. Under high stratification conditions the mass-diffusion of the species is influential in determining flow aspects. Even when the calculation is initiated with species separation, the flow never returns to this condition as turbulence stirs the flow and convects species throughout the domain. Thus, in these small domains in which gravity effects are small, species separation is never observed, independent of the number of species or of the altitude.

To simulate the entire Venus lower atmosphere and include gravity effects, it is required to include the interaction of the fluid with the Venus surface within a nominal altitude $H \ll 0.4$ km. Once this information becomes available, it will permit conducting Large Eddy Simulations (LES) of the entire Venus lower atmosphere at the high Reynolds number values shown to prevail on the planet; such simulations will allow addressing pending questions regarding the super-rotation and the planet moment of inertia. Such LES simulations could also enhance the understanding of recently postulated volcanic activity on Venus (Gülcher et al., 2020).

Towards the goal of performing LES, the present DNS database can be used as good starting point in understanding the small-scale modeling requirements

stemming from the mixing of species. Moreover, current interest in Venus missions with landers able to sustain the harsh conditions of the Venus lower atmosphere as far as material integrity is concerned (e.g. melting, corrosion (for modeling reactions under high-pressure turbulent conditions see Bellan, 2017a, Bellan, 2017b)) make simulations of the Venus lower atmosphere a necessary component of mission design. Thus science and engineering are entirely coupled; one can use science for engineering purposes and the missions resulting from engineering can refine the scientific knowledge. Additionally, proliferation of experimental facilities for simulating the Venus environment (e.g. Kremic et al., 2016; Lambert et al., 2010) – for the purpose of understanding the effects of species mixing on engineering systems and understanding geological materials reacting under the Venus thermodynamic conditions – is to date unsupported by a theoretical framework. The present model and study, and the potential it has for future simulations, would provide the much needed coupling of the experiment with theory in order to create a concerted effort to develop new science.

Acknowledgments

This work was conducted at the Jet Propulsion Laboratory (JPL) of the California Institute of Technology (Caltech) and sponsored by JPL internal development funds. This study is part of Stefano Morellina's (SM) Master thesis and was performed while he was an intern at JPL. The contributions of Dr. Aswin Gnanaskandan and Dr. Luca Sciacovelli in helping SM understand the DNS code are thankfully recognized. Stefano Morellina's Master thesis supervisor, Dr. Francesco Creta, and the co-supervisor, Dr. Pasquale E. Lapenna, are thanked for their advice. The Institut Supérieur de l'Aéronautique et de l'Espace (ISAE-SUPAERO), the Sapienza University of Rome, and the Italian Space Agency are thanked for providing support to SM during his internship at JPL. The computational resources were provided by the NASA Advanced Supercomputing at Ames Research Center under the Science Mission Directorate program. The discussions with and guidance from Dr. J. Cutts of JPL are gratefully acknowledged.

9 Copyright

Copyright 2020. All rights reserved until the copyright is transferred to the publisher.

A Governing equations for three-dimensional time-dependent simulations of the lower Venus atmosphere

The governing equations are the conservation equations coupled to the equation of state.

A.1 Conservation equations

The conservation equations for mass, momentum, energy and species valid for high- p conditions (Masi et al., 2013) are listed below

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x_j} [\rho u_j] = 0, \quad (\text{A.1})$$

$$\frac{\partial}{\partial t} (\rho u_i) + \frac{\partial}{\partial x_j} [\rho u_i u_j + p \delta_{ij} - \sigma_{ij}] = 0, \quad (\text{A.2})$$

$$\frac{\partial}{\partial t} (\rho e_t) + \frac{\partial}{\partial x_j} [(\rho e_t + p) u_j - u_i \sigma_{ij} + q_j] = 0, \quad (\text{A.3})$$

$$\frac{\partial}{\partial t} (\rho Y_\alpha) + \frac{\partial}{\partial x_j} [\rho Y_\alpha u_j + J_{\alpha j}] = 0, \quad (\text{A.4})$$

where $\alpha \in [1, N-1]$, t denotes the time, x is a Cartesian coordinate, subscripts i and j refer to the spatial coordinates, u_i is the velocity, $e_t = e + u_i u_i / 2$ is the total energy (i.e. internal energy, e , plus kinetic energy), Y_α is the mass fraction of species α and N is the number of species, σ_{ij} is the Newtonian viscous stress tensor

$$\sigma_{ij} = \mu \left(2S_{ij} - \frac{2}{3} S_{kk} \delta_{ij} \right), \quad S_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right), \quad (\text{A.5})$$

where μ is the viscosity, S_{ij} is the strain-rate tensor, and $J_{\alpha j}$ and q_j are the j -direction species- α mass flux and heat flux, respectively.

The full matrices of mass-diffusion coefficients and thermal-diffusion factors derived by Harstad and Bellan (2004a) are used to express the mass and heat fluxes. Instead of using a set of N dependent species equations for Eq. (A.4), a set of $(N-1)$ independent species equations are solved for the species mass fractions. $\mathbf{J}_\alpha$ and $\mathbf{q}$ are expressed as follows:

$$\mathbf{J}_\alpha = -\rho \left[Y_\alpha (D_{T,\alpha}) \frac{\nabla T}{T} + Y_\alpha (D_{p,\alpha}) \frac{\nabla p}{p} + \sum_{\beta=1}^{N-1} \left(D'_{\alpha\beta} \frac{m_\alpha}{m_\beta} \right) \nabla Y_\beta \right], \quad (\text{A.6})$$

$$\mathbf{q} = -\lambda \nabla T + \sum_{\alpha=1}^{N-1} \mathbf{J}_{\alpha} \left[\left(\frac{h_{\alpha}}{m_{\alpha}} - \frac{h_N}{m_N} \right) - R_u T \left(\frac{\bar{\alpha}_{T,\alpha}^b}{m_{\alpha}} - \frac{\bar{\alpha}_{T,N}^b}{m_N} \right) \right] \quad (\text{A.7})$$

973 where

$$D_{T,\alpha} = - \sum_{\beta=1}^N \bar{\alpha}_{T,\beta}^b \mathbb{D}_{\beta\alpha}, \quad D_{p,\alpha} = \frac{p}{R_u T} \sum_{\beta=1}^N v_{\beta} \mathbb{D}_{\beta\alpha}, \quad (\text{A.8})$$

$$D_{\alpha\gamma} = \sum_{\beta=1}^N \mathbb{D}_{\alpha\beta} \alpha_{D\beta\gamma}, \quad (\text{A.9})$$

$$\bar{\alpha}_{T,\alpha}^b = \sum_{\beta=1}^N X_{\beta} \alpha_{T,\beta\alpha}^b, \quad (\text{A.10})$$

$$D'_{\alpha\beta} = D_{\alpha\beta} - \left(1 - \frac{m_{\beta}}{m_N} \right) \left(\sum_{\gamma=1}^{N-1} D_{\alpha\gamma} X_{\gamma} \right). \quad (\text{A.11})$$

974 wherein $X_{\alpha} = Y_{\alpha} m / m_{\alpha}$ represents the species molar fraction; $v_{\alpha} = (\partial v / \partial X_{\alpha})_{T,p,X_{\beta}(\beta \neq \alpha)}$
 975 is the partial molar volume, where the molar volume is $v = 1/n$ and $n = \rho/m$
 976 is the molar density; $h_{\alpha} = (\partial h / \partial X_{\alpha})_{T,p,X_{\beta}(\beta \neq \alpha)}$ is the partial molar enthalpy,
 977 where the molar enthalpy is $h = G - T(\partial G / \partial T)_{p,X}$ with G being the Gibbs
 978 energy; R_u is the universal gas constant; $D_{\alpha\gamma}$ are the pairwise mass diffusion
 979 coefficients; $\alpha_{T,\alpha\beta}^b$ are the binary thermal diffusion factors; and λ is the thermal
 980 conductivity. The mass-diffusion factors, $\alpha_{D\alpha\beta}$, are calculated from thermo-
 981 dynamics (see Harstad and Bellan, 2004a; Masi et al., 2013; Castiglioni and
 982 Bellan, 2018) as

$$\alpha_{D\alpha\beta} \equiv \frac{1}{R_u T} X_{\alpha} \frac{\partial \xi_{\alpha}}{\partial X_{\beta}} = (\delta_{\alpha\beta} - \delta_{\alpha N}) + X_{\alpha} (R_{\alpha\beta} - R_{\alpha N}) \quad (\text{A.12})$$

983 with $1 \leq \alpha \leq N$, $1 \leq \beta \leq N-1$, and

$$R_{\alpha\beta} \equiv \frac{\partial \ln \gamma_{\alpha}}{\partial X_{\beta}} \quad (\text{A.13})$$

984 with $1 \leq \alpha \leq N$, $1 \leq \beta \leq N$. Here, ξ_{α} is the chemical potential of species
 985 α written in terms of $N-1$ species; $\gamma_{\alpha} \equiv \varphi_{\alpha} / \varphi_{\alpha}^o$ where φ is the fugacity
 986 coefficient written in terms of N species and the superscript o denotes the pure
 987 ($X_{\alpha} = 1$) limit. The calculation of the fugacity from the PR EoS is provided
 988 in Appendix C of Castiglioni and Bellan (2018). The non-linear coupling of
 989 transport and thermodynamics, through v_{β} in Eq. (A.8) and $\alpha_{D\beta\gamma}$ in Eq. (A.9),
 990 indicates that a real-gas EoS should be used; here the PR EoS is coupled to
 991 the conservation equations.

992 Matrix elements $\mathbb{D}_{\beta\gamma}$ are the solution of the mixing rules equations (Harstad
993 and Bellan, 2004a)

$$\sum_{\beta=1}^N \left[\delta_{\alpha\beta} - (1 - \delta_{\alpha\beta}) X_{\beta} \frac{\bar{\mathcal{D}}_{\alpha}}{\mathcal{D}_{\alpha\beta}^b} \right] \frac{\mathbb{D}_{\beta\gamma}}{X_{\beta}} = \bar{\mathcal{D}}_{\alpha} \frac{(\delta_{\alpha\gamma} - Y_{\alpha})}{X_{\alpha}} \quad (\text{A.14})$$

994 where

$$\bar{\mathcal{D}}_{\alpha} = 1 / \sum_{\substack{\beta=1 \\ \beta \neq \alpha}}^N \left(\frac{X_{\beta}}{\mathcal{D}_{\alpha\beta}^b} \right). \quad (\text{A.15})$$

995 Solutions for $\mathbb{D}_{\beta\gamma}$ may be obtained by an approximate inversion (Ern and
996 Giovangigli, 1998) as follows:

$$\mathbb{D}_{\beta\gamma} \simeq X_{\beta} \mathbb{D}_{\beta\gamma}^{(1)}, \quad (\text{A.16})$$

$$\mathbb{D}_{\alpha\beta}^{(1)} = \frac{(1 + Y_{\alpha})}{X_{\alpha}} \mathcal{D}_{\alpha}^* \delta_{\alpha\beta} + (1 - \delta_{\alpha\beta}) \frac{\mathcal{D}_{\alpha}^* \mathcal{D}_{\beta}^*}{\mathcal{D}_{\alpha\beta}^b} - (\sigma_{\alpha} \mathcal{D}_{\alpha}^* + \sigma_{\beta} \mathcal{D}_{\beta}^*) + \sum_{\gamma=1}^N (Y_{\gamma} \sigma_{\gamma} \mathcal{D}_{\gamma}^*), \quad (\text{A.17})$$

$$\mathcal{D}_{\alpha}^* = (1 - Y_{\alpha}) \bar{\mathcal{D}}_{\alpha}, \quad (\text{A.18})$$

$$\sigma_{\alpha} = \frac{m_{\alpha}}{m} (1 + Y_{\alpha}) + \sum_{\substack{\beta=1 \\ \beta \neq \alpha}}^N Y_{\beta} \frac{\mathcal{D}_{\beta}^*}{\mathcal{D}_{\alpha\beta}^b} \quad (\text{A.19})$$

997 where $\mathcal{D}_{\alpha\beta}^b$ is the full approximation binary-diffusion matrix. This method
998 leads to a singularity when the mixture is composed of only one species. In that
999 case Eq. (A.15) is no longer used and the diffusion coefficients are evaluated
1000 using the binary-diffusion matrix, by setting $\mathcal{D}_{\alpha}^* = \mathcal{D}_{\alpha N}^b$ where N represents
1001 the index associated with the solvent. This method was tested against an exact
1002 Gauss inversion (not shown) and it gave the same results, with an additional
1003 gain in computational time. Defining $\mathcal{D}_{\alpha\beta}$ as the first approximation of the
1004 binary diffusion matrix and realizing that the deviation of the ratio $\mathcal{D}_{\alpha\beta}^b / \mathcal{D}_{\alpha\beta}$
1005 from unity is comparable to uncertainties in binary diffusion coefficients values
1006 (Harstad and Bellan, 2004a), we assume $\mathcal{D}_{\alpha\beta}^b = \mathcal{D}_{\alpha\beta}$. The computation of $\mathcal{D}_{\alpha\beta}$
1007 and $\alpha_{T,\alpha\beta}^b$ is described in Section B.

A.2 Equation of state

Equations (A.1)-(A.4) are coupled with the Peng-Robinson (PR) **EoS** (Lopez-Echeverry et al., 2017)

$$p = \frac{R_u T \left(\sum_{\alpha=1}^N X_{\alpha} \right)}{(v_{PR} - b_{mix})} - \frac{a_{mix}}{(v_{PR}^2 + 2b_{mix}v_{PR} - b_{mix}^2)} \quad (\text{A.20})$$

from which T and p are obtained as an iterative solution which satisfies both values of ρ and of e , as obtained from the conservation equations (Okong'o et al., 2002). Here v_{PR} is the molar PR volume, and $v = v_{PR} + v_s$ where v_s is the volume shift introduced for improving the accuracy of the PR EoS at high p (Harstad et al., 1997); a_{mix} and b_{mix} are functions of T and X_i (see Appendix C). The v_s computation was described in detail elsewhere (Okong'o et al., 2002). In that study, a v_s correction was used to enhance the PR-EoS accuracy for those particular species and mixtures of species, whereas in the present study it was verified that random inputs to v_s for the minor (i.e. trace) species made no difference in the predictions, meaning that v_s correction is negligible for the minor species in the specific mixtures used here.

B Transport property models

The conservation Eqs. (A.1) - (A.4) are coupled with the PR EoS, Eq. (A.20).

The mixture physical viscosity, μ_{ph} , is computed following the Wilke method (Reid et al., 1987) described in Section B.1, and the physical mixture thermal conductivity, λ_{ph} , is computed using the Wassiljewa-Mason-Saxena method (Poling et al., 2001) according to the formulas of Section B.2. To complete the description of the models for computing transport properties, the formulations to calculate the binary mass diffusion coefficients and the binary thermal diffusion factors are presented in Sections B.3 and B.4, respectively.

B.1 Mixture viscosity

The computation of individual species viscosity, μ_{α} , was described in lengthy detail in Morellina et al. (2020) and thus will not be reproduced here. The model for computing the mixture viscosity, μ , has also been provided in Morel-

lina et al. (2020) but is provided here for completeness.

$$\mu = \sum_{\alpha=1}^N X_{\alpha} \omega_{\alpha}^M \mu_{\alpha} \quad (\text{B.1})$$

is computed using the Wilke method (Reid et al., 1987) where

$$(\omega_{\alpha}^M)^{-1} = \sum_{\beta=1}^N \phi_{\alpha\beta} X_{\beta} \quad (\text{B.2})$$

$$\phi_{\alpha\beta} = \frac{\left[1 + (\mu_{\alpha}/\mu_{\beta})^{1/2} (m_{\beta}/m_{\alpha})^{1/4}\right]^2}{[8(1 + m_{\alpha}/m_{\beta})]^{1/2}} \quad (\text{B.3})$$

in which ω_{α}^M are weighting factors (Reid et al., 1987).

B.2 Mixture thermal conductivity

The complete details of calculating the individual species viscosity, λ_{α} , were included in Morellina et al. (2020) and will not be duplicated here, for brevity. As explained in Morellina et al. (2020), once all λ_{α} are computed, the mixture molecular thermal conductivity is calculated following the Wassiljewa-Mason-Saxena method (Poling et al., 2001):

$$\lambda = \sum_{\alpha=1}^N X_{\alpha} \omega_{\alpha}^Q \lambda_{\alpha} \quad (\text{B.4})$$

where according to the assumption made by Reid et al. (1987),

$$\omega_{\alpha}^Q = \omega_{\alpha}^M. \quad (\text{B.5})$$

B.3 Binary mass diffusivities

Matrix elements $\mathcal{D}_{\alpha\gamma}^b$ are the building blocks of $\mathbb{D}_{\alpha\gamma}$ and basically of $D'_{\alpha\gamma}$. To compute $\mathcal{D}_{\alpha\gamma}^b = \mathcal{D}_{\alpha\gamma}$, we adopt the method of Harstad and Bellan, 2004b which gives (in cgs units)

$$n\mathcal{D}_{\alpha\gamma} = 2.81 \times 10^{-5} \frac{f_{D,\alpha\gamma}(T)}{r_D v_{c,\alpha\gamma}^{2/3}} \left[\left(\frac{1}{m_{\alpha}} + \frac{1}{m_{\gamma}} \right) T \right]^{1/2} \quad (\text{B.6})$$

where $f_{D,\alpha\gamma}(T)$ is generically defined for each matrix element as $f_D(T) \equiv (T_{red})^s$ with $\ln s = \sum_{\zeta=0}^5 a_{\zeta}^s (\ln T_{red})^{\zeta}$ where the a^s vector has elements $\{-0.84211, -0.32643, -0.10053, 0.07747, 0.0127, -0.00995\}$, and r_D is a constant $O(1)$ which provides an empirical adjustment for the specifics of the collisional interactions of a selected pair of species. $T_{red,\alpha\gamma} \equiv T/T_{c,\alpha\gamma}$ with $T_{c,\alpha\gamma}$; $v_{c,\alpha\gamma}$ is computed as in Section C.

B.4 Binary thermal diffusion factors

According to Harstad and Bellan (2004a)

$$\alpha_{T,\alpha\gamma}^b = \zeta_{\alpha\gamma} \frac{(m_{\alpha}\omega_{\gamma}^T - m_{\gamma}\omega_{\alpha}^T)}{(m_{\alpha} + m_{\gamma})\mathcal{D}_{\alpha\gamma}} \quad (\text{B.7})$$

$$\omega_{\alpha}^T = \frac{\omega_{\alpha}^Q \lambda_{\alpha}}{R_u n}, \quad \zeta_{\alpha\gamma} = \frac{6}{5} C_{\alpha\gamma}^* - 1 \quad (\text{B.8})$$

where ω_{α}^Q is computed from Eqs. (B.2) and (B.5), and $C_{\alpha\gamma}^*$ is given by Hirshfelder et al., 1964 and is function of a normalized temperature including the characteristic molecular interaction potential (Harstad and Bellan, 2004a).

C Equation of state details

Miscellaneous relationships relevant to the EoS are

$$a_{mix} = \sum_{\alpha} \sum_{\gamma} X_{\alpha} X_{\gamma} a_{\alpha\gamma}(T), \quad b_{mix} = \sum_{\alpha} X_{\alpha} b_{\alpha}, \quad (\text{C.1})$$

where indices do not follow the Einstein notation, and

$$a_{\alpha\gamma} = (1 - k'_{\alpha\gamma}) \sqrt{\alpha_{\alpha\alpha} \alpha_{\gamma\gamma}}, \quad (\text{C.2})$$

$$\alpha_{\alpha\alpha}(T) \equiv 0.457236 (R_u T_{c,\alpha})^2 \times \frac{[1 + c_{\alpha}(1 - \sqrt{T_{red,\alpha}})]^2}{p_{c,\alpha}}, \quad (\text{C.3})$$

$$c_{\alpha} = 0.37464 + 1.54226 \omega_{\alpha} - 0.26992 \omega_{\alpha}^2, \quad (\text{C.4})$$

1063 where $T_{red,\alpha} \equiv T/T_{c,\alpha}$, $T_{c,\alpha}$ is the critical temperature and ω_α is the acentric
 1064 factor. Also,

$$b_\alpha = 0.077796 \frac{R_u T_{c,\alpha}}{p_{c,\alpha}}, \quad (C.5)$$

$$T_{c,\alpha\gamma} = (1 - k_{\alpha\gamma}) \sqrt{T_{c,\alpha} T_{c,\gamma}} \text{ with } k_{\alpha\alpha} = 0, \quad (C.6)$$

$$v_{c,\alpha\gamma} = \frac{1}{8} \left(v_{c,\alpha}^{1/3} + v_{c,\gamma}^{1/3} \right)^3, \quad (C.7)$$

$$Z_{c,\alpha\gamma} = \frac{1}{2} (Z_{c,\alpha} + Z_{c,\gamma}), \quad (C.8)$$

$$p_{c,\alpha\gamma} = \frac{R_u T_{c,\alpha\gamma} Z_{c,\alpha\gamma}}{v_{c,\alpha\gamma}}, \quad (C.9)$$

1065 with $T_{red,\alpha\gamma} \equiv T/T_{c,\alpha\gamma}$, $Z_{c,\alpha}$ being the critical compressibility factor with the
 1066 compressibility factor defined as $Z = p/(\rho T R_u/m)$, $v_{c,\alpha}$ being the critical vol-
 1067 ume, and $p_{c,\alpha}$ being the critical pressure. $k_{\alpha\gamma}$ is an empirical mixing parameter.
 1068 The relationship between parameters $k_{\alpha\gamma}$ and $k'_{\alpha\gamma}$ is

$$(1 - k_{\alpha\gamma}) = (1 - k'_{\alpha\gamma}) \frac{(v_{c,\alpha} v_{c,\gamma})^{1/2}}{v_{c,\alpha\gamma}}. \quad (C.10)$$

1069 and for all pairs not in Table C.1, $k'_{\alpha\gamma} = 0$ is used.

Species 1	Species 2	k'
CO ₂	N ₂	-0.017
CO ₂	H ₂ O	0.12
CO ₂	H ₂ S	0.0974
N ₂	SO ₂	0.08
N ₂	H ₂ S	0.1767
H ₂ O	H ₂ S	0.04

Table C.1

Binary interaction parameters when the first species has a relatively low molar mass.
 Parameters not listed are set to be null. The reference is Knapp et al. (1982).

1070 D Models for the functional derivatives

1071 According to Masi et al. (2013), if one defines

$$C_{\beta\alpha} \equiv \frac{\delta Y_\beta}{\delta Y_\alpha}, \quad C_{\beta T} \equiv \frac{\delta Y_\beta}{\delta T}, \quad (\text{D.1})$$

$$C_{T\alpha} \equiv \frac{\delta T}{\delta Y_\alpha}, \quad (\text{D.2})$$

$$C_{p\alpha} \equiv \frac{\delta p}{\delta Y_\alpha}, \quad C_{pT} \equiv \frac{\delta p}{\delta T}, \quad (\text{D.3})$$

for a flow with turbulent characteristics, these quantities can be modeled as follows

$$C_{\beta\alpha} = \sum_{i=1}^{i=3} \left(\frac{\partial Y_\beta}{\partial x_i} \frac{\partial Y_\alpha}{\partial x_i} \right) / \sum_{i=1}^{i=3} \left(\frac{\partial Y_\alpha}{\partial x_i} \frac{\partial Y_\alpha}{\partial x_i} \right), \quad C_{\beta T} = \sum_{i=1}^{i=3} \left(\frac{\partial Y_\beta}{\partial x_i} \frac{\partial T}{\partial x_i} \right) / \sum_{i=1}^{i=3} \left(\frac{\partial T}{\partial x_i} \frac{\partial T}{\partial x_i} \right), \quad (\text{D.4})$$

$$C_{T\alpha} = \sum_{i=1}^{i=3} \left(\frac{\partial T}{\partial x_i} \frac{\partial Y_\alpha}{\partial x_i} \right) / \sum_{i=1}^{i=3} \left(\frac{\partial Y_\alpha}{\partial x_i} \frac{\partial Y_\alpha}{\partial x_i} \right), \quad (\text{D.5})$$

$$C_{p\alpha} = \sum_{i=1}^{i=3} \left(\frac{\partial p}{\partial x_i} \frac{\partial Y_\alpha}{\partial x_i} \right) / \sum_{i=1}^{i=3} \left(\frac{\partial Y_\alpha}{\partial x_i} \frac{\partial Y_\alpha}{\partial x_i} \right), \quad C_{pT} = \sum_{i=1}^{i=3} \left(\frac{\partial p}{\partial x_i} \frac{\partial T}{\partial x_i} \right) / \sum_{i=1}^{i=3} \left(\frac{\partial T}{\partial x_i} \frac{\partial T}{\partial x_i} \right). \quad (\text{D.6})$$

Not only does the model of equations (D.4)-(D.6) render the coefficients independent of directional variation, but it also avoids potential singularities occurring when there are very small gradients. Only some of the (D.4)-(D.6) relationships are independent, and only N coefficients out of the total $N \times N$ must be computed (without counting coefficients $C_{\alpha\alpha} = 1$).

References

- Alexakis, A, Biferale, L., 2018. Cascades and transitions in turbulent flows. Physics Reports, 767–769, 1–101.
- Almagro, A., Garcia-Villalba, M., Flores, O., 2017. A numerical study of a variable density low-speed turbulent mixing layer. J. Fluid Mech., 830, 569-601.
- Ando, H., Imamura, T., Tsuda, T., Tellmann, S., Pätzold, M., Häusler, B., 2015. Vertical wavenumber spectra of gravity waves in the Venus atmosphere obtained from Venus Express radio occultation data: Evidence for saturation. J. Atmos. Sci. 72, 2318-2329.
- Batchelor, G. K., 1999. An Introduction to Fluid Dynamics. Cambridge University Press.

- 1090 Bellan, J., 2017a. Direct numerical simulation of a high-pressure turbulent reacting
1091 temporal mixing layer. *Combust. Flame* 176, 245–262.
- 1092 Bellan, J., 2017b. Evaluation of mixture-fraction-based turbulent-reaction-rate
1093 model assumptions for high-pressure reactive flows, *Combust. Flame*, 179, 253–266.
- 1094 Bellan, J., 2020 Future challenges in the modelling and simulations of
1095 high-pressure flows, *Combustion Science and Technology*, 192(7), 1199–1218.
1096 doi.org/10.1080/00102202.2020.1719404
- 1097 Bierson, C.J. , Zhang, X., 2020. Chemical cycling in the Venusian atmosphere:
1098 A full photochemical model from the surface to 110 km. *J. G.R. Planets*
1099 doi.org/10.1029/2019JE006159
- 1100 Borghesi, G., Bellan, J., 2015. A priori and a posteriori investigations for developing
1101 large eddy simulations of multi-species turbulent mixing under high-pressure
1102 conditions, *Phys. Fluids* 27, 035117.
- 1103 Castiglioni, G., Bellan, J., 2018. On models for predicting thermodynamic regimes
1104 in high-pressure turbulent mixing and combustion of multispecies mixtures. *J. Fluid*
1105 *Mech.* 843, 536–574.
- 1106 Cordier, D., Bonhommeau, D.A., Port, S., Chevrier, V., Lebonnois, S., García-
1107 Sánchez, F., 2019. The physical origin of the Venus low atmosphere chemical
1108 gradient. *The Astrophysical Journal*, 880-82 (8pp).
- 1109 De Groot, S. R., Mazur, P. 1984 *Non-equilibrium Thermodynamics*. Dover.
- 1110 Duncan, J.B., Toor, H.L., 1962 . An experimental study of three component gas
1111 diffusion. *AIChE J.* 8 (1), 38–41.
- 1112 Ern, A., Giovangigli, V., 1998. Thermal diffusion effects in hydrogen–air and
1113 methane–air flames. *Combust. Theory Modelling* 2, 349–372.
- 1114 Gaitonde, D. V., Visbal, M.R., 1998. High-order schemes for Navier-Stokes
1115 equations: algorithm and implementation into FDL3DI. Air Force Research Lab
1116 Wright-Patterson AFB OH Air Vehicles Directorate AFRL-VA-WP-TR-1998-3060.
- 1117 Germano, M., Piomelli, U., Moin, P., Cabot, W. H., 1991. A dynamic subgrid-scale
1118 eddy viscosity model. *Phys. Fluids A.: Fluid Dynamics*, 3(7), 1760–1765.
- 1119 Giovangigli, V., Matuszewsky, L., Dupoirieux, F. 2011. Detailed modeling of planar
1120 transcritical H₂-O₂-N₂ flames. *Comb. Th. Mod.* 15, 141–182.
- 1121 Gnanaskandan, A., Bellan, J. 2020. Large Eddy Simulations of high pressure jets :
1122 Effect of subgrid scale modeling. Chapter 11, 461–481, AIAA Progress Series book
1123 titled *High Pressure Flows for Propulsion Applications* (Ed. J. Bellan).
- 1124 Goto, S., Kida, S., 1999. Passive scalar spectrum in isotropic turbulence: prediction
1125 by the Lagrangian direct-interaction approximation. *Phys. Fluids* 11 (7) 1936–1952.
- 1126 Gülcher, A. J. P., Gerya, T. V., Montési, L. G. J., Munch, J., 2020. Corona structures
1127 driven by plume–lithosphere interactions and evidence for ongoing plume activity
1128 on Venus. *Nature Geoscience* 13, 547–554.

- 1129 Hannoun, I. A., Fernando, H.J.S., List, E.J., 1988. Turbulence structure near a
1130 sharp density interface. *J. Fluid Mech.* 189, 189-209.
- 1131 Harstad, K., Miller, R. S., Bellan, J., 1997. Efficient High-Pressure State Equations,
1132 *A.I.Ch.E. J.*, 43(6), 1605-1610.
- 1133 Harstad, K.G., Bellan, J., 2004a. Mixing rules for multicomponent mixture mass
1134 diffusion coefficients and thermal diffusion factors. *J. Chem. Phys.* 120(12), 5664–
1135 5673.
- 1136 Harstad, K.G., Bellan, J. 2004b. High-pressure binary mass-diffusion coefficients for
1137 combustion applications. *Ind. & Eng. Chem. Res.* 43(2), 645–654.
- 1138 Harstad, K.G., Bellan, J., 2011. Computation of Laminar Premixed Flames Using
1139 Reduced Kinetics Based on Constituents and Species. *AIAA-2011-415*.
- 1140 Hirshfelder, J., Curtis, C., Bird, R., 1964. *Molecular Theory of Gases and Liquids*.
1141 John Wiley and Sons.
- 1142 Holton, J. R. 2004. *An Introduction to Dynamic Meteorology*. Academic Press. p.
1143 64. ISBN 0-12-354015-1.
- 1144 Izakov, N. N. 2010. Dissipation of buoyancy waves and turbulence in the atmosphere
1145 of Venus Solar System Research, 44, 475-486.
- 1146 Jacobson, N. S., Kulis, M., Radoman-Shaw, B., Harvey, R., Myers, D.L., Schaefer,
1147 L., Fegley, Jr., B., 2017. Thermodynamic Constraints in the Lower Atmosphere of
1148 Venus. *ACS Earth and Space Chem.* 1, 422-430.
- 1149 Johnson, N. M., de Oliveira, M.R.R., 2019. Venus atmospheric composition in situ
1150 data: a compilation. *Earth and Space Science* 6, 1299–1318.
- 1151 Kawai, S., 2019. Heated transcritical and unheated non-transcritical turbulent
1152 boundary layers at supercritical pressures. *J. Fluid Mech.*, 865, 563-601.
- 1153 Keizer, J., 1987. *Statistical Thermodynamics of Nonequilibrium Processes*.
1154 Springer-Verlag, New York.
- 1155 Kit, E., C. Hocut, D. Liberzon, Fernando, H. J. S 2017. Fine-scale turbulent bursts
1156 in stable atmospheric boundary layer in complex terrain. *J. Fluid Mech.* 833, 745-
1157 772.
- 1158 Knapp, H., Döring, R., Oelrich, L., Plöcker, U., Prausnitz, J.M., 1982. Vapor-liquid
1159 Equilibria for Mixtures of Low Boiling Substances, vol VI. Dechema.
- 1160 Kremic, T., Nakley, L., Vento, D., Balcerski, J., Kulis, M. J., Jacobson, N. S. Costa,
1161 G. C. C. 2016. Glem Extreme Environments Rig (GEER) for planetary science, 47th
1162 Lunar and Planetary Science Conference, paper 2146
- 1163 Lambert, J., Morookian, J., Roberts, T., Polk, J., Smrekar, S., Clegg, S. M., Wiens,
1164 R. C., Dyar, M. D., Treiman A., 2010. Standoff LIBS and Raman Spectroscopy
1165 under Venus Conditions, 41st Lunar and Planetary Science Conference, paper 2608

- 1166 Lebonnois, S., Schubert, G., 2017. The deep atmosphere of Venus and the possible
1167 role of density-driven separation of CO₂ and N₂. *Nat. Geosci.* 10, 473-477.
- 1168 Lebonnois, S., Schubert, G., Forget, F., Spiga, A., 2018. Planetary boundary layer
1169 and slope winds on Venus. *Icarus*, 314, 149-158.
- 1170 Lebonnois, S., Schubert, G., Kremic, T., Nakley, L., Phillips, K., Bellan, J.,
1171 Cordier, D., 2020. An experimental study of the mixing of CO₂ and N₂
1172 under conditions found at the surface of Venus. *Icarus*, 338, 113550, 2020
1173 doi.org/10.1016/j.icarus.2019.113550
- 1174 Lele, S.K., 1992. Compact finite difference schemes with spectral-like resolution.
1175 *Journal of computational physics* 103(1), 16–42.
- 1176 Limaye, S. S., Grassi, D., Mahieux, A., Migliorini, A., Tellmann, S., Titov, D.,
1177 2018. Venus Atmospheric Thermal Structure and Radiative Balance. *Space Science*
1178 *Reviews* 214 (5) doi: 10.1007/s11214-018-0525-2.
- 1179 Lopez-Echeverry, J. S., Reif-Ackerman, S., Aruajo-Lopez, E., 2017. Peng-Robinson
1180 equation of state: 40 years through cubics. *Fluid Phase Eq.* 447, 39-71.
- 1181 Ma, P. C., Yang, X. I. A., Ihme, M., 2018. Structure of Wall-bounded Flows at
1182 Transcritical Conditions. *Physical Review Fluids*, 3, 034609.
- 1183 Masi, E., Bellan, J., Harstad, K.G., Okong'o, N.A., 2013. Multi-species
1184 turbulent mixing under supercritical-pressure conditions: modelling, direct numerical
1185 simulation and analysis revealing species spinodal decomposition. *J. Fluid Mech.* 721,
1186 578-626.
- 1187 Mayer, W., Telaar, J., Branam, R., Schneider, G. and Hussong, J., 2003. Raman
1188 measurements of cryogenic injection at supercritical pressure. *Heat and Mass*
1189 *Transfer*, 39(8-9), 709-719.
- 1190 Miller, R. S., Harstad, K., Bellan, J., 2001. Direct Numerical Simulations of
1191 Supercritical Fluid Mixing Layers Applied to Heptane – Nitrogen, *J. Fluid Mech.*,
1192 436, 1-39.
- 1193 Moin, P., Mahesh, K., 1998. Direct Numerical Simulation: A Tool in Turbulence
1194 Research. *Annu. Rev. Fluid Mech.* 30, 539-578.
- 1195 Morellina, S., Bellan, J., Cutts, J., 2020. Global thermodynamic, transport-property
1196 and dynamic characteristics of the Venus lower atmosphere below the cloud layer.
1197 *Icarus* 350, 113761, 2020 doi.org/10.1016/j.icarus.2020.113761
- 1198 Moser, R., Rogers, M., 1991. Mixing transition and the cascade to small scales in a
1199 plane mixing layer. *Phys. Fluids A* 3(5), 1128–1134.
- 1200 Moser, R. D., Rogers, M. M. 1993. The three-dimensional evolution of a plane mixing
1201 layer: pairing and transition to turbulence. *J. Fluid Mech.* 247, 275-320.
- 1202 Muller, S.M., Scheerer, D., 1991. A method to parallelize tridiagonal solvers. *Parallel*
1203 *Computing* 17, 181–188.

- Okong'o, N., Bellan, J., 2002. Consistent Boundary Conditions for Multicomponent Real Gas Mixtures Based on Characteristic Waves, *Journal of Computational Physics* 176(2), 330-344.
- Okong'o, N., Harstad, K., Bellan, J., 2002. Direct numerical simulations of O_2/H_2 temporal mixing layers under supercritical conditions. *AIAA J.* 40(5), 914-926.
- Okong'o, N., Bellan, J. 2004. Perturbation and initial Reynolds number effects on transition attainment of supercritical mixing layers, *Computers and Fluids*, 33(8), 1023-1046.
- Onsager, L., 1931. Reciprocal Relations in Irreversible Processes. I. *Physical Review. American Physical Society (APS)*. 37 (4), 405-426. doi:10.1103/physrev.37.405
- Oswald, M., Schik, A., 1999. Supercritical nitrogen free jet investigated by spontaneous Raman scattering. *Exps. Fluids* 27, 497-506.
- Oswald, M., Schik, A., Klar, M., Mayer, W., 1999. Investigation of coaxial LN_2/GH_2 -injection at supercritical pressure by spontaneous Raman scattering. *AIAA Paper* 99-2887.
- Pantano, C., Sarkar, S., 2002. A study of compressibility effects in the high-speed turbulent shear layer using direct simulation. *J. Fluid Mech.* 451, 329-371.
- Papamoshou, D., Roshko, A., 1988. The compressible turbulent shear layer: an experimental study, *Journal of Fluid Mechanics*, 197, 453-477.
- Polikhov, S., Segal, C., 2007. Subcritical to supercritical jet mixing. *AIAA Paper* 2007-0569.
- Poling, B. E., Prausnitz, J. M., O'Connell, J.P., 2001. *The Properties of Gases and Liquids*. McGraw-Hill.
- Rapp, B. E., 2017. *Fluids, Microfluidics: Modelling, Mechanics and Mathematics*, Chapter 9., 243-263., Elsevier
- Reid, R.C., Prausnitz, J.M., Poling, B.E., 1987. *The Properties of Gases and Liquids*. 4th edn. McGraw-Hill.
- Selle, L.C., Okong'o, N.A., Bellan, J., Harstad, K.G., 2007. Modeling of subgrid scale phenomena in supercritical transitional mixing layers: an a priori study, *J. Fluid Mech.* 593, 57-91.
- Svedhem, H.S., Titov, D.V., Taylor, F.V., Witasse, O., 2007. Venus as a more Earth-like planet. *Nature* 450 (7170): 629-632.
- Taşkinoglu, E.S., Bellan, J., 2010. A posteriori study using a DNS database describing fluid disintegration and binary-species mixing under supercritical pressure: Heptane and Nitrogen, *J. Fluid Mech.*, 645, 211-254.
- Taşkinoglu, E.S., Bellan, J., 2011. Subgrid scale models and Large Eddy Simulation of oxygen stream disintegration and mixing with a hydrogen or helium stream at supercritical pressure, *J. Fluid Mech.*, 679, 156-193.

- 1243 Taylor, R., Krishna, R., 1993. Multicomponent Mass Transfer. Wiley Series in
1244 Chemical Engineering. Wiley.
- 1245 van Duin, Adri C. T., Dasgupta, S., Lorant, F., Goddard, W. A., 2001. ReaxFF:
1246 A reactive force field for hydrocarbons, Journal of Physical Chemistry A, 105 (41):
1247 9396–9409. doi:10.1021/jp004368u
- 1248 von Kármán, Th. 1930 Mechanische Ähnlichkeit und Turbulenz, Nachrichten von
1249 der Gesellschaft der Wissenschaften zu Göttingen, Fachgruppe 1 (Mathematik), 5,
1250 58–76.
- 1251 Wang, G., Yang, F., Wu, K., Ma, Y., Peng, C., Liu, T., Wang, L.-P., 2021 Estimation
1252 of the dissipation rate of turbulent kinetic energy: A review. Chem. Eng. Sci., 229,
1253 116133.
- 1254 Yamamoto, M., 2011 Microscale simulations of Venus convective adjustment and
1255 mixing near the surface: Thermal and material transport processes, Icarus, 211(2),
1256 993-1006.
- 1257 Zhiyin, Y., 2015 Large-eddy simulation: Past, present and the future Chinese
1258 Journal of Aeronautics, 28(1), 11-24.

Highlights

- Used a parameter-free model to study portions of the Venus lower atmosphere
- The model describes compressible high-pressure turbulent species mixing
- Simulations are performed in temporal mixing-layer small domains at three altitudes
- The initial composition represents either large or small species stratification
- The results do not support a literature-existing species-separation hypothesis