

## Influence of solubility effects and diffusion coefficient models on the drop vaporization rate at high pressure

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### Introduction

In modern rocket engines, gas turbines and internal combustion engines, fluids are injected in a high pressures atmosphere at fuel states either close to or exceeding the critical point. Under these conditions, fuel droplets may experience a thermodynamic transition into a supercritical state during thier lifetime. Comprehensive reviews on the subject can be found in Givler and Abraham [1] Yang [2] and in Bellan [3]. Recently, Crua et al. [4] introduced an empirical regime map to predict the transition of microscopic droplets from classical evaporation to the diffusive mixing regime. In the present work, we analyze the influence of solubility effects and of diffusion coefficient models on the droplet vaporisation rate.

### Influence of diffusion coefficient models

Most diffusion models used in droplet evaporation studies are based on an expression derived from the Chapman-Enskog or the hard-spheres theory [5]. At low and moderate pressures, the binary diffusion coefficient ( $\mathcal{D}$ ) is inversely proportional to pressure (or density) variations and directly proportional to temperature with exponents varying in the range  $1.5 < n < 1.75$ . This dependency can be found in the correlations of Wilke & Lee (WL) and Fuller et al. (FSG) [5] and it basically implies that, for a given temperature, the product  $\rho\mathcal{D}$  is constant. At high pressure, the product ( $\rho\mathcal{D}$ ) is no longer constant but decreases with increasing density, due to gas non-idealities and mixture composition effects. Several approaches have been proposed to model these more complex dependencies. Lito et al. [6] introduced a correlation based on Chapman-Enskog theory, especially tailored for application to supercritical fluid extraction. Alternatively, ideal diffusion coefficient models are corrected by including empirical factors that include an explicit density and composition dependence. In this context, Riazi et al. [7] introduced a density-dependent and a viscosity-dependent correction factors. Harstad and Bellan [8], instead, employed a kinetic theory expression similar to Wilke & Lee. The correlation is then corrected by two empirical factors that have been fitted to experimental data. Finally, Krishna and van Baten [9] proposed a thermodynamic correction factor  $\Gamma$  that results in a reduction of the effective diffusion coefficient close to the critical point or close to the binodal curve. According to [9], the binary diffusion coefficient can be expressed as

$$\mathcal{D} = \mathcal{D}_{id} Z \Gamma \quad (1)$$

where  $Z$  is the compressibility that describes the deviation of a real gas from ideal gas behavior. The correction factor  $\Gamma$  is defined as

$$\Gamma = 1 + x_g \partial \ln \phi_g / \partial x_g \quad (2)$$

where  $x_g$  is the gas mole fraction and  $\phi_g$  represents the gas fugacity coefficient. An overview of the different models is provided in Table 1.

### Influence of solubility effects

For a quantitative description of solubility effects, one can introduce the so-called enhancement factor  $f_e$ . The latter represents the increase in the vapour saturation pressure due to the solubility of an inert gas in the liquid phase and it is defined as

$$f_e = y_{v,eq} p / p_{v,sat} \quad (3)$$

**Table 1.** Overview of binary diffusion coefficient models and relative correction factors.  $\Omega(p)$  is the collision integral and  $E_d$  is a mixture specific energy parameter fitted to experimental data,  $\omega(\rho)$  is a reduced density dependent high-pressure correction factor,  $p_c$  is the critical pressure and  $F$  is a correction factor.

	Ideal gas	$p$ -dependence	$T$ -dependence	$x$ -dependence
Wilke-Lee [5]	Yes	$p^{-1}$	$T^{1.5}, \Omega(p)$	none
Fuller et al. (FSG) [5]	Yes	$p^{-1}$	$T^{1.75}$	none
Riazi et al. [7]	No	$\rho(p)$	$\mu(T)/\mu_{id}(T), \mathcal{D}_{id}(T), \rho_{id}(T)/\rho(T)$	$\mu(x)/\mu_{id}(x), p_c(x), \rho_{id}(x)/\rho(x)$
Harstad-Bellan [8]	No	$\rho(p)$	$T^{0.5}, \rho(T), \Omega(p)$	$\rho(x), \omega(\rho)$
Lito et al. [6]	No	$\rho(p)$	$T, \rho(T), \exp[(-E_d)/(R_g T)]$	$\rho(x), F(\rho)$
Z-corr. FSG [9]	No	$p^{-1}, Z(p)$	$T^{1.75}, Z(T)$	$Z(x)$
$\Gamma/Z$ -corr. FSG [9]	No	$p^{-1}, Z(p)$	$T^{1.75}, Z(T)$	$Z(x), \Gamma(x)$

where  $y_{v,eq}$  represent the equilibrium vapor mass fraction at the droplet interface and  $p_{v,sat}$  the saturation pressure of the pure vapor. The enhancement factor takes into account the following effects, namely non-idealities in the liquid and gaseous phase, inert gas mole fraction dissolved in the liquid phase and the so-called Poynting effect. The latter represents the sorrection to the equilibrium mass fraction  $y_{v,eq}$  due to the high-pressure conditions. Taking into account that the driving force for phase transition is the difference in chemical potential, the Gibbs-Duhem relation yields:

$$\Delta\mu = v(\Delta p_v) - s\Delta T \quad (4)$$

where  $\Delta p_v = (p_{v,s} - p_{v,\infty})$ . Being  $p_{v,s} = y_{v,eq} p = f_e p_{v,sat}$ , it follows that solubility effects may lead to a significant increase of the rate of vaporization, when  $f_e$  is larger than one. Note that the above definition of the enhancement factor relies on a binary fluid phase-equilibrium calculation. Basically, for a given ambient pressure and temperature, it assumes that the inert gas dissolves instantaneously in the liquid drop. In reality, the actual vapor mass fraction ( $y_{v,eff} \neq y_{v,eq}$ ) depends upon the rate of inert gas diffusion in the liquid phase. Given the uncertainty in the modelling of binary diffusion coefficients in compressible liquids, no accurate and reliable estimate of  $y_{v,eff}$  can be currently obtained.

## Results and Discussion

The present section is organized as follows. First, the accuracy of the different binary diffusion coefficient models - listed in Table 1 - is analyzed by including a direct comparison with the available experimental data. Second, the influence of binary diffusion coefficient models on solubility effects and consequently on the droplet vaporization rate is discussed. Third the possible evolution path of the droplet state is analyzed from a thermodynamic point of view.

As can be seen in Figure 1(a), the pressure dependence is well described over a large range of pressure by all models considered. Deviations from the ideal gas (alias  $p^{-1}$ ) trend are observed only at chamber pressures as high as 800-1000 bar. Note, in addition, that  $\Gamma$ -corrected  $\mathcal{D}_{id}$ -models are as accurate as the Lito et al.'s model [6], developed specifically for supercritical fluids. A good agreement throughout the entire pressure range is provided only by the Harstad & Bellan correlation [8], which is fitted to the experimental data. Larger discrepancies are observed when considering the temperature dependence. As shown in Figure 1(b), ideal models (e.g. Wilke/Lee or Fuller et al.) greatly overestimate the experimental values for the binary diffusion coefficient close to the critical mixture temperature. At the same time, the introduction of the  $\Gamma$ -correction to  $\mathcal{D}_{id}$ -models results in a considerable improvement in the predictions, which is comparable in accuracy to the Lito et al. correlation, developed specifically for high pressure conditions.

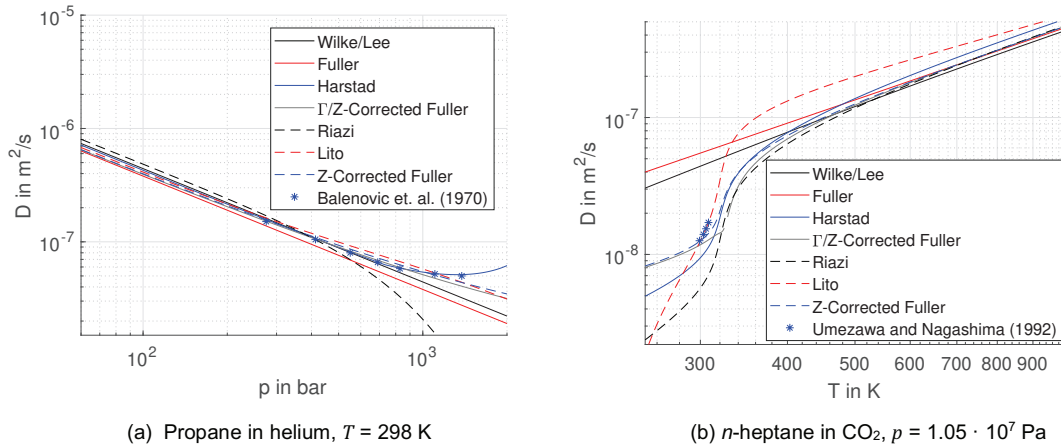


Figure 1. Pressure and temperature dependence of different binary diffusion coefficient models and comparison with experiments.

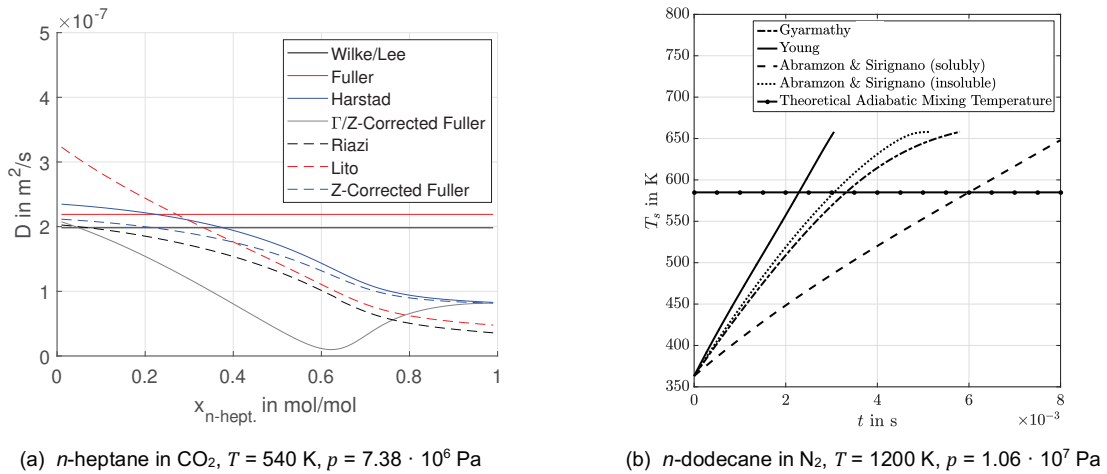


Figure 2. Concentration dependence of different binary diffusion coefficient models and influence on the droplet evaporation rate. Initial droplet temperature:  $363 \text{ K}$

Concerning the dependence on mixture composition,  $D_{id}$ -models are independent upon the inert gas concentration. All other non-ideal models show a similar trend in the gaseous region (i.e.  $x_{n\text{-hept}} < 0.63$ ), dominated by a strong density dependency. At the critical mixture composition (roughly  $x_{n\text{-hept}} = 0.63$ ), only the  $\Gamma/Z$ -corrected model exhibits a minimum. Large discrepancies in models' predictions are, instead, observed in the liquid-like region ( $x_{n\text{-hept}} > 0.63$ ), where the use of gas-derived corrections is not recommended. Non-ideal liquid diffusion models or empirical correlations should be preferred in the liquid-like region. This uncertainty in the estimation of the binary diffusion coefficient in the liquid droplet hampers the correct estimation of the actual vapor mass fraction ( $y_{v,eff}$ ) at the droplet surface. As explained in the previous section, this leads to an inaccurate estimation of the vapor pressure at the droplet surface and ultimately to an erroneous evaluation of the droplet vaporization rate. The importance of solubility effect is shown in Figure 2(b) for two limiting cases, namely zero and complete solubility of inert gas. As can be seen, the droplet lifetime is almost doubled, when solubility effects are encompassed under the assumption of instantaneous relaxation to a state of binary fluid phase-equilibrium (i.e.  $p_{v,s} = y_{v,eq} p$ ), as shown by the simulations with the Abramzon and Sirignano evaporation model. In reality, the effective vapor mass fraction ( $y_{v,eff}$ ) is lower than the equilibrium vapor mass fraction ( $y_{v,eq}$ ) due to the finite inert gas diffusion rate into the liquid droplet. Consequently, the actual evaporation rate will be intermediate among the due limiting cases, considered in Figure 2(b). Given the uncertainty in the modelling of binary diffusion coefficients in compressible liquids, no accurate and reliable estimate of  $y_{v,eff}$  can be currently obtained, leading to high uncertainties in the modelling of droplet evaporation at high pressure conditions.

As final remark, we would like to point out that the evaporation process has an important influence on the thermodynamic evolution of the liquid droplet. Indeed, the progression of the droplet temperature is controlled by three energetic contributions according to

$$m_d c_{p,l} \frac{dT}{dt} = -\dot{E}_g - \dot{M}L - \dot{M}h_{vs} \quad (5)$$

where  $\dot{E}_g$  represents the energy transfer from the gaseous region,  $\dot{M}L$  and  $\dot{M}h_{vs}$  the droplet cooling rate due to evaporation. Consequently, for low volatile fluids and high energy transfer rates from the gas phase, the drop gradually heats up to the critical mixing temperature, thus causing the disintegration of the immiscible interface due to the vanishing of surface tension and the transition to the dense-fluid mixing regime. This situation is depicted in Figure 3(a). The opposite occurs for high volatile fluids and low energy transfer from the gas phase, as shown in Figure 3(b). In this case, the drop slowly relaxes towards its equilibrium temperature and the mixture formation is controlled by the evaporation process and not by dense gas mixing.

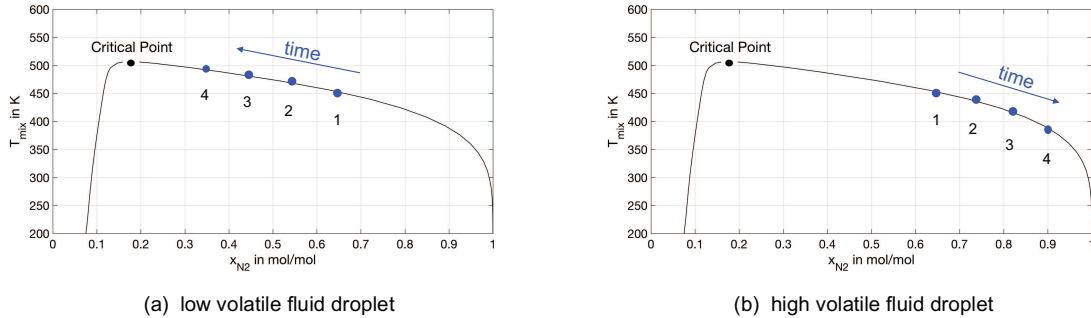


Figure 3. Possible evolution paths for an evaporating droplet: (a) high volatile fluids and (b) low volatile fluids.

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