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Reflectivity of diffuse, transcritical interfaces

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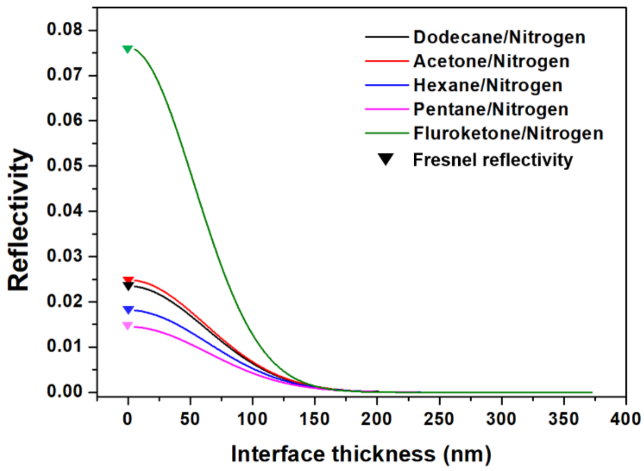
Abstract In this letter, we evaluate evidence for interface scattering that can occur even when the interface is assumed to have broken down in a supercritical jet. To evaluate this phenomenon, we report estimates of the optical reflectivity for a diffuse, transcritical interface, including various liquids of current interest. We rely upon prior work to explain the phenomenon and to estimate how strong it is for the cases of interest to the community.

Graphical Abstract



1 Introduction

Interest in transcritical fuel injection has increased recently, owing to the fact that the combustion chambers in modern engines operate at high pressure and temperature for improved efficiency. Some fuels could potentially be above their critical points if injected into such an environment. If a liquid becomes supercritical, the surface tension goes to zero (in addition to other changes in physical properties). If surface tension disappears during injection, what was a spray will transition into a dense gas jet. The dynamics of fuel/air mixture preparation would change significantly in such a case. These changes are established at equilibrium, however, and the question of how much time is required to achieve equilibrium has not been fully settled.

Recent work, experimental and theoretical, has been reviewed extensively in the book edited by Bellan (2021), with chapters contributed by many members of the research community.

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We have recently conducted experiments on a laminar jet of pure liquid (fluoroketone during initial experiments) injected into high pressure and temperature nitrogen. We have generated planar laser induced fluorescence (PLIF) images of the jet under various thermodynamic conditions.

The sheet of laser light for PLIF (at 355 nm for fluoroketone) will also scatter elastically from an intact liquid interface. Scattering is often thought to occur when the interface is effectively infinitely thin, as established by surface tension, via Fresnel reflection. Loss of surface tension would then result in loss of interface scattering. In our work, the laser sheet scattering signal was used to detect when the interface was strong, when it was weakening, and when it had disappeared. For the most part that scheme is successful.

We are not the only group to use elastic scattering to detect interface strength. To quantify transcritical phenomena, for example, a German consortium has been studying drops and jets in a high pressure and temperature chamber [see e.g. Chapter 2 in Bellan (2021) for a review of their work]. They have studied a number of fluids released into high pressure and temperature nitrogen. This group has combined shadowgraphy and interface back-scattering, with the same goal to observe interface breakdown. They call the technique “front-lighted shadowgraphy”. In a more recent publication by the same group, Gerber et al. (2021) employed planar

Mie scattering at 90°. They discuss the scattered light signal produced by this technique, mentioning a weakening of the signal as conditions approach and then exceed the critical point.

Because our subcritical jets were not optically thick, the laser sheet entered and was reflected around inside the liquid column before exiting towards the camera. The camera collected image signatures of randomly varying caustics for that reason. These caustics were often similar in appearance to the signal generated during Interferometric Laser Imaging Droplet Sizing (ILIDS, Ragucci et al., 1990). In ILIDS, scattering from the input face interferes with the first internal light to exit a drop (it is internally reflected once from the opposite surface of the drop and then refracted as it leaves the liquid and propagates towards the camera), generating an obvious fringe pattern which is a function of drop size. Thus, jet-induced caustics contain evidence of an intact interface. When surface tension was present, the jet was in the Rayleigh breakup regime, and small wave structures were developed across the interface and these structures located the strongest caustics.

The impetus for this Letter arose when the injected fluid was supercritical inside the nozzle, and the chamber was also operating under supercritical conditions for the fluoroketone/nitrogen mixtures (based on vapor/liquid equilibrium calculations). On average, we recorded no interfacial elastic scattering signal under supercritical conditions, which was expected. Very infrequently, however, a random caustic would appear momentarily. It always appeared close to the nozzle exit where shear-based wave structures existed (as observed in PLIF images). An example caustic under supercritical conditions is contained in Figure 1.

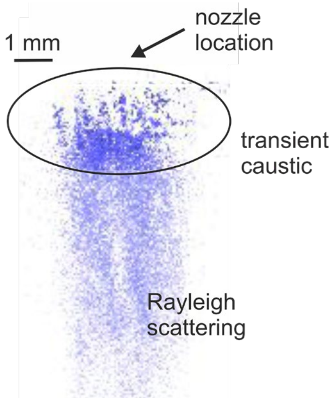

Figure 1. Transient image of elastic scattering from a laminar, supercritical jet of fluoroketone. Under normal circumstances one would expect to see only Rayleigh scattering. The caustic is recognizable by an interference pattern, similar to the signal produced by ILIDS. Note that under supercritical conditions, reflectivity is thought to be 10^{-7} of the reflectivity under subcritical conditions (Huang and Webb, 1969), which is why the signal is weak.

Our laser sheet scattering experiments indicate strong Rayleigh scattering from a supercritical (i.e. very dense) jet, but the caustics were clearly caused by some other phenomenon. We hypothesized that thin density gradients might be generated randomly by the shear-based wave structures; they could potentially generate some thin-interface reflectivity, and that could be the source of the momentary caustics. The same phenomenon could potentially be observed in other, related experiments so an investigation was warranted.

Our goal in this work was two-fold. The first goal was to test this hypothesis. As such, a highly accurate determination of reflectivity is unnecessary; trends can confirm the hypothesis. The second goal was to alert the community to the possibility that reflectivity may exist even when an interface has broken down.

2. Prior work

In 1965, Gilmer et al. used a treatment of electron penetration into a potential barrier by Eckart (1930) to develop a theory for the reflectivity of a diffuse index gradient profile. The theory was used in conjunction with backscattering experiments. In their initial work, they studied a binary system of cyclohexane and methanol in a heated high pressure cell. They illuminated the horizontal fluid interface under nearly critical conditions, at normal incidence, using a mercury arc lamp, and then detected the reflected light. They measured reflectivity at five wavelengths using bandpass filters in front of the mercury lamp as they varied the cell thermodynamic conditions, because their theory depends upon the optical wavelength. The multi-wavelength approach added fidelity to the measurements. Unfortunately, they were unable to measure reflectivity as they neared the critical point in this first experiment.

Gilmer and co-workers used Gradient Theory (van der Waals, 1893, and Cahn and Hilliard, 1958) for the spatial dependence of the fluid density normal to the interface, and assumed that the index is linearly proportional to density. Their model was able to reproduce Fresnel reflection values for an infinitely thin interface, and reflectivity dropped as the interface grew in thickness. The results at the five wavelengths were consistent with each other. The approach was proposed as a means to measure the thickness of the interface, and by using their reflectivity measurements Gilmer et al. estimated a thickness on the order of 100 nm.

In subsequent work, the same group (Huang and Webb, 1969) evaluated various models for the density distribution at the interface using the same model for reflectivity. They compared the results to similar mercury lamp experiments on the same binary mixture, but the setup had been substantially improved. This allowed them to more closely approach the critical point, but as they mention, reflectivity could be reduced by a factor of 10^{-7} going from fully subcritical to fully supercritical. This dynamic range presented a serious challenge.

Meunier and Langevin (1982) revisited the issue of density profiles, discussing the fact that chemical-potential-based models ignore the degradation of reflectivity based on thermal fluctuations. They proposed a modified reflectivity model that would take into account both processes (density gradient and thermal fluctuation). Unfortunately, the thermal fluctuation model required knowledge of the correlation length in the interface, and it was unknown.

3. Modelling reflectivity in recent experiments

In the work described here, we applied the reflectivity models listed in Huang and Webb (1969) to evaluate our hypothesis. The equations are based on various models for the density distribution in the interface, including: a linear model, exponential model, hyperbolic tangent model, and error function model. These profiles were folded into the reflectivity equation which was based upon the original work by Eckart (1930), to generate four simplified models:

$$R = R_F (\sin kL / kL)^2 \tag{1}$$

$$R = R_F [1/(1+k^2L^2)]^2 \tag{2}$$

$$R = R_F [\pi kL / 2\sinh(\pi kL/2)]^2 \tag{3}$$

$$R = R_F \exp(-2k^2L^2/\pi) \tag{4}$$

where R_F is the Fresnel reflectivity (P-polarization case), and k is the average wave vector of light in the interfacial region. L is the thickness of the interface. R_F and k are given by:

$$R_F(P\text{-polarization}) = \left[\frac{n_1 \cos\theta_2 - n_2 \cos\theta_1}{n_1 \cos\theta_2 + n_2 \cos\theta_1}\right]^2 \tag{5}$$

$$k = (n_1 + n_2)\pi/\lambda \tag{6}$$

where n_1 and n_2 are the refractive indices of the materials in the core and at the edge of the interface respectively. These values were inferred here by reference to the density profiles published by Dahms et al. (2015) (including a 363 K liquid phase injected into 900 K, 60 bar nitrogen). The angles θ_1 and θ_2 are for incidence and refraction, and λ is the wavelength of incident light (532nm light is adopted here).

Similar to prior work, we assume the refractive index depends linearly on the mass density. In the optical regime, the index is also temperature dependent via temperature dependence of the molecular dipole moments, but it the case under consideration it is a lesser effect. Index is also dependent on the composition, but in this binary mixture the fluoroketone index dominates. The reflectivity calculation results are shown in Figure 2.

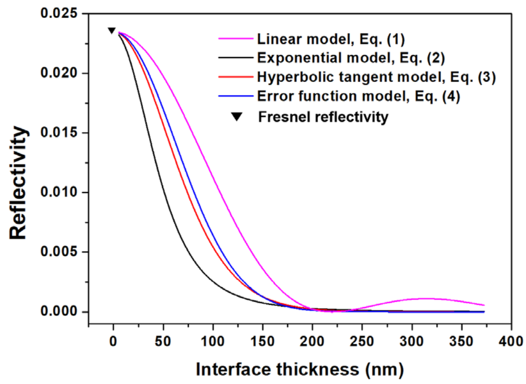

Figure 2. Normal incidence reflectivity of various interfaces (Dodecane/nitrogen mixture).

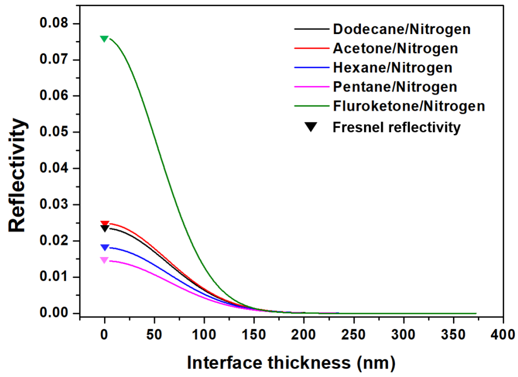

Figure 3. Normal incidence reflectivity for various mixtures using the error function model for the density distribution.

Next, various mixtures (acetone/nitrogen, hexane/nitrogen, pentane/nitrogen, and fluroketone/nitrogen) were calculated assuming the same conditions reported by Dahms et al. (2015). Both NIST REFPROP (Lemmon et al. 2018) and FluidProp (Colonna et al. 2014) were used to calculate densities. The error function model (equation 4) was used to calculate reflectivity for the cases shown in Figure 3. Our goal was to infer the effect of changes in refractive index for the various fluid mixtures of interest. We assumed similar density profiles for each curve, which is why the profiles are similar in shape for all fluids considered.

4. Discussion

The values of reflectivity presented in Figure 2 clearly support our hypothesis that specific fluid dynamics can generate intermittent, thin density profiles with a finite reflectivity, even when the fluid is supercritical. While this finding does not negate the value of using average observations of scattering to identify a weakened interface, one should be aware that this phenomenon can occur.

5. Future possibilities

The early researchers in this field were required to model the interface density distribution and the thermal fluctuations. Moreover, while they were very careful experimentalists, generating impressive results with limited equipment, modern equipment would significantly improve capabilities.

For more accurate reflectivity modelling, numerical predictions of the interfacial density profile (see e.g. the associated chapters in Bellan, 2021) could be used. Molecular dynamics modelling could provide a coherence length, for use in the scattering theory. For high fidelity, models for refractive index including composition and temperature could be applied. With these more accurate model results in hand, a more accurate reflectivity theory could be numerically integrated to provide a higher fidelity analysis of the measurements.

For experiments, a modern supercontinuum laser could illuminate the surface, and reflection could be monitored as a function of many wavelengths simultaneously. For low reflectivity measurements, averaging or phase sensitive detection could be used, generating signals even at low reflectance (note that we did detect intermittent interface scattering even under supercritical conditions, albeit weakly, within an 8 ns pulse).

It should be noted that this technique was developed for interfaces at equilibrium. It would develop significant uncertainties in a jet, for example, where thermodynamic equilibrium has not been reached. A properly designed experiment, however, could create the necessary conditions.

6. Conclusions

We have used a model originating in 1930 to support a hypothesis based on observations of intermittent scattering under supercritical conditions. We report the outcome here because it can have an impact on scattering measurements in transcritical flows going forward. Figure 3 indicates that all fluids of interest can undergo this process, although it would be less noticeable with hydrocarbon fuels. These observations could also potentially lead to the re-development of a useful diagnostic for these interfaces.

Declarations

Ethics approval and consent to participate

Not applicable

Consent for publication

Not applicable

Availability of data and materials

The relevant data and materials are presented in this Letter.

Competing interests

The authors have no competing interests to declare that are relevant to the content of this article.

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Authors' contributions

Dr Yang helped the literature review and developed the numerical models. He generated the plots of results (Figures 2 and 3).

Mr Kasapis set up the experiment and acquired the image in Figure 1.

Prof Linne was the leader of the group, he generated the hypothesis, did much of the literature review, and wrote much of the text.

Acknowledgements

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