Studying Near-Critical and Super-Critical Fluids in Reduced Gravity

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Critical and supercritical fluids have a variety of applications, from use as machine lubricants in high pressure or high temperature environments to the manufacturing of materials such as aerogel. The optical properties of fluids undergo rapid changes near the critical point resulting in a rapid increase in turbidity known as critical opalescence. These optical changes can be used to probe the universality of critical behavior. As a fluid approaches the critical point, the compressibility rapidly increases. In a gravitational field, this increase in compressibility leads to near-critical fluids stratifying by phase and density, making it difficult to observe the optical properties of the fluid. Therefore it becomes necessary to study critical fluids in a reduced gravity environment. The HYdrogen Levitation DEvice (HYLDE) apparatus at CEA-Grenoble was used to study cells filled with oxygen and hydrogen suspended in a magnetic field as they were gradually decreased from the critical temperature (T_c). Using shadowgraph methods, we analyzed intensity map data to determine the light transmission and turbidity of critical and near critical hydrogen and oxygen. Turbidity measurements were made for a hydrogen filled cell at light wavelengths of 465.2 nm, 519.4 nm, and 669.4 nm. The turbidity of the oxygen filled cell was measured at 400 nm, 450 nm, 500 nm, and 650 nm.

Background

The critical point

At high enough temperature or pressure, the liquid and gas phases of a fluid become indistinguishable [1,2]. The temperature and pressure corresponding with this phenomenon are called the critical point, and are usually denoted in a phase diagram at the termination point of the gas-liquid line, as shown in Figure 1. The critical point can be referred to by either the critical pressure P_c or the critical temperature T_c.

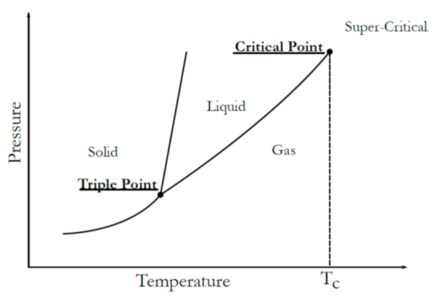

Figure 1. Phase diagram of a pure substance showing the critical point.

Correlation length and the critical exponents

Super critical and near critical phenomena can described by a set of exponents called the critical exponents [1,2]. The phenomena can be parameterized by a general function $f(\varepsilon)$, which is dependent on the dimensionless value of the reduced temperature

$$\epsilon = \frac{T - T_c}{T_c},$$

where T is the temperature of the fluid and T_c is the critical temperature specific to that fluid. For small values of ε [1], a critical exponent can then be defined as

$$\lambda = \lim_{\varepsilon \to 0} \frac{\ln f(\epsilon)}{\ln \epsilon} \ .$$

Some of the critical exponents can be used to describe more than one property of a fluid near its critical point. For example, as shown in Table 1, λ is used in the parametrization of susceptibility, and specific heat, as well as the compressibility (not shown). This makes the critical exponents a useful tool for understanding the physics of near critical phenomena. Moreover, the exponents are universal, meaning that if λ is experimentally determined to be *1.239* for one critical fluid that number will hold for all other pure fluids [2].

Compressibility and gravity

The isothermal compressibility is defined by

$$K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

where V is the volume and P is the pressure [2]. K_T approaches infinity as T approaches T_c. Under a gravitational field, the increase in compressibility leads to stratification of a fluid by density. At the critical point, this can also lead to separation and stratification by phases of a fluid. Because many of the optical properties of a fluid, such as refractive index, are dependent on the density and phase of the fluid, this can make it difficult to analyze a near critical fluid using optical methods.

Since hydrogen is diamagnetic with a strong negative magnetic susceptibility, and oxygen is paramagnetic with a strong positive magnetic susceptibility, a magnetic field can be used to compensate for and reduce the effects of gravity on these fluids [3].

Table 1. Critical exponents and their associated definitions and properties.

Exponent	Definition	Quantity	Value
$\boldsymbol{\beta}$	$\rho_L - \rho_G \sim (-\epsilon)^\beta$	Liquid-gas density difference	$\beta = 0.326$
$\boldsymbol{\gamma}$	$K_T \sim \epsilon^{-\gamma}$	Isothermal compressibility	$\gamma = 1.239$

Methods

Experimental setup: the HYdrogen Levitation Device (HYLDE)

The HYdrogen Levitation Device (HYLDE), shown in Figure 2a, at CEA-Grenoble can reduce the effects of gravity on a fluid filled cell using a magnetic field, while simultaneously gathering optical data on the cell. This is achieved using a *10 T* superconductive cylindrical coil. Due to its paramagnetic properties, total gravity compensation for oxygen occurs at *8.15* T^2m^{-1} and for hydrogen at approximately *980* T^2m^{-1} [3].

As a fluid approaches the critical point, the transmission rapidly changes. This effect is known as critical opalescence. Because this change in opacity is caused by Rayleigh scattering from density fluctuations [4,5], the transmission of light through a near-critical fluid can be used to probe some of the critical exponents related to susceptibility and compressibility such as γ, shown in Table 1 [6]. The transmission of a material

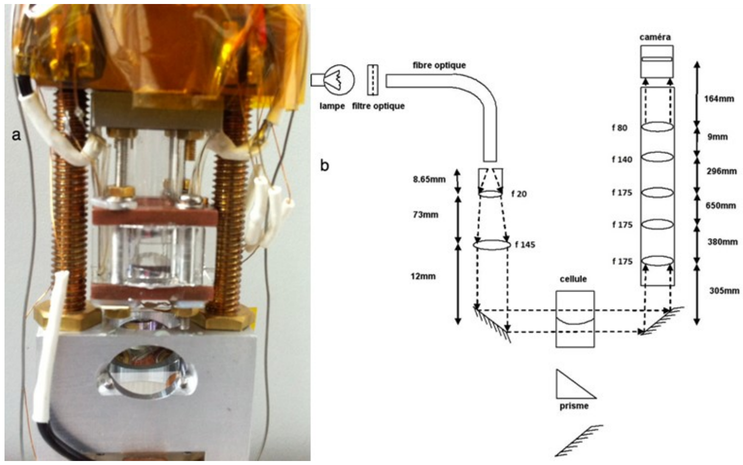

Figure 2. Close up image of the fluid-filled cell in the HYLDE (a) and the schematic representation of optical path of the HYLDE device (b)

$$T_r = \frac{I_T}{I_0},$$

is a unit-less measure of the attenuation of an initial light intensity I_0 as it passes through the material and I_T is the intensity of light measured after passing through the material.

The turbidity can then be determined by

$$\tau = -\frac{1}{e}\ln T_r$$

where e is the distance that light travels through the material, or in this case, the thickness of the fluid-filled cell. For hydrogen $e = 21\ mm$ and for oxygen $e = 18\ mm$. Since I_0 can simply be measured as the intensity of the light without the cell, and does not vary over time, then the turbidity, τ can be rewritten as

$$\tau = -\frac{1}{e}\ln(I_T) + C$$

where C is simply a constant [7]. I_T can then be measured at multiple points in the cell by passing light through the cell and into a CCD. The optical path for the HYLDE experiments is shown in Figure 2b.

Image Analysis Methods

The fluid-filled cell is gradually heated up to the fluids critical point, and then the temperature is reduced incrementally. As the fluid drops from its critical point, a CCD is used to take images of light passing through the cell. For oxygen, $T_c = 154.6\ K$, and for hydrogen, $T_c = 33\ K$. These images can then be used to determine the transmission T of the fluid at different temperatures near the critical point. Small fluctuations in density, and turbulence caused by changing temperature cause the transmission of light through the cell to be non-uniform. It is also likely that edge effects near the borders of the cell also contribute to non-uniform illumination. Therefore, in order to gain an accurate representation of the transmission through the cell, multiple sampling windows, as shown in Figure 3a where chosen to average the intensity of light passing through the cell.

The light intensity maps for near critical oxygen, shown in Figure 3b, were also taken. A window sampling scheme similar to that used for the hydrogen data sets was used, with the windows centered on the image, and different sampling sizes chosen according to Table2.

Intensity maps for both oxygen and hydrogen where using a monochromatic light source. For hydrogen, images where taken for a *465.2 nm*, *519.4 nm*, and *669.4 nm* light source. Intensity map images of the oxygen filled cell where taken for a *400 nm*, *450 nm*, *500 nm*, and *650 nm* light source.

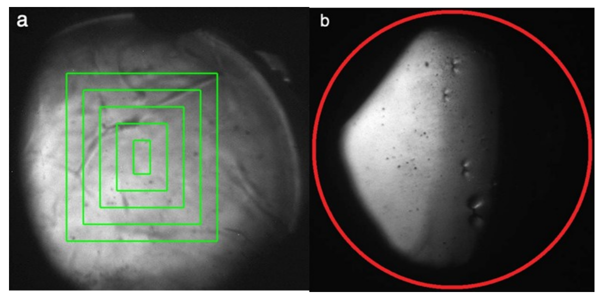

Figure 3. Light intensity map of a critical hydrogen-filled cell (a) and oxygen-filled cell (b).

Table 2. Size of image processing windows (in pixels) used to find average transmission for oxygen-filled cell.

Width (px)	Height (px)
400	400
500	500
600	600
700	700
800	800
900	900
1000	1000

Results

Transmission

The transmission for both near-critical hydrogen, and oxygen filled cells was determined by averaging the intensity of light passing through the cells at differing wavelengths. For hydrogen, shown in Figure 4, transmission was determined for a *465.2 nm* (Figure 4a), *519.4 nm* (Figure 4b), and *669.4 nm* (Figure 4c) light source.

For oxygen, shown in Figure 5, transmission was determined for a *400 nm* (Figure 5a), *450 nm* (Figure 5b), *500 nm* (Figure 5c), and *650 nm* (Figure 5d) light source.

At low values of T-T_c, when the cells were close to the corresponding critical temperatures for oxygen and hydrogen, the transmission was extremely low, and the intensity of light passing through the cell is greatly attenuated by the critical opalescence. As T-T_c increases and the temperature is further reduced from the critical temperature, the transmission increased as the fluid began to coalesce back into the liquid

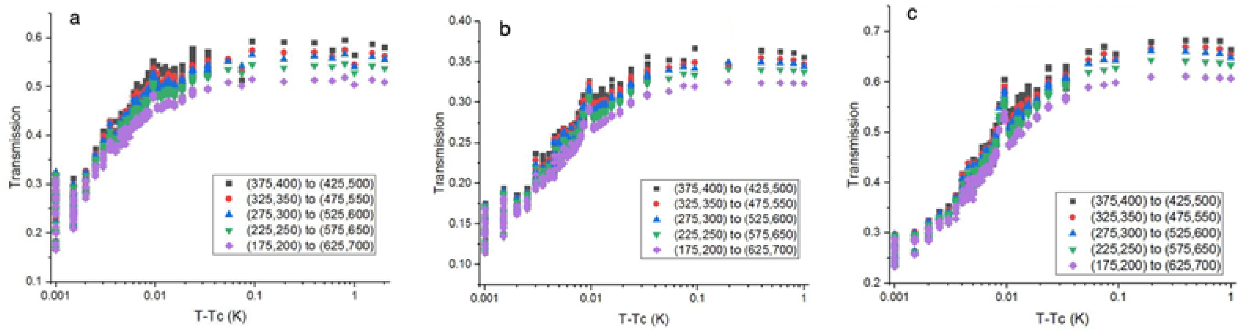

Figure 4. Transmission of light through a hydrogen-filled cell at different temperatures for red 669.4 nm (a), green 519.4 nm (b), and blue 465.2 nm (c).

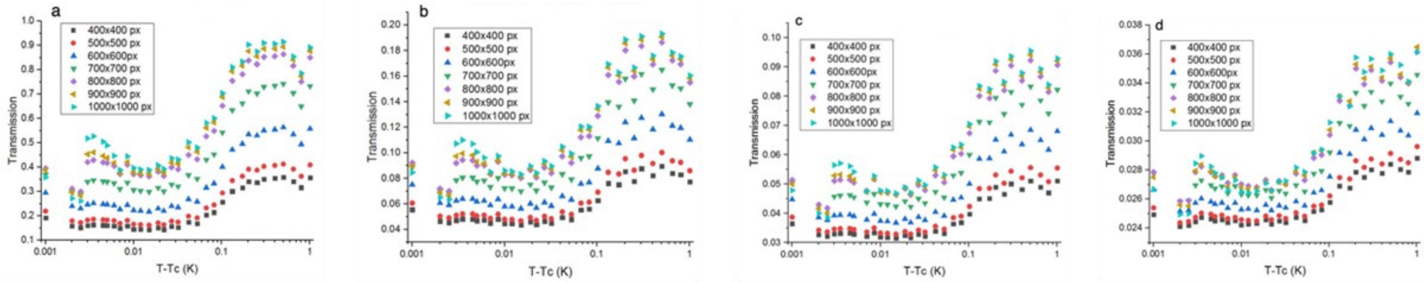

Figure 5. Transmission of light through an oxygen-filled cell at different temperatures for red 650 nm (a), green 500 nm (b), blue 450 nm (c), and violet 400 nm (d).

and gas phases. The sampling windows for oxygen showed much greater variance, due to the greater variation in intensity of the oxygen images.

Turbidity

Once the transmission coefficient is known, the turbidity can be determined using the same data processing windows. The turbidity for near-critical hydrogen was determined for *465.2 nm*, *519.4 nm*, and *669.4 nm* wavelengths, and is shown in Figure 6.

Likewise, the turbidity for near-critical oxygen was determined for *400 nm, 450 nm*, *500 nm*, and *650 nm* wavelengths, and is shown in Figure 7.

As $T-T_c$ increased, and the temperature of the cells where reduced from the critical point, the turbidity rapidly decreased. Again, the variation in sampling windows is much higher for oxygen (Figures 5 and 7) compared to that of hydrogen (Figures 4 and 6).

As a fluid approaches the critical point, the compressibility approaches infinity. This can be parameterized by the critical exponent γ, which can also be used to parameterize the susceptibility of a near-critical fluid and whose currently accepted value is $\gamma = 1.239$. Because the transmittance of a near critical fluid is greatly affected by Rayleigh scattering of light due to density fluctuations, these parameterized exponent γ can be probed using optical methods [4,5]. By measuring the transmittance of

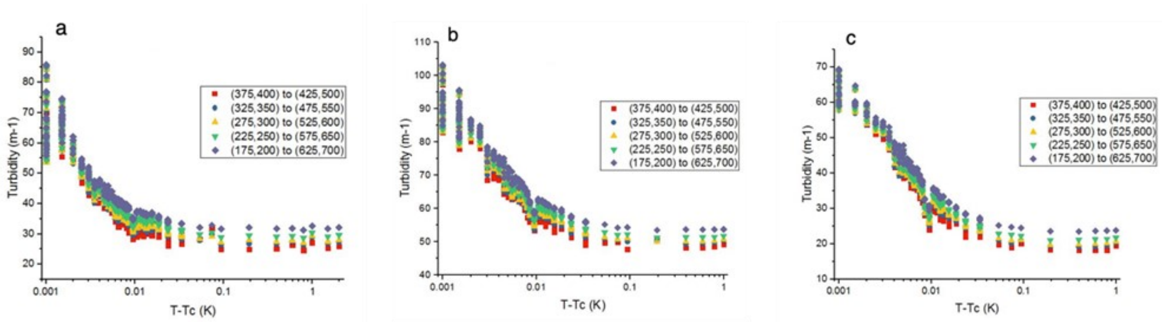

Figure 6. Turbidity of light through a hydrogen-filled cell at different temperatures for red 669.4 nm (a), green 519.4 nm (b), and blue 465.2 nm (c).

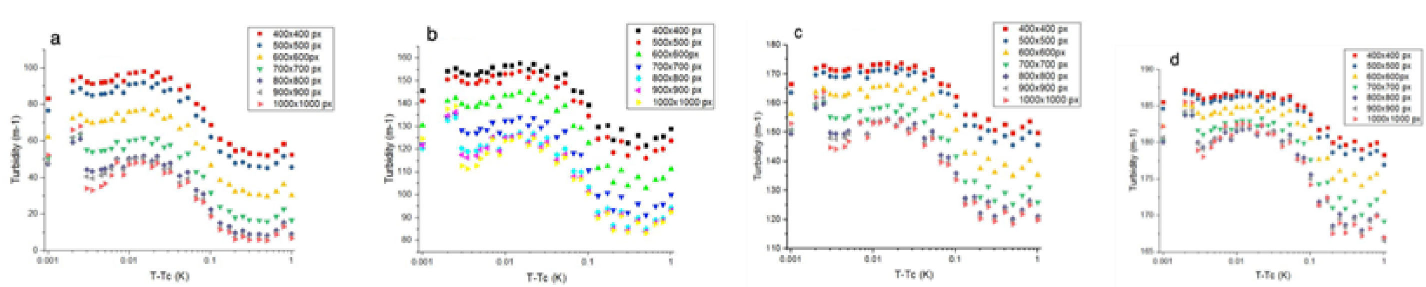

Figure 7. Turbidity of light through an oxygen-filled cell at different temperatures for red 650 nm (a), green 500 nm (b), blue 450 nm (c), and violet 400 nm (d).

light through a near-critical fluid filled cell, the turbidity can be determined and γ can be fit to the turbidity as shown in Figure 8, where the value of γ is the slope of line fit against the change in turbidity as $T-T_c$ is increased, or as the fluid is cooled down from the critical point.

Conclusions

While a magnetic field can be used to reduce the effects of gravity, variations will exist in density inside of the fluid. These variations are seen on an intensity map image such as Figure 3 as darker spots, corresponding to the increased light attenuation of regions of the fluid that are closer to the critical point. Even in true microgravity, density gradients can be caused by a temperature gradient inside the cell or by turbulence inside the cell. By averaging the intensity of light over a larger area on the image, and therefore including more variation, this effect can be reduced. For the hydrogen-filled cells which appeared fairly homogeneous, the transmission (Figure 4) and turbidity (Figure 6) measurements where very tightly clustered. For oxygen, which showed strong variation in light attenuation, the transmission (Figure 5) and turbidity (Figure 7) measurements were much more spread out. This variation may have also been enhanced by a temperature gradient, which would have caused density fluctuations and stratification, or by the cell misalignment with the magnetic field, resulting in stratification by phase and density in regions of the cell.

Notes and References

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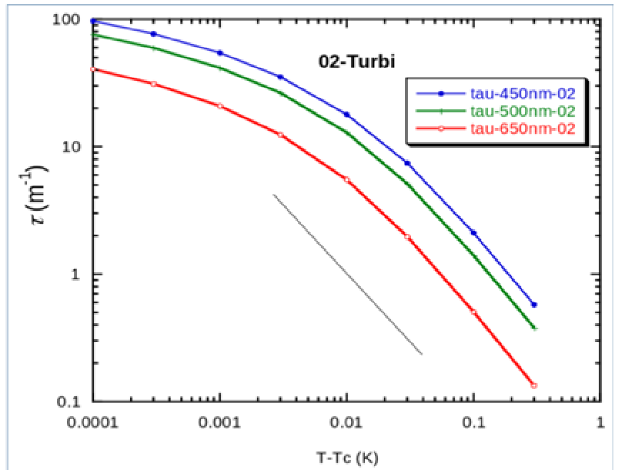

Figure 8. Isothermal compressibility shown in black, along with turbidity of red (650 nm), green (500 nm), and blue (450 nm) light plotted against T-T_c.