An undergraduate laboratory experiment to determine the critical point of SF$_6$ using light scattering at selected wavelengths

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Abstract

Molecules and atoms that are normally gaseous at room temperature and pressure will liquefy or solidify as their temperature reduces or their pressure increases. In the apparatus detailed here a commercial cell contains pressurized SF$_6$ so that it exists in both gaseous and liquid states, with the density of both being similar at room temperature. The critical point on the phase diagram can then be investigated, by elevating the temperature of the cell so the densities of liquid and gas equalize. Under these conditions light passing through the cell is highly scattered by density fluctuations in the fluid. By measuring the transmitted light as a function of both temperature and wavelength, the critical exponent can be derived and the effects of light scattering with wavelength investigated.

Keywords: critical opalescence, critical exponent, light scattering, undergraduate experiment

(Some figures may appear in colour only in the online journal)

1. Introduction

The thermodynamic properties of a material show how it responds to pressure, temperature, volume changes and other external factors. The equations governing these interactions are a macroscopic representation of the microscopic changes that occur when the molecules in the material interact. For gases, the molecules are often considered as individual particles with average inter-molecular distances that are large compared to their size. Collisions between

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the molecules and any container walls are elastic under normal laboratory conditions of temperature and pressure. Gases are hence easy to compress, and their properties can to a good approximation be represented by simple analytic expressions that relate the pressure to the temperature, volume and density of the gas [1]. As the pressure or density increases, modifications to the ideal gas law are required that allow for inter-molecular interactions often represented by van der Waals forces. This leads to a modification of the equations of state that allows for the size of the molecules and the interactions between them. By contrast, in liquids and solids the molecular separations are comparable to their size so that inter-molecular interactions dominate. Liquids and solids are hence far more difficult to compress than gases, and require more complex analysis to determine how the energy of the system changes under external perturbations.

At elevated pressures a material that is normally gaseous at room temperature will partially condense into a liquid, so that both states are present within an enclosed volume. Gravity keeps the liquid at the bottom of the container, and an interface forms between gas and liquid. In equilibrium there is an equal exchange of molecules from the gas to the liquid and from liquid to gas. A further increase in the pressure or temperature will increase the density of the gaseous state until at the critical point the densities of both gas and liquid are equal. Under these conditions the gas and liquid cannot be distinguished, and the interface disappears.

The dynamics of the molecules under these conditions is complex, since the isothermal compressibility $\kappa_T$ of the material is large, resulting in large fluctuations in the local density of the liquid and gas. Close to the critical point, $\kappa_T$ is proportional to $|T - T_c|^{-\gamma}$ where $T$ is the temperature, $T_c$ is the critical temperature and $\gamma$ the critical exponent. The exponent $\gamma$ is found to be largely independent of the material, and has an experimentally determined value $\gamma = 1.239 \pm 0.002$ [2, 3].

Far from the critical point the density is uniform, and so light passing through the material is only weakly scattered. Light propagating in the forward direction hence has almost no loss of intensity [3]. As the critical point is approached (usually by changing the temperature) the material compresses and expands easily, with very little energy required to promote density changes on a local scale. When the length scale of these variations becomes comparable to the wavelength of light passing through the material the light scatters strongly, resulting in a large reduction in intensity in the forward direction. Einstein first modeled these effects in 1910 [4] to explain the experimental results of Smoluchowski [5]. He showed that the scattering of radiation followed that predicted by Rayleigh [6], leading to an intensity decrease that also depended on wavelength. This phenomenon is called opalescence, as it is the same process that occurs in opals to produce their many different colours.

Light scattering is an established technique used in science and industry to investigate particle sizing and their characteristics. A review of these methods for particle characterization can be found in [7], whereas [8] presents theoretical light scattering techniques including that of opalescence in condensed matter. The thermodynamics of critical points and the associated opalescence are finding new application in ultra-cold physics [9] and in Bose–Einstein condensates [10], and recent work has been carried out considering opalescence in dielectric media [11]. These new studies demonstrate this area continues to have topicality in emerging areas of physics.

The aim of the undergraduate experiment described here is for students to determine the critical exponent $\gamma$ and to establish the wavelength relationship of the scattered light close to the critical point. A pressurized cell containing SF$_6$ that is heated through the critical temperature is used, and six different coloured light sources allow the wavelength effect on the scattering process to be investigated. By carefully measuring the opalescence under different conditions,
students can then compare their results to the model predictions, as are detailed in the following sections.

2. Theory of light scattering near the critical point

The forward intensity of radiation passing through a material reduces due to scattering and absorption according to the Beer–Lambert–Bouguer law [12] so that

$$I(z) = I_0 \exp(-\eta z)$$

where $I_0$ is the light intensity at the entrance to the material, and $\eta$ is the attenuation coefficient. At visible wavelengths (as used here) the effects due to absorption are negligible, and so scattering processes then dominate the measurements. For a fluid near the critical point that has density fluctuations $\Delta \rho$ in a typical volume $v$, the attenuation coefficient can be calculated from the results of Einstein [4] and Smoluchowski [5] to be

$$\eta = \frac{8\pi^3 (\alpha')^2}{\lambda p v} v (\Delta \rho)^2$$

where $\lambda$ is the wavelength of the radiation and $\alpha'$ is the molecular polarizability. Assuming purely dipolar interactions the exponent is given by $p = 4.0$, however it can deviate slightly from this value due to changes in the refractive index of the material, and due to the anisotropy of the molecules [13–15]. The fluctuation density $\Delta \rho$ is related to the isothermal compressibility $\kappa_T$ through the relationship [3, 16]:

$$(\Delta \rho)^2 \sim \frac{kT}{v \rho^2} \kappa_T$$

and so the attenuation coefficient is given by

$$\eta = \frac{8\pi^3 (\alpha')^2}{\lambda p v} v (\Delta \rho)^2 \sim \frac{8\pi^3 (\alpha')^2 kT \rho^2}{\lambda p} \kappa_T.$$  

As noted above, close to the critical point the isothermal compressibility $\kappa_T = \kappa_C |T - T_C|^{-\gamma}$ where $\kappa_C$ is a constant of proportionality, and so the attenuation coefficient is then given by

$$\eta = \left( \frac{8\pi^3 \kappa_C (\alpha')^2 \rho \lambda p}{\lambda p} \right)^\frac{T}{|T - T_C|} = \left( \frac{\beta_{\text{atten}}}{\lambda p} \right)^\frac{T}{|T - T_C|^{-\gamma}}$$

where $\beta_{\text{atten}} = 8k \pi^3 \kappa_C (\rho \alpha')^2$ is a constant. The attenuation of light near the critical point hence depends upon the wavelength, temperature and optical path-length and is given by

$$I(z, T, \lambda) = I_0 \exp\left(-\frac{\beta_{\text{atten}}}{\lambda p} \frac{T}{|T - T_C|^{-\gamma}} \right).$$

It is this expression that is the basis for the experiments described in this paper.

2.1. The experimental apparatus

The molecule used in these experiments is sulfur hexafluoride (SF$_6$) that is contained in a pressurized steel cell obtained from Leybold Didactic [17]. This is used since the critical
Figure 1. Diagram of the apparatus. Selected LEDs produce light of different wavelengths that passes through the SF6 cell after collimation by a 25 mm focal length lens. Transmitted light from the cell is imaged onto an amplified photodiode by a 50 mm diameter, $f = 100$ mm lens. The cell is heated using three 50 W power resistors affixed to the bottom of the cell using heat-sink glue. A type-K thermocouple monitors the internal temperature of the cell as it heats and cools. The cell is secured in a 3D-printed insulated housing to reduce the cooling rate during measurements. The outputs from the photodiode and thermocouple pass to the control electronics that amplify and digitize the signals using an ESP32 microcontroller. The digitized signals are then passed to a dedicated LabVIEW program on an external PC so they can be analyzed.

The temperature of SF6 is $T_C = 318.7$ K (45.5 °C), which is easy to obtain in undergraduate laboratories. The gas pressure near the critical point is around 37 bar, and so the cell must withstand this high pressure. The windows are hence constructed of glass with a thickness $\sim 20$ mm, and the cell is sealed using o-ring washers compressed between the cell wall and windows. At room temperature the cell contains $\sim 50\%$ liquid by volume, and has an optical path-length between the windows of $z_{SF6} \sim 10$ mm.

Since the path-length $z_{SF6}$ inside the cell is fixed, equation (6) only depends upon the incident wavelength and cell temperature. Under typical operating conditions the temperature change $\Delta T = T - T_C$ is much smaller than $T_C$, and so equation (6) may be rewritten as

$$I(z, T, \lambda) \xrightarrow{T_C >> \Delta T} I_0 \exp \left( -\frac{\beta_{atten} z_{SF6} T_C}{\lambda p |\Delta T|} \right) = I_0 \exp \left( -\frac{\mu C}{\lambda p |\Delta T|} \right)$$

(7)

where $\mu C = \beta_{atten} z_{SF6} T_C$ is a constant. By measuring $I/I_0$ as a function of both $\lambda$ and $\Delta T$ the critical exponent $\gamma$ can hence be ascertained, and the prediction that $I \propto \lambda^{-p}$ where $p$ is around 4.0 can be tested. $I_0$ can be estimated by setting $T \gg T_C$ and $T_C$ determined from the data since $I/I_0 \xrightarrow{T \gg T_C} 0$. In practice setting $T \sim T_C + 5^\circ$ allows a good estimate of $I_0$ to be made. Since thermal gradients may occur in the cell as it cools back through the critical point, a small non-zero intensity is usually seen at the critical temperature, which can be estimated from the position of the intensity minimum.

Figure 1 shows a block diagram of the apparatus. The light is produced from a selection of six different light emitting diodes (LEDs) that range in wavelength from $\sim 400$ nm to $\sim 700$ nm. Light emitted by the selected LED is quasi-collimated by a 25 mm focal length lens so that it enters the cell. The cell has a clear aperture of $\sim 12$ mm diameter through which the light passes.
Figure 2. The housing for the LEDs is secured to the optical table as in figure 1, through which the power supply is connected. Each LED is mounted in an aluminium holder that acts as a heat sink. The LED holder is inserted into the housing as shown. Connection from the constant current supply to each LED is made by soldering wires to two offset Nd magnets with opposite polarities in the housing. In a similar way the LED is connected to two Nd magnets in the holder. As the holder slides into the housing, the magnets attract each other and current flows as a connection is made.

A 50 mm diameter 100 mm focal length lens collects the transmitted light and images the cell onto an amplified photodiode. The pressurized cell is held in an insulated plastic housing so that it cools slowly after being heated beyond $T_C$. The thermocouple and heaters are secured to the cell so they remain undisturbed when students adjust the optical components. The LED housing, lenses, SF$_6$ cell and photodiode are fixed using posts clamped onto a breadboard, allowing students to adjust their relative positions so as to optimize signal onto the photodetector. The photodiode amplifier gain can be adjusted using an external 10-turn potentiometer so that the intensity $I_0 \sim I (T_C + 5^\circ)$ from the different LED’s produces the same output. This normalizes the signal for the different emission efficiencies of the LED’s and the photodiode spectral response. The signal from the photodiode amplifier is directed via coaxial cable to an analogue to digital converter (ADC) via a buffer stage (see figure 4 for details).

The cell is heated using the 9 V AC output from a 50 VA toroidal transformer that is directed to three 50 W, 10 $\Omega$ power resistors fixed to the bottom of the cell using heat-conducting glue. The heater supply current passes through a temperature-controlled switch to prevent overheating. A low voltage AC supply is adopted as it is safe for students to use. The heater supply is switched off during opalescence measurements, to eliminate electrical noise from the heating process on the photodiode or thermocouple signals as the experiment proceeds. This is important particularly for the thermocouple signal which at source is only $\sim 1–5$ mV at these temperatures.

The temperature is measured using a type-K thermocouple embedded in the cell close to the SF$_6$ chamber. The thermocouple signal is directed using shielded type-K cable to the input of the thermocouple amplifier that has two outputs. The first monitors the full temperature range used in the experiment, whereas the second produces an output that spans around the critical point. It is the second output that is used in equation (7). Both amplifier outputs are directed through buffer amplifiers before being digitized by ADCs.

If students forget to turn off the current as the cell heats, the temperature controller will automatically switch off the 9 V$_{AC}$ supply if the cell rises above 50 $^\circ$C. This ensures the cell remains at a temperature well below its safe operating point ($\sim 90$ $^\circ$C). Due to thermal lag the temperature of the cell tends to rise to $\sim 53$ $^\circ$C after the current has been switched off by the failsafe circuit.

Six different LEDs rated at 3 W are used with peak wavelengths from 415 nm to 659 nm. The spectral characteristics of each differ slightly, however all have bandwidths $\sim 20$ nm with similar peak intensities when driven by a constant current, as measured using a spectrophotometer. The LEDs are mounted on individual aluminium holders as shown in figure 2, so they can be exchanged easily without needing to adjust the optical arrangement. The connections
are made by soldering wires onto small neodymium (Nd) magnets on both the housing and LED holder. The magnet poles (N–S) are set so that the correct polarity voltage is connected to the LEDs, the individual magnets strongly attracting each other to make a secure connection.

Central to the experiment is the ESP32 microcontroller that monitors the digitized thermocouple outputs and photodiode output using a serial peripheral interface (SPI) to the ADCs. This microcontroller sends information to a 20 character by 4 row LCD display on the front panel of the interface unit, allowing students to continuously monitor the experimental status. The ESP32 averages the measurements from the amplifiers to reduce sampling noise, and calibrates these to produce the temperature in Celsius or Kelvin and the photodiode output in volts. The conditioned signals are then directed to an external PC via USB, where a dedicated LabVIEW program produces plots of the different signals that are required. Students can then save the data in comma separated variable (.csv) files for further analysis.

2.2. The control hardware

Several printed circuit boards (PCBs) are used in the experiment. These are located in the interface unit, apart from the photodiode amplifier located on the optical breadboard (see figure 1). Three separate power supplies are used to minimize crosstalk between the electronics, as shown in figure 3. A 50 VA toroidal transformer supplies current for the heaters and associated control electronics and the LEDs, and on-board 3.2 VA isolation transformers are used for all other supplies. The heater current is sourced directly from the secondary of the toroidal transformer via the switching control system (see figure 4(b)), whose DC supply operates at ±9 VDC as shown. All DC supplies use similar components, consisting of a full-wave rectifier (either 1N4007 discrete diodes or W08 bridge), electrolytic smoothing capacitors (2200 μF or 6800 μF), tantalum capacitors for high-frequency noise rejection, and either 78xx and 79xx regulators that deliver a fixed voltage, or LM317/337 variable regulators that produce ±6 VDC for the photodiode amplifier. The LED constant current supply uses an LM317 variable regulator. The drive current is set by the 2 × 100 Ω resistors, since the regulator adjusts its output to maintain the voltage difference across the resistors at 1.25 VDC. In this example the current is hence 1.25 V/50 Ω = 25 mA irrespective of the load. This is beneficial here as each LED requires a different operating voltage, whereas the output intensity of the LEDs is proportional to the current passing through them.

Figure 4 shows schematics of the analogue systems that are used. The photodiode is an OSD15-5T that is reverse-biased to ensure linearity with the input light intensity. An OPA277 operational amplifier provides an adjustable positive output (set by the 50 kΩ 10-turn potentiometer) that connects to the interface unit via shielded cable. The response time of the amplifier is set by the 820 nF capacitor in parallel with the feedback resistors. The dedicated power supply for this amplifier is adjusted to deliver around ±6 VDC to ensure the output does not rise above +5 V (due to the operational amplifiers output range being around ±1 V less than the rail to rail voltage), thereby preventing damage to the digital systems. A (normally reverse biased) 1N914 small signal diode is included to prevent the output becoming more negative than −0.6 VDC in the event of failure of the photodiode amplifier.

The failsafe control system for the heaters is shown in figure 4(b). The temperature monitor board is adjusted to give an output of +5 VDC at a temperature of 50 °C, and this feeds the negative input of the LM741 operational amplifier as shown. The LM741 acts as a comparator, with hysteresis set by the 820 kΩ resistor in the feedback path. The positive pin of the LM741 is adjusted to 5 VDC using the 5 kΩ trim potentiometer, so that if the temperature is below 50 °C the comparator output is around +8 VDC. This turns on the TIP121 Darlington transistor and engages the relay, allowing heater current to flow. A front panel switch allows manual control
Figure 3. Power supplies used in the experiment. (a) The 9V AC supply used to power the heaters (from A & B) and the DC supply for the control board that prevents overheating. The 50VA toroidal transformer also supplies current for the constant current supply that drives the LEDs. (b) The supply used for the photodiode amplifier located on the optical breadboard and the supply for the thermocouple amplifiers. (c) The dedicated supply for the ESP32 board, which uses separate supplies for the digital and analogue components on this board.

of the current, so that under normal conditions the students can control the upper temperature of the cell.

If the cell heating is left unmonitored the reference voltage will reach $+5 \, \text{V}_{\text{DC}}$ at $50 \, ^\circ \text{C}$. At this time the comparator output will switch to around $-8 \, \text{V}_{\text{DC}}$ which switches off the TIP121 so that the heater current ceases. Hysteresis in this circuit keeps the current off until the cell has cooled to $\sim 47 \, ^\circ \text{C}$, at which point the heater re-engages. In practice the cell cycles between $\sim 53 \, ^\circ \text{C}$ and $\sim 45 \, ^\circ \text{C}$ under these failsafe conditions due to thermal lag. This circuit hence prevents cell damage due to overheating.

Figure 4(c) shows the amplifiers used to monitor the cell temperature. An AD8495 thermocouple amplifier interfaces the type-K thermocouple to the main amplifier board. The AD8495 is a surface mount device and is soldered onto a daughter board so it can be inserted into a DIP-8 socket for easy replacement if damaged. The AD8495 produces 190 mV at $25 \, ^\circ \text{C}$ which
Figure 4. Analogue amplifiers and control systems used in the experiment. (a) A schematic of the photodiode amplifier located on the optical breadboard. The output is sent to the interface unit via coaxial cable as shown. (b) The circuit used to control the heater current, so that this is switched off if the cell rises above 50 °C. (c) A schematic of the thermocouple interface electronics that amplifies the signal from the thermocouple, applies an offset and further amplifies the signal for plotting the response of the light scattering to the SF6 temperature.

rises to 318 mV at 50 °C when using a type-K thermocouple, and it has a cold junction compensation circuit to achieve good linearity with temperature. The output from the AD8495 is amplified by one of four operational amplifiers in an OPA4277 package. The non-inverting amplifier A4/1 is set to have a gain of 9.8814 by adjusting the 500 Ω trim-potentiometer. This then feeds A4/4, which is a unity gain inverting stage with a time constant $\tau \sim 360$ ms as set by the feedback resistor and capacitors. This reduces high-frequency noise that may be picked up by the feed wires from the thermocouple to the interface unit. A REF02 precision 5 VDC reference is buffered by A4/2 which produces an output of 2.613 V as set by the 1 kΩ trim-potentiometer. This voltage is added to the output of A4/4 using A4/3, which is a summing amplifier with a gain of 10. The output of A4/3 hence ranges from $-7.5$ V to $+5$ V at 50 °C, and is 0 V at 40 °C. A 1N914 diode prevents the output becoming more negative than $-0.6$ VDC, so that the output to the ADC1 circuit from this stage then ranges from $-0.6$ V to 0 V when the temperature changes from 20 °C to 40 °C, and subsequently produces a linear output with temperature from 0 V at 40 °C to $+5$ V at 50 °C. The output from this amplifier is also directed to the cell heater control board as discussed above.

The output from A4/1 is taken to a second ADC circuit so the temperature of the cell can be directly monitored. This has reduced precision compared to the output from A4/3 and so is used as a monitor for students to see how the cell is heating and cooling over the full temperature range of the experiment.
Figure 5. The ADC board and ESP32 microcontroller schematic showing the input buffer amplifiers, quad ADC and precision reference, ESP32 microcontroller and LCD screen.

Typical values of voltages measured in the circuit are shown in figure 4(c). A shunt between the AD8495 and A4/1 allows the AD8495 output to be monitored directly by a high precision voltmeter, so the circuit can be calibrated with respect to temperature. Each AD8495 is found to produce a slightly different output, and so it is necessary to adjust the trim potentiometers to ensure the ADC inputs are set correctly. Once the output range from the AD8495 is known, the gain of A4/1 and A4/4 can be adjusted (with the shunt removed), by feeding a precise voltage into pin 3 of A4/1 and then monitoring the output of A4/4.

The three analogue outputs from the thermocouple and photodiode amplifiers are input to the ADC board as shown in figure 5. The inputs are buffered using an OPA4277 whose operational amplifiers act as unity gain non-inverting amplifiers. The outputs of each buffer feed an MCP3204 12-bit ADC to digitize the analogue signals. A REF02 precision 5 V reference sets the conversion range for the ADC so that the digital output is 0 at 0 V and is 4095 at +5 V on each input. It is important to ensure any unused inputs at the buffers are connected to 0 V (AGND), or incorrect analogue conversions can occur on active inputs.

The ESP32 addresses the MCP3204 ADC via a serial peripheral interface (SPI) and reads the output at a rate of 7 kHz. This allows the embedded software to determine an average value, thereby reducing the effects of any high-frequency noise that may occur on the signals. The ESP32 converts the digitized signals to temperature in °C or K for the thermocouple circuit, and outputs the digitized signal from the photodiode amplifier as a voltage. These are written to the LCD screen located on the front panel of the interface unit using the inter-integrated circuit (I2C) protocol, and are also sent to the external PC via serial communication over a USB interface for input to the LabVIEW program.

To reduce noise on the buffer amplifiers from digital switching, two separate supplies are used for the ESP32 board as shown in figure 3. The OPA4277 and REF02 are supplied from the ±9 VDC supply and the 0 V from this supply is connected to AGND on the MCP3204 ADC. The ESP32, MCP3204 and LCD digital components all use the ±5 VDC supply shown in figure 3(c), with 0 V set as DGND. The negative 5 VDC supply is not used in the present configuration.
2.3. The control and interface software

The control and logging system uses an ESP32 microcontroller [18] that is programmed using the Arduino software framework, with programs written in C/C++ [19]. All firmware and software described here is available online under an open source licence [20].

The firmware is relatively simple. Once powered on, the following initialization take place:

- The universal asynchronous receiver/transmitter (UART) connected to the USB interface is initialized as a serial port to communicate with the PC running LabVIEW.
- The SPI interface is initialized to communicate with the MCP3204 ADC.
- Calibration factors are recalled from onboard non-volatile memory in order to convert ADC readings to appropriate units.
- The I2C interface is configured to communicate with the LCD display. The LCD shows the cell temperature, the higher resolution measurement from 40 °C to 50 °C, the photodiode output and the default time-step \( dt \) for the measurement rate (which is adjustable via LabVIEW).

The firmware then enters a loop (figure 6) operating at 7 kHz that does the following:

(a) The serial port is checked for commands from the PC. These are for setting and obtaining the calibration coefficients, the default measurement time-step, and saving the values to non-volatile memory. The unit responds to an identification request with the string ‘CO’ (critical opalescence) to differentiate it from any other data loggers connected to the PC on different ports. The readings sent to the PC can be enabled or disabled to prevent pile-up at the serial port buffer on the PC when LabVIEW is not running.

(b) The data are read by the ADCs and added to running totals, and the ‘number of readings’ counter is incremented. Once the measurement time \( dt \) has elapsed an average is calculated, and the main loop is notified that a new reading is available. A typical value of \( dt \) is 100 ms so each reading is an average of 700 samples.

(c) If an update is available, the latest readings are sent to the LCD and the three averaged values are sent to the PC via a serial message, if the PC readings are enabled.

(d) The loop then returns to step 1.

A PC communicates with and receives data via USB from the ESP32 which is set as a simple serial peripheral device in Microsoft Windows. The LabVIEW program handles serial communications and plots the photodiode output against temperature in real time. The program
features a graphical user interface (GUI) that allows the user to view and save the data as required.

The LabVIEW program identifies the ESP32 serial port by sending a request to all connected peripherals so a connection can be established. The ESP32 is then requested to send the data as comma separated ASCII strings terminated with a ‘\n’ newline character. The main loop then commences, which responds to user inputs and plots the data from the ESP32 as follows:

1. Respond to any of the following user inputs:
   - Change the time-step \(dt\) by sending a new time-step to the ESP32.
   - Reset all graphs for a new experimental run.
   - Save data to a comma separated variable (.csv) file.
   - Start and stop logging from the ESP32 by sending an \textit{enable} or \textit{disable} request.
   - Change maximum log time & send request to the ESP32 to stop logging messages.
   - Exit program and return to Microsoft Windows.

2. If logging is enabled, parse in data from the ESP32, and update plots displayed on the GUI.

3. The loop then returns to step 1.

The ESP32 firmware described here uses a simple serial communications protocol, and so to keep costs down a PC running LabVIEW is not necessary to communicate with and log the data. Any computer with a serial port can hence be used (e.g. a Raspberry Pi [21] running python could log the data to a USB memory stick).

2.4. Examples of experimental results

The equation used for data analysis in the experiment is the non-linear equation (7). The critical exponent can be obtained from a non-linear fit to the data (using e.g. a Marquardt method), or the equation can be further manipulated to allow a linear fit to be used, which is more suitable for undergraduate students who may not have seen non-linear fitting methods in their studies. Linear fitting requires manipulation of equation (7) as shown below, where the wavelength exponent is here also set as a parameter to be obtained from experiment. Equation (7) is hence given by

\[
I(z, \Delta T, \lambda) = I_0 \exp \left( -\frac{\mu C}{\lambda^p |\Delta T|^\gamma} \right) \Rightarrow \ln \left( \frac{I_0}{I(z, \Delta T, \lambda)} \right) = \left( \frac{\mu C}{\lambda^p} \right) |\Delta T|^{-\gamma} = \left( \frac{\mu C}{|\Delta T|^p} \right) \lambda^{-p}.
\]

(8)

If the temperature difference \(\Delta T\) is fixed, equation (8) can be rewritten as a linear equation:

\[
\ln \left( \ln \left( \frac{I_0}{I(z, \Delta T_{const}, \lambda)} \right) \right) = \ln \left( \frac{\mu C}{|\Delta T_{const}|^p} \right) - p \ln (\lambda) = \Xi_{const} - p \ln (\lambda).
\]

(9)

By fitting the double logarithm of the intensity ratio to \(\log_e (\lambda)\) using a linear fitting routine the slope yields the exponent \(p\), with \(\Xi_{const}\) the intercept. To establish the critical exponent \(\gamma\), the wavelength is held constant and so

\[
\ln \left( \ln \left( \frac{I_0}{I(z, \Delta T_{const}, \lambda)} \right) \right) = \ln \left( \frac{\mu C}{\lambda_{const}^p} \right) - \gamma \ln (|\Delta T|) = \Psi_{const} - \gamma \ln (|\Delta T|).
\]

(10)
Figure 7. Results from experiment for the different LEDs. (a) Experimental data for red, green and blue LED. The blue light is seen to be more highly scattered than the red light as expected. (b) A non-linear Marquardt fit to the red LED data, where the horizontal axis in (a) and (b) is $\Delta T = T - T_C$. The fit is sensitive to both $I_0$ (normalized to unity here) and the experimentally determined critical temperature $T_C$. (c) Linear fits to the manipulated data at fixed $\Delta T$ from 0.05 K to 0.60 K. The slope of the fit yields the wavelength exponent, here found to be $\langle p \rangle = 3.80 \pm 0.09$. (d) Fits at fixed wavelengths from 0.05 K to 0.60 K where the manipulated data was found to be reasonably linear. The averaged critical exponent from the fit is $\langle \gamma \rangle = 1.21 \pm 0.03$.

Now $\Psi_{\text{const}}$ is the intercept and the slope produces $\gamma$. From [2] the expected value of $\gamma$ should be around 1.23, whereas $p$ should be around 4.0 as noted above.

Figure 7 shows data from experiments carried out in the teaching laboratory in Manchester using the apparatus described here. Figure 7(a) shows measurements from 1.5 K above the critical temperature $T_C$ to $\sim 0.3$ K below this temperature, for three different LEDS. The effect of wavelength on the scattering process is clearly seen, the data for 415 nm showing significantly more light scattering than for 659 nm as expected. At temperatures below $T_C$ large variations are observed in the transmitted intensity due to turbulence and bubbles in the SF6. A non-linear fit to the red data is shown in figure 7(b), which is plotted over a wider range of temperature to accurately determine $I_0$ (normalized to unity here). This fit produces a value $\gamma = 1.26 \pm 0.05$. The uncertainty was estimated by adjusting the values of $\gamma$ around the fitted value so as to produce a change of $\pm 1$ in the reduced $\chi^2$. This technique was adopted as the Marquardt algorithm failed to produce a sensible uncertainty from the covariance matrix. It was also noted that a difference of 20 mK in the value of $T_C$ would change the fitted exponent by up to 20%, demonstrating the sensitivity of the algorithm to this parameter.
Figure 7(c) shows a plot of the double logarithm of the intensity ratio against $\log_e (\lambda)$, allowing equation (9) to be used to establish $p$. In both figures 7(c) and (d) the chosen temperature range is from 0.05 K to 0.60 K above $T_C$, since the double logarithm was found to be reasonably linear in this region. Linear fits were carried out at intervals of 0.05 K for the six LED wavelengths in figure 7(c), and the averaged slopes used to calculate $\langle p \rangle = 3.80 \pm 0.09$. This is within 2 standard deviations of the ideal value of $p = 4.0$. Figure 7(d) plots the double logarithm of the intensity ratio against $\log_e (\Delta T)$, as in equation (10). The slopes of the linear fits to each curve are then averaged to yield $\langle \gamma \rangle = 1.21 \pm 0.03$.

For this series of experiments the calculated value of $\gamma$ is found to be within two standard deviations of the reported value. Recent work using cavity ring down spectroscopy [22] has been carried out on SF$_6$ gas at pressures up to 20 bar, and these authors calculated the exponent $p$ for this gas at a wavelength of 1180 nm. They compared their results to other authors who used different wavelengths, and estimated an average value for SF$_6$ of $p = 4.28 \pm 0.05$. This is slightly outside the measurements from the experiments described here. These authors found that deviations to the scattering cross section occur at higher pressures, and this will slightly change the exponent value under the high pressure conditions ($\sim 37$ bar) that are found in the SF$_6$ cell used here.

The calculated exponents from the current measurements are very sensitive to both the value of $I_0$ and $T_C$ as found from experiment, and so it is important that students establish both as precisely as possible. The measured value of $T_C$ can vary from the accepted value of $T_C = 45.5^\circ$C for SF$_6$ due to thermal lag as the cell cools, and so $\Delta T$ is defined by measuring the change with respect to the temperature where the intensity is a minimum (i.e. maximum scattering of the transmitted light). This point is difficult to determine accurately due to the steepness of the change as shown in figures 7(a) and (b), and so it is sensible for students to repeat the experiment several times to reduce the uncertainty in this parameter. It is also important to establish $I_0$ accurately, so that the intensity ratio in equations (7)–(10) as the cell cools can be determined. It is hence necessary to heat the cell to $\sim 5^\circ$C higher than the measured critical temperature, so that $I \sim I_0$ provides a good approximation at all wavelengths.

### 3. Conclusion & summary

In this paper an undergraduate laboratory experiment has been described that measures the critical exponent as SF$_6$ transitions through the critical point where the density of the gas and liquid in a cell become equal. Under these conditions the localised density of the fluid fluctuates markedly since the isothermal compressibility becomes very large. Light passing through the fluid then undergoes large scattering, which reduces the intensity effectively to zero at the critical point. By measuring the scattered light as a function of temperature the critical region can hence be investigated for comparison with thermodynamic models. By choosing different wavelengths, it is also possible to establish if the scattering process follows that predicted by Einstein and others.

Although the high-pressure cell used here is sourced from a commercial supplier for safety reasons, all other components have been designed and built ‘in house’, significantly reducing the cost of building the experiments. The hardware and software have been described in detail, and results have been presented to show how the data can be analyzed in different ways. The derived results agree with accepted values, showing that with careful experimentation this apparatus can be used to effectively explore this unusual region of thermodynamic phase space.

Further details (CAD drawings, PCB layouts, etc) of the apparatus and electronic systems are available from the authors on request.
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