Critical Temperature Shift in Pure Fluid SF_6 Caused by an Electric Field

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A systematic study of the effect of an electric field on the critical temperature of a pure fluid is made for the first time to our knowledge. An ac electric field is applied to a spherical capacitor filled with SF_6 at its critical density, while the temperature is slowly ramped down through its critical temperature T_c. By continuously observing the light transmission through the fluid during the temperature ramp, a shift in T_c, ΔT_c, is found at various electric fields. By shining the light vertically through the fluid, we utilize the density gradient induced by the fluid's weight to compensate for the effects of density changes from electrostriction. This technique effectively keeps the system at constant critical density with respect to the observation of T_c. We observe an increase in T_c as expected from thermodynamic stability and renormalization group theory, but quantitatively larger by an order of magnitude.

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Our understanding of the singular behavior near a thermodynamic critical point has seen great progress in recent times [1]. In fact, systems near their critical point remain the most experimentally accessible systems for rigorous tests of the renormalization group theory [2]. The liquid-gas critical point initially attracted many great scientists because it gave direct evidence of thermal fluctuations [1]. This spectacular critical opalescence, where ordinarily transparent fluids suddenly become a "liquid pearl," occurs over a small fraction of a degree Kelvin, exactly where the difference between gas and liquid disappears. It was explained as a manifestation of light scattering from large domains of correlated density fluctuations (~ 500 nm). These density fluctuations make the fluid highly compressible, such that the hydrostatic pressure from a gravitational field in a ~ 1 cm column of fluid may induce an $\sim 10\%$ density change (see Fig. 1). Precision measurements in a homogeneous system require weightlessness [3]. This fascinating behavior in a gravitational field begs other questions; the most obvious is the behavior in an electric field. Although such studies have been performed in more complex systems, e.g., liquid mixtures, there appears to be no study of the electric field in the much simpler system of a pure fluid.

In this work we have studied, for the first time to our knowledge, the influence of an electric field on the critical point. We first present previous contradictory theories, the experimental system, the results that show T_c increases with increasing E field, and how this is required by thermodynamic stability.

Different theories predict upward or downward shifts in the critical temperature when an electric field is applied to a substance [4–7]. Some experiments have reported a downward shift in the critical temperature for polymers and binary mixtures [6–8]. These previous experiments have also been criticized for not controlling heating effects and for ignoring pressure and density changes from an external mass reservoir [4]. This experiment has avoided these difficulties. Using a spherical capacitor filled with highly insulating SF_6 (99.99% pure) between the inner and the outer sphere, we have applied an ac field, thus avoiding joule heating. These experiments are performed in a ground-based environment so that a gravitationally induced density gradient assures a horizontal layer of fluid at the critical density in the capacitor. Monochromatic light is then passed through this layer; i.e., the optical axis of the light beam is vertically oriented; see Fig. 2. An upward shift in the critical temperature that depends on the electric field, as predicted separately in Refs. [4,5,9], is found. This shift is

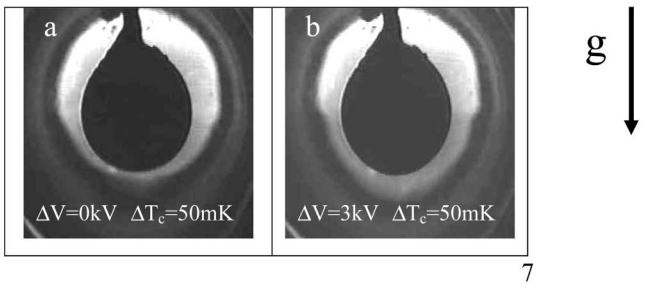

FIG. 1. Shown above are images, with the camera axis horizontal, of a spherical electrode surrounded by turbid fluid. Images (a) and (b) are both $\cong 50$ mK above their respective critical temperatures T_c. In this sample, the height of the critical density is below the sphere's equator (this is because the roughly symmetric cell has been filled to a density that is below the critical density ρ_c). This layer is dark near T_c from critical opalescence. This layer also significantly refracts light as seen by the deformation of the annular (lighter) region around the central electrode. Image (a) at $\Delta V = 0$ has a temperature that is $\cong 30$ mK lower than image (b) at $\Delta V = 3$ kV. Although the two images have different temperatures, they appear to have similar turbidities. The data in Fig. 4 uses the same cell filled to the critical density and rotated 90°, so that the optical axis is vertical and the image is uniform.

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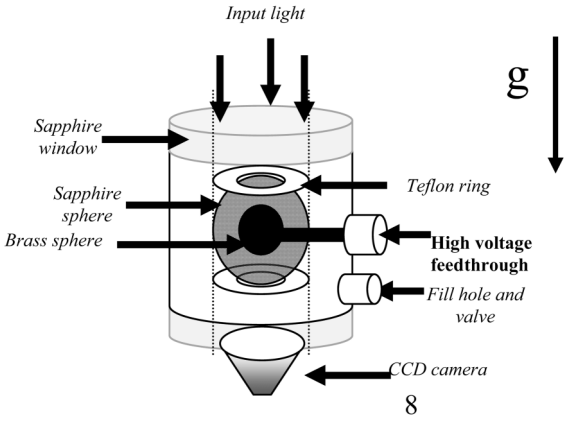

FIG. 2. Two sapphire windows seal a cylindrical copper cell ($1.5''$ in diameter cavity in a $3''$ diameter cell that is $3''$ in length) containing SF_6. Concentric electrodes (brass inner sphere 6.35 mm diameter and indium tin oxide coated sapphire outer sphere of 25.4 mm inner diameter) at the center of the cell make the spherical capacitor. Light passes vertically through a horizontally oriented critical density layer. This layer is located at the equator of the concentric spheres.

repeatable and is found by measuring the light transmission through the vertical density gradient while slowly decreasing the temperature through the critical temperature at a given voltage. At a sufficient low ramping rate, we found a repeatable upward shift of the critical temperature as a function of the applied electric field.

An electric field applied to a neutrally charged dielectric fluid introduces another thermodynamic variable. In a nonuniform field, or an electric field *gradient*, a polarized molecule feels a net force from the field toward the region of higher field intensity [9]. The result in the continuum limit is a body force, the so-called pondermotive force in the fluid. In a fluid of constant composition and temperature, this stress is often called electrostriction. In an ac field, the dipole moment remains aligned with the field, preserving the attraction toward the higher field gradient. In this spherical geometry, shown in Fig. 2, the electric field gradient produces a central body force [10].

Inside of the critical fluid cell is a spherical capacitor described in Ref. [10] except for the following differences: the brass inner sphere has an outer diameter of 6.35 mm, the outer sphere is grounded while ΔV is applied to the inner sphere, and the inner sphere is not heated. This capacitor is placed inside of the cell as shown in Fig. 2 so that it contains SF_6 fluid at its critical density between the electrodes. The outer sphere is positioned inside of the critical fluid cell using two Teflon rings. An ac voltage of up to 3 kV may then be applied to the inner sphere, this being the limit of a high voltage feedthrough. The optical axis of the cell and charge-coupled device (CCD) camera can be orientated in either the horizontal (as shown in Fig. 1) or the vertical direction (as shown in Fig. 2). The test cell is set up so that light may shine through the fluid between the inner and the outer sphere of the spherical capacitor, as shown in Fig. 2. An external HeNe light source shines onto a light diffuser. This produces a uniform illumination. The image of the center electrode is then to be focused into a CCD camera, so that it may serve as the object for the optical system and the focal plane is within the critical layer of fluid. The average light intensity of the annular region of uniform intensity is calculated. This average transmitted light intensity is measured as a function of temperature, and the temperature of the minimum light intensity is taken as T_c. The critical fluid cell is placed inside of several thermal shields so that temperature fluctuations from the environment are filtered.

The compressible near-critical fluid in our cell is SF_6 and is chosen for its relatively low critical pressure P_c ($P_c = 37.7$ bars), low critical temperature T_c ($T_c = 45.54\,^{\circ}\mathrm{C}$), and high breakdown voltage (> 100 kV/cm). A cylindrical cell is filled with SF_6 to within 0.01% of the critical density ρ_c and is then sealed. This precision is obtained by observing the volume fraction as a function of T [11]. The closed cell constrains the fluid to a constant volume and a constant mass (a constant average density), so that the temperature is the only independent thermodynamic variable.

In normal terrestrial gravity, a highly compressible near-critical fluid stratifies under its own weight. The response to input heat is, however, more complicated. Experiment and theory have found that the high compressibility and thermal expansion coefficients, together with the very small thermal diffusivity, lead to a very fast initial thermal response [12–14]. The input heat at the wall expands so that the bulk of the fluid is compressed to higher temperature (in a constant volume sample) almost immediately. The density response is very slow, being slaved to the small temperature gradients through the large thermal expansion and the very slow temperature relaxation (small diffusivity). The presence of the gravitational field has been shown to increase this response considerably, at least by an order of magnitude, from the resulting convection [12]. In fact, when the cylindrical cavity of the cell is horizontal (see Fig. 1), any heating induces convection, as is to be expected when a horizontal temperature gradient is present. This convection generally occurs in a thin layer adjacent to the wall, consistent with the above picture of a thermal boundary layer of considerable density difference.

To find an appropriate ramping rate, we found the minimum light transmission at various ramping rates as shown in Fig. 3. This shows how T_c is affected by the ramping rate when $\Delta V = 0$. All ramps were started at $\cong$ 1 K above T_c. The very slow ramps were done in three stages: the temperature is ramped at 2.00 mK/min, then 0.02 mK/min, and finally at the slow rate indicated in the

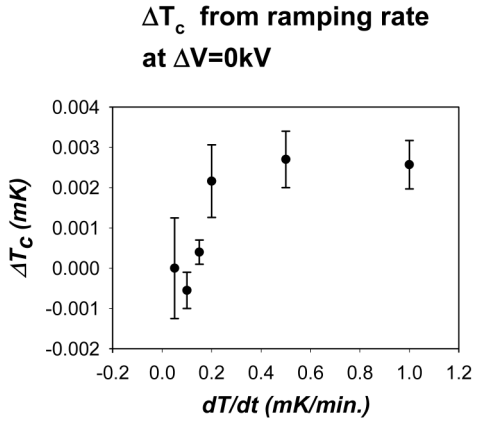

FIG. 3. Shown above are the results of T_c measured at various ramping rates at $\Delta V = 0$. The faster ramping rates have a lower minimum of light transmission, the measure of T_c. The slow relaxation of density in a near-critical fluid due to residual temperature gradients does not allow enough time for a well developed density gradient to form, so lower ramping rates are closer to equilibrium conditions.

figure. Total ramping times are typically 24–36 h. The large error bars at the lowest ramping rate are indicative of the very slight changes in the transmitted intensity with temperature at the minimum of intensity at these very slow ramps. Slower ramps were attempted with little success. We observed that the largest T_c shift was at the slowest ramping rate. Figure 4 shows the shift in T_c as the voltage is increased, where each data point was obtained at the lowest ramping rate in Fig. 3.

Previous experiments in near-critical fluids performed in weightlessness showed a density change when a relatively weak electric field gradient was applied [5]. We also

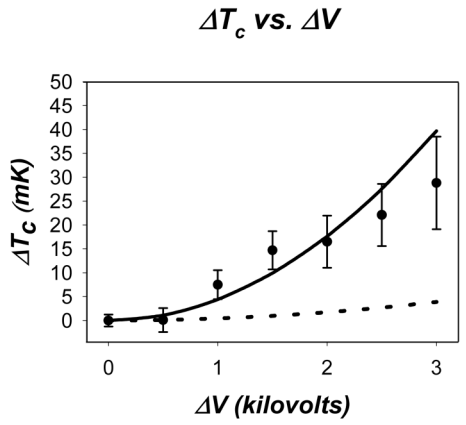

FIG. 4. Shown above are the main results. T_c measured at a ramping rate of $dT/dt = 0.04$ mK/min. The critical temperature is clearly shifted upward as ΔV increases, consistent with thermodynamic stability and renormalization theory. The solid line is a fit to a parabolic curve and the dashed line is the renormalization theory.

visualized changes in the vertical density gradient in weightlessness (this apparatus was in a KC-135 jet that performs a sinusoidal flight path to repeatedly produce $\cong$ 20 s of weightlessness) [15]. Without an electric field, the horizontal critical density layer quickly expanded as the hydrostatic pressure gradient was removed. In order to observe the effect of the E field in the very limited time available in weightlessness, we switched the voltage on and off, producing an approximate square wave in voltage with a period of 2 s. When the 3 kV ac potential was applied, the horizontal critical density layer was clearly distorted such that the center electrode tended to compress the fluid. In the configuration shown in Figs. 1 and 2, we should expect the inhomogeneous density distribution to produce large-scale refraction that may possibly modify the transmitted light intensity. The superposition of the gravitational force (directed along the optical axis) and radial electrostriction produces an axially symmetric density distribution. This bends the light toward the center axis of the cell. At T_c, however, we expect the maximum refraction from the maximum compressibility and the maximum light extinction from refraction. Refraction can amplify only the light extinction process that already exists from critical opalescence. We also note that an increase in the density of the fluid in the capacitor from the electrostriction would produce an apparent decrease in ΔT_c because the coexistence temperature for phase separation is always less than T_c.

These observations clearly demonstrated the contributions of the two external fields to the fluid's free energy density F. In fact, the density distribution of the fluid should be such that the total free energy $\mathcal{F} = \int dVF$ is a minimum. Previous attempts to calculate ΔT_c followed Landau and Lifshitz, who showed that the usual chemical potential μ_o is modified in the presence of an E field to $\mu = \mu_o - \frac{1}{2}\varepsilon_o E^2(\partial\kappa/\partial\rho)_T$. At the critical point the usual thermodynamic stability condition $(\partial\mu/\partial\rho)_{E,T} > 0$ becomes $(\partial\mu/\partial\rho)_{E,T} = (\partial\mu_o/\partial\rho)_{E,T} - \frac{1}{2}\varepsilon_o E^2(\partial^2\kappa/\partial\rho^2)_T = 0$ and the stability condition becomes $(\partial^2\mu/\partial\rho^2)_{E,T} = 0$. Zimmerli *et al.* [5] used the restricted cubic model and the Clausius-Mossetti formula in the above equations to evaluate both ΔT_c and the shift in the critical density $\Delta\rho_c$. In this system at $\Delta V = 3$ kV, using their approach we calculate $\Delta T_c = 0.06$ mK and $\Delta\rho_c$ is insignificant. The measured ΔT_c is 3 orders of magnitude larger.

Onuki predicted an increase in T_c from two separate mechanisms. The first increase is from the shift in the stability condition as outlined above. The second contribution is from a dipole-dipole interaction between density fluctuations. The external E field induces a dipole moment in each density fluctuation, and these dipole moments interact. This interaction changes F and further increases T_c. Using a renormalization group calculation, Onuki predicted an increase in ΔT_c, also quadratic in the E field

as it suppresses fluctuations in the E field's direction, thus decreasing the critical dimensionality from 4 to 3. This crossover to the "strong field" regime occurs when the compressibility $\Gamma = \Gamma_0(T/T_c - 1)^{-\gamma}$ is greater than the parameter C_E^{-1}, where $C_E = (\kappa/\varepsilon_0)[\rho_c(d\kappa/d\rho)E]^2$ (derived from the dipole-dipole interaction). This parameter has been rescaled to make it dimensionally consistent in the pure fluid case. Because of the slow ramping procedure, this condition is always satisfied. The shift is then given, after a renormalization calculation, by $\Delta T_c = \frac{\pi}{108} C_E \Gamma_0 T_c = 4.31 \times 10^{-10}\ (^\circ\mathrm{C/volts}^2)V^2$. The data shows that the corresponding coefficient is $4.41 \times 10^{-9}\ (^\circ\mathrm{C/volts}^2)$, so this theory is closer but still predicts a shift that is an order of magnitude too small. We note that this theory assumes a homogeneous field and a homogeneous fluid, where here we have a diverging radial field $\mathbf{E}$, in addition to $\mathbf{g}$, inducing a cylindrically symmetric density distribution. Because of the dominance of $\mathbf{g}$ in this case, the critical density is mostly in the equatorial plane of the center electrode and the large fluctuations in this plane would still be perpendicular to the local $\mathbf{E}$ field. If $\mathbf{g}$ were also suppressing the fluctuations, then the critical dimension would be less than 3 and this may qualitatively explain the larger than expected shift.

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[1] C. Domb, *The Critical Point: A Historical Introduction* (Taylor & Francis, Bristol, PA, 1996).
[2] J. A. Lipa, D. R. Swanson, J. A. Nissen, T. C. P. Chui, and U. E. Israelsson, Phys. Rev. Lett. **76**, 944 (1996).
[3] M. R. Moldover, J. V. Sengers, R. W. Gammon, and R. J. Hocken, Rev. Mod. Phys. **51**, 79 (1979).
[4] A. Onuki, Europhys. Lett. **29**, 611 (1995).
[5] G. A. Zimmerli, R. A. Wilkinson, R. A. Ferrell, and M. R. Moldover, Phys. Rev. E **59**, 5862 (1999). Also see Phys. Rev. Lett. **82**, 5253 (1999).
[6] P. Debye and K. Kleboth, J. Chem. Phys. **42**, 3155 (1965).
[7] D. Beaglehole, J. Chem. Phys. **74**, 5251 (1981).
[8] D. Wirtz and G. G. Fuller, Phys. Rev. Lett. **71**, 2236 (1991).
[9] L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media* (Addison-Wesley, Reading, MA, 1960).
[10] K. Amara and J. Hegseth, J. Fluid Mech. **450**, 297 (2002).
[11] C. Morteau, M. Zalzmann, Y. Garrabos, and D. Beysens, in *Fluids in Space*, edited by A. Viviani (Edizioni Jean Gilder Congressi srl, Naples, 1996), p. 327.
[12] A. Onuki and R. A. Ferrell, Physica (Amsterdam) **164A**, 245 (1990). Also see A. Onuki, H. Hong, and R. A. Ferrell, Phys. Rev. A **41**, 2256 (1990).
[13] H. Boukari, R. L. Pego, and R. W. Gammon, Phys. Rev. E **52**, 1614 (1995).
[14] D. Bailly and B. Zappoli, Phys. Rev. E **62**, 2353 (2000).
[15] J. Hegseth and K. Amara, Ann. N.Y. Acad. Sci. **974**, 10 (2002).