Viscoelasticity of Xenon near the Critical Point

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Using a novel, overdamped, oscillator flown aboard the space shuttle, we measured the viscosity of xenon near the liquid-vapor critical point in the frequency range $2 \text{ Hz} \leq f \leq 12 \text{ Hz}$. The measured viscosity divergence is characterized by the exponent $z_\eta = 0.0690 \pm 0.0006$, in agreement with the value $z_\eta = 0.067 \pm 0.002$ calculated from a two-loop perturbation expansion. Viscoelastic behavior was evident when $t = (T - T_c)/T_c < 10^{-5}$ and dominant when $t < 10^{-6}$, further from T_c than predicted. Viscoelastic behavior scales as $Af\tau$ where τ is the fluctuation decay time. The measured value of A is 2.0 ± 0.3 times the result of a one-loop calculation. (Uncertainties stated are one standard uncertainty.) [S0031-9007(98)08357-4]

PACS numbers: 51.20.+d, 05.70.Jk, 64.60.Ht, 83.50.Fc

As the liquid-vapor critical point is approached, the shear viscosity $\eta(\xi)$ measured in the limit of zero frequency diverges as ξ^{z_η}, where ξ is the correlation length, which itself diverges on the critical isochore as $t^{-\nu}$. [Here, $t \equiv (T - T_c)/T_c$, T_c is the critical temperature, and $\nu = 0.630$.] Because the critical viscosity exponent $z_\eta = 0.069$ is so small, it is very difficult to measure accurately on Earth in a pure fluid such as xenon. Close to the critical point, gravity causes stratification of the very compressible xenon and blunts the divergence of the viscosity in a manner that depends upon the height of the viscometer. Far from the critical point, the separation of the viscosity into critical and background contributions is uncertain; the critical contribution is a small fraction of the total, and the separation depends sensitively upon the "crossover function," which is known only approximately.

At nonzero frequencies f, $\eta(\xi, f)$ is complex in nearcritical fluids, even at the subaudio frequencies used here. Ordinarily, viscoelasticity (i.e., a partly elastic response to shear stress) is seen either at much higher frequencies or in complicated fluids such as polymer melts. Bhattacharjee and Ferrell [1] calculated the scaling function $S(z)$ for near-critical viscoelasticity. Their result can be combined with the crossover function $H(\xi)$ from Ref. [2] and the background viscosity $\eta_0(T, \rho)$ from Appendix C of Ref. [3] to obtain the prediction

$$\eta(\xi, f) = \eta_0(T, \rho) \exp[z_\eta H(\xi)][S(Az)]^{-z_\eta/(3+z_\eta)}. \tag{1}$$

Here, the scaled frequency is defined by $z \equiv -i\pi f\tau$, where the fluctuation-decay time is $\tau \equiv 6\pi\eta\xi^3/k_B T_c = \tau_0 t^{-\nu(3+z_\eta)}$. We introduced the parameter $A = 2.0 \pm 0.3$ into the argument of the scaling function $S(z)$ to obtain agreement with our data. (All uncertainties stated are a single standard uncertainty.) Accurate measurements of the scaling function require accurate measurements of $\eta(\xi, f)$ in the region where ξ is large and where z spans

the range $z \ll 1$ to $z \gg 1$. Prior measurements were unable to achieve these conditions [4,5].

We developed a novel viscometer, integrated it into the "critical viscosity of xenon" (CVX) experiment package, and operated it aboard the Space Shuttle Mission STS-85. Figure 1 shows that the shuttle's microgravity environment enabled CVX to make accurate viscosity measurements two decades in reduced temperature closer to T_c than the best ground-based measurements. The data for the real part of the viscosity $\text{Re}(\eta)$ lead to the result $z_\eta = 0.0690 \pm 0.0006$, in agreement with the value $z_\eta = 0.067 \pm 0.002$ obtained from a recent two-loop perturbation expansion [6].

As CVX approached the critical temperature, viscoelasticity caused $\text{Re}(\eta)$ to depart from the asymptotic powerlaw divergence, first at high frequencies and then at low frequencies as shown in Fig. 2. In the same temperature range, $\text{Im}(\eta)$ decreased from zero. [$\text{Im}(\eta)$ is the ratio of
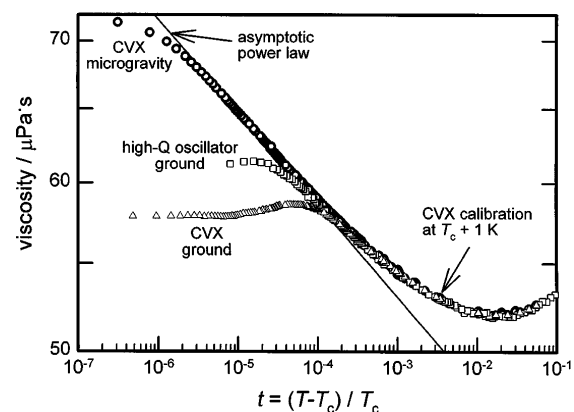

FIG. 1. Log-log plot of xenon's viscosity measured near the critical point. The asymptotic line has the slope $z_\eta/\nu = 0.0435$ deduced from the present microgravity data. Near T_c, the CVX microgravity data [$\text{Re}(\eta)$ at 2 Hz] depart from the asymptotic line because of the viscoelasticity. The two sets of ground data depart from the asymptotic line further from T_c because the xenon stratifies in Earth's gravity.
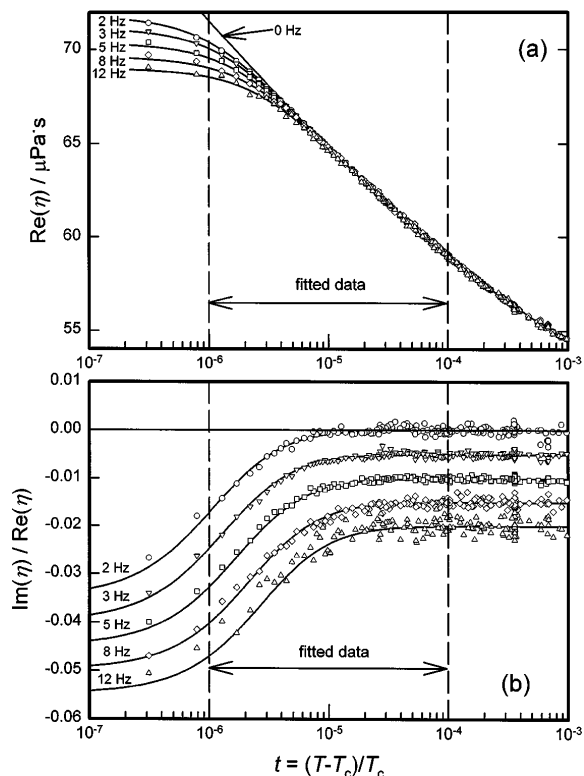
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FIG. 2. Xenon's viscosity at critical density measured at 2–12 Hz. The solid curves resulted from fitting Eq. (1) to the data in the range $10^{-6} < t < 10^{-4}$. (a) The real viscosity $\mathrm{Re}(\eta)$. Near $t = 10^{-5}$, the data depart from the 0 Hz curve because of viscoelasticity. (b) The ratio $\mathrm{Im}(\eta)/\mathrm{Re}(\eta)$. For clarity, the ratio data at frequencies above 2 Hz are displaced downward by integer multiples of 0.005; otherwise, they would coincide at $t > 10^{-5}$.

the quadrature component of drag on the viscometer to the driving force.] This viscoelastic behavior was evident when $t < 10^{-5}$ and dominant at $t < 10^{-6}$, further from T_c than predicted by Bhattacharjee and Ferrell's one-loop calculation [1]. The fitted value $A = 2.0 \pm 0.3$ means that viscoelastic relaxation in xenon is 2 times slower than predicted. This factor is a challenge to the present one-loop theory; however, the challenge is comparable to one that Bhattacharjee and Ferrell met when scaling ultrasonic attenuation and dispersion in near-critical liquid mixtures. When they replaced the one-loop acoustic theory with a more sophisticated theory [7], the ultrasonic frequency scale changed by a factor of 1.6.

The unique CVX viscometer, shown schematically in Fig. 3, was a thin rectangular nickel screen (19 mm long and 8 mm wide) composed of 0.03 mm wide electrode-posited wires spaced 0.85 mm apart. A wire in the middle of the screen was extended and soldered to a supporting yoke, permitting the screen to oscillate in the xenon much like a child's seesaw. These torsional oscillations were driven and detected by nearby electrodes. The torque applied to the screen was derived from a repeated, 32-s long waveform that had equally weighted frequency compo-
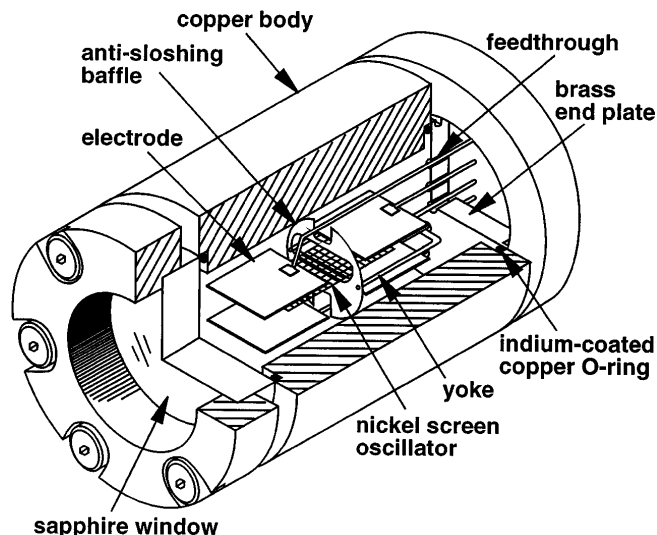

FIG. 3. Cutaway view of the CVX viscometer cell. The cylindrical volume occupied by the xenon was 38 mm long and 19 mm in diameter. The screen was oscillated by applying voltages to the four electrodes. The electrodes were also components of a 10 kHz capacitance bridge that detected the screen's motion.

nents in the range 0.03 Hz $< f <$ 12.5 Hz. The corresponding viscous penetration length $\delta \equiv [\eta/(\rho \pi f)]^{1/2}$ ranged from 800 to 40 μm.

The screen had a complicated geometry; thus, the viscosity could not be calculated from its dimensions and its response to the applied torque. Instead, we relied on a hydrodynamic similarity argument [8] which shows that the drag on the screen was proportional to $f^2 B(\delta)$ and we determined the calibration function $B(\delta)$ from the viscosity data taken at $T_{\mathrm{cal}} = T_c + 1$ K while CVX was in orbit. The calibration procedure and tests of the similarity argument were described in our earlier work [8]. Because $\mathrm{Im}(\eta) \approx 0$ under the conditions of the calibration, we deduced $\mathrm{Re}(\eta)$ and $\mathrm{Im}(\eta)$ from the magnitude and the phase of the screen's response to the applied torques by analytic continuation of $B(\delta)$ to complex arguments.

We used data outside the viscoelastic region to check the calibration procedure in three ways. First, the values of $\mathrm{Re}(\eta)$ were examined at 2, 3, 5, 8, and 12 Hz for frequency dependence. None was found. Second, the values of $\mathrm{Re}(\eta)$ were compared with our previous data [3] taken on Earth with a high-Q, 7 mm high, oscillating-cylinder viscometer. They agreed throughout the range $3 \times 10^{-4} < t < 5 \times 10^{-2}$, where the data sets overlap and where the high-Q data were not greatly affected by stratification. Third, the values of $\mathrm{Im}(\eta)$ were examined for departures from zero. The examination revealed departures from zero that were less than $0.002\,\mathrm{Re}(\eta)$ and were a weak function of $\log_{10}(T - T_{\mathrm{cal}})$, suggesting that the screen was influenced by an additional force not proportional to $f^2 B(\delta)$. We applied a corresponding correction proportional to $\log_{10}(T - T_{\mathrm{cal}})$, and we extrapolated

this correction to $\text{Im}(\eta)$ inside the viscoelastic region. We checked the validity of this extrapolation by fitting A separately to $\text{Re}(\eta)$ and $\text{Im}(\eta)$ inside the viscoelastic region. The two values of A agreed within 4%. [If we had assumed the correction to $\text{Im}(\eta)$ were proportional to $(T - T_{cal})$ raised to a small power such as z_η, our results would be unchanged.]

The maximum displacement of the screen was 0.03 mm and the maximum shear rate was 9 s^{-1}. The product (shear rate) $\times$ (fluctuation-decay time) was always sufficiently small that CVX did not encounter near-critical shear thinning [9]. The oscillating screen had a mass of only 1 mg; thus, its operation was relatively insensitive to the in-orbit vibrations of the shuttle, and it survived the rigors of launch and landing with a large margin of safety.

The CVX cell and thermostat were designed such that the xenon sample would be isothermal within 0.2 μK at $T_c \approx 290$ K. Tests indicated that the thermostat's performance was 4 times better than this [10]. Calculations ignoring convection showed that the CVX sample was too large to attain thermal equilibrium very close to T_c during the 11-day flight. This led to the concern that once large density inhomogeneities were generated, for example, by cooling the sample below T_c, they would persist. To alleviate this concern, the sample's temperature was programmed to minimize density inhomogeneities. The sample was fully equilibrated at $T_c + 100$ mK to achieve a homogeneous density. The subsequent cooling ramps towards T_c reduced the density in the interior of the cell by at most $0.0013\rho_c$, according to a conservative, convection-free, one-dimensional, thermal model. Electric-field induced convection of the sample and heat conduction along the metal components within the cell could only reduce density inhomogeneities.

Key portions of the CVX data were taken as the temperature was ramped downward through T_c. The first ramp, at the rate -1 μK/s, started at $T_c + 0.05$ K. The second ramp was 20 times slower; it started at $T_c + 0.003$ K and had the rate -0.05 μK/s. Above T_c, the data from the two ramps were indistinguishable; the viscosity increased monotonically, becoming complex and frequency dependent as T_c was approached. Below T_c, the data from the slower ramp indicated higher viscosities in the phase-separating sample.

In Eq. (1), the background viscosity was described by the sum of analytic functions of the density ρ and the temperature: $\eta_0(T, \rho) = \eta_{00}(T) + \eta_{01}(\rho)$. (See Appendix C of Ref. [3].) These functions were determined from the viscosity measured by others far from the critical point. For consistency with the measurements of Ref. [3] and the value $\rho_c = 1116$ kg/m^3, we set $\eta_0(T_c, \rho_c) = 51.3 \pm 0.4$ μPa s. The present results are not sensitive to this description of η_0 [3,11].

The CVX viscosity data at 2, 3, 5, 8, and 12 Hz were used to determine five parameters. Two are the "universal" parameters z_η and A, two are the wave vectors q_C and q_D that occur in the crossover function for xenon, and one is the value of T_c on CVX's temperature scale. When all of the data within the range $10^{-6} < t < 10^{-4}$ were fitted for these parameters, the results included $z_\eta = 0.0690 \pm 0.0006$, $q_C\xi_0 = 0.051 \pm 0.007$, and $q_D\xi_0 = 0.16 \pm 0.05$, where the standard uncertainties quoted allow for the correlations among the parameters. The same fit determined the product $A\tau_0$ with a fractional standard uncertainty of 0.03. However, the fractional uncertainty of A itself is 0.17 because of the larger uncertainty of the fluctuation decay-time amplitude τ_0 given by

$$\tau_0 = \left[\frac{2\xi_0}{e^{4/3}(q_C^{-1} + q_D^{-1})} \right]^{z_\eta} \frac{6\pi\eta_0\xi_0^3}{k_B T_c}. \qquad (2)$$

For xenon, $\tau_0 = (1.15 \pm 0.17) \times 10^{-12}$ s and the uncertainty of τ_0 is dominated by the uncertainty of xenon's correlation length amplitude $\xi_0 = 0.184 \pm 0.009$ nm which we estimated [11] as the difference between the two measurements reported in [12].

The fit to the data more than 290 μK above T_c determined T_c with a standard uncertainty of 8 μK. It is reassuring that, for every frequency examined, both $\text{Re}(\eta)$ and $\text{Im}(\eta)$ showed extrema within 60 μK of the fitted value of T_c. Equally reassuring, the fitted value of $q_C\xi_0$ agrees with the value $q_C\xi_0 = 0.059 \pm 0.004$ determined from independently published data that do not include the near-critical viscosity [3,11].

Figure 2(b) shows the ratio $\text{Im}(\eta)/\text{Re}(\eta)$. This ratio is independent of the background viscosity η_0 and the crossover function $H(\xi)$; thus, these data are sensitive only to A, T_c, and the scaling function. Figure 2 demonstrates that the functional form $S(Az)$ describes both $\text{Re}(\eta)$ and $\text{Im}(\eta)$ in the ranges $10^{-6} < t < 10^{-5}$ and 2 Hz $< f <$ 12 Hz, corresponding to $0.06 < Az < 33$, provided that the factor A that sets the frequency scale has the value 2.0.

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