LOW-FREQUENCY VISCOSITY MEASUREMENTS NEAR THE CRITICAL POINT OF CARBON DIOXIDE ☆

L. BRUSCHI and G. TORZO
Dipartimento di Fisica dell'Università di Padova, Padua, Italy
and Gruppo Nazionale Struttura della Materia, Padua, Italy

Received 5 July 1983

Preliminary CO_2 viscosity measurements have been performed along an isochore near to the critical one. Particular care was taken to avoid gravitational and frequency effects. The results are in agreement with the theoretical prediction of a divergent viscosity critical behaviour.

Near the critical point of a classical fluid, the theory of critical dynamics [1–6] predicts an asymptotical divergence of the shear viscosity η:

$$\eta/\bar{\eta} = (q\xi)^{\phi}\,, \tag{1}$$

$\bar{\eta}$ is the so-called normal viscosity, ξ the correlation length, q a fluid-dependent parameter, and ϕ a universal exponent spanning the range

$$0.054 < \phi < 0.065\,. \tag{2}$$

Experiments on various fluids have been performed by several authors [7–15]. All of them confirm the existence of an anomalous viscosity enhancement near the critical point [16–18]. However an accurate experimental test of (1) is quite difficult, since two effects limit the measurement accuracy close to the critical point. The first one is the gravitational effect: the local fluid density may be very different from the average density if the fluid sample has a large vertical thickness. To overcome this difficulty we performed experiments with a vibrating wire viscosimeter [13,15], which allows simultaneous density and viscosity measurements in a thin layer of fluid. The second one is a frequency effect [19]. If viscosity measurements are performed at a finite frequency one may observe a deviation from the hydrodynamic behaviour, since the characteristic fluid relaxation rate diverges. This effect was probably present in a previous work [13, 15], where we obtained a non-divergent viscosity behaviour.

To avoid this second difficulty we recently developed a new type of viscosimeter [20]. It allows measurements at very low shear rate in a thin horizontal layer of a small fluid sample. With the viscosimeter the viscosity is obtained by measuring the drag moment exerted by the fluid on a rotating disk.

Here we only give a schematic description of the viscosimeter, since it will be extensively described elsewhere [20]. In fig. 1a we show the experimental apparatus. A cylindrical cavity (2 cm diameter and 0.08 cm height) is cut inside a massive copper cell. A copper disk (1.8 cm diameter and 0.02 cm thickness) is axially held inside the cavity by means of a steel pivot. The pivot is soldered on the disk and clamped between two rubies fixed onto the cell walls. The cavity is filled through a stainless steel capillary and sealed by a metal-to-metal needle valve built in the cell body. Therefore the sample fluid is entirely confined inside the measuring cavity.

The disk is set into motion by means of eddy currents induced on the disk itself. Two electromagnets (fig. 1a), respectively excited by simusoidal currents having the same frequency ν(= 1560 Hz) but a phase difference equal to $\pi/2$, yield two magnetic fields perpendicular to the disk surface:

☆ Work sponsored by Consiglio Nazionale delle Ricerche, Rome, Italy.

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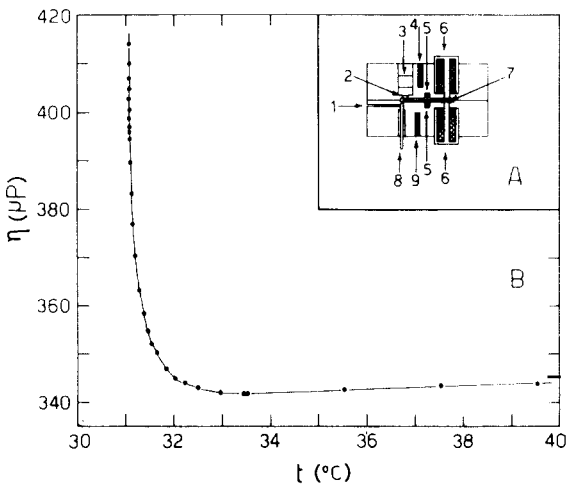

Fig. 1. A. Schematic view of the measuring cell: 1 fluid inlet, 2 optical window, 3 optical device, 4 secondary thermometer, 5 rubies, 6 electromagnets, 7 rotating disk, 8 needle valve, 9 main thermometer. B. Measured viscosity versus temperature at $\rho = 0.4739\ \mathrm{g/cm^3}$.

$$B_1 = B_{10}\cos(2\pi\nu t), \quad B_2 = B_{20}\cos(2\pi\nu t + \pi/2). \quad (3)$$

The eddy currents, induced on the disk, generate a mean driving moment:

$$\tau_m = K B_{10} B_{20}, \quad (4)$$

and a mean decelerating moment:

$$\tau_e = -(K_1 B_{10}^2 + K_2 B_{20}^2)\,\omega. \quad (5)$$

In the present experiment ($\omega \approx 17\ \mathrm{rad\ s^{-1}}$) τ_e is negligible with respect to τ_m [20], so that in a stationary situation we have

$$\tau_\eta = \tau_m - \tau_0, \quad (6)$$

where $-\tau_0$ is the frictional moment due to the disk bearings, and $-\tau_\eta$ is the viscous moment, which is a function of ω, η, and the fluid density ρ. The ratio τ_0/τ_m is of the order of 3×10^{-2}. Our experiment was performed at constant exciting current amplitudes. In this case $\tau_m - \tau_0$ turns out to be a weak function of temperature only, this dependence being essentially due to the temperature coefficient of the electrical resistivity of copper.

The angular velocity ω and the critical temperature T_c are measured by an optical device. A light beam, emitted by a light emitter diode, is reflected by the disk surface and the reflected beam intensity is monitored by a phototransistor. A small light adsorbing spot, on the disk surface, produces a spike in the phototransistor signal, through which the angular velocity ω can be easily measured.

With such an apparatus we are able to measure ω with a maximum error of 0.05%. The temperature T_c is detected by critical opalescence. When opalescence occurs we observe a lower intensity of the reflected beam. We assume that T_c is the temperature corresponding to the minimum reflected beam intensity. Two NTC thermistors, one at the top and the other at the bottom of the cell, are used as thermometers. The temperature resolution is about 2×10^{-5} °C. To obtain a thermoregulation, of the same order as the temperature resolution, the cell is placed inside a three-stage thermostat, identical to the one described in a previous paper [15].

The viscosity can be determined by measuring the angular velocity ω, the fluid density ρ and by means of eq. (6), once an explicit expression for the viscous moment τ_η is given. τ_η has a simple form in two limiting cases [21]:

$$\tau_\eta \propto \eta\omega/b, \quad \text{for } \delta \gg b,$$
$$\propto \eta\omega/\delta, \quad \text{for } \delta \ll b, \quad (7)$$

where b is the gap between the disk surfaces and the cavity walls, and $\delta = (\eta/\rho\omega)^{1/2}$ is the boundary layer thickness. A general analytical expression for τ_η is not known, while it is difficult to give a precise estimate for $\tau_m - \tau_0$. Following a procedure extensively used with the oscillating disk viscosimeter [8,22–25], we performed calibration measurements with a fluid of known density and viscosity. The measured ω was then fitted by the relationship

$$\eta\omega = A f(\delta), \quad (8)$$

where $f(\delta)$ is an empirical function of δ:

$$f(\delta) = b(1 + \delta/\delta_0) - \{[b(1 + \delta/\delta_0) - 1]^2 + 2b - 1\}^{1/2},$$
$$b = b_0 + b_1[(\delta - \delta_0)^2 + b_2]^{-1}, \quad (9)$$

and A is proportional to $\tau_m - \tau_0$.

The calibration has been performed with nitrogen at 30°C in the pressure range 1–80 atm. The nitrogen viscosity data are reproduced by (8) with a standard deviation of 0.075%.

The temperature dependence of A has been measured at low densities, where $f(\delta)$ is nearly constant ($\delta > b$), in the temperature range 25–40°C. The nitrogen viscosity temperature dependence was obtained by a Keyes-type formula [22].

The calibration procedure was tested in CO_2, by measuring the viscosity at 31.63°C in the density range $2 \times 10^{-3} - 3 \times 10^{-1}$ g/cm^3 [20]. Comparing our results with those obtained by Kestin et al. [25], at the same temperature and in the same density range, we found agreement within 0.5%.

In the present paper we report preliminary CO_2 viscosity measurements along the isochore $\delta = 0.4730$ g/cm^3, as a function of temperature (fig. 1b). The critical temperature turns out to be 31.77°C.

The measurements were performed in the reduced temperature range $1.6 \times 10^{-5} < (T - T_c)/T_c < 2.8 \times 10^{-2}$. The lower limit is not due to apparatus temperature resolution but to thermal gradients arising from the power ($\approx$ 20 mW) dissipated in the driving electromagnets. The observed temperature differences between the upper and the lower thermometer are of the order of 2×10^{-4} °C. To avoid large errors in the reduced temperature, we have then limited its measurement range.

To test relation (1) it is necessary to know the behaviour of the normal viscosity $\bar{\eta}$. This can be expressed as [17]:

$$\bar{\eta}(\rho, t) = \eta_0(t) + \eta_e(\rho, t) , \qquad (10)$$

where η_0 is the "zero density viscosity", and η_e the "excess viscosity" which is a slowly varying function of temperature.

At present our measurements do not yield the full η_0 temperature dependence. Therefore, we have used for it a linear dependence as obtained by fitting data from other authors [14].

In the investigated temperature range, we consider η_e as temperature independent. If we make the hypothesis

$$\eta(\rho, t_1) = \bar{\eta}(\rho, t_1) , \qquad (11)$$

where $\eta(\rho, t_1)$ is the viscosity value obtained with our apparatus at the highest temperature t_1 ($\approx$39.5°C), we obtain

$$\eta_e(\rho) = \eta(\rho, t_1) - \eta_0(t_1) . \qquad (12)$$

In this manner we are able to describe the temperature dependence of normal viscosity at $\rho = 0.4730$ g/cm^3:

$$\bar{\eta}(\rho, t) = 324.74 + 0.4831\, t \qquad (13)$$

where $\bar{\eta}$ is in μP and t in °C.

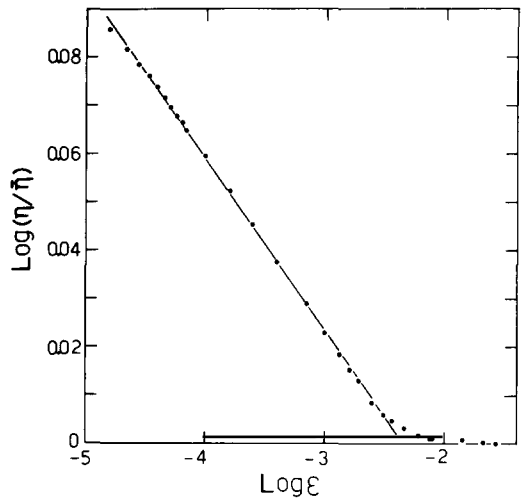

Fig. 2. Log–log plot of $\eta/\bar{\eta}$ versus the reduced temperature $\epsilon = (T - T_c)/T_c$. The experimental errors are of the same size as the dots.

A log–log plot of $\eta/\bar{\eta}$ versus the reduced temperature $\epsilon = (T - T_c)/T_c$ is shown in fig. 2. The experimental errors are of the same size as the dots.

The experimental data for $\epsilon < 3.7 \times 10^{-3}$ are well fitted by

$$\eta/\bar{\eta} = B\, \epsilon^{-x} , \qquad (14)$$

where

$$x = 0.0356 \pm 0.002 , \quad B = 0.8250 \pm 0.0014 . \qquad (15)$$

Along the critical isochore ($\rho_c = 0.468$ g/cm^3) the correlation length behaviour is

$$\xi = \xi_0\, \epsilon^{-\nu} . \qquad (16)$$

So at $\rho = \rho_c$ (1) may be written:

$$\eta/\bar{\eta} = (\xi_0 q)^{\phi} \epsilon^{-\nu\phi} . \qquad (17)$$

Our measurements were performed at a density differing from the critical one by only 1%. Comparing (14) to (17), we have

$$\phi = 0.0563 , \quad q^{-1} = 4.6 \times 10^{-7} \text{ cm} , \qquad (18)$$

by using $\nu = 0.633$, $\xi_0 = 1.5 \times 10^{-8}$ cm.

The ϕ value lies within the predicted range (2). The q^{-1} value may be compared with the one given by the approximate relationship [17]:

$$q^{-1} \approx \frac{8\pi\bar{\eta}\bar{\lambda}\xi^2}{kT\rho(C_p - C_V)} \approx 4.7 \times 10^{-7} \text{ cm}. \quad (19)$$

As a conclusion, in the investigated temperature range, our results show that CO_2 shear viscosity accurately obeys eq. (1), thus yielding an experimental confirmation of critical dynamics theory.

An improved version of rotating disk viscometer is in progress, to further remove the small thermal gradients that are still present in our apparatus, and that prevent us from reaching smaller ϵ values.

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