

Viscosity of nitrogen near the liquid-vapor critical point

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The viscosity of nitrogen in the vicinity of the liquid-vapor critical point at distances from T_c down to 0.01 °K is measured by determining the damping of rotational oscillations of a stack of disks. An anomalous increase in the viscosity is observed in the critical region [$\epsilon \equiv (T - T_c)/T_c \lesssim 10^{-2}$, which amounts to 37% of the excess viscosity at the critical point. The behavior of the singular part of the viscosity satisfies the relations of scaling transformation theory and can be described by a power function (10) on the critical isochor.

The theoretical and experimental data that exist at the present time do not allow unambiguous resolution of the question of the character of the behavior of the shear viscosity near the critical point of a pure liquid. In most theoretical researches^[1-6], the existence of an anomaly in the viscosity in the temperature dependence is assumed but its character is assumed to be different by the different authors: a sharp finite peak, a weak logarithmic singularity, or a stronger power-law divergence. The results of experimental investigations are also contradictory. Measurements of the viscosity in the immediate neighborhood of the critical point have been carried out earlier, primarily for carbon dioxide. The anomalously large increase in the viscosity of carbon dioxide gas near T_c , obtained by Mitchell and co-workers^[7], is of little reliability in view of the unsuitability of the capillary method then used for the measurements in a liquid with infinite compressibility. Researches in which the method of damping of the rotational oscillations of a disk^[8,9] was employed, gave compatible results—a small "hump" of the order of 10% is obtained on the curve of the density dependence of the viscosity in the critical-point region. But since the values of the density were found by calculation with accuracy of the same order as the effect, the problem of the singularity of the viscosity remains open. Recently, another work has been published,^[10] in which the viscosity of carbon dioxide gas was measured accurate to 5% by the method of torsional vibrations of a quartz crystal. The authors worked along an isotherm that lies 1°C above the critical temperature, and no anomalies were discovered.

Experimental investigations of the physical properties of liquids near the critical point entail appreciable difficulties. The greatest obstacles arise from the fact that the compressibility of the pure substance tends to infinity as the critical point is approached, as a consequence of which the gravitational field of the earth produces a significant vertical gradient of the density of the material in the container, and consequently, inhomogeneities of all the other properties. Such a situation sharply limits the possibilities of the experimenter. For example, in order to prevent averaging of the measured value of the viscosity over the height of the container, the measuring element of the viscosimeter should have minimum height and should not introduce any appreciable perturbations in the surrounding medium, in view of its extraordinarily high compressibility. Moreover, in almost every method of measurement of the viscosity, the value of the density of the medium enters into the calculation formula and, as is well known, the equation of state in the critical region is a problem in itself. But even if an equation of state is available, the errors in the established values of the critical parameters, the impossibility of reproduction of specific con-

ditions in the experiment with the required absolute accuracy, and the action of the gravitational effect, all will cause the values of the density obtained by calculation to differ significantly from the actual values, thus leading to large errors both in the determination of the viscosity and in the obtained density dependence of the viscosity. Thus the necessity of the simultaneous measurement of the viscosity and density in the same layer of the liquid in the container is quite evident.

In this connection, a new attempt was undertaken to study experimentally the behavior of the viscosity of a pure material close to the liquid-vapor critical point. Nitrogen was chosen as the subject of the study. Preliminary results were published earlier^[11], but subsequent improvement in the accuracy has shown that the preliminary values of the viscosity were overestimated and the densities underestimated because of errors in calibration that was carried out with the use of the inaccurate data of Forster on the viscosity of liquid nitrogen.

METHOD OF MEASUREMENT

For the simultaneous measurement of the viscosity and density of nitrogen in the region of the critical point, we used the method of an oscillating stack of disks, which had been used previously for measurement of the density of the normal component in liquid helium.^[12] The theory of the damped torsional oscillations executed by a stack of disks suspended from a thin elastic wire in a liquid medium, has been treated by a number of authors,^[12-14] who obtained equations connecting the viscosity η and the density of the medium ρ with the geometric characteristics of the disks and the oscillation parameters. For our case, when we can neglect the effect of the walls of the surrounding chambers, Eqs. (30a, b) were used; these were obtained by Dash and Taylor.^[14] These equations, with account of the quantities $(1 \pm \delta)^{1/2}$ and the correction found by Folse and Hussey^[15], are of the form

$$(\rho\eta)^{1/2} = \frac{2J[\delta(\tau^2/\tau_0^2 + 1) - 2\delta_0\tau/\tau_0]}{[\pi\tau(1-\delta)]^{1/2}[N(r^2-r_1^2)F_1+r^4+2hr^2+8\nu\lambda r^3+3h\lambda r^2]}, \quad (1)$$

$$(\rho\eta)^{1/2} = \frac{2J(\tau^2/\tau_0^2 - 1)}{[\pi\tau(1+\delta)]^{1/2}[N(r^2-r_1^2)F_2+r^4+2hr^2]}. \quad (2)$$

Here τ_0 and τ are the periods of oscillation of the system of disks in a vacuum and in the medium, J is the moment of inertia of the suspended system, r is the radius of the disks, r_1 is the radius of the washer separating the disks, $N + 1$ is the number of disks in the stack, h is the height of the stack, ν is the coefficient of "angular correction," $\lambda = (\tau\eta/\pi\rho)^{1/2}$ is the penetration depth of the viscous wave; the functions F_1 and F_2 are of the form

$$F_{1,2} = \frac{\text{sh}[(1-\delta)^{1/2}s/\lambda] \mp \text{sin}[(1+\delta)^{1/2}s/\lambda](1 \pm \delta)}{\text{ch}[(1-\delta)^{1/2}s/\lambda] + \text{cos}[(1+\delta)^{1/2}s/\lambda]}$$

where the upper sign is for F_1 and the lower for F_2 ; s is the value of the gap between disks and the condition $s \lesssim 2\lambda$ is satisfied.

Expanding the trigonometric functions in the expressions for F_1 and F_2 in series and discarding the small terms of the expansion, we find that, with an accuracy acceptable for our experiment, we can assume

$$F_1 \approx s^2/6\lambda^2 - \delta s/\lambda, \quad F_2 \approx s/\lambda.$$

Then Eqs. (1) and (2) reduce to the following form:

$$\eta^{1/2} = \frac{\delta(\tau^2/\tau_0^2 + 1) - 2\delta_0\tau/\tau_0}{[\tau_0(1-\delta)]^{1/2}(c+d\lambda - e\delta/\lambda + f/\lambda^2)}, \quad (3)$$

$$\rho = \frac{\tau^2/\tau_0^2 - 1}{(1+\delta)^{1/2}(a+b\lambda)}, \quad (4)$$

where

$$a = \frac{\pi}{2J} N(r^4 - r_1^4)s, \quad b = \frac{\pi}{2J}(r^4 + 2hr^3), \quad c = \frac{b}{\sqrt{\pi}},$$

$$d = \frac{\sqrt{\pi}}{2J}(8vr^3 + 3hr^2), \quad e = \frac{a}{\sqrt{\pi}}, \quad f = \frac{as^2}{6\sqrt{\pi}}.$$

In view of the difficulty of calculation of the numerical coefficients a, b, c, d, e and f for a real stack of disks with the necessary accuracy and with the aim of taking into account the influence of the suspension system, we have determined their values by calibration measurements with gaseous argon at a temperature of -100°C and nitrogen at a temperature of -90°C in the density range from 0.04 to 0.35 g/cm³, using the reliable experimental data on the viscosity and density published in^[16, 17] (the error was no greater than 0.2% for the viscosity and no greater than 0.1% for the density). The following values were obtained for the numerical coefficients: $a = 0.603$, $b = 3.20$, $c = 1.805$, $d = 1.17$, $e = 0.34$ and $f = 1.6 \times 10^{-4}$.

The proper damping decrement of the oscillations of the suspension system δ_0 and the zeroth period of oscillations τ_0 were measured in a vacuum of $\sim 10^{-6}$ mm Hg; here δ_0 amounted to 5×10^{-5} , and for τ_0 we obtained experimentally a relation that took into account the effect of the variations of the elasticity of the filament and of the dimensions of the stack of disks with temperature:

$$\tau_0[\text{sec}] = 30.987 + 10^{-4}(5.2T + 57t_f),$$

here T is the temperature of the disks in $^\circ\text{K}$, and t_f is the temperature of the filament in $^\circ\text{C}$, estimated from the temperature of the tube in which the filament was located.

The values of η and ρ were found from the experimentally determined τ and δ by simultaneously solving (3) and (4). The solution was carried out with the help of an M-20 electronic computer.

We now consider the following question: do Eqs. (1) and (2) remain valid for specific critical conditions, in view of the divergence of the compressibility and the singularities of the kinetic coefficients at the critical point? The general equations of motion for small oscillations of a body in a viscous compressible fluid are of the form^[18]

$$\rho \partial \mathbf{v} / \partial t = -\text{grad } P + \eta \Delta \mathbf{v} + (\zeta + \eta/3) \text{grad div } \mathbf{v}, \quad (5)$$

$$\partial \rho / \partial t + \text{div } \rho \mathbf{v} = 0. \quad (6)$$

In all the theories of the method of the oscillating disk or stack of disks, the authors assume the liquid to

be incompressible and set $\text{div } \mathbf{v} = 0$ in the equations of motion. We shall see how close to the critical point such an assumption is valid. With this purpose, we compare the orders of magnitude of the terms $(\zeta + \eta/3) \text{grad div } \mathbf{v}$ and $\eta \Delta \mathbf{v}$ in the Navier-Stokes equation (5).

The stack of disks executes harmonic rotational oscillations with an angular amplitude α and frequency ω ; consequently, the amplitude of the linear velocity in the liquid is $\mathbf{v} = \alpha r \omega$. The oscillations of the pressure in the liquid $\Delta P \sim \rho v^2$ then produce density changes $\Delta \rho \sim \rho K_T \rho v^2$, where K_T is the isothermal compressibility. These density changes have a frequency ω and range in space over a distance of the order of r , i.e., $\partial \rho / \partial t \sim K_T \rho^2 v^2 \omega$ and $\text{grad } \rho \sim K_T \rho^2 v^2 / r$. We then have from the continuity equation (6)

$$\text{div } \mathbf{v} = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial t} + \text{grad } \rho \cdot \mathbf{v} \right) \sim \rho K_T v^2 \omega (1 + \alpha) \approx \rho K_T v^2 \omega.$$

The value of $\text{div } \mathbf{v}$ undergoes a significant change (of the order of the quantity $\text{div } \mathbf{v}$ itself) over distances of the order of r ; therefore, $\text{grad div } \mathbf{v} \sim \rho K_T v^2 \omega / r$. It has been established experimentally^[19] that the isothermal compressibility of a simple liquid diverges at the critical point according to the law

$$K_T \approx \Gamma \epsilon^{-1.25}, \quad \epsilon = (T - T_c) / T_c,$$

where $\Gamma P_c \approx 0.05$; then

$$\text{grad div } \mathbf{v} \sim 0.05 \rho v^2 \omega \epsilon^{-1.25} / P_c r.$$

The order of magnitude of the factor $\zeta + \eta/3$ is determined essentially by the value of the bulk viscosity ζ , which, according to theory^[3] is of the order of $\zeta \sim \zeta_0 \epsilon^{-2}$ near the critical point. Thus,

$$(\zeta + \eta/3) \text{grad div } \mathbf{v} \sim 0.05 \zeta_0 \rho v^2 \omega \epsilon^{-3.25} / P_c r. \quad (7)$$

The order of magnitude of $\eta \Delta \mathbf{v}$ is found from the following considerations: inasmuch as the velocity of the transverse wave in the liquid falls off with distance l to the surface of the vibrating body, according to the law $v \sim l^{-1/2}$ ^[18], we have $\Delta \mathbf{v} \sim \mathbf{v} / \lambda^2$ and

$$\eta \Delta \mathbf{v} \sim \eta v / \lambda^2 = v \omega \rho / 2. \quad (8)$$

Dividing (7) by (8), we get

$$(\zeta + \eta/3) \text{grad div } \mathbf{v} / \eta \Delta \mathbf{v} \sim 10^{-1} \zeta_0 \alpha \omega \epsilon^{-3.25} / P_c. \quad (9)$$

From data on the ultrasonic absorption in nitrogen,^[20] we find $\zeta_0 \sim 10^{-6}$ g/cm-sec (as $\omega \rightarrow 0$). Substituting this value of ζ_0 and $\alpha \approx 0.1$ rad, $\omega = 2\pi/\tau \approx 0.2$ sec⁻¹, $P_c = 33.5$ atm (for our case) in (9), we obtain

$$(\zeta + \eta/3) \text{grad div } \mathbf{v} / \eta \Delta \mathbf{v} \sim 10^{-1} \zeta_0 \alpha \omega \epsilon^{-3.25} / P_c. \quad (9)$$

It follows from this relation that the contribution of the term $(\zeta + \eta/3) \text{grad div } \mathbf{v}$ in the Navier-Stokes equation rises swiftly with approach to the critical point, but for $\epsilon = 10^{-4}$ (the usual experimental limit) it is still small, amounting to $\sim 0.1\%$.

Thus Eqs. (1) and (2), which were obtained on the basis of the simplified equations of motion, remain in force at $\epsilon \lesssim 10^{-4}$. We also note that the method of oscillating disks allows us to move close to the critical point in a hydrodynamic regime, i.e., maintaining the condition $k\xi \ll 1$, since the oscillatory processes in the liquid in this case are characterized by small wave numbers k ($k = \lambda^{-1}$). Actually, if $k \approx 10$ cm⁻¹ in our case and, according to^[21], the correlation length $\xi \approx 1.5 \epsilon^{-0.63}$ Å, then for $\epsilon = 10^{-6}$, for example, $k\xi \approx 10^{-3} \ll 1$.

EXPERIMENTAL PART

Figure 1 shows a diagram of the cryostat with the viscosimeter. The stack 1 consists of six disks of diameter 4.2 cm, made out of copper sheet. The disks were assembled on a shaft and spaced 0.053 cm apart by interlining washers of 1 cm diameter. Thus the height of the stacks amounted to 0.325 cm. The shaft of the stack was fastened to glass rod 2 (diameter 0.1 cm), the upper end of which was inserted in the holder 3 with a small mirror of dimensions 0.3×0.5 cm. This entire system was suspended from a phosphor bronze wire filament 4, which had a diameter of 40μ and a free length of 25 cm. The point of suspension was located on a rotatable sleeve controlled by the electromagnet 5. The system was given its initial oscillations by means of a short-time twisting of the upper end of the wire. The amplitudes of the oscillations were determined with the help of the little mirror and scale, for which a glass window 6 was provided. The scale of length 1.3 m was made of plastic and was fastened on a circle with radius 2.5 m and with center on the axis of the suspension system. It had millimeter divisions, drawn with an error not greater than 0.03 cm over a length of 100 cm. The amplitudes were measured with a terrestrial telescope with an accuracy to within ± 0.04 cm. Counting of the periods of oscillations was performed in the following manner: as the oscillatory system passed through the null position, the light beam reflected from the mirror intercepted a photodiode and the intervals of time between the electric impulses produced in it were recorded by an electronic frequency meter ChZ-3A. The error in the measurement of the periods of oscillation amounted to several milliseconds.

The low-temperature part of the apparatus consisted of a massive cylindrical chamber 7, in the hollow part of which the oscillations of the stack of disks take place. There are gaps between the stack and the surfaces of the cavity—1 cm above and below and 0.5 cm laterally. The chamber is suspended on a stainless steel tube in the

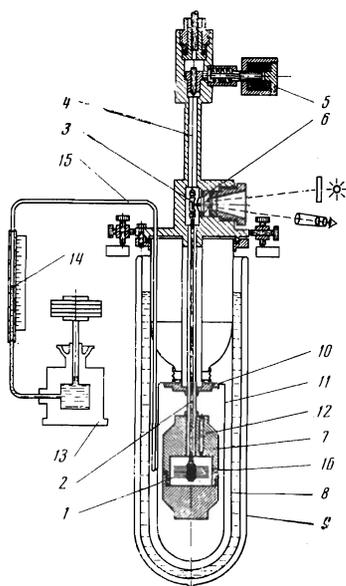


FIG. 1. Diagram of cryostat with viscosimeter: 1 — stack of disks; 2 — glass rod; 3 — holder for mirror; 4 — phosphor bronze wire; 5 — electromagnet; 6 — window; 7 — copper chamber; 8 — vacuum cylinder; 9 — dewar with liquid nitrogen; 10 — copper cap; 11 — radiation screen; 12 — platinum screen; 13 — loading-piston manometer MP-60 14 — oil pressure gauge; 15 — tube for pressure measurement; 16 — capillary tube.

evacuated cylinder 8, the lower end of which is immersed in the liquid-nitrogen filled dewar 9. The chamber is cooled to the specified temperature by means of a heat-exchange gas which is then pumped out to a pressure of not more than 10^{-4} mm Hg. To eliminate temperature gradients in the chamber, the latter is screened from above by a copper cap 10, which diverts the thermal influx along the tube and supporting wires, and by a radiation screen 11. The temperature of the cap is maintained at several hundredths of a degree higher than that of the chamber, to eliminate the possibility of convection of the liquid. The temperature of the screen is set at several tenths of a degree below the temperature of the chamber. The specified values of the temperature of the chamber and the temperature difference between it, the screen, and the cap are maintained by automatic regulators (based on photoelectric amplifiers F-116), which control the corresponding heating coils. Differential copper-constantan thermocouples serve as temperature pickups for the cap and screen, and a thermistor of a germanium crystal, alloyed with gold are used for the chamber. The steep temperature characteristic of the thermistor made it possible to stabilize the temperature of the chamber to within 0.0005°K . The measurement of the temperature was carried out with a platinum resistance thermometer 12 in a usual potentiometer circuit with absolute accuracy $\pm 0.01^\circ\text{K}$ and sensitivity to a temperature change of 0.0005°K .

The upper part of the viscosimeter communicates with the gas-filling system through a thin tube. Measurement of the pressure is carried out by means of a loading-piston manometer 13 (type MP-60 class 0.05) in conjunction with a differential oil pressure gauge 14 with a pressure sensitivity 0.0002 kg/cm^2 . The tube 15 for measurement of the pressure in the chamber is let out at the level of the disks. The temperature of the vertical part of the tube was kept constant (equal to the room temperature) with the help of an automatic regulator, and the transition from the chamber temperature to room temperature was accomplished with a horizontal loop of stainless steel capillary tube 16. Such a method makes it possible to take into account the correction to the pressure for the weight of the column of gas in the tube, and the density distribution on the horizontal part, which cannot be accounted for, does not contribute to the value of the pressure.

In the present investigation, nitrogen of 99.97% purity was used for the measurements. The measurements were performed along fourteen isotherms in the temperature range from 126.16 to 135.00°K and at densities from 0.20 to 0.45 g/cm^3 . The viscosimeter was filled with nitrogen in an amount approximately corresponding to the specified value of the density in the measurement chamber, and then the necessary temperature was established. By changing the nitrogen content of the chamber, a systematic passage along the isotherm was guaranteed from the subcritical values of the density to supercritical and reverse. The meniscus, or the level of the liquid with the maximum density gradient, moved in this case along the height of the chamber and passed through the stack of disks, which assured a closer approach to the critical point with respect to all parameters. After each filling of the chamber and stabilization of the temperature, the pressure was measured as well as the period and amplitude of the oscillations. For each point, the measurements were repeated every 15–30 min with the aim of making clear the time required to establish thermodynamic equilibrium. It was found that the time

in which the measured parameters did not change increases for the homogeneous state from about ten minutes for points very far removed from the critical point to 10 hours for points very close to it. An even longer time was required to establish the two-phase state near the critical point, where separation into phases takes place very slowly.

In the course of measurement, the amplitudes of the oscillations were read beginning with the value $A_n = 100-120$ cm and ending with the amplitude $A_{n+m} = 10-15$ cm, where m was equal to 7-15. The damping decrement was determined from the formula

$$\delta = \frac{1}{2\pi m} \ln \frac{A_n}{A_{n+m}}$$

(it varied between the limits 0.028-0.055) with an error not worse than 0.15%. The absolute accuracy of the values of η and ρ , obtained from Eqs. (1) and (2), depends on the reliability of the theory of the method and on the accuracy of the calibration and the accuracy of the measured parameters, and is estimated in the given case to be 1% for the density and 2% for the viscosity.

EXPERIMENTAL RESULTS AND THEIR DISCUSSION

Table I gives the experimental results of the measurements of the density and viscosity of nitrogen for four supercritical isotherms: 127.00, 128.00, 130.00 and 135.00°K, and Figs. 2 and 3 show the immediate near-critical region, where the minimum step for the isotherms is equal to 0.01°K. The $P - \rho - T$ dependence (see Fig. 3) was used to find the most probable value of the critical temperature, $T_c = 126.21^\circ$ K, and other parameters of the critical point of nitrogen, namely $\rho_c = 0.311 \pm 0.003$ g/cm³ and $P_c = 34.65 \pm 0.02$ kg/cm². Thus the isotherms 126.16, 126.18, and 126.20° K lie in the two-phase region, and the remainder are above the critical point.

Table II gives the results of the measurement of P , ρ and η for the critical isotherm with the primary experimental data (as an example)—the oscillation periods and damping decrements. Attention is called in Fig. 2 to the presence of a break in the isotherms, located in the vicinity of $\sim 0.05^\circ$ K from the critical temperature. The occurrence of this break is due to the anomalous increase in the viscosity, which is clearly seen in the

TABLE I. Viscosity of nitrogen in the supercritical region*

T = 127.00° K			T = 128.00° K			T = 130.00° K			T = 135.00° K		
P	ρ	$\eta \cdot 10^6$									
34.790	0.202	128	35.77	0.200	127.5	37.29	0.191	127	43.11	0.208	137
34.972	0.208	131	36.36	0.218	134.5	37.97	0.204	131	45.09	0.235	149
35.374	0.226	138.5	36.63	0.232	143	38.52	0.217	136.5	46.32	0.255	158
35.551	0.240	144.5	36.78	0.236	143.5	39.02	0.229	142.5	47.25	0.271	166
35.696	0.254	152	37.08	0.253	154	39.46	0.243	148.5	47.98	0.283	172
35.742	0.260	154.5	37.29	0.280	166.5	39.84	0.257	155	48.70	0.297	179
35.784	0.266	158.5	37.56	0.300	176	40.17	0.270	162	49.39	0.309	186
35.890	0.288	171	37.73	0.315	187	40.49	0.285	170	50.12	0.321	193
35.898	0.290	173.5	37.83	0.327	193	40.71	0.293	175	50.86	0.334	200.5
35.939	0.300	180	37.92	0.335	199	40.93	0.305	180.5	52.01	0.349	211.5
35.971	0.309	184.5	38.09	0.350	207	41.15	0.316	187	53.65	0.370	225
36.013	0.322	191	38.29	0.363	215	41.38	0.326	192.5	55.05	0.385	234
36.056	0.331	196	38.39	0.368	219	41.59	0.335	198	57.01	0.403	248.5
36.112	0.344	205	38.57	0.376	226	41.82	0.344	204	59.05	0.418	261.5
36.196	0.356	211.5	38.63	0.380	226.5	42.09	0.352	209.5	61.16	0.431	275
36.297	0.367	219	39.29	0.400	242.5	42.41	0.362	216	65.21	0.450	292
36.441	0.378	225	40.15	0.415	255	42.93	0.375	225.5			
36.643	0.389	235	41.45	0.431	271	43.58	0.390	236.5			
37.236	0.410	251	42.07	0.441	278.5	44.36	0.403	246.5			
37.893	0.423	262	43.32	0.454	293	45.36	0.416	257			
39.650	0.447	284				47.00	0.434	272.5			
						49.00	0.448	286			

*Here and below in Tables II and III, we give P in kg/cm², ρ in g/cm³, $\eta \cdot 10^6$ in g/cm-sec.

TABLE II. Experimental data* for the critical isotherm $T_c = 126.21^\circ$ K.

P	τ	τ_0	δ	ρ	$\eta \cdot 10^6$	P	τ	τ_0	δ	ρ	$\eta \cdot 10^6$
33.842	33.795	31.187	0.02740	0.198	126	34.651	35.370	31.165	0.04207	0.320	217
34.026	33.884	31.185	0.02820	0.205	130	34.652	35.417	31.180	0.04213	0.324	214
34.195	33.983	31.188	0.02903	0.213	133	34.651	35.425	31.178	0.04225	0.324	216
34.342	34.061	31.165	0.03000	0.222	138	34.652	35.465	31.165	0.04258	0.330	215
34.438	34.180	31.185	0.03081	0.231	139	34.653	35.471	31.171	0.04247	0.330	214
34.472	34.221	31.170	0.03120	0.235	140.5	34.651	35.534	31.187	0.04277	0.334	213.5
34.541	34.327	31.176	0.03221	0.243	146	34.653	35.517	31.167	0.04279	0.335	213
34.571	34.383	31.169	0.03264	0.248	148	34.656	35.598	31.173	0.04316	0.342	212
34.578	34.409	31.173	0.03289	0.249	151	34.657	35.629	31.178	0.04327	0.345	211
34.622	34.557	31.167	0.03424	0.262	157	34.666	35.725	31.177	0.04370	0.353	212
34.626	34.590	31.178	0.03442	0.263	158.5	34.684	35.861	31.182	0.04489	0.365	216
34.640	34.706	31.192	0.03538	0.270	166	34.700	35.898	31.179	0.04520	0.368	218
34.647	34.793	31.173	0.03637	0.278	172	34.717	35.977	31.184	0.04579	0.374	222
34.648	34.857	31.178	0.03702	0.282	178	34.763	36.054	31.182	0.04646	0.380	227
34.650	34.955	31.164	0.03810	0.290	186	34.825	36.117	31.172	0.04710	0.386	232
34.651	35.051	31.175	0.03896	0.296	193	34.949	36.258	31.171	0.04824	0.397	240
34.651	35.090	31.178	0.03943	0.298	199	35.136	36.363	31.172	0.04907	0.405	245.5
34.651	35.114	31.181	0.03965	0.299	200.5	35.438	36.509	31.174	0.05025	0.415	254
34.651	35.199	31.180	0.04050	0.303	210	35.788	36.638	31.185	0.05117	0.424	261
34.652	35.233	31.178	0.04108	0.306	215	36.227	36.744	31.174	0.05216	0.433	270
34.652	35.281	31.178	0.04129	0.311	214						
34.651	35.325	31.163	0.04175	0.316	215.5						
34.651	35.348	31.172	0.04188	0.317	217						

*Here τ and τ_0 are given in seconds, while the units of measurement of the other quantities are the same as in Table I.

density dependence of the so-called excess viscosity $\tilde{\eta} = \eta - \eta(0, T)$, where η is the measured viscosity and $\eta(0, T)$ the viscosity as $\rho \rightarrow 0$ and at the temperature at which the value for η is taken.

Figure 4 (upper curves) shows the excess viscosity of nitrogen for our measurements along all the isotherms from 126.16 to 135.00°K and also the data obtained by others for the temperatures -90° and -50° C^[16,17]. The values of $\eta(0, T)$ in the calculation of $\tilde{\eta}$ were taken from^[22]. As has been well established,^[16,17,23] the excess viscosity of nitrogen does not have an appreciable temperature dependence over a wide range of temperatures and densities far from the critical point, and is a function of the density only. Actually, as follows from Fig. 4, the points for the isotherms 130.00 and 135.00°K which are the farthest from critical fit, within the accuracy of the experiment, are on one common curve, with the data of^[16,17] at the temperatures -90 and -50° C. The points for the other isotherms, much closer to the critical, also fit this common curve, denoted by $\tilde{\eta}_{id}$ in Fig. 4, but far from the critical density. In the density range 0.25-0.37 g/cm³, a bump appears on the isotherms, beginning with a temperature of 128.00°K; this bump grows upon approach to the critical temperature. The greatest deviation from the smooth curve amounts to 37%. The isotherms 126.20, 126.21 and 126.22°K are almost identical, i.e., a change of the temperature by $\pm 0.01^\circ$ K relative to its critical value does not affect the amount of the singularity; this can be attributed to the limited resolving power of the given method of measurement and also possibly to the effect of impurities. Actually, the stack of disks averages the measured properties in a layer of thickness ~ 5 mm (the height of the stack plus the thickness of the boundary layer), while the critical conditions are achieved only in a limitingly thin layer.^[24]

To explain the character of the singularity, we isolate the anomalous part of the viscosity, i.e., the contribution $\Delta\eta$ to this "ideal" viscosity $\tilde{\eta}_{id}$, the value of which is obtained by extrapolation from points far removed from the critical region. We obtain the value of $\Delta\eta$ from the relations

$$\Delta\eta = \tilde{\eta} - \tilde{\eta}_{id}, \quad \tilde{\eta}_{id} = \eta_{id} - \eta(\rho, T)$$

where $\tilde{\eta}_{id}$ is the excess viscosity far from the critical

$\eta \cdot 10^6, \text{ g/cm-sec}$

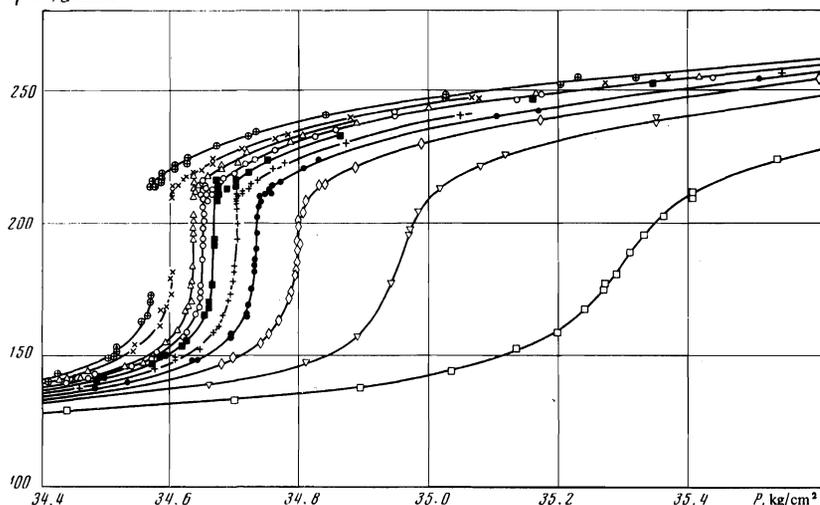


FIG. 2. Dependence of the viscosity of liquid nitrogen on the pressure in the critical region along the isotherms (T in $^{\circ}\text{K}$): \oplus -126.16, \times -126.18, Δ -126.20, \circ -126.21, \blacksquare -126.22, $+$ -126.24, \bullet -126.26, \diamond -126.30, ∇ -126.40, \square -126.60.

$\rho, \text{ g/cm}^3$

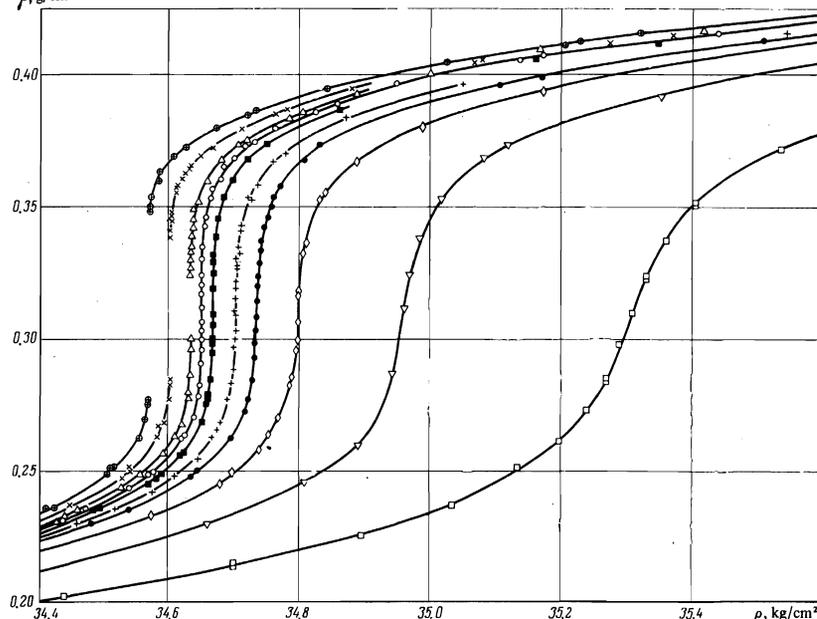


FIG. 3. Density of nitrogen as a function of the pressure in the critical region along the various isotherms. Notation the same as in Fig. 2.

TABLE III. Anomalous part of the viscosity of nitrogen in the critical region

ρ	$\Delta\eta \cdot 10^6$	ρ	$\Delta\eta \cdot 10^6$	ρ	$\Delta\eta \cdot 10^6$	ρ	$\Delta\eta \cdot 10^6$	ρ	$\Delta\eta \cdot 10^6$
$T - T_c = 0.03^{\circ}\text{K}$									
0.265	4	0.331	16	0.3225	20	0.316	16	0.338	4.5
0.277	8	0.339	11	0.323	19	0.318	14	0.351	2.5
0.284	11.5	0.341	11	0.325	17	0.332	10		
0.288	13.5	0.344	9	0.328	15				
0.2995	18			0.330	15.5				
0.3025	21			0.333	14				
0.305	24			0.335	13.5				
0.310	25.5			0.343	8.5				
0.315	25			0.354	4				
0.319	24								
0.323	22.5								
0.328	19								
0.329	18.5								
$T - T_c = 0.05^{\circ}\text{K}$									
		0.330	15.5						
		0.333	14						
		0.335	13.5						
		0.343	8.5						
		0.354	4						
$T - T_c = 0.09^{\circ}\text{K}$									
		0.269	4.5						
		0.308	8.5						
		0.294	11						
$T - T_c = 0.39^{\circ}\text{K}$									
		0.285	6						
		0.297	7						
		0.3095	8						
$T - T_c = 0.79^{\circ}\text{K}$									
		0.288	3						
		0.290	4						
		0.300	5						
		0.309	4						
		0.322	3.5						
		0.331	2.5						
		0.344	2.5						

point, given in Fig. 4. The anomalous part of the viscosity of nitrogen thus calculated is given in Table III and shown in Fig. 4 (the lower graph). The temperature dependence of $\Delta\eta$ along the critical isochor was obtained from this graph with the cross section $\rho_c = 0.311 \text{ g/cm}^3$. This temperature dependence is shown in Fig. 5 in logarithmic and semilogarithmic scales. The singularity of the viscosity turned out to be stronger than logarithmic

and could be approximated by the power function

$$\Delta\eta = H\epsilon^{-f}, \quad H = 0.5 \cdot 10^{-6} \text{ g/cm-sec}, \quad \Phi = 0.47^{+0.15}_{-0.12} \quad (10)$$

The accuracy of the parameter Φ is determined by the fact that $T_c = 126.21^{\circ}\text{K}$ is known with accuracy of $\pm 0.01^{\circ}\text{K}$, and $\Delta\eta$ with an accuracy of $\pm 2 \times 10^{-6} \text{ g/cm-sec}$. For comparison, we shall show that the calculation from the theory of Fixman,^[1] who obtained the power-law singularity $\Delta\eta = H\epsilon^{-1/2}$, gives a value of H for nitrogen that is about three times that obtained in the present work.

We now consider whether the behavior of the particular part of the viscosity $\Delta\eta$ satisfies the laws of the scaling transformation theory, for which, by analogy with what was done by Sengers for the thermal conductivity of carbon dioxide gas^[25], we test the feasibility of a scaling relation of the form

$$\frac{\Delta\eta}{H|\Delta\rho'|^{-\Phi/\beta}} = f\left(\frac{x+x_0}{x_0}\right), \quad (11)$$

where f is a function of the single scaling parameter x ,

$$x = \frac{\epsilon}{|\Delta\rho'|^{1/\beta}}, \quad x_0 = B^{-1/\beta}, \quad \Delta\rho' = \frac{\rho - \rho_c}{\rho_c}$$

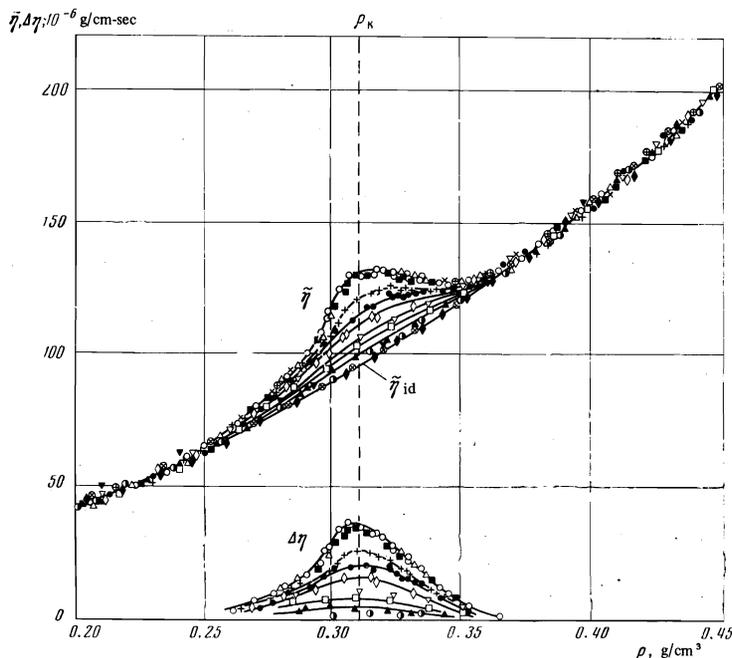


FIG. 4. Dependence of the excess ($\bar{\eta}$) and anomalous ($\Delta\eta$) parts of the viscosity on the density for different temperatures. The notation is the same as in Fig. 2, and also \blacktriangle — $T = 127.00^\circ\text{K}$; \bullet — 128.00°K ; \blacklozenge — 130.00°K ; \oplus — 135.00°K ; ∇ —for -90 and -50°C from [16,17].

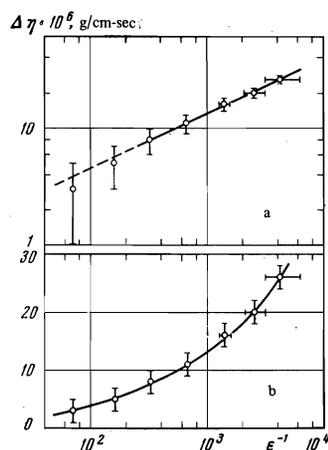


FIG. 5. Determination of the character of the singularity of the viscosity: temperature dependence of the anomalous increment $\Delta\eta$ along the critical isochor in logarithmic (a) and semi-logarithmic (b) scales.

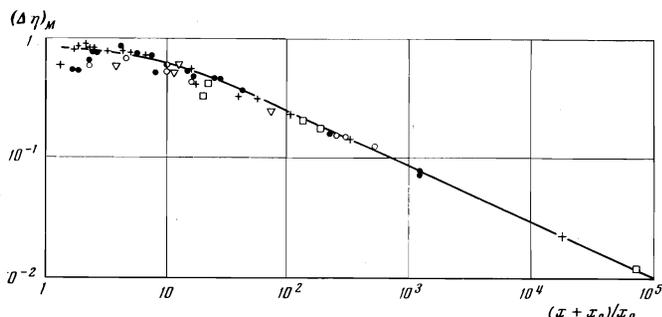


FIG. 6. The "scaled" special part of the viscosity of nitrogen $(\Delta\eta)_M = \Delta\eta/H|\Delta\rho^*|^{-\phi/\beta}$ as a function of $(x + x_0)/x_0$ for the following values of $T - T_c$ (in $^\circ\text{K}$): $+ - 0.03$; $\bullet - 0.05$; $\circ - 0.09$; $\nabla - 0.19$; $\square - 0.39$.

β and B are parameters in the formula for the coexistence curve $|\Delta\rho^*| = B|\epsilon|^\beta$. The relation (11), calculated from the experimental data given in Table 3, is shown in Fig. 6 in logarithmic coordinates. In the calculation, the following values of the constants were used: $\rho_c = 0.311 \text{ g/cm}^3$, $T_c = 126.21^\circ\text{K}$, $\phi = 0.47$, $H = 0.5 \times 10^{-6} \text{ g/cm-sec}$ and the values $\beta = 0.35$ and $x_0 = 0.181$ were obtained from our experimental data for the coexistence curve of nitrogen. Figure 6 demonstrates that

the "scaled" $\Delta\eta$ is well approximated by a function of only a single scaling parameter x .

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