

# Viscosity of nitrogen measured to pressures of 7 GPa and temperatures of 573 K

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Shear viscosities of supercritical nitrogen have been measured to 573 K and 7 GPa (70 kbars). Measurements were made in a diamond-anvil cell with a rolling-ball technique. Individual isotherms are well fitted by a modified Doolittle equation. The data demonstrate a close relation between viscosities and excess entropy; this relation is further explored for the systems argon, oxygen, carbon dioxide, sodium, cesium, and a Lennard-Jones fluid.

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## I. INTRODUCTION

The last two decades have seen increased attention paid to the transport properties of highly compressed fluids. Interest has been driven by applications to fields such as geo- and planetary physics, explosives modeling, glass formation, and high-pressure chemistry, but also by the tremendous increase in available computing power which has made molecular dynamics simulation a routine tool. In fact, the relative difficulty of experimentation at the necessary high pressures has led to a situation in which computational studies are far more numerous than their experimental counterparts. In the absence of data, both simulations and fundamental theories of dense fluids remain substantially unchallenged by experiment. In this laboratory we have begun a program of measuring viscosities to the pressures and temperatures available in the high-pressure diamond-anvil cell. Here, we report the viscosities of fluid nitrogen to pressures of 7 GPa, temperatures of 573 K, and densities of five times the critical value. The relation between viscosity and entropy is explored in the context of these data and of other data taken from the literature.

## II. EXPERIMENT

Viscosities were measured with a rolling-ball technique in a high-pressure diamond-anvil cell. The technique is described more fully in Refs. [1–3]. Briefly, a platinum sphere of diameter 30–60  $\mu\text{m}$  is allowed to roll down the inner diamond face of the cell. The speed at which the sphere rolls is measured with a videocamera. Viscosity is inversely proportional to the derivative of speed with respect to the sine of the angle of inclination; the constant of proportionality differs for each sphere and is most easily found by calibration with fluids of known viscosity, in this case water [4], oxygen [2], and toluene [5].

The cell was of modified Merrill-Bassett design [6], enclosed within an oven, with temperature measured to within 1 K. Nitrogen (99.995%) was condensed at 77 K and loaded as the fluid. Pressures were determined [7–9] by way of included chips of either ruby or  $\text{Sm}:\text{SrB}_4\text{O}_7$ .

## III. RESULTS AND DISCUSSION

Measured viscosities [10] are plotted in Fig. 1 along isotherms of 294, 373, 473 and 573 K. Data previously taken to 0.65 GPa at 298 K (and 0.1 GPa at 369 K) [11], and up to 0.4 GPa at 293 and 373 K [12], are shown in the inset. The current data, in conjunction with dilute gas viscosities [13], were fitted to a modified Doolittle equation [2] along each isotherm:

$$\ln(\eta) = \ln \left[ \frac{\eta_{\text{dilute}} \rho_0}{(B-1)\rho + \rho_0} \right] + B \left[ \frac{\rho}{\rho_0 - \rho} \right] \quad (1)$$

(solid lines in Fig. 1), with a rms deviation of 3%. In this equation,  $B$  and  $\rho_0$  are fitting constants (Table I),  $\eta_{\text{dilute}}$  is the viscosity of the dilute gas at that temperature, and the density  $\rho$  is given by Ref. [14].

Clearer comparisons with the older, lower-pressure data are made in Fig. 2 as fractional differences from the fits. Included in this figure are the predictions of Lemmon and Jacobsen [13], based on a compilation of data taken from the literature. Below 0.1 GPa the simple form of Eq. (1) clearly produces a systematic error of  $\sim 4\%$ . At higher pressures the

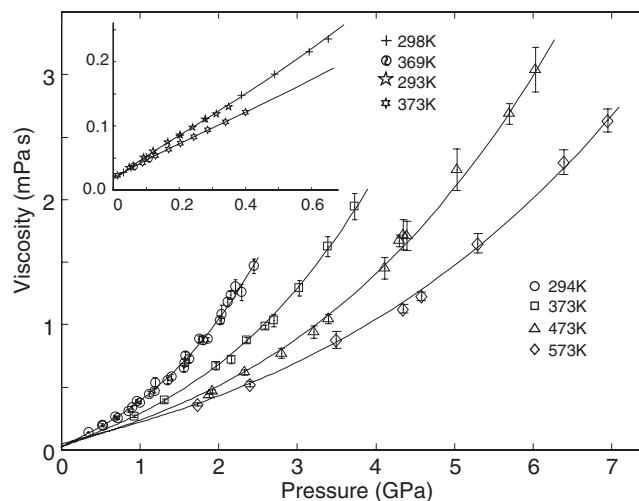


FIG. 1. Viscosities (mPa s) are plotted against pressure (GPa) on isotherms of 294, 373, 473, and 573 K. Error bars approximate 1 $\sigma$  values. Curves are fits of the data to Eq. (1). The inset shows data from Vermeese at 298 and 369 K [11], and of Golubev and Kurin at 293 and 373 K [12].

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TABLE I. Parameters for Eq. (1).

$T$ (K)	$\eta_{\text{dilute}}$ ( $\mu\text{Pa s}$ )	$B$	$\rho_0$ ( $\text{g/cm}^3$ )
294	17.6	12.79	4.217
373	21.1	13.26	4.593
473	25.1	14.70	5.204
573	28.7	16.04	5.810

current fits agree with previous data to within the probable error of the latter, and to the results of Lemmon and Jacobsen over the range for which data existed. In passing we note that Eq. (1), while not attaining the accuracy of published formulations at lower pressures [13,15] where a substantial body of work exists, does appear capable of providing useful estimates at intermediate pressures where both conventional and diamond-anvil cells prove difficult to operate.

### A. Viscosity and entropy

In dense fluids, the fluidity (inverse viscosity) might be expected to be proportional to the number of new configurations available to the relaxing fluid, and thus be an exponential function of the entropy. Simple relations which give viscosities (or diffusivities) as functions of entropy have long been posited [16–19]. On the basis of molecular dynamics simulations of several different systems of structureless particles, Rosenfeld [20] proposed the following relation between a reduced viscosity and reduced excess entropy:

$$\eta_{\text{red}} = 0.2e^{0.8s}, \quad \eta_{\text{red}} = \eta \rho_N^{-2/3} / (mkT)^{1/2},$$

$$s = -(S - S_{\text{ideal gas}}) / Nk, \quad (2)$$

for values of  $s$  roughly between 1 and 4. Here,  $\rho_N$ ,  $m$ , and  $S$

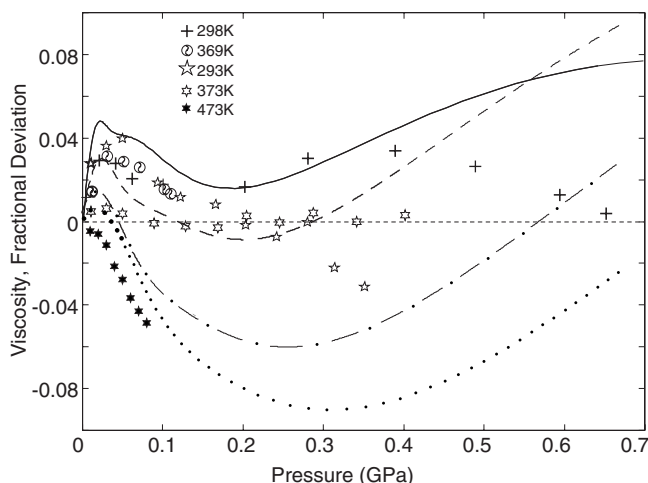


FIG. 2. Viscosities from the literature are plotted against pressure as fractional differences from fits to Eq. (1),  $(\eta_{\text{lit}} - \eta_{\text{calc}}) / \eta_{\text{calc}}$ . Data are those of the inset in Fig. 1 [11,12], with several additional points from Golubev and Kurin at 473 K. Results of the formulation of Lemmon and Jacobsen [13] are given at 294, 373, 473, and 573 K by solid, dashed, dot-dashed, and dotted lines, respectively; pressures at which previous data existed are marked in thicker lines.

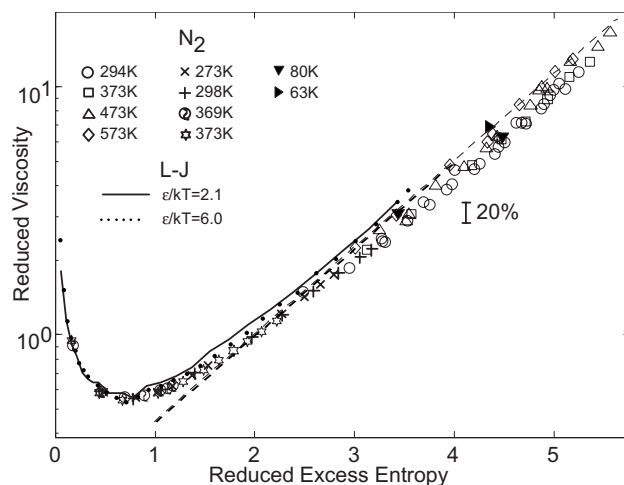


FIG. 3. Reduced viscosity is plotted against reduced excess entropy [Eqs. (2)]. Data are those of Fig. 1, from this study and Refs. [11,12]; additionally, the formulation of Lemmon and Jacobsen [13] is used to give two points at the minimum and maximum extent of the 80 K liquid (i.e., pressures of boiling and solidification), and the triple point at 63 K. The solid and dotted lines are results from molecular dynamics simulations of a Lennard-Jones fluid [21–23] at reduced temperatures of 2.1 and 6.0, respectively. The dashed line represents Rosenfeld's hypothesis; it is plotted with a thicker weight over the range of  $s \approx 1$  to 4 for which various molecular dynamics simulations existed.

are the particle density, particle mass, and entropy, respectively, and  $S_{\text{ideal gas}}$  is the entropy the fluid would have if it were an ideal gas at the same density and temperature. These reduced variables have been shown [3] to organize the viscosities of water into a single curve, roughly parallel to the line suggested by Rosenfeld, but rising to higher viscosities in the 1 bar, supercooled region as the effects of hydrogen bonding increase, and displaced by an amount suggestive of the effects of quenched rotation in the fluid.

It could be guessed that nitrogen, consisting of approximately spherical molecules without strong intermolecular bonding, would be more consistent with the simulations upon which Rosenfeld based his hypothesis; as seen in Fig. 3, this is indeed the case. At reduced entropies above  $\sim 1$  the data fall within 20% of the proposed line, while necessarily increasing without bound as  $s$  approaches 0. Even viscosities of the liquid lie within the same cluster of points, as shown in Fig. 3 for the span between the vapor pressure ( $s=3.3$ ) and freezing ( $s=4.5$ ) at 80 K, and for the triple point at 63 K. For comparison, viscosities of a simulated, monatomic Lennard-Jones fluid [21–23], plotted at reduced temperatures of 2.1 and 6, lie slightly ( $\sim 10\%$ ) above Rosenfeld's estimated line when close to their melting points ( $s \sim 3.5$ ) and curve upward along with the real data at lower values of  $s$ .

In order to avoid the divergence at  $s=0$  the density in Eq. (2) might be replaced by the particle density at the critical point to give

$$\eta_{\text{red}}^* = \eta \rho_{N, \text{crit}}^{-2/3} / (mkT)^{1/2}. \quad (3)$$

As seen in Fig. 4, the data are also reasonably well described by a single curve,  $\eta_{\text{red}}^* = 0.3e^{0.88s}$ , from roughly the critical

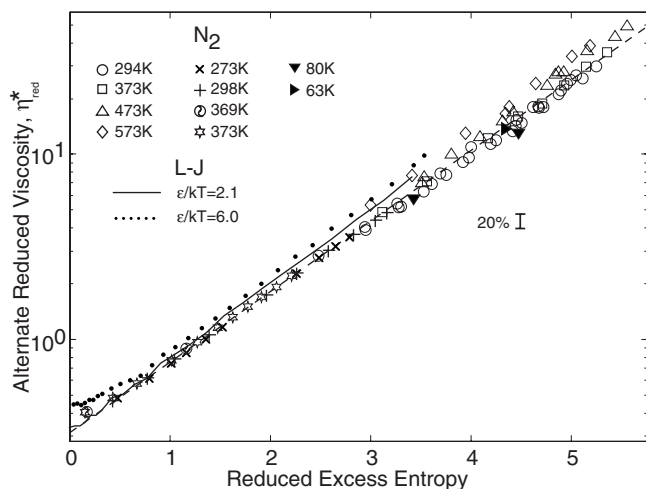


FIG. 4. Another version of the reduced viscosity  $\eta_{red}^*$  [Eq. (3)] plotted against reduced excess entropy. Data are the same as in Fig. 3. The dashed line represents the equation  $\eta_{red}^* = 0.3e^{0.88s}$ .

density ( $s \sim 0.6$  at these temperatures) to the melting line.

It is not clear whether the displacements among nitrogen’s isotherms, seen in Figs. 3 and 4, are real or are due to error in the calculated entropies. Entropies (and densities) are given by an equation of state [14] which is based mostly on data below 2.2 GPa, but formulated as an expansion of the Helmholtz energy with terms designed to extrapolate well [24]. Uncertainties in the absolute entropy were not given, but at pressures of 2 GPa the authors’ “conservative” estimates for uncertainty in  $C_p$  exceed 2%. Even an error of 2% in  $C_p$ , integrated between 294 and 573 K, amounts to a relative error of 0.07 in reduced excess entropy, which is comparable to the displacement between those isotherms in the plots.

Neither of these two reduced viscosities ( $\eta_{red}$  or  $\eta_{red}^*$ ) increases directly in proportion to the loss of available configurations, instead rising to lesser powers (0.80 and 0.88); nonetheless, the fact that these powers are close to 1.0, and more impressively that viscosities over a large range of densities and temperatures all reduce to the same curves when plotted in this fashion, suggests an essential truth to the original conjecture.

### B. Viscosity and entropy in other systems

Equations (2) and similar relations have been explored for a variety of simulated fluids (hard sphere, soft sphere, Lennard-Jones, one-component plasma, Yukawa, and simulated metal melts) [17–20,25–28], but seldom for real fluids. In the last figure (Fig. 5) we plot  $\eta_{red}$  for several other (non-associative) fluids. We were particularly interested in the extent to which nonspherical or metallic fluids would deviate from the patterns of Fig. 3. Not surprisingly, the viscosity of argon [29–32], which has been measured up to 0.9 GPa at room temperature, falls on the Lennard-Jones curves (Fig. 3) to within probable errors. It is remarkable that a (supplementary) point taken during this study for supercritical argon at 294 K, 1.0 GPa, and  $\rho = 1.8 \text{ g/cm}^3$ , when plotted in this

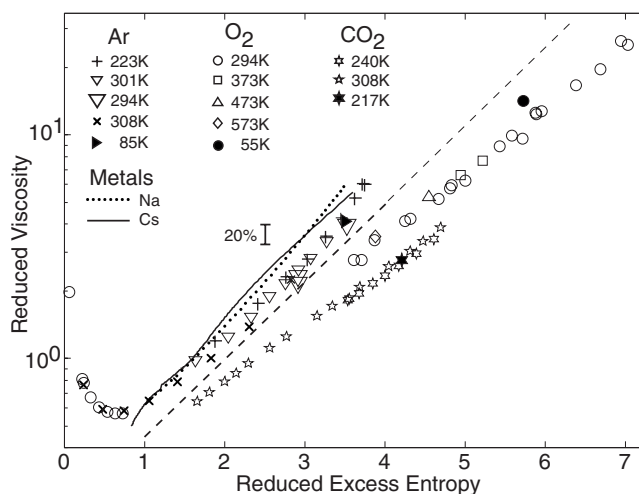


FIG. 5. Reduced viscosity plotted against reduced excess entropy [Eqs. (2)] for several other nonassociative systems: argon at 223 and 301 K [31], 308 K [30], 294 K (this work, the three larger triangles), and just above the triple point at 85 K [32]; oxygen at 294 K (lower pressures [33], higher pressures [2]), the triple point at 55 K [13], and 373, 473, and 573 K (this work); carbon dioxide at 240 and 308 K [40], and the triple point at 217 K [51]; sodium [42] and cesium [43] along their lines of liquid-vapor equilibrium up to temperatures of  $\sim 0.85T_{crit}$  (2100 and 1700 K, respectively). The dashed line represents Rosenfeld’s hypothesis as in Fig. 3.

manner, coincides with that for the liquid at the triple point (84 K,  $\rho = 1.4 \text{ g/cm}^3$ ).

The viscosities of oxygen [2,33], reported at room temperature up to 6 GPa, have here been supplemented with a few new points at 373, 473, and 573 K. Unfortunately, no equation of state (EOS) suitable for the higher-pressure data is available. We therefore approximated the densities and entropies by combination of an EOS of oxygen meant for low pressures [34], and a similar EOS for nitrogen [14] useful for higher pressures, taking the ideal gas contribution to the Helmholtz energy from the first and the residual contribution from the second, after substituting the appropriate mass, critical density, and critical temperature. To the extent that oxygen and nitrogen adhere to a law of corresponding states, this should yield a useful EOS. Happily, the result predicts measured speeds of sound [35] to within 2% from 1 to 6 GPa (at 294 and 473 K), and also correctly predicts the Hugoniot [36], i.e., the locus of pressure-density points achieved by shocking the fluid, up to  $\sim 15 \text{ GPa}$  (and to  $\sim 50 \text{ GPa}$  for a model [37] of the “nonreactive” fluid). As a further check, the entropy of the fluid at the melting point of 5.7 GPa and 294 K may separately be approximated by the Clapeyron equation in conjunction with the density of the solid [38], the slope of the melting curve [35], and an entropy for the solid calculated from either of two alternate lattice-dynamic models [39]. The results,  $s = 7.0$  or  $7.5$  depending on the lattice model, are close to the 7.0 computed from the EOS. We therefore believe that the oxygen data shown in Fig. 5 are plotted with sufficient accuracy to state that the three isotherms in the plot fall together, within probable errors, and describe a straight line. The difference between the slope of this line and that of the nitrogen data (compare their respec-

tive positions in Figs. 3 and 5 with the line suggested by Rosenfeld) is probably due to error in oxygen's EOS (this is the only system seen so far in which the position of the triple point, also plotted [13], appears to depart significantly from the other data), but possibly to the slightly less spherical nature of the oxygen molecule.

The viscosities of carbon dioxide have so far been measured [40] only up to 0.45 GPa and, at these higher pressures, subcritical temperatures; the EOS employed here [41] is expected to be adequate for these pressures. While still approximating a straight line, the plotted data clearly tend to higher reduced entropies for a given viscosity. We consider this to be most probably a result of quenched rotation, such that the reduced excess entropy is no longer solely a measure of lost configurations and is therefore overestimated for the purposes of calculating viscosity.

Finally, we consider the viscosities of two simple metals, sodium [42] and cesium [43], along their lines of vapor-liquid equilibrium. Thermodynamic quantities are taken or calculated from Refs. [44,45]; reduced excess entropies are now taken as  $s = -(S - S_{\text{elec}} - S_{\text{ideal gas}})/Nk$ , where the electronic contribution to the entropy,  $S_{\text{elec}}$ , is calculated as that of an ideal Fermi-Dirac gas to first order in  $kT/E_{\text{Fermi}}$ . From the melting point up to about  $0.85T_{\text{crit}}$  the viscosities of these metals parallel those of argon and nitrogen, even as the latter vary isothermally under the influence of applied pressure.

The (configurational) entropies of pure metals around their normal melting points have been explored [46–48] in several interesting papers. It was found that the reduced entropies of simple metals fall mostly in the range of 3.5–4.0

and are strongly correlated with viscosity. Separately, Andrade's [49] estimate of the viscosities of the "simplest liquids" at their melting points, liquid metals [50] in particular, may be rearranged to yield a universal, reduced viscosity at melting of  $\sim 5.3$ . In Fig. 5 it is seen that sodium, cesium, and also argon, are in agreement with both of these observations. This suggests that simple liquid metals, and the rare gases, would fall close to the same curves as seen in Fig. 5, not only at their melting points, but likely at all combinations of temperature and pressure for which they exist as monatomic fluids.

#### IV. CONCLUSIONS

Shear viscosities of supercritical nitrogen were measured up to a temperature of 573 K and a pressure of 7 GPa. From the dilute gas to the highest densities the isotherms deviate by less than 4% from a modified Doolittle equation with two variable parameters. For these almost spherical molecules there is a good correspondence between excess entropy and two different reduced viscosities. Similar correspondences were shown to exist for several other fluids, including metals; greater nonsphericity of the particles will cause deviations to lower viscosities for a given (thermodynamic) entropy.

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