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Viscosity of carbon dioxide measured to a pressure of 8 GPa and temperature of 673 K

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Shear viscosities of supercritical carbon dioxide have been measured to 673 K and 8 GPa (80 kbar). Measurements were made in a diamond-anvil cell with a rolling-ball technique. Individual isotherms are well fit by a modified free-volume equation. The data demonstrate a close relation between viscosity and residual entropy.

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I. INTRODUCTION

By application of the high pressures achievable in a diamond-anvil cell, fluid densities can be continuously increased to many times the critical value. This realization of density as an experimentally independent variable offers obvious opportunities for advancing the general theory of fluids. Fluid carbon dioxide, the subject of this paper, is of particular interest as a constituent of planetary interiors and of explosive products. As with other high-pressure substances, the bulk of what is known concerns its thermodynamics while viscosities and other transport properties remain largely unmeasured.

Published viscosities of carbon dioxide were previously available to a maximum pressure of 0.45 GPa at 308 K [1]. Here I report measurements up to a pressure of 8 GPa and temperature of 673 K. The data are fit to a modified free-volume formula and the connection between viscosity and residual entropy is further explored.

II. EXPERIMENTAL

Viscosities were measured with a rolling-ball technique in a high-pressure, diamond-anvil cell. The technique is described more fully in references [2–4]. Briefly, a platinum sphere of diameter 25–60 μm is allowed to roll down the inner, diamond face of the cell. The speed at which the sphere rolls is recorded and measured with a video camera. A plot of speed with respect to the sine of the angle of inclination yields a straight line the slope of which is inversely proportional to the viscosity; the constant of proportionality differs for each sphere and is most easily found by calibration with fluids of known viscosity, in this case toluene [5] and carbon dioxide [1] at 0.4 GPa and 308 K.

Carbon dioxide (obtained from Praxair, Inc. with a stated purity of 99.995%) was loaded under its own vapor pressure at 21 °C. The diamond-anvil cell was of modified Merrill-Bassett design [6], enclosed within an oven. Chromel-alumel thermocouples were used to measure the temperature to within 1 K. Pressures were determined [7,8] by way of included chips of either ruby or Sm-doped SrB_4O_7.

III. RESULTS AND DISCUSSION

Viscosities of carbon dioxide at pressures in excess of 0.3 GPa have been reported twice previously. Van der Gulik [1] made measurements over the entire liquid range ($T_{\mathrm{triple}}=217$ K; $T_{\mathrm{critical}}=304$ K), and to maximal pressure and temperature of 0.45 GPa at 308 K. Data have also been collected at the somewhat higher temperature of 423 K [9] but only to 0.35 GPa. Results of prior work are summarized and fitted to a formulation in Refs. [10,11].

The current data [12] are plotted in Fig. 1 along isotherms of 308, 373, 473, 573, and 673 K. At these pressures the isotherms are well represented by the modified free-volume equation [3]:

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

where η_{dilute} is the viscosity of the dilute gas [10] at the given temperature, while B and ρ_0 are constants for each isotherm. The density, ρ, is given by Ref. [13]. A simultaneous fit to all the data (curves in Fig. 1) with $B=17.925+3.0305\times10^{-3}$ T and $\rho_0(\mathrm{g\ cm^{-3}})=4.9106+5.5400\times10^{-3}$ T provides a root-mean-square misfit of 4.3%, consistent with random scatter, and differs by less than 3.5% at any point from best fits along individual isotherms. Given the above-mentioned scatter, a 2.7% rms misfit of the calibrants, and an apparent absence of significant systematic error as evidenced by consistency in the results for several loads with different spheres rolling at different speeds (see also Refs. [3,4]), the overall error of the viscosities averaged

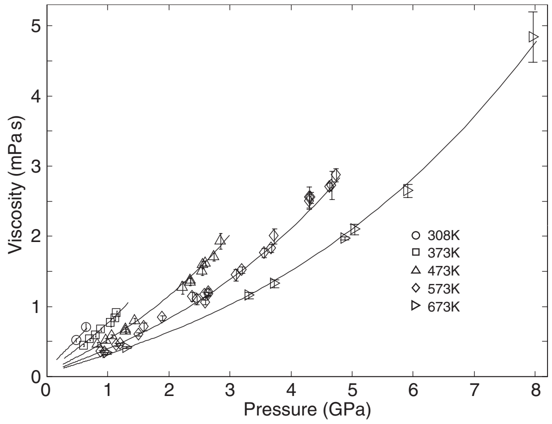

FIG. 1. Viscosities (mPa s) are plotted against pressure (GPa) on isotherms of 308, 373, 473, 573, and 673 K. Error bars approximate 1σ values. Curves are overall fits of the data to Eq. (1) with temperature-dependent coefficients as given in the text.

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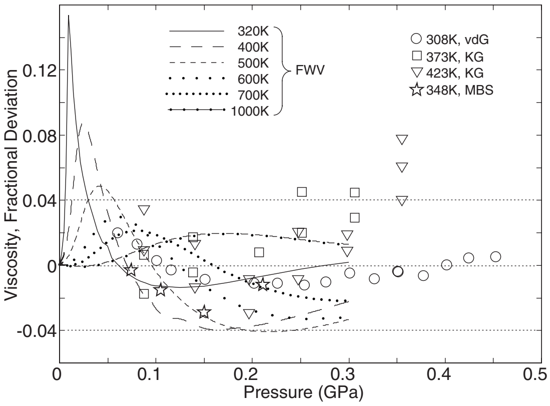

FIG. 2. Viscosities from the literature (vdG [1]; KG [9]; MBS [21]) are plotted against pressure as fractional differences from the overall fit to Eq. (1), $(\eta_{lit}-\eta_{calc})/\eta_{calc}$. Curves (FWV) represent a formulation [11] which has an estimated uncertainty of 4% above 400 K.

along any one isotherm with this fitting function is expected to be less than 5%. No useful interpretation of the fitted values of ρ_0 and B is evident [3], although they are still of the magnitude expected from the original theory [14,15] where they represent, respectively, the maximum density of the fluid (absent voids) and the ratio of the minimum volume of a void allowing effective diffusion to that of a single molecule. Extrapolation of these fits to higher densities is likely to provide poor results, although modest extrapolation in temperature may be useful.

Shown in Fig. 2 are deviations of prior data from the curves of Fig. 1. In the region of pressures less than 0.1 GPa combined with temperatures less than 600 K the modified free-volume expression is inaccurate; plotted against density (not shown) the greatest misfits are seen to be around the critical density (although these deviations are not a critical effect). Above either 0.1 GPa or 600 K the fit is within probable error of prior data, and also matches the 1998 formulation of Fenghour *et al.* [11] up to 0.3 GPa within their estimated uncertainty of 4%. The latter formulation was designed for a maximum pressure of 0.3 GPa and does not extrapolate well in the range of the new data.

Rosenfeld [16] proposed a relationship between a reduced viscosity, η_{red}, and reduced residual entropy, s,

$$\eta_{red} = a e^{bs},$$

with

$$\eta_{red} = \eta \rho_N^{-2/3} (mkT)^{-1/2}$$

and

$$s = -(S - S_{ideal})/Nk. \tag{2}$$

Here, ρ_N and m are the particle density and particle mass, a and b are constants which vary with the fluid, and S is the entropy while S_{ideal} is the entropy the fluid would have if it were an ideal gas at the same density and temperature. The range of applicability is for liquidlike densities with $s \sim > 2$. Equations (2) were originally suggested for systems of structureless particles on the basis of a few molecular dynamic simulations; they have now been seen to fit closely the viscosities of rare gases, expanded alkali metals, and also the molecules nitrogen and oxygen [17].

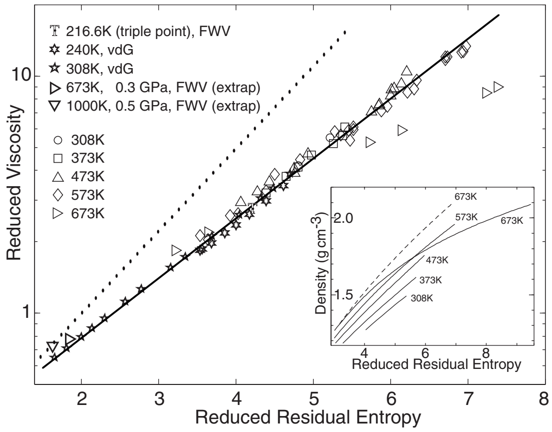

FIG. 3. Reduced viscosity (η_{red}) is plotted against reduced residual entropy (s). Data are those of Fig. 1 from this study (lighter symbols) and Ref. [1] (vdG, bold symbols); additionally, the formulation of Fenghour *et al.* [11] is used to give values at the triple point, and two points at 673 and 1000 K extrapolated to pressures beyond their available data (FWV, bold symbols). The straight, solid line is drawn through the 308 K data. The dotted line represents Rosenfeld's suggestion for a fluid of structureless particles. Shown in the inset are isotherms of density (g cm^{-3}) plotted against s for the equation of state used [19] (solid lines); the dashed line represents a suggested 673 K isotherm which would cause the 673 K η_{red} to fall on the same straight line as the other data in the main figure.

The quantity s is assumed to quantify the loss of configurations available for translational motion. In the cases of molecules such as nitrogen and oxygen, the damping of rotational motion within the fluid might be expected to be relatively small, thus contributing little to s. For larger molecules in which rotation would be hindered by high densities, s as defined is expected to overestimate the loss of translational possibilities. In the case of water, subject to both a quenched rotational entropy and also extensive hydrogen bonding, there remains a correlation between the two reduced variables [4] however it is shifted to higher s as expected and also assumes a significant curvature in a semilogarithmic plot. Carbon dioxide represents an intermediate case in which effects of quenched rotational entropy should be seen without the further complications of a strong intermolecular bonding.

Figure 3 presents a plot of the data in these new coordinates. Where adequate thermodynamic data exist, roughly from the triple point up to 0.45 GPa and 308 K, all reduced viscosities fall within 7% of a single curve with $a \approx 0.25$ and $b \approx 0.58$. As expected, for any given η_{red} this curve is shifted to higher s than Rosenfeld's line for structureless particles ($a \approx 0.2$ and $b \approx 0.8$).

Unfortunately, in the range of the new data, none of the published equations of state (EOSs) is likely to provide entropies with an accuracy sufficient to our current purpose. If the data in Fig. 3 are plotted using the EOS of Span and Wagner [13] reduced viscosities begin deviating from a single line exactly at the pressures and temperatures where experimental thermodynamic data used to define that EOS were lacking. This is not surprising as the EOS also fails to match either newly available speeds of sound at these higher pressures or older shock data [18] (at $P > 10$ GPa). In order to plot the higher pressure ($P > 0.5$ GPa) points in Fig. 3, I have therefore used the EOS of Giordano *et al.* [19] which is based on those authors' recent measurements of Brillouin spectra up to pressures of 8 GPa and, separately, of refractive index. This EOS is clearly more accurate at pressures and temperatures within the range of the Brillouin data [20], however tight constraints on the calculated entropies (obtained from integration of $(\partial S/\partial P)_T = -(\partial V/\partial T)_P$) are precluded both by uncertainties in the interpretation of the data and also by the simple form used to parametrize the densities. Nevertheless, through use of this improved EOS all data in the figure fall close to a single line, with the exception of the higher pressure points at 673 K (two such points, with $s = 8.2$ and 10.2, are not even plotted). To explain these errant points we may consider a plot of density against s (inset, Fig. 3) where we see that the calculated 673 K isotherm begins to diverge from the others at $s \approx 4$, just where there is also a divergence of the η_{red} in the main figure. The Brillouin spectra on which this EOS is based were taken up to 700 K, and it is probable that the form of parametrization chosen distorts the EOS near the boundaries of the data. The dashed curve in the same inset indicates values along this isotherm which if adopted would cause the 673 K η_{red} to fall on the same straight line as all the rest of the points. This last curve matches the pattern of the other isotherms and is likely to be a better approximation to the true EOS.

In summary, the data for carbon dioxide exhibit a close correlation between viscosity and entropy, consistent with that proposed by Rosenfeld. Below the critical temperature reduced viscosities deviate by at most 7% from a single line, and in the supercritical fluid deviations between measured viscosities and an exact correlation are within the uncertainties of the calculated entropies. A more definitive appreciation of the correlation thus awaits further progress on the thermodynamics of carbon dioxide.

IV. CONCLUSIONS

Viscosities of carbon dioxide have been measured up to a pressure of 8 GPa and temperature of 673 K, with an estimated mean accuracy of 5%. The data are well fit by a modified free-volume equation as long as the pressures are in excess of 0.1 GPa or the temperatures in excess of 600 K. A close correlation of reduced viscosity and residual entropy is seen, and is consistent with the form proposed by Rosenfeld within the uncertainty of the calculated entropies.

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