

## THERMOPHYSICAL PROPERTIES OF PORE-CONFINED SUPERCRITICAL CO<sub>2</sub> BY VIBRATING TUBE DENSIMETRY

Mirosław S. Gruskiewicz<sup>1</sup>, David J. Wesolowski<sup>1</sup> and David R. Cole<sup>2</sup>

<sup>1</sup>Oak Ridge National Laboratory, Chemical Sciences Division  
Oak Ridge, Tennessee 37831-6110, USA  
e-mail: [gruskiewicz@ornl.gov](mailto:gruskiewicz@ornl.gov)

<sup>2</sup>Ohio State University, School of Earth Sciences  
Columbus, Ohio 43210, USA

### **ABSTRACT**

Properties of fluids confined in pore systems are needed for modeling fluid flow, fluid-rock interactions, and changes in reservoir porosity. The properties of CO<sub>2</sub>-rich fluids are particularly relevant to geothermal heat mining using carbon dioxide instead of water. While manometric, volumetric, and gravimetric techniques have been used successfully to investigate adsorption of low-density subcritical vapors, the results have not been satisfactory at higher, liquid-like densities of supercritical fluids. Even if the requirements for high experimental accuracy in the neighborhood of the critical region were met, these methods are fundamentally unable to deliver the total adsorption capacity, since the properties (e.g. density) of the adsorbed phase are in general not known.

In this work we utilize vibrating tube densimetry for the first time to measure the total amount of fluid contained within a mesoporous solid. The method is first demonstrated using propane at subcritical and supercritical temperatures between 35 °C and 97 °C confined in silica aerogel (density 0.2 g·cm<sup>-3</sup>, porosity 90%) that was synthesized inside Hastelloy U-tubes. Sorption and desorption of carbon dioxide on the same solid was measured at 35 °C at pressures to 120 bar (density to 0.767 g·cm<sup>-3</sup>). The results show total adsorption increasing monotonically with increasing pressure, unlike excess adsorption isotherms which show a maximum close to the critical density.

### **INTRODUCTION**

#### **Enhanced Geothermal Systems (EGS) using CO<sub>2</sub> as the heat mining fluid**

Development of two technologies are increasingly viewed as central to a sustainable energy future: 1) commercially viable methods for geothermal energy

mining from vast resources of hot rocks, initially without sufficient permeability and/or water resources (EGS systems), and (2) effective and safe sequestration of carbon dioxide in deep geological formations. Using compressed CO<sub>2</sub> instead of water for reservoir creation and heat mining, proposed by Brown (2000), may contribute to greenhouse gas reduction by producing renewable energy more efficiently with practically no new emissions, as well as permanently sequestering some CO<sub>2</sub> through carbonate mineral formation. Brown (2000), Fouillac *et al.* (2004), Pruess (2006), Pruess and Azaroual (2006) and Xu *et al.* (2008) discussed a number of benefits of this concept including saving water resources, efficient permeability creation using supercritical gas, better fluid flow and heat transfer properties, and finally, weaker interactions with engineered materials, due to nonionic character of CO<sub>2</sub>. This latter difference between dry CO<sub>2</sub> and water promises far less pronounced scaling problems in underground and in-plant plumbing, and therefore better compatibility with energy conversion equipment such as heat exchangers, as well as potentially greater control over mineral dissolution, solute transport and precipitation inside the reservoir.

Experimental and numerical studies of the creation and operation of EGS using CO<sub>2</sub> injection have led to a vision of a geothermal reservoir divided into several zones differing in water content and hence with different controlling processes. In the central zone in the direct vicinity of the injectors most water will be expelled shortly after injection of pressurized fluid as new fractures and cracks are created. Some minerals will dehydrate leading to an additional increase of porosity. Some remaining brine will dissolve into the CO<sub>2</sub> and form homogeneous fluid phases. In the peripheral zones carbonate minerals would precipitate in the pore network as CO<sub>2</sub> slowly diffuses away from the wells. These processes could

create a confined and sealed engineered geothermal system. Accurate modeling of the processes outlined above requires accurate properties of CO<sub>2</sub>-rich fluids and quantitative information on fluid-rock reactivity that are not currently available. Existing data are particularly inadequate for predicting the behavior of multicomponent CO<sub>2</sub>-rich phases under EGS conditions, but discrepancies and gaps exist even for the essential CO<sub>2</sub>-H<sub>2</sub>O binary system. While dry CO<sub>2</sub> is not a polar and strongly ionizing solvent like water, addition of water to CO<sub>2</sub> induces formation and dissociation of carbonic acid, H<sub>2</sub>CO<sub>3</sub>. The spatial limits of the zones described above and the extent of carbonate formation at the peripheries of the reservoir will depend on mutual solubilities between supercritical carbon dioxide and aqueous brines.

Although CO<sub>2</sub> is less viscous than water, it is generally recognized that, in the vicinity of injection wells, only macroscopic cleats and fractures can provide the fluid flow required for economical energy mining. However, additional issues originating at the fluid-solid interface inside pore systems, and similar to those associated with geologic carbon sequestration, emerge in geothermal systems using CO<sub>2</sub> as the heat transfer fluid. The composition of the fluids and reservoir sealing are determined by fluid-matrix processes occurring in large volumes of mesoporous and microporous rocks that may be located away from cleats and fractures and/or far from the wells. All four CO<sub>2</sub> trapping/storage mechanisms (structural, capillary, solubility and mineral) can be potentially affected by the presence of water and modification of fluid properties by confinement in pore systems. It is not surprising that accurate fundamental properties, such as multicomponent fluid phase densities and compositions of confined fluids at the fluid-mineral interface are crucial for modeling of reactive transport of fluids and prediction of the behavior of vast reservoir volumes.

### **Previous research of the properties of pore fluids**

Studies of adsorbed or confined fluids indicate that pore size, shape, distribution, interconnectivity and chemistry can have a profound effect on densities, phase equilibria and transport properties. Research on phase separation and phase equilibria in confined systems has been reviewed by Gelb *et al.* (1999). More recently Cole *et al.* (2010) summarized the current state of knowledge about the behavior of pore-confined supercritical fluids, in particular CO<sub>2</sub>, in geologic formations. Inside micropores or microfractures, liquid-vapor demixing, density changes, solid solubility, and heterogeneous reactions may occur at different temperatures and pressures

than in bulk fluids. Vapor-liquid phase equilibria for pure compounds were investigated by measuring adsorption (capillary condensation) isotherms in porous materials such as Vycor pore glass, controlled pore glass (CPG), porous silica, silica gel, silica aerogels, activated carbon fibers, zeolites, etc. The results were interpreted as “hysteresis phase diagrams” and compared with bulk gas-liquid coexistence curves, although the “gas” and liquid “phases” identified on the opposite sides of the adsorption hysteresis loop are not necessarily coexisting phases in thermodynamic equilibrium. For example, for CO<sub>2</sub> adsorbed in Vycor glass, the hysteresis critical temperature was found to be about 40 °C lower than the critical temperature of CO<sub>2</sub> (Burgess *et al.*, 1989). A limited number of binary systems with liquid-liquid equilibria in porous glasses and silica gels have been investigated using such methods as light scattering, small angle neutron scattering, neutron transmission, light transmission, Raman spectroscopy, electrical permittivity measurements, and positron annihilation. Solid-liquid transitions were investigated using differential scanning calorimetry, NMR, and X-ray diffraction.

Classical experimental adsorption methods using volumetric, manometric and gravimetric measurements are well established and accurate as long as the density of the (liquid-like) adsorbed phase is much higher than the density of the bulk phase (gas-like). However, as these densities converge when approaching the critical point and for supercritical fluids with increasing pressure, it becomes clear that total adsorption capacity cannot be obtained. The measured quantity is best characterized as Gibbs excess sorption, although the exact meaning depends on the details of the experimental procedure and the interpretation of experimental results and is not always equivalent to the definitions used in computational models (Cole *et al.*, 2010). While macroscopically interpreted excess sorption is sufficient for most chemical process design purposes (Sircar, 1999) even without any information on the properties of the actual adsorbed phase (such as its volume or local density), the knowledge of total adsorption is still useful for at least two reasons. First, it is important to know the total capacity of a geothermal reservoir for fluid storage, e.g. to balance the flows and account for fluid losses, and second, a simultaneous analysis of total and excess adsorption can provide an estimate of the density of the adsorbed phase – a nanoscale property. Thus the advantage of total sorption data is an additional opportunity to better understand both the large-scale functioning of geothermal systems and, at the same time, the molecular-scale processes at the fluid-solid interface underpinning their

behavior. The desired end result is a further advance in the accuracy of comprehensive reservoir modeling.

Noteworthy progress in the application of small angle neutron scattering (SANS) and neutron transmission techniques to the study of the local properties of nanoconfined phases is demonstrated by a few recent studies of fluid-saturated nanoporous silica aerogels (Melnichenko *et al.*, 2006; Rother *et al.*, 2007). The experimental data and the newly developed Adsorbed Phase Model (Rother *et al.*, 2007) yield the mean density and the volume of the sorption phase and thus allow for determination of excess and total sorption.

### **The advantage of vibrating tube densimetry (VTD) for investigation of confined fluids**

The ultimate motivation for this project was to develop a new macroscopic method for obtaining total adsorption data, complementary to SANS. The significance of total adsorption is illustrated in Fig. 1., taken from Siemons and Busch (2007), which shows the 45 °C isotherm of excess adsorption determined using a volumetric-manometric method (the red curve) and the corresponding total adsorption isotherms calculated from the simple relation,

$$n_{\text{tot}} = n_{\text{ex}} \rho_{\text{ads}} / (\rho_{\text{ads}} - \rho_{\text{bulk}}), \quad (1)$$

where  $\rho_{\text{ads}}$  is the density of the adsorbed phase (assumed here to be constant) and  $\rho_{\text{bulk}}$  is the density of CO<sub>2</sub> obtained from an equation of state for the bulk phase at each pressure. Each total adsorption isotherm corresponds to a different value of  $\rho_{\text{ads}}$ .

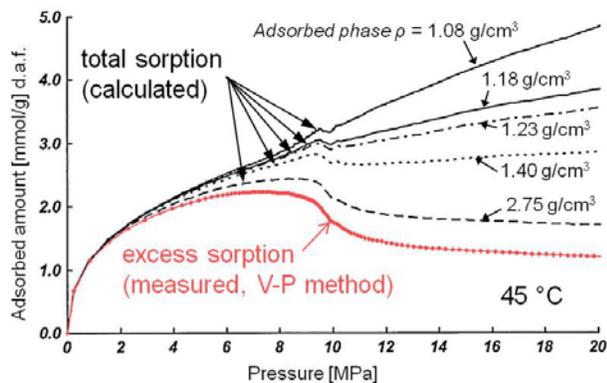


Figure 1: Calculation of total sorption of CO<sub>2</sub> on coal (per gram of dry ash free substrate) taking into account various densities of sorbed CO<sub>2</sub> (based on Siemons and Busch, 2007).

Three of the adsorbed phase densities marked in Fig. 1 are previously published results obtained from modeling adsorption of CO<sub>2</sub> on coal samples (1.08 g/cm<sup>3</sup> and 1.40 g/cm<sup>3</sup>) and activated carbon (2.75 g/cm<sup>3</sup>). The remaining two densities are saturated liquid density at triple point (1.178 g/cm<sup>3</sup>) and the liquid density at boiling point (1.227 g/cm<sup>3</sup>). The simplified model represented in Fig. 1 demonstrates the dependence of total adsorption on the density of the adsorbed phase which is an essential quantity for understanding sorption of fluids in the critical and supercritical regions, but impossible to estimate with sufficient accuracy using conventional macroscopic methods.

Measurements of density using the vibrating tube method differ fundamentally from the gravimetric method, where the adsorbed amount is determined from the weight of the sample, or manometric /volumetric methods, where the adsorbed amount is determined from changes of pressure measured in a calibrated volume of fluid. To correct for either the sample buoyancy in bulk adsorbate, or the pressure change due to the changing volume of the adsorbed phase, both of these methods require the knowledge of the volume of the fluid present in the pores, which is difficult to estimate. Since these methods rely in principle on measurements of the difference between two quantities that may be close or equal to each other (the densities of bulk and adsorbed phases), errors are difficult to avoid. Both buoyancy and volume corrections are considerable at densities close to their critical values. With the vibrating tube method, the mass is directly measured as the inertia of the fluid imbibed in the solid sample without significant errors caused by excess free fluid present.

In this first report on the application of the vibrating tube method to obtain directly the densities of confined fluids, we follow the strategy delineated by Cole *et al.* (2010) and focus on the proof of principle using a well defined and uniform engineered porous solid (silica aerogel). We first explore both the subcritical region with liquid-vapor equilibria and the supercritical region using a relatively inert adsorbate fluid (propane) and then measure adsorption of supercritical CO<sub>2</sub> in the same material.

The advantage of these well-defined relatively simple systems is the ability to compare the results with molecular-level computational simulations including Monte Carlo and Molecular Dynamics methods. In addition, the results of this work are complementary and comparable to the results of recent SANS/neutron transmission experiments with the same and similar substrates (CO<sub>2</sub> + silica aerogel; Melnichenko *et al.* 2006 and deuterated propane +

silica aerogel; Rother *et al.* 2007). The SANS studies are capable of providing the mean density and volume of the sorption phase (as well as the fraction of unadsorbed fluid) as a function of pressure. The results reveal an interesting phenomenon of critical depletion involving a decrease of the density of the sorbed phase as bulk fluid density crosses over the critical value. We anticipate that with the aid of the new vibrating tube density data the gap between macroscopic results obtained by volumetric or gravimetric sorption and micro-structural information obtained by SANS can be bridged as the results obtained by different approaches are cross-verified.

Characterization of multicomponent CO<sub>2</sub>-bearing fluids, both bulk and pore-confined, at the conditions relevant to geothermal energy production, is an important part of the research funded by US DOE Geothermal Program at Oak Ridge National Laboratory. The ultimate goal is to develop a sound basis for development of geothermal power through reliable predictive modeling starting from molecular scale interfacial regions, through pore and fracture scales, to the entire reservoir. Predictive models are needed that are applicable at every stage, starting from site identification, to reservoir creation, operation, and stimulation. Using two high-temperature high-pressure vibrating tube densimeters (VTD) we plan to extend the measurements to multicomponent CO<sub>2</sub>-rich mixtures, both bulk and pore-confined to obtain accurate densities and phase boundaries for subsurface fluids relevant to EGS. We are also planning to develop experimental methods for using the VTD apparatus with porous and particulate materials other than synthetic silica gels.

The following sections describe the details of the experimental method, including in particular the calibration methods adopted to obtain quantitative results, and the results for propane, argon, and CO<sub>2</sub>.

## **EXPERIMENTAL**

### **Apparatus**

High pressure-temperature flow vibrating tube densimeters, (Simonson *et al.*, 1994; Blencoe *et al.*, 1996) designed and custom built at ORNL, were modified for measurements of confined fluid densities. The most important modification of the Simonson apparatus was the replacement of the existing U-tube (OD = 1.59 mm), previously welded to the supporting mount, with a new Hastelloy C22 U-tube containing the porous solid (OD = 3.17 mm, ID = 1.78 mm; the length of the vibrating section = 90 mm). The U-tube was clamped in a new mount designed to facilitate future tube replacements. The

apparatus consisted of a solid cylindrical block made of silver and placed inside a cylindrical furnace. The U-tube was placed upside-down inside a cavity in the silver block. The U-tube had a permanent Alnico V rod magnet attached to one of its arms using a small titanium clamp, about 24 mm below its tip. Inlet and outlet tubing (OD = 1.59 mm) was fitted to the ends of the U-tube and placed in matching grooves cut in the silver block for efficient heat exchange. A spiral heater tube (OD = 1.59 mm) was wound around the silver block to provide precise temperature control. A preheater for the inlet tubing was also provided by winding it together with another heater around a separate cylindrical block placed above the main block containing the vibrating U-tube. Two ceramic (Macor) electromagnet coils (one exciting the vibrations and the other sensing the resonance frequency) were installed in openings in the main block to accommodate the ends of the permanent magnet attached to the U-tube. The pressure in the system was measured using two digital piezoresistive transducers (345 bar and 552 bar full scale) calibrated by the manufacturer (Keller America, Inc.) with total error band of  $\pm 0.1\%$  of the full scale. The temperature was controlled roughly using the furnace and precisely using the small heater wound around the silver block. The temperature of the silver block was maintained constant within  $\pm 0.002$  K of the setpoint. The temperature was measured by means of a platinum RTD and an Instrulab Inc. digital thermometer calibrated to an accuracy of  $\pm 0.02$  °C to 400 °C by ORNL Metrology using fixed-point standards traceable to NIST. Temperature, pressure, and vibration period data were continuously recorded, and plotted on the screen by a custom made computer data acquisition program. The remaining details of the experimental setup were the same as described by Simonson *et al.* (1994).

### **Materials**

Supercritical alcohol-dried silica aerogel (density = 0.2 g/cm<sup>3</sup>) was synthesized inside Hastelloy C22 U-tubes by Oscellus Technologies, Inc., Livermore, California, USA. Assuming the skeletal density of 2.02 g/cm<sup>3</sup>, the porosity of this sample was over 90% with estimated specific surface area in the range 700 m<sup>2</sup>/g to 800 m<sup>2</sup>/g. The silica aerogel is an open structure of thin silica strands with mesh size between 10 and 20 nm (Fig. 2).

The grades and nominal purities of the gases used were as follows: propane: Matheson Tri Gas Research Purity, (99.993%); helium: Air Liquide Ultra High Purity (99.999%); argon: Airgas Research Plus (99.9999%), and carbon dioxide: Matheson Tri Gas Research Grade (99.999%).

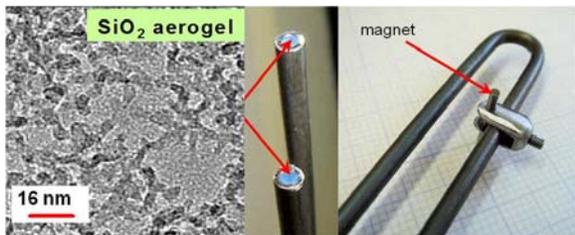


Figure 2: TEM image of the silica aerogel structure (silica strands are darker) and the Hastelloy U-tube with silica aerogel synthesized inside and the magnet clamp attached.

### VTD operation and calibration

Vibrating tube densimetry consisting of a U-tube forming a uniform cantilever is based on the linear dependence of the vibration period on the square root of the linear specific mass of the cantilever. In practice, the most accurate measurements of the unknown density  $\rho$  of the fluid inside the tube can be obtained by calibration using reference fluids of known density. The difference between the unknown density  $\rho$  and reference density  $\rho_0$  is given by:

$$\rho - \rho_0 = K(\tau^2 - \tau_0^2), \quad (2)$$

where  $\tau$  and  $\tau_0$  are the vibration periods of the fluid under investigation and the reference fluid, respectively. The temperature-dependent slope  $K$  can be determined using two reference fluids. Vacuum is often used as one reference, and water as the second. While reference fluids with densities close to the unknown density would provide the best accuracy, past experience shows that the deviation from linearity of the relationship between the fluid density and the square of the vibration period is very small in comparison with other sources of error, so that usually there is no need to calibrate with more than two fluids or introduce calibration equations of orders higher than the linear equation (2). This is due to (i) close to ideal harmonic vibrations assured by the small amplitude, and (ii) relatively small mass of the fluid in comparison to the mass of the tube. In general, the high accuracy that can be achieved using the vibrating tube method can be attributed to very high accuracy of the measurement of time (frequency). In this work the vibration frequency of the evacuated tube filled with silica aerogel was about 263 Hz and the frequency reduction due to saturation with CO<sub>2</sub> at 35 °C and 139 bar (0.8 g/cm<sup>3</sup>)

was approximately 4 Hz. The periods of vibration (~3.8 ms, averaged over 40 s intervals), were measured and recorded continuously with the resolution of 1 ns (seven digits).

Since the average density of the pore-confined fluid is, in general, unknown and different from the density of the free fluid remaining in equilibrium with it, calibration is not as straightforward for confined fluids as for bulk fluids. To obtain absolute values of confined fluid density we made the following assumptions: (i) excess adsorption of inert gases at 35 °C, far above their critical temperature, is negligible; and (ii) the average densities of confined liquids will approach the bulk liquid density at high pressure. Additionally, a theoretical calculation of the slope  $K$  in equation (1) was made using geometrical and mechanical properties of the vibrating cantilever.

Fig. 3 shows the densities of confined propane measured at pressures between vacuum and 19 bar during adsorption (blue) and desorption (green) at 35 °C. Also shown is the density of bulk propane (purple). The vibration period vs. density slope  $K$  of equation (2) was determined by assuming that at 19 bar the densities of confined and bulk propane are equal (also, that both are zero at vacuum). With this assumption, the compressibilities of confined (measured) and bulk (EOS) fluids also become equal.

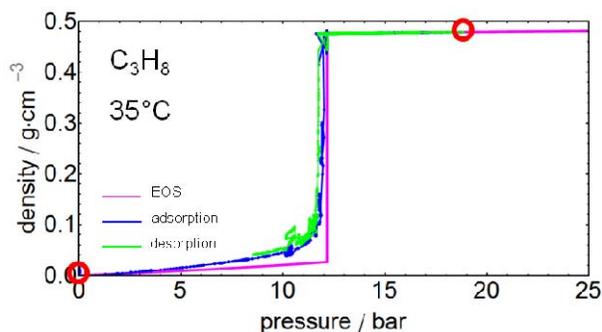


Figure 3: Measured density of confined (blue and green) and bulk propane (purple) at 35 °C. The red circles indicate the points used to calculate  $K$  in equation (1) (at vacuum and at 19 bars where the densities of confined and bulk fluids were assumed to be equal).

Fig. 4 shows the corresponding diagram for argon at the same temperature. The vibrating period data were converted to densities using the value of  $K$  determined from the propane data as described above.

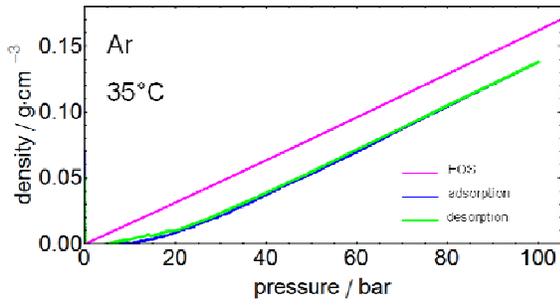


Figure 4: Measured density of pore-confined argon compared with bulk gas density.

Parallel lines in Fig. 4 demonstrate that the isotherms for confined argon scaled using the same calibration equation as for propane and show the same compressibility as bulk argon. This is expected, assuming that excess adsorption on silica aerogel is negligible at the temperature nearly 160 K above critical (for argon  $T_c = -122.46$  °C). The difference between bulk and confined densities in Fig. 4 (less than  $0.03$  g/cm<sup>3</sup>) is within the experimental error of the vibration period at vacuum.

While the agreement between the results for propane and argon was better than expected, there is no guarantee that the same assumptions will be valid for every combination of porous solid and fluid adsorbate. It should be expected that for materials characterized as microporous, the density difference between confined and bulk fluid could persist to higher pressures, and filling of the pores of molecular sizes would be more strongly affected by the size and geometry of the fluid molecules.

It should be kept in mind that even if accurate absolute values of density could not be obtained from calibration using reference fluids, vibrating tube densimetry would still provide valuable information of the relative changes of the density of the confined fluids with pressure, possible phase transitions, and relative densities for different fluids. However, absolute values of density, although usually of lesser accuracy than those calibrated with reference fluids, can be also obtained by calculation of the resonance frequency from the geometry and mechanical properties of the vibrating tube, as described below.

For an evacuated U-tube ( $\rho_0 = 0$ ) the slope  $K$  in equation (2) can be calculated from

$$K = \left( \frac{n^2}{2\pi L} \right)^2 \frac{EI}{V_{pore}}, \quad (3)$$

where  $E$  is the Young's modulus of elasticity for Hastelloy C22;  $I$  is the second moment of tube cross-section area,  $I = \pi/64 (OD^4 - ID^4)$ ;  $n$  is the characteristic constant for the principal mode of vibration, and  $L$  is the length of the cantilever. The vibration period for the tube filled with porous solid and evacuated is then,

$$\tau_0 = \sqrt{\frac{m_0}{K V_{pore}}}, \quad (4)$$

where  $m_0$  is the mass of empty tube and porous solid per unit length, and the other symbols have the meanings as defined above.

The data used for calculation of  $K$  and  $\tau_0$  from equations (3) and (4) included nominal outer and inner diameters of the tubing, the typical Young's modulus for Hastelloy C22, the measured length of the U-tube, the weighed mass of empty and solid-filled tubes, and the pore volume estimated from the difference. A correction was applied for the additional point-mass of the magnet located about 24 mm from the free end of the cantilever (Fig. 2). The parameters of equation (2), obtained from the calibration and the calculation as described above, are summarized in Table 1.

Table 1. The parameters of equation (2) from calibration and calculation.

	Calibrated	Calculated	Difference
$K$ (g·cm <sup>-3</sup> ·ms <sup>-2</sup> )	1.713	1.876	+10%
$\tau_0$ (ms)	3.805	3.470	-10%

Agreement within 10% of the calibrated value is quite satisfactory, taking into account the accuracy of the data used in equations (3) and (4) and in particular in comparison with the accuracy of other methods used to estimate the density of confined fluids.

Additionally, the dependence of the vibration period on temperature at constant pressure was determined experimentally at constant pressure. This linear relationship was used to estimate  $\tau_0$  whenever it was not measured, although in principle  $\tau_0$  can be measured directly at each temperature. Additional measurements of the density of pore-confined helium at 35 °C were used to demonstrate negligible adsorption of helium and lack of any significant pressure effect on the calibration of the vibrating tube at least to 120 bar.

## RESULTS AND DISCUSSION

The summary of the proof-of-principle results for VTD measurements of the density of pore-confined propane are shown in Fig. 5.

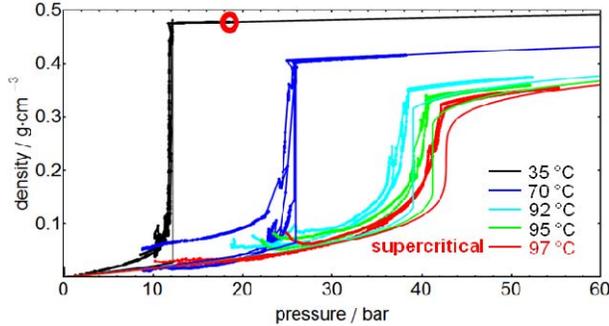


Figure 5: Densities of propane confined in the pores of silica aerogel at subcritical and supercritical temperatures plotted as a function of pressure.

Measurements were made at four subcritical temperatures (35, 70, 92, and 95 °C) and at 97 °C, about 0.3 K above the critical temperature ( $T_c = 96.7$  °C). The thinner smooth lines in Fig. 5 represent the equation of state for (bulk) propane (Lemmon *et al.*, 2007; 2009). The isotherms show large increase in density due to the onset of condensation in the pores which starts significantly earlier in the smallest pores than the condensation of bulk fluid.

The calibration using the point on the 35 °C isotherm (marked by a red circle in Figures 3 and 5) produces results consistent with the EOS data at higher temperature. At the temperatures closer to the critical point (92 °C and higher) and the pressure above the saturation pressure of the bulk fluid, the pore liquid is clearly denser and less compressible than the bulk fluid (the slopes are less steep for confined fluid in Figure 5). As the pressure is increased, the densities and the compressibilities of the confined and bulk fluids converge. The increased average density of the confined fluid in the vicinity of the bulk fluid saturation pressure represents excess adsorption.

Figure 6 shows the analogous plot for carbon dioxide at 35 °C, about 4 K above its critical temperature (31.0 °C). The purple curve represents the equation of state for bulk CO<sub>2</sub> (Span and Wagner, 1996) as implemented by Lemmon *et al.* (2007). The same slope  $K$  for equation (2) as determined for propane and listed in Table 1, was used for CO<sub>2</sub>. The results for propane and CO<sub>2</sub> are consistent, with the adsorption hysteresis loop narrowing and excess adsorption decreasing with increasing reduced temperature ( $T/T_c$ ).

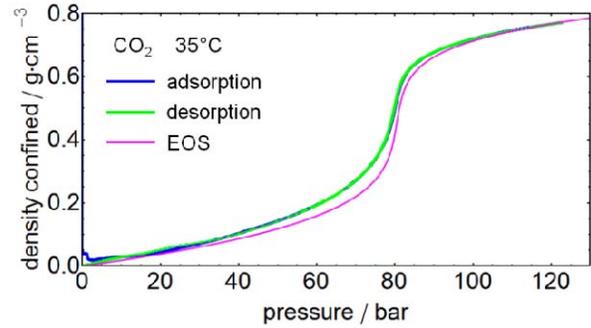


Figure 6: Densities of CO<sub>2</sub> confined in the pores of silica aerogel at 35 °C.

Figure 7 shows the densities of confined supercritical propane and carbon dioxide plotted vs. the density of the bulk fluid. This diagram presents total adsorption isotherms. Reduced densities ( $\rho/\rho_c$ ) were used to emphasize the corresponding states similarity of the fluids.

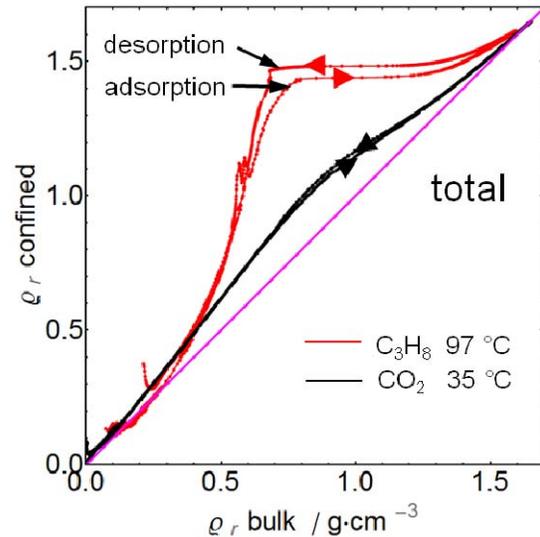


Figure 7: Total adsorption isotherms for supercritical C<sub>3</sub>H<sub>8</sub> and CO<sub>2</sub> plotted in terms of reduced densities. The diagonal line represents the bulk fluid.

The total adsorption isotherm for supercritical propane at 97 °C, just above its critical temperature, features a nearly horizontal section remaining as a vestige of the condensation of the bulk fluid below the critical temperature. By comparing with CO<sub>2</sub> and applying the principle of corresponding states it can be expected that the slope of this section will increase as the temperature increases and the shape of the isotherm for propane at a higher reduced temperature will approach the shape of the isotherm for CO<sub>2</sub> shown in Figure 7.

All total adsorption isotherms obtained in this work increased monotonically with pressure. This is in general agreement with the neutron scattering results (Rother *et al.*, 2007) for total adsorption of deuterated propane in a similar silica aerogel with a density lower by a factor of two ( $0.1 \text{ g/cm}^3$ ). It should be noted that unlike the macroscopic VTD technique described here, the neutron scattering methods and associated models are capable of differentiating between adsorbed and unadsorbed pore fluid. Melnichenko *et al.* (2006) and Rother *et al.* (2006) found pronounced depletion of the adsorbed fluid density in the vicinity of the critical point. However, this apparent exchange of material between the adsorbed and unadsorbed phases of the model did not cause a significant change in total adsorption. This finding is confirmed by the present work. The crucial aspect the Adsorbed Phase Model is the quantitative distribution of the pore fluid between adsorbed and unadsorbed phases, leading to the ability of distinguishing between absolute adsorption, referring to the adsorbed phase, directly affected by the solid-fluid interface, and total adsorption referring to all fluid contained in the pore system. Future VTD experiments with fluids confined in microporous solids and adsorption systems with stronger fluid-solid interactions (where most or all fluid can be treated as adsorbed phase) can provide even more insight leading to further verification and refinement of both VTD and SANS data interpretation and modeling.

## SUMMARY AND CONCLUSIONS

We applied vibrating tube densimetry for the first time to measure the density of pore-confined fluids. The principal advantage of this method is the ability to obtain total adsorption isotherms, unlike classical manometric/volumetric and gravimetric methods which can only determine excess adsorption. This experimental approach is much more flexible for exploring wide ranges of temperature/pressure/composition for pure and mixed fluids and thus serves as a powerful complement to SANS experiments. Furthermore, the VTD allows mapping of fluid phase boundaries, since the vibration frequency exhibits pronounced changes when droplets condense or bubbles form in a homogeneous fluid within the tube. Experiments were carried out with silica aerogel as a prototype porous solid synthesized inside vibrating U-tubes. The results described here as the proof-of-principle for propane from  $35 \text{ }^\circ\text{C}$  to  $97 \text{ }^\circ\text{C}$  and for carbon dioxide at  $35^\circ\text{C}$  demonstrate total adsorption isotherms monotonically increasing with increasing pressure.

Since excess adsorption isotherms can be also obtained from VTD results, direct comparisons can

be made not only with recently reported neutron scattering data but also with traditional thermophysical methods. Figure 8 shows excess adsorption isotherms for supercritical propane and carbon dioxide at  $35 \text{ }^\circ\text{C}$  corresponding to the total adsorption isotherms plotted in Figure 7. The shapes of the excess adsorption isotherms plotted as a function of bulk gas density are similar e.g. to those reported by Gensterblum *et al.* (2009) for adsorption of  $\text{CO}_2$  on activated carbon and our new (to be published) results for  $\text{CO}_2$  on silica aerogel obtained gravimetrically.

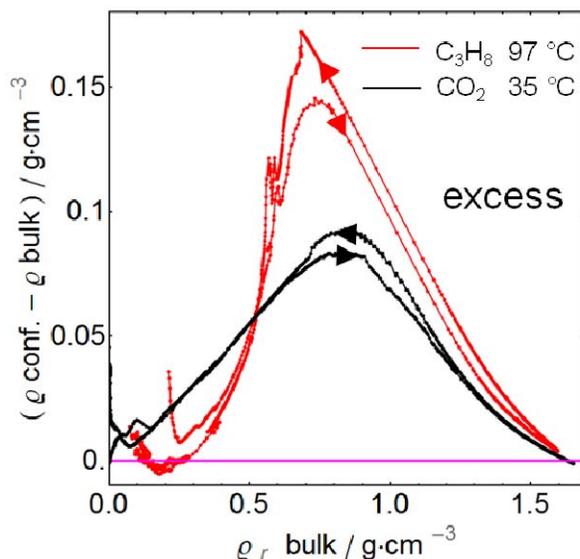


Figure 8: Absolute excess adsorption isotherms for supercritical  $\text{C}_3\text{H}_8$  and  $\text{CO}_2$  plotted in as a function of reduced bulk fluid density.

The present work provides a clear interpretation of the excess adsorption isotherms by reference to the total adsorption isotherms (Fig. 7) and to the results for propane below its critical temperature. Since traces of vapor-liquid equilibrium persist above the critical temperature, approximately along the critical isochore, the decreasing part of the isotherm corresponds to the vapor-liquid equilibrium tie line (a straight line connecting vapor and liquid phases in equilibrium). For this reason, the slope of the decreasing part of the excess adsorption isotherm should reach a limiting value of -1 at the critical point (this slope is zero for the total adsorption isotherm in Figure 7). On the other hand, the slope of the increasing part of the isotherm depends in general on pore size distribution. It could reach the value of 1 for excess adsorption isotherms (corresponding to a steep vertical slope of total adsorption) e.g. in the cases where adsorption (condensation) occurs rapidly in a narrow range of pressures for uniform pores.

Vibrating tube densimetry of bulk fluids is based on accurate and simple calibration using reference fluids with accurately known densities. For confined fluids calibration is not as straightforward since there are no standards for confined fluids. We have demonstrated three methods of obtaining quantitative results based on the assumed behavior of confined fluids at certain conditions or an analysis of the geometry and mechanical properties of the vibrating tube. We estimate the accuracy of total adsorption measured by VTD as better than  $\pm 10\%$ .

Regardless of the absolute density accuracy that can be achieved, even uncalibrated VTD data proportional to confined fluid density can provide information on the behavior of confined fluids in a wide range of temperature and pressure conditions including e.g. the phenomena of critical depletion of the adsorbed phase and phase transitions.

For propane confined inside the pore system of silica aerogel we did not detect any lowering of the critical point relative to the bulk fluid. As can be seen in Figure 5, a distinct change in the character of vapor-liquid transition was not observed. One of the contributing factors could be a relatively wide distribution of pore sizes. This is another case where SANS and VTD studies are complementary, since SANS can probe the pore size distribution. A well defined transition to low-compressibility fluid, probably corresponding to complete filling of the widest pores by the liquid-like denser phase, persisted even above the critical point. Additional isotherms closer to the critical point are needed to verify if this is also true for carbon dioxide. Such data will also validate the applicability of the principle of corresponding states to confined fluids.

The results of this initial study show that vibrating tube densimetry can bring new insights into the behavior of confined fluids. It seems likely that a simultaneous analysis of VTD data in conjunction with other approaches, including in particular small angle neutron scattering has the potential to deliver the missing quantitative information of the  $PVT_x$  properties needed for reliable modeling of enhanced geothermal systems, starting from molecular scale interfacial regions, through pore and fracture scales, to whole reservoir modeling.

We intend to extend the initial research described here to measurements of mixed aqueous  $\text{CO}_2$ -rich fluids and also explore the techniques for filling the tube with other porous solids more closely matching the materials that can be encountered by  $\text{CO}_2$  injected into geothermal reservoirs.

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