LETTER TO THE EDITOR

Hysteresis at the gas–liquid and liquid–solid phase transitions of capillary confined CO_2: a positronium annihilation study

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Abstract. The hysteresis behaviour of capillary confined CO_2 gas is studied through the positron/positronium annihilation technique. The arrangement of the confining medium (VYCOR glass) allowed simultaneous measurement of the bulk and pore confined phase behaviour. Isobaric temperature cycling showed marked hysteresis at the gas–liquid and liquid–solid phase boundaries for the confined gas. Observations at the gas–liquid transition are in agreement with capillary condensation theories and simple ideas are proposed to explain the liquid–solid transition behaviour.

In recent years, positron and positronium annihilation techniques have seen some interesting applications in the studies of gas adsorption at internal surfaces [1]. Lately the technique has also been successfully applied in the investigation of phase behaviour of gases confined in interconnected cylindrical pores (radius ~20 Å) in VYCOR glass [2, 3]. The phase behaviour under such conditions are markedly different compared to those in the bulk gas, due to the combined effects of finite pore size and substrate forces [4, 5, 6].

Previous isothermal measurements, using different techniques [2, 3, 4, 7, 8] on a number of gases at the gas–liquid transition in confined geometry, show capillary condensation of the gas to a dense liquid-like state, that fills the pores at a pressure less than the saturated vapour pressure (P_{sat}) for the bulk. Measured through increasing and decreasing pressure cycles, the isotherms show significant hysteresis which diminishes and eventually disappears as the bulk critical temperature is approached [2, 4, 7]. If measurements are conducted at constant pressure, the gas–liquid transition occurs at a higher temperature compared to that of the bulk. It is conceivable that hysteresis of the type seen in the isotherms should also occur during isobaric measurements.

There have been a number of studies at the liquid-solid boundary for ^{4}He confined in pores of average radius ~60 Å [9, 10, 11]. General observation points to a shifting of the liquid–solid transition towards lower temperatures at constant pressure. SANS experiments in a mixture of H_2O/D_2O in VYCOR glass [8] and picosecond optical investigations of oxygen in sol-gel glasses containing pores of radii between 20–50 Å [12] indicate a similar behaviour. More recently, there has been a comprehensive study of the liquid–solid transitions and hysteresis behaviour in VYCOR glass (average pore radius 18 Å) and silica xerogel (average pore radius 25 Å) by Molz et al [13] using specific heat and ultrasonic measurements.

Here, we report our positron/positronium annihilation observations of hysteresis during isobaric phase transitions across both the gas–liquid and liquid–solid phase boundaries for

CO_2 in VYCOR glass, containing interconnected cylindrical pores of average radius $\sim$20 Å. The positron technique has the potential to investigate all phase behaviour for a wide variety of gases. Moreover, the positron is an effective probe that seeks out the pores where the phase transitions occur.

Upon entering a porous glass sample, energetic ($\leqslant$ 0.5 MeV) positrons from a radioisotope (usually ^{22}Na) attain thermal equilibrium with the glass matrix within a very short period of time (typically a few ps). Thermalized positrons may either annihilate as free positrons in the glass matrix, or diffuse to the pores and form positronium there (Ps: a hydrogen–like entity with the proton replaced by a positron). Consideration of the total spin of the bound pair and the total number of possible states, requires that three quarters of these will be ortho-positronium (o-Ps: positron and electron spins parallel) and one quarter para-positronium (p-Ps: spins anti-parallel). In vacuum, the relatively long lived ($\sim$140 ns) o-Ps decays via the emission of 3γ photons. p-Ps has a considerably shorter lifetime of $\sim$125 ps and annihilates into 2γ photons. In a small pore (pore radius < o-Ps mean free path) even a thermalized o-Ps will undergo a large number of collisions with the pore walls during its relatively long lifetime. This may result in the annihilation of the positron with an electron of opposite spin from the pore wall. Such annihilations can proceed via a variety of ways, commonly termed as quenching [14], which lead to a shortening of the o-Ps lifetime and annihilation into 2γ photons. In the presence of gas in the pores, the gas molecules will contribute to the quenching, increasing the 2γ contribution to annihilation. The extent to which a surrounding medium will lead to o-Ps quenching is likely to depend on the density of the medium. A substantial increase in the 2γ contribution will occur at the gas–liquid transition within the pores, as a result of the significant increase in the density of the fluid. Similar effects are to be expected at gas–solid and, perhaps to a lesser extent, at liquid–solid transitions. Thus, the monitoring of $3\gamma/2\gamma$ annihilation ratio provides a novel way of probing phase behaviour under such conditions. However, when interpreting positron/positronium annihilation data, account must also be taken of the total Ps population. If a significant volume of gas condenses near the positron source, a large fraction of positrons will thermalize within the liquid and some may form Ps there. In contrast, one may observe an inhibition of Ps formation in the solid phase. Any process which increases the amount of Ps formed will tend to increase the ratio of $3\gamma/2\gamma$ annihilation, unless such processes also increase the o-Ps quenching rate, decreasing $3\gamma/2\gamma$. As a consequence, the precise balance of Ps formation and o-Ps quenching is likely to be complex and will be discussed below as circumstances require.

The experiments were performed in a purpose designed small pressure cell of volume $\sim$110 mm^3, which was housed in a sample chamber with associated automated and computer controlled specimen cooling, heating and evacuation facilities [15]. The porous samples were commercially available VYCOR glass containing interconnecting cylindrical pores of average radius of $\sim$20 Å, occupying $\sim$30% of the total volume of the glass [16]. The gas investigated was 5N pure CO_2, chosen for the easy attainability of experimental pressures and temperatures across the relevant phase boundaries. Experiments were carried out in the form of isobaric phase transitions in the pressure and temperature ranges of 5–10 bar and 180–300 K respectively. Two identical samples were sandwiched around a positron source of $\sim$30 μCi ^{22}Na deposited on a $\sim$8 μm Kapton foil, and the assembly inserted in the cell. The VYCOR specimens were thick enough to contain almost all the positrons within the sandwich. A small gap (a few microns) was created between the source and the samples to allow simultaneous measurement of the bulk phase transitions. The gas was bled into the cell through a computer controlled pressure system, incorporating a pressure reservoir and associated valve-assembly. Pressure stability (to an accuracy of $\pm$0.05 bar) was achieved

using a computer controlled digital pressure gauge and the temperature was controlled via a commercially available Eurotherm unit. Measurements of the phase behaviour in the pores were complemented by an independent assessment of the pure bulk phase diagram, using the same pressure cell containing a suspended positron source. The phase behaviour was monitored through measurements of the energy distributions of the annihilation photons. The data were analysed using a parameter $N(3\gamma/2\gamma)$ representing the total counts in the region 340–490 keV (3γ) divided by the total counts in the region 491–540 keV (2γ).
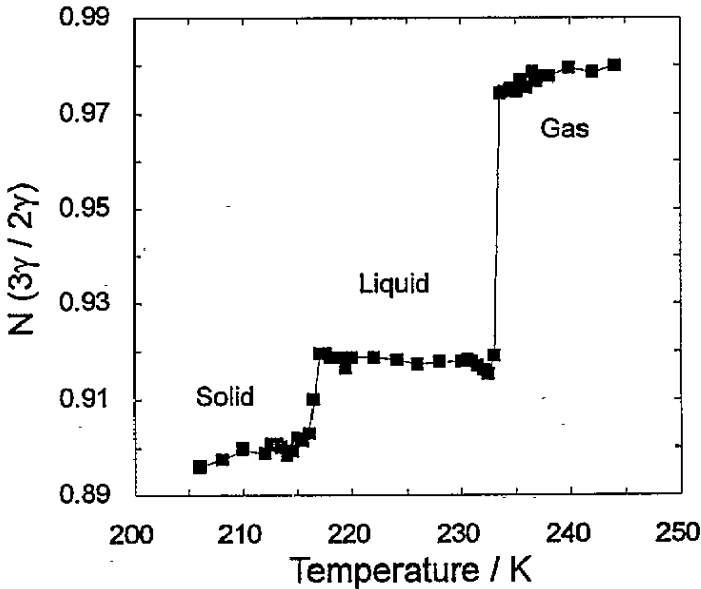

Figure 1. $N(3\gamma/2\gamma)$ as a function of decreasing temperature for bulk carbon dioxide at 10 bar, showing the gas–liquid and liquid–solid phase transitions.

Figure 1 shows a typical isobar for bulk CO_2 gas, where $N(3\gamma/2\gamma)$ is presented at a constant pressure of 10 bar, measured as a function of decreasing temperature. $N(3\gamma/2\gamma)$ remains fairly constant until a sharp drop is registered at the expected gas–liquid transition temperature of ~233 K. Following a plateau region in $N(3\gamma/2\gamma)$ a further small, but sharp decrease is noted at the expected liquid–solid transition temperature (~216 K). These stepwise decreases in N result from a combination of increased o-Ps quenching and inhibition of Ps formation as a function of the medium density.

$N(3\gamma/2\gamma)$ at the same pressure of 10 bar, but with the porous VYCOR glass inserted is presented in figure 2 as a function of decreasing (closed squares) and increasing (open squares) temperature. During the adsorption cycle (decreasing in temperature from the gaseous state) we observe a sharp drop in N at ~237 K, ~4 K above the bulk gas–liquid transition (figure 1), which we interpret as the occurrence of the liquid phase in the pores. This shift of the gas–liquid transition to higher temperatures is consistent with ours and others' previous results [2, 3, 7, 8]. A sharp increase in N follows at ~233 K, the same temperature for the bulk gas–liquid transition. Such an increase is seen in all our isobaric experiments [15] at the relevant bulk gas–liquid transition temperature and we assign this increase in N to the bulk gas–liquid transition of CO_2 in the gap between the VYCOR specimens [3]. When the gap between the glass specimens is filled with liquid, a fraction of the positrons will be stopped in the liquid leading to a higher proportion of the positrons
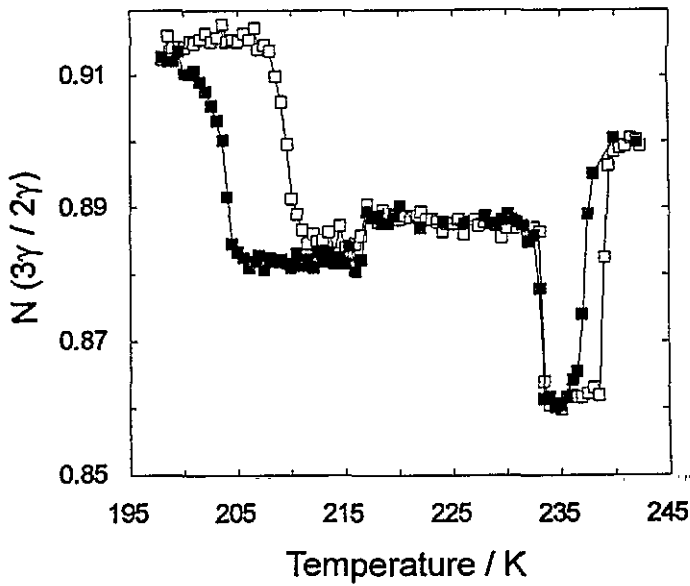
Figure 2. $N(3\gamma/2\gamma)$ as a function of decreasing temperature (solid symbols) and increasing temperature (open symbols) for carbon dioxide at 10 bar with VYCOR samples present. Hysteresis is observed in the phase transitions of the confined gas but not in the corresponding bulk phase transitions.

forming Ps.

At the bulk liquid–solid transition temperature ($\sim$216 K), we again observe a small but sharp drop in N, most likely due to the inhibition of Ps formation in solid gas (compared to the liquid gas) in the gap between the VYCOR samples. At a lower temperature, we note a final increase in N at $\sim$204 K (the midpoint temperature) which we believe is due to liquid–solid transition in the pores. Such an increase is contradictory to intuition (and to observation of the bulk gas above) but can be understood in light of the experimental arrangements. Since the bulk liquid–solid transition occurs at a higher temperature compared to that in the pores, the specimens are already surrounded by solid CO_2 at $T < 216$ K and no additional gas from the CO_2 reservoir can reach the pores. Consequently, when the liquid in the pores freezes a considerable fraction of the pore volume may become empty, as the density of solid CO_2 is substantially higher than that of the liquid (1.5 times greater in bulk CO_2). The availability of the open space is likely to increase the probability of Ps formation and hence increase 3γ annihilation. In addition, it is possible that the presence of solid CO_2 in the pores may further enhance the Ps fraction by providing a large surface area of solid gas where the balance between the electron and positron work functions and the binding energy of Ps is more favourable towards Ps formation (a Ps forms at a surface if the sum of the electron and positron workfunctions is less than the Ps binding energy of 6.8 eV [14]). Further evidence of this being a liquid–solid transition can be found in the fact that above the adsorption triple point in the pore this transition occurs at the same temperature of $\sim$204 K for all pressures, producing the familiar picture of a near vertical solidus line [3].

During the increasing temperature cycle, we find distinct evidence of hysteresis at both transitions in the pores, while no hysteresis is observed at the corresponding bulk transitions in the same experiment. The hysteresis at the liquid–solid–liquid transition ($\Delta T \sim 6$ K) is

much more pronounced than that in the gas–liquid–gas transition ($\Delta T \sim 2$ K). The 'melting' in the pores occurs approximately halfway between the bulk and pore freezing points which is consistent with results obtained by Molz *et al* [13] for a number of gases. When the gas is frozen in the pores, in the absence of pressure propagation from the gas reservoir and due to the creation of empty volume in the pores, it is possible that the equilibrium pressure there is much less than the ambient pressure applied. If this is the case, the 'melting' process is likely to be complex and it is conceivable that it initially proceeds via evaporation. If this conjecture is true, this will explain the much more extended hysteresis at the liquid–solid transition. Further work is under way to probe the possibility of partial pore filling following the freezing transition in CO_2 in pores and its implications for the melting behaviour.

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