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Positron and positronium annihilation studies of the phase behaviour of fluids in Vycor

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Abstract. We summarize the results of a recent positron annihilation study of the phase behaviour of CO₂ confined in Vycor glass. Particular emphasis is placed on the phase diagram of the confined fluid and on the usefulness of the positron annihilation technique in determining the mechanisms underlying phase transitions of fluids in porous solids.

1. Introduction

The phase behaviour of fluids adsorbed into small nanometre-scale pores poses an interesting fundamental problem for physics and chemistry. When a material is confined in a pore, its phase behaviour can be dramatically modified from that in bulk. The combined effects of finite pore size, substrate–fluid forces and the disorder introduced by the pore walls [1] may broaden first-order phase transitions and may shift the location of the phase boundaries in the (P, T) plane. Moreover, the individual transitions often show hysteresis on adsorption and desorption which results in distinctly different ‘phase diagrams’ for cooling and heating of a confined fluid.

Many experimental techniques have been used to study the properties of such systems. These include mass and volume adsorption, heat capacity, attenuation of sound, x-ray and neutron diffraction. Here, we describe a successful complement to these—namely, positron and positronium (Ps) annihilation spectroscopy. The sensitive response of a positron to its local surroundings, reflected either by its direct annihilation radiation or by the formation of positronium prior to annihilation, makes the positron a valuable probe of phase transitions. We describe some recent results using this technique to study fluids adsorbed in the nanopores of Vycor glass, and discuss the usefulness of positron/positronium spectroscopy for determining phase behaviour in these systems.

2. Background to the use of positrons

In a porous medium, such as Vycor glass, positrons thermalize in the glass matrix and a fraction form positronium (Ps) at the matrix/pore interface or in the matrix where they can diffuse to the pores prior to annihilation [2]. Roughly three quarters of the Ps formed will be ortho-Ps (oPs) and one quarter para-Ps (pPs). In vacuum, oPs decays via the emission of 3γ -photons and has a relatively long lifetime of ~ 140 ns and a broad, roughly triangular photon energy distribution extending from 0–511 keV [3]. pPs has a much shorter lifetime of ~ 125 ps and annihilates into 2γ -photons with a narrow energy distribution centred around

511 keV. In a small pore (pore radius $<$ oPs mean free path) even a thermalized oPs will collide many times with the pore wall during its long lifetime. This may result in the positronium of the oPs annihilating with an electron of opposite spin from the pore wall, and thereby decaying via 2γ -photons instead of 3γ -photons. Such a process is termed ‘oPs quenching’ [3]. If a fluid is present in the pores, the extent of oPs quenching will depend on the local density and thus is expected to increase at the gas \Rightarrow liquid and gas \Rightarrow solid transitions and, to a lesser extent, at the liquid \Rightarrow solid transition. In addition, any condition which changes the total positronium population will also affect the ratio of 3γ - to 2γ -annihilation. If the Ps is thermalized prior to annihilation then the formation of additional pPs will provide its own signature of phase transitions in the form of increased counts near the 511 keV annihilation photo-peak. Clearly, the precise balance of positronium formation and oPs quenching in confining geometry is likely to be complex and will depend on the amount and density of any confined fluid.

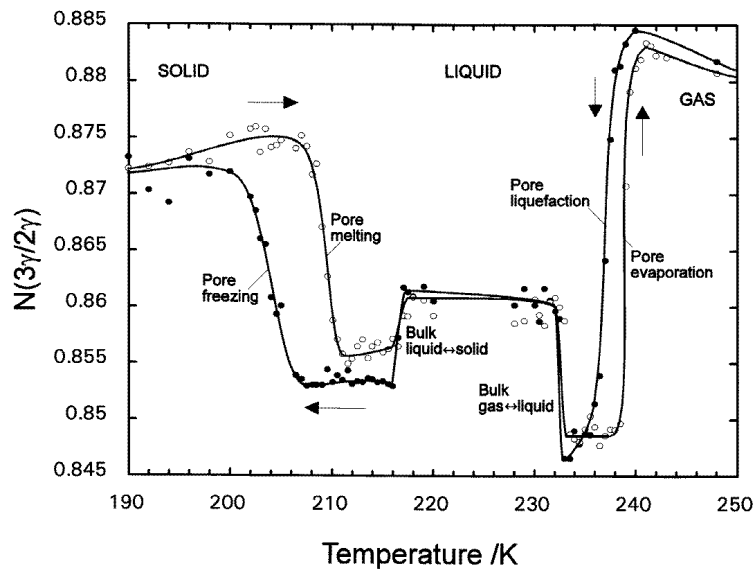


Figure 1. The ratio $N(3\gamma/2\gamma)$ as a function of decreasing (solid symbols) and increasing (open symbols) temperature measured along an isobar for CO_2 in Vycor at $P = 10$ bar.

3. Experimental details

The majority of our experiments [2, 4–9] have been performed using porous Vycor glass with interconnecting cylindrical pores of radius ~ 20 Å and occupying $\sim 30\%$ of the total sample volume. In these experiments, two porous Vycor glass samples were sandwiched around a ^{22}Na positron source (~ 20 – 30 μCi) and inserted into the pressure cell [5, 6]. A gap of a few tens of μm between the source and the Vycor samples was created to allow simultaneous study of the bulk and confined-fluid phase behaviour. The energy spectrum of the positron annihilation radiation was collected at each temperature and pressure for 30 minutes, using a Ge solid-state detector. Each energy spectrum was analysed using two parameters, $N(3\gamma/2\gamma)$ and S . $N(3\gamma/2\gamma)$ is defined as the ratio of the number of counts in the region 340–490 keV to the region centred on the 511 keV peak (491–540 keV). This

ratio reflects the balance of 3γ - to 2γ -annihilation and will be high if there is a lot of Ps formation and much unquenched oPs. If the oPs is quenched, due to its interactions with the surroundings, then $N(3\gamma/2\gamma)$ will fall. The second parameter S is simply a ratio of the counts in two regions (510.5–511.5 keV) and (507–515 keV) centred on 511 keV. This ratio is slightly more difficult to interpret since it contains several positron and positronium annihilation contributions (e.g. pPs, free-electron–positron annihilation and quenched oPs), but it can be considered to reflect the amount of pPs (and hence total Ps) formed.

4. Results

4.1. Bulk fluids (no Vycor)

The phase behaviour of several gases has been investigated, but our most comprehensive study so far has involved CO₂. This is due to the relatively easy experimental access to the relevant parts of the (P, T) phase diagram [5, 6]. Using the experimental cell described above but with no Vycor samples present, one finds [4, 5] a stepwise decrease in $N(3\gamma/2\gamma)$ as the fluid changes from gas \Rightarrow liquid \Rightarrow solid, i.e. there is increased oPs quenching and Ps inhibition as the fluid density increases. For an isobar of 10 bar these steps occur at \sim 233 K and \sim 216 K, which are close to the respective bulk gas–liquid and liquid–solid transition temperatures found in the literature. The gas intake from the reservoir was monitored throughout, and was found to increase at these temperatures by an amount consistent with the volume of the cell and the bulk densities [4, 5]. We therefore assign these step-like discontinuities to the bulk phase transitions.

4.2. The confined fluid and its phase behaviour

Figure 1 shows $N(3\gamma/2\gamma)$ for the same pressure (10 bar) but with the Vycor glass inserted. Both the adsorption (decreasing T) and desorption (increasing T) isobars are shown. Similar results are found for all other isobars which lie above the bulk triple point. The first points to note are the steps at 216 K and 233 K which show no significant hysteresis on heating and cooling. The sharpness of the features and their lack of hysteresis leads us to assign these to the bulk solid–liquid and liquid–gas transitions respectively.

If we now turn to the pore transitions, we find that as the temperature is *decreased*, $N(3\gamma/2\gamma)$ falls at the pore gas \Rightarrow liquid transition (237 K), due to increased Ps quenching in the liquid. There is also hysteresis of a few degrees between liquefaction and evaporation. This shift and hysteresis is consistent with the findings of adsorption measurements for CO₂ in a similar Vycor glass [10]. We attribute the step-like features near 205 K and 211 K to the confined freezing and melting transitions, respectively. These show a greater degree of hysteresis ($\Delta T \sim 6$ K) than at the gas–liquid boundary ($\Delta T \sim 2$ K) which is consistent with results found by other techniques [10–15]. The increase in $N(3\gamma/2\gamma)$ at the formation (on cooling) of what should be a dense CO₂ solid phase filling the pores may be explained by a combination of factors. Since the bulk fluid surrounding the Vycor sample freezes first (figure 1), no further CO₂ molecules from the reservoir can reach the pores. Empty volume could be created in the pores if the solid phase is more dense than the liquid (in bulk CO₂, the density of the solid is \sim 1.4 times that of the liquid at temperatures near the triple point). The presence of ‘empty’ space would facilitate the creation of more unquenched oPs (increasing 3γ) compared to when the pores are fully filled with liquid. The distribution of this open space is uncertain. Pores may freeze individually creating empty space within each pore, or if the CO₂ is able to flow slightly as it freezes, as one pore freezes other

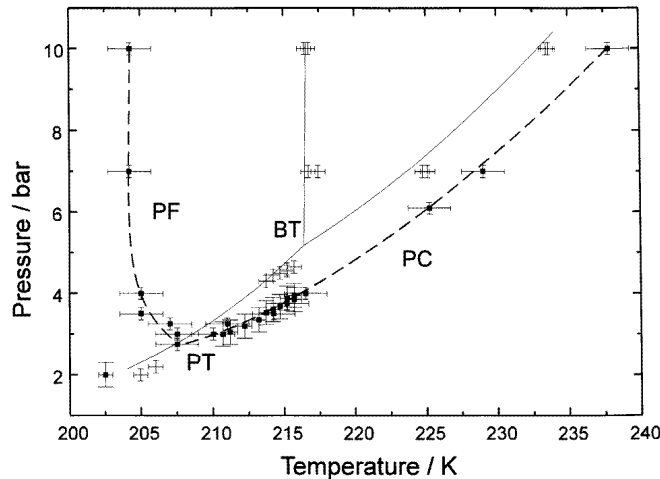


Figure 2. The adsorption phase diagram for CO₂ in Vycor. The solid curves are the known bulk phase boundaries [16]. For details of the other symbols see the text.

unfrozen material may enter the pore via a neck, resulting in large empty spaces in some parts of the sample, with other parts being full. It should be pointed out that Molz *et al* [14] found some vacancy-assisted diffusion of solid argon into Vycor; however, this occurred when a frozen sample was subject to ultrasonic stresses during the ultrasound experiment. We are performing experiments on frozen argon in Vycor to help clarify this point.

By plotting the loci of the rapid changes ('steps') in $N(3\gamma/2\gamma)$ obtained from about 50 measured isobars and isotherms, we constructed a phase diagram [5, 8] for CO₂ adsorbed in Vycor (figure 2). The solid lines indicate the accepted bulk phase boundaries for CO₂ [16] and the symbols (+) near them indicate our bulk transition data measured with and without the Vycor. The filled symbols are the positions of shifted (pore) transitions and the dashed line is there to guide the eye. Three conclusions can be made. (i) Gas \Rightarrow liquid condensation in the pores (pore condensation (PC) line) is shifted up in temperature relative to the bulk, in agreement with experiment and theory [1]. The shift is about 5 K for the higher pressures. (ii) The liquid \Rightarrow solid phase transition (pore freezing (PF) line) in the pores is also shifted, but towards lower temperatures, by approximately 12 K on cooling. Similar shifts, based on other experimental techniques (usually at a single pressure), have been reported for the freezing of several simple fluids in Vycor and other porous solids. (iii) We see a merging of the condensation and freezing lines as the pressure is lowered. These results, together with our (sparse) data at low pressures (<2.6 bar) which indicate a single gas–solid transition, suggest that there is a point PT which can be identified as a shifted triple point for CO₂ confined in Vycor. This point is lowered by about 10 K in temperature and by more than 2 bar in pressure with respect to the bulk triple point BT. We believe that figure 2 constitutes the first attempt at piecing together a complete adsorption phase diagram of a confined classical fluid near its bulk triple point.

However, given the nature of the experiment, it is important to reiterate some remarks made in [8] on the interpretation of figure 2 as a genuine phase diagram. (i) When the bulk fluid around the sample freezes, the fluid within the porous medium is sealed at the externally applied pressure. On further cooling the internal (pore) pressure may change. This should be a small effect prior to freezing of the confined fluid. Nevertheless, it should

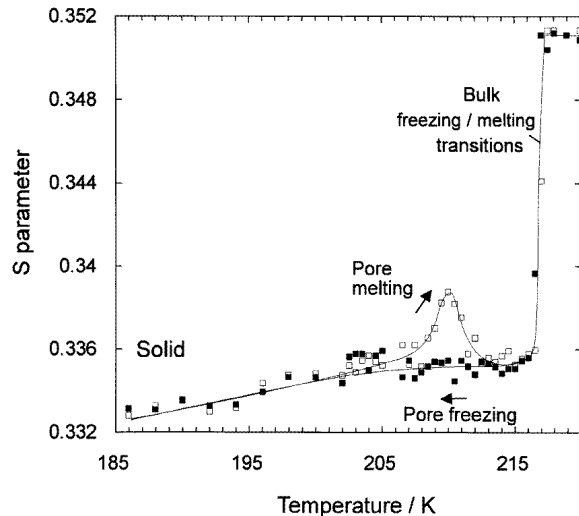


Figure 3. The S -parameter as a function of decreasing (solid symbols) and increasing (open symbols) temperature for CO_2 in Vycor at $P = 10$ bar.

be borne in mind when interpreting the line marked PF. (ii) Hysteresis effects are large. The data here refer to cooling only and a very different phase diagram results if we plot positions for heating (desorption). (iii) First-order phase transitions are not expected to be sharp for fluids confined in Vycor. Since there is a distribution of pore sizes, one expects that all phase transitions will be rounded [1]. We should, perhaps, refer to the lines in figure 2 as lines of quasi-transitions and the point PT as a quasi-triple point.

4.3. Hysteresis at the liquid–solid boundary

The freezing/melting behaviour in pores ($T < 216$ K in figure 1) is intriguing. As the pore solid is heated, we observe a small but clear rise in $N(3\gamma/2\gamma)$ before melting begins. On the apparent ‘completion’ of melting in the pores (>210 K), $N(3\gamma/2\gamma)$ has a distinctly higher value than the pre-frozen state. Subsequent freezing–melting cycles in the pores do not change this value provided the temperature is kept below the bulk melting temperature. However, if the temperature is raised so that the bulk melts and the sample is cooled back down below 216 K, $N(3\gamma/2\gamma)$ returns to its original value. This would suggest that there has been a non-reversible rearrangement of the material in the pores caused by the freezing or melting processes within them.

If the S -parameter is plotted (figure 3) a peak is seen in the second half of the melting transition, similar to that seen in our work on the gas–liquid transition [5, 7]. There we found an enhancement in the pPs signature as the pores filled with liquid but not during emptying. We argued this was due to additional positronium formation at large gas–liquid interfaces created during the filling process. Once the pores are full the interfaces disappear and the pPs signature decreases. Our results showed the magnitude of the pPs signature depended on how complete the pore emptying process was. If the pores were substantially emptied the effect was very similar to that seen for complete hysteresis. Conversely, if only a small amount of emptying had occurred, the signature was smaller. This enhancement of Ps (and pPs) is only seen in the 2γ -radiation; the absence of a similar feature in $N(3\gamma/2\gamma)$

was explained by assuming that any additional oPs was rapidly quenched and not seen. A recent ultrasonic attenuation and light scattering study of spatial correlations [17] found analogous features when filling Vycor pores with liquid hexane. They found no long-range correlations on adsorption and proposed the formation of a large number of vapour bubbles before complete pore filling. It remains to be seen whether in our case the enhanced pPs feature is a consequence of large liquid–gas interfaces as we suggest, or is due to the formation of micro-bubbles. Returning to the liquid–solid phase boundary, the peak in S is a signature of enhanced pPs formation during melting but not freezing. This may indicate that melting also proceeds via the creation of large interfaces. As we mentioned before, the confined liquid–solid boundary is shifted *down* in temperature below the bulk transition, so the samples are effectively sealed when the fluid freezes in the pores. In the absence of pressure propagation from the gas reservoir and with the creation of empty volume in the pores, it is possible that the internal pressure drops below the external applied pressure and follows the solid–gas line in confinement. If this is the case, the melting process is likely to be complex and may initially proceed via sublimation [5, 9]. Eventually the pressure is sufficient for liquid to form and features arise that are akin to those seen during the gas \Rightarrow liquid transition.

Scanning hysteresis of the liquid–solid transition reveals further information [5, 9]. We find that any solid (no matter how little) frozen in the pores is relatively stable under heating. In contrast if the solid is partially melted it can be made to refreeze almost immediately by lowering the temperature slightly, suggesting the presence of nucleation centres. For further details of the melting and freezing behaviour in pores, the reader is referred to [5, 9].

5. Discussion

Capillary condensation (the shifted gas–liquid transition) is usually interpreted on the basis of a competition between bulk and surface contributions to the total free energy of the confined fluid [1]. Since the pore walls prefer liquid to gas, the wall–liquid surface tension is lower than the wall–gas surface tension. This leads to condensation at lower pressures than in bulk [1]. Capillary freezing is a more subtle phenomenon. The naive explanation for the shift of the freezing line to lower temperatures is that the walls prefer liquid to crystal [1]. Whether this reflects some intrinsic property of the substrate material (Vycor is mainly silica), or whether it reflects the disorder of the porous network, i.e. the formation of the crystalline phase at the substrate is hindered, is not completely clear. Recent computer simulations of freezing of fluids in idealized single pores have shown that the transition can occur at lower or higher temperatures than in bulk [18]; the direction of the shift depends on the nature of the various interparticle potentials. Thus it is not yet established whether figure 2 is a generic phase diagram for any simple fluid confined in a mesoporous solid.

Acknowledgments

In summary, we have shown that positron and positronium annihilation provides a valuable new technique for monitoring phase transitions of confined fluids. Taken in conjunction with the more established methods, this technique can provide new insight into phase behaviour. We thank the EPSRC, UK, and the Royal Commission for the Exhibition of 1851 for financial support.

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