Phase transitions of CO_2 confined in nanometer pores as revealed by positronium annihilation

LETTER TO THE EDITOR

Phase transitions of CO_2 confined in nanometer pores as revealed by positronium annihilation

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Abstract. The results of a comprehensive positronium annihilation study of the phase behaviour of carbon dioxide in porous Vycor glass are presented. Isobaric measurements of the $3\gamma{:}2\gamma$ annihilation ratio show that on cooling, the gas–liquid phase boundary is raised by ~5 K while the liquid–solid transition is depressed by ~12 K relative to the bulk. The resulting phase diagram suggests the existence of a 'triple point' of the confined fluid at a temperature ~10 K and a pressure ~2 bar below the bulk triple point.

When fluids are confined in mesoporous solids their phase behaviour can be dramatically different from that found in bulk. The effects of finite pore size, substrate–fluid forces and the disorder associated with the porous medium broaden first-order phase transitions and may shift the location of phase boundaries. Volumetric and gravimetric adsorption isotherm measurements [1] show that a dilute gas capillary condenses [2] to a dense liquid in the pores at pressures below the bulk saturated vapour pressure. The liquid–solid transition has been investigated using a variety of experimental techniques [3–8] and data for a wide range of fluids in various porous substrates show a marked depression of the freezing temperature. However, apart from work on the freezing and melting lines of ^{4}He in Vycor glass (see [9] and references therein) we are not aware of systematic determinations of the three phase boundaries for a confined fluid and, in particular, of attempts to locate any triple point. There is a long-standing and diverse interest in such problems, ranging from attempts to understand the freezing of water in cracks and soils [10, 11, 12] to the basic statistical mechanics of finite-size effects on phase transitions [2]. Here we report the results of positron/positronium annihilation experiments which enable us to map out substantial sections of the gas–liquid, liquid–solid and gas–solid phase boundaries for CO_2 adsorbed in Vycor containing interconnected 'cylindrical' pores of average radius ~20 Å, occupying ~30% of the total volume [13].

The novel positronium technique was developed in our earlier investigation [14] of capillary condensation of N_2 in Vycor. Upon entering an evacuated Vycor sample, positrons from a ^{22}Na source thermalize in the glass matrix and a fraction form positronium (Ps), either in the matrix or at the matrix/pore interface, and diffuse to the pores prior to annihilation. Roughly three quarters of the Ps will be ortho-Ps (o-Ps) and one quarter para-Ps (p-Ps). In vacuum, o-Ps decays via the emission of 3γ photons and has a relatively long lifetime of ~140 ns leading to a broad and roughly triangular photon energy distribution extending from 0 to 511 keV. p-Ps has a considerably 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 < o-Ps mean free path) even a thermalized o-Ps will collide many times with the pore walls during its long lifetime. This may result in the positron of the o-Ps annihilating with

an electron of opposite spin from the pore wall, and thereby emitting 2γ photons instead of 3γ. Such a process is termed 'o-Ps quenching' [15]. When there is fluid present, the extent of o-Ps quenching depends on the local density and thus is expected to increase at the gas–liquid and gas–solid transitions and, to a lesser extent, at the liquid–solid transition. However, any condition which changes the total positronium population will also affect the ratio of 3γ to 2γ annihilation. Consequently, the precise balance of positronium formation and o-Ps quenching in confining geometry is likely to be complex and cases of specific interest should be discussed in the light of relevant data.

The various phase transitions were monitored by plotting the $3\gamma{:}2\gamma$ ratio, $N(3\gamma/2\gamma)$, derived from the measured annihilation energy spectra, for a set of about 50 isobars and isotherms. This ratio is the total counts in the interval 340–490 keV (3γ) divided by the total counts in the interval 491–540 keV (2γ). Two identical Vycor specimens were sandwiched around a positron source and placed inside the pressure chamber containing 99.999% pure carbon dioxide. The chamber was designed with a gap of a few microns between the specimens and source enabling us to monitor simultaneously the bulk (in the gap) and confined (in the porous medium) phase transitions. Additional studies of bulk phase equilibria were performed in the chamber with the Vycor specimens removed.

In figure 1(a) we present $N(3\gamma/2\gamma)$ for bulk CO_2 measured as a function of decreasing temperature at a constant pressure of 7 bar. Two sharp steps in $N(3\gamma/2\gamma)$ are registered at $\sim$225 K and $\sim$216 K, which are close to the known bulk gas–liquid and liquid–solid phase transitions at this pressure [16]. We therefore assign these steplike discontinuities to the bulk phase transitions, in line with our previous results [17].
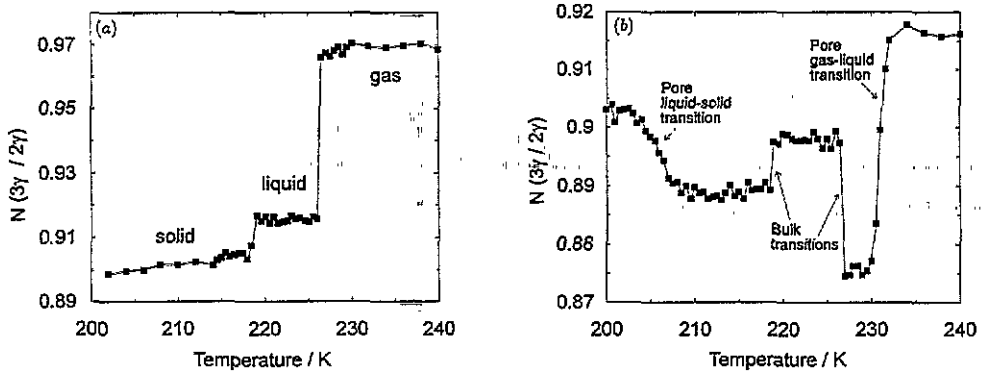
Figure 1. The $N(3\gamma/2\gamma)$ ratio measured at a constant pressure of 7 bar. In (a) there is no Vycor present and the steps occur at temperatures equal to those of the bulk phase transitions for this pressure. There is no significant hysteresis observed on cooling and heating. In (b) Vycor is present in the cell. The steps near 225 K and 216 K are associated with the gas–liquid and liquid–solid transitions of bulk fluid in the gap between the specimens. The rapid decrease in $N(3\gamma/2\gamma)$ near 229 K corresponds to capillary condensation of gaseous CO_2 to liquid CO_2 in the Vycor pores. The increase near 204 K is attributed to freezing of the pore liquid. These results refer to cooling. On heating, melting and evaporation in the pores occur near 210 K and 232 K, respectively (see text).

Figure 1(b) shows $N(3\gamma/2\gamma)$ for the same isobar, but with the porous Vycor glass inserted. Similar results are found for all other isobars which lie above the bulk triple point. As the temperature is *decreased*, the first sharp drop occurs at $\sim$229 K, i.e. $\sim$4 K above the bulk gas–liquid transition. This is attributed to capillary condensation in the pores and is consistent with our previous results [14] for N_2 in Vycor.

A sharp increase of $N(3\gamma/2\gamma)$ follows at $\sim$225 K, coincident with the bulk gas–liquid

transition. Whereas in the bulk (figure 1(a)) this ratio decreased, it now clearly increases as the bulk liquid phase forms. Our explanation for such apparently contradictory behaviour is that as the bulk fluid 'liquefies' additional positrons thermalize in the gap before reaching the specimens, leading to increased positronium formation and a sharp increase in $N(3\gamma/2\gamma)$.

Support for the above phase transition interpretation of positron annihilation data is given by the following. (i) The gas flow from the reservoir into the sample cell assembly was monitored throughout the experiment. The amount of gas flowing into the cell during the transition at ~229 K was consistent with the additional gas required to completely fill the empty volume within the porous specimens with liquid CO_2. In the same fashion, the gas intake by the cell at the transition at ~225 K was compatible with the additional amount of gas required to fill the open volume of the cell around the specimens. (ii) During an increasing temperature cycle, hysteresis was observed [17] at the liquid–gas transition at 229 K (pore) but not at 225 K (bulk). (iii) An independent set of measurements showed that the bulk 225 K transition vanished when the gap was closed. The above confirms our assertion that the transitions in the positron annihilation data at 229 K and 225 K are due to capillary condensation in the pores and bulk gas–liquid transitions, respectively.

At ~216 K, we observe a small but sharp drop in $N(3\gamma/2\gamma)$ which occurs at the same temperature as the bulk liquid–solid transition (figure 1(a)). On subsequent reheating [17] this transition showed no hysteresis and given the sharpness of the feature we assign it to the bulk liquid–solid transition. The decrease in $N(3\gamma/2\gamma)$ is due to an inhibition (relative to the liquid) of positronium formation in the solid phase which forms in the gap.

Finally, we note a sharp increase in $N(3\gamma/2\gamma)$ near 204 K and for the following reasons we assign this increase to a liquid–solid transition within the pore: (i) the rise occurs at approximately the same temperature for all isobars, including pressures appreciably below that of the bulk triple point. The resulting locus is a near vertical line in the conventional $p(T)$ phase diagram which has the appearance of a shifted bulk freezing line (see figure 2); (ii) the hysteresis observed during cooling and heating is similar to that found in other investigations of the liquid–solid transition in mesoporous solids. Picosecond optical [3], differential scanning calorimetry [4, 5], AC heat-capacity [6], ultrasonic attenuation and sound velocity [6], nuclear magnetic resonance [7] and neutron diffraction [8] measurements all indicate that the freezing temperature is lowered relative to the bulk by an amount which appears to be inversely proportional to the mean pore radius [3, 5], a result predicted by simple (Gibbs–Thompson) thermodynamic arguments which balance bulk and surface contributions to the total free energy. Most of these studies report pronounced hysteresis, whose nature is not fully understood, with melting usually occurring at a temperature well above that for which freezing first takes place. In keeping with these studies [6, 9], we find 'melting', as signalled by a sharp decrease in $N(3\gamma/2\gamma)$, occurs at temperatures approximately midway between pore 'freezing' and the bulk freezing transition. Note that the *increase* in $N(3\gamma/2\gamma)$ at the formation (on cooling) of what should be a dense CO_2 solid phase, filling the pores, may be explained by a combination of factors. Since the bulk gas surrounding the Vycor sample freezes first (figure 1(b)), no further CO_2 molecules from the reservoir can reach the pores. As a result, when the liquid within the pores freezes, substantial empty volume could be created; recall that in bulk CO_2 the density of the solid is about 1.4 times that of the liquid at temperatures near the triple point. This would enhance the probability of positronium formation and 3γ annihilation. It is also possible that a large solid–'fluid' surface area in the pores would provide favourable conditions for positronium formation [14, 15].

By plotting the loci of the rapid changes ('steps') in $N(3\gamma/2\gamma)$, we constructed a phase diagram for CO_2 adsorbed in Vycor (figure 2). Our estimates of the bulk phase boundaries,
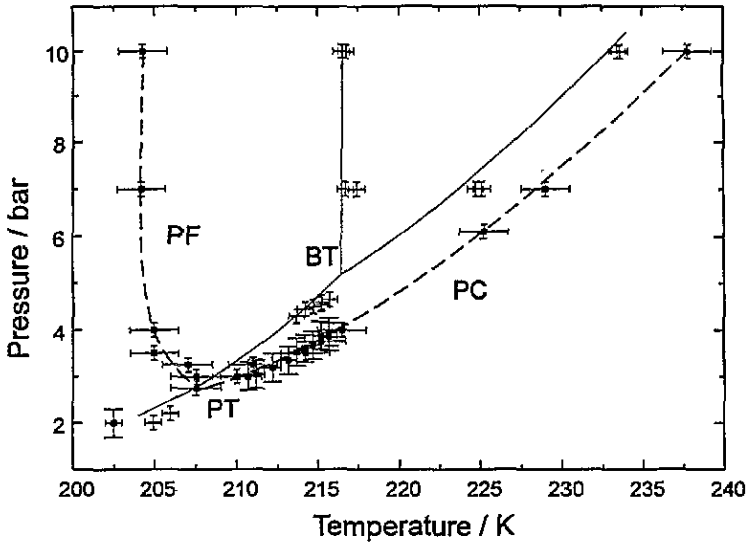
Figure 2. Phase diagram for CO_2. The symbols (+) refer to steps in $N(3\gamma/2\gamma)$ obtained for bulk fluids. These points lie very close to the known bulk phase boundaries (solid curves). The solid symbols refer to steps in $N(3\gamma/2\gamma)$ for CO_2 confined in porous Vycor. All data refer to cooling the samples at fixed pressure. The dashed lines (drawn to guide the eye) joining these symbols are the loci of pore condensation (PC) and pore freezing (PF). At pressures below about 2.6 bar only a single step is seen in $N(3\gamma/2\gamma)$ and this points to a single (gas–solid) transition in the pores at a temperature close to the corresponding bulk transition (see text).

obtained both with and without the Vycor present, are quite close to the accepted literature values [16]. Three main conclusions can be drawn from our results. First, gas–liquid condensation in the pores (PC line) is shifted towards higher temperatures, in accordance with earlier adsorption measurements [1] and general theoretical predictions [2]. The shift is about 5 degrees for the higher pressures. Second, the liquid–solid phase transition (PF line) is also shifted, but towards lower temperatures, by approximately 12 degrees on cooling. Similar shifts, based on other experimental techniques but usually at a single pressure, have been reported for the freezing of several simple fluids in Vycor and other porous solids. Figure 2 also shows a merging of the condensation and freezing lines as the pressure is lowered. These results together with the fact that our (sparse) data in the low-pressure (<2.6 bar) regime indicate there is only a single transition, which we identify as a gas–solid transition, suggest that there is a point PT which can be identified as a shifted triple point for CO_2 confined in Vycor. This point, which refers to measurements taken on cooling (adsorption), is lowered in temperature by about 10 K and lowered in pressure by more than 2 bar with respect to the bulk triple point BT.

We believe that figure 2 constitutes the first set of results for phase behaviour of a confined classical fluid near its bulk triple point. However, given the nature of the sample, it is important to make some remarks in connection with 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 pore freezing of the confined fluid. Nevertheless, this should be borne in mind when interpreting the line marked PF. (ii) Hysteresis effects are large. The results displayed here refer to

cooling only. Quantitatively different phase diagrams would result if we plotted results for heating (desorption). (iii) First-order phase transitions are not expected to be sharp for fluids confined in Vycor. Since the pore volume is finite and there is a distribution of pore sizes, one expects that all phase transitions will be rounded [2]. In the light of these remarks we should, perhaps, refer to the lines in figure 2 as lines of quasi-transitions and the point PT as a quasi-triple-point.

Finally, we note that CO_2 was chosen for this first study simply because its bulk triple point is readily accessible. Whether figure 2 constitutes a generic phase diagram for fluids confined in a mesoporous solid remains to be seen. Positron investigations for other fluids and porous materials are under way.

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