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Freezing and melting of Ar in mesopores studied by optical transmission

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Ar condensates in a porous Vycor glass with an average pore diameter of 10 nm have been studied by optical transmission. Cooling-heating cycles have been performed through the freezing and melting transition for samples with different fractional fillings. Freezing leads to a decrease of the transmission up to four orders of magnitude due to material transport in the pore network that leads to a coarsening of the pore filling. The results are compared with transmission data on isothermal filling and draining and with heat-capacity data on freezing and melting.

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I. INTRODUCTION

Liquids such as water, organic solvents, and cryoliquids condensed into small pores freeze and melt at different temperatures T_{f} and T_{m}, which are both lower than the bulk triple-point temperature T_3.[1–3] The understanding of this behavior is not only of academic interest as an example of a first-order transition in a confined geometry, but is also of practical importance. The phenomenon of frost heave, that is, the growth of ice lenses in soil, rocks, and masonry, relies on the flow of liquid through pores at temperatures below T_3.

For simple van der Waals systems such as Ar and porous silica substrates, it is established that the pore condensate consists of an adsorbed layer on the pore walls, typically two or three monolayers thick, and the capillary condensate in the pore center.[4] This latter fraction usually shows, in contrast to the ‘‘dead’’ wall coating, the phase transitions of its bulk counterpart, though with lower transition temperatures and thermal hysteresis,[4,5] the freezing and melting transition being the most prominent example. Our recent studies of vapor pressure isotherms, x-ray diffraction,[4] and heat capacity[6] on Ar in Vycor glass and xerogels have given some further insights. The temperatures T_{f} and T_{m} are related, respectively, to the vapor pressures p_{a} of capillary condensation and p_{d} of capillary evaporation. The heat-capacity anomaly of freezing is narrower than that of melting and is different for partially filled pores prepared by adsorption and desorption. Additionally the freezing anomaly of samples with lower fillings has a satellite about 10 K below T_{f}.

These observations suggest that for partially filled pores the distribution of the material in the pore network is of importance and that this distribution can change upon phase transitions. For the liquid-vapor transition, which is usually probed by vapor pressure isotherms, this view is in fact widely accepted. Page *et al.*[7] have observed that Vycor samples partially filled with hexane prepared by adsorption are transparent, but for samples prepared by desorption the transmission is lower by several orders of magnitude due to ‘‘pore-space correlations.’’ In the present paper we will report on such transmission measurements performed on isothermal adsorption and desorption of Ar in Vycor, and then, in the main part of the paper, apply this method to thermal cycles through the freezing and melting transition.

II. EXPERIMENT AND RESULTS

The porous matrix used in this study is Vycor glass code 7930. The Vycor sample has been taken from the same batch as the one used in our recent heat-capacity study.[6] The average pore diameter is slightly higher than the standard, about 10 nm instead of the usual 7 nm, and the porosity is about 30%. A monolithic disk of Vycor 3 mm thick and 10 mm in diameter is placed in a cell that is mounted to the cold plate of a closed-cycle refrigerator and is connected via a thin tubing to an all-metal gas manifold. The dead volume of the cell and of the tubing up to the first valve of the manifold is 8 cm^3.

The cell has two flat windows. The beam of a He-Ne laser is directed through the sample at normal incidence. The incoming and the transmitted intensities, I_0 and I, have been measured with photo-resistors. The symbol I represents the integrated intensity across a pinhole 3 mm in diameter in the straight-through position 20 cm after the sample. For the measurement of I_0, a beam splitter has been placed in front of the sample.

In a preparatory experiment the vapor pressure and the transmission have been measured simultaneously along an isotherm at 86 K, on adsorption and on desorption. At this temperature both bulk and pore condensed Ar are liquid. The vapor pressure isotherm that is the relation of the vapor pressure p and the amount N of adsorbed Ar is shown in Fig. 1. It is practically identical to that on the sample of the heat-capacity study.[6] The units used are the fractional filling $f = N/N_0$ and the reduced vapor pressure $p = P/P_0$, P_0 is the saturated vapor pressure of bulk Ar (about 960 mbar) and N_0 is the amount necessary for complete filling at 86 K. Figure 1 (lower panel) and Fig. 2 show the transmission $\tau = I/I_0$ as function of p and f, respectively.

Several fillings f ranging from 0.05 to an overfilled state, $f > 1$, have been prepared by adsorption at 86 K and have been cooled through the solidification temperature T_{f} down to 50 K and heated through the melting temperature T_{m} back

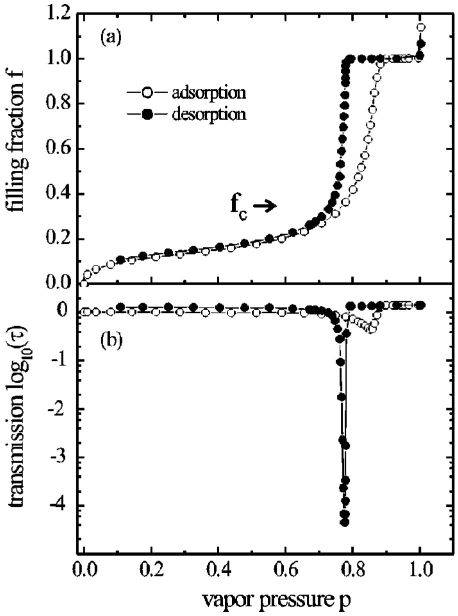

FIG. 1. (a) The fractional pore filling $f=N/N_0$ and (b) the optical transmission τ as function of the reduced vapor pressure $p=P/P_0$ of Ar in Vycor at 86 K.

up to 86 K. Such temperature cycles extended over two days. During the cycles the valve of the sample cell was closed in order to keep the dead volume as small as possible, but doing so the variation of p and of f as function of T is not known. The f value of the preparation is a lower bound for the actual filling fraction at lower T. At 50 K the vapor pressure is negligible. Here an upper limit for the actual filling can be obtained by assuming that all the vapor remaining in the dead volume at 86 K has condensed into the pores on cooling. The difference between the upper and the lower bound is 0.19 for lower f and increases to 0.29 for $f=1$. (This would mean that for $f=0.80$ the pores should be occupied completely at 50 K. We leave this problem till later). Thus the cooling-heating cycles are not really isosteric.

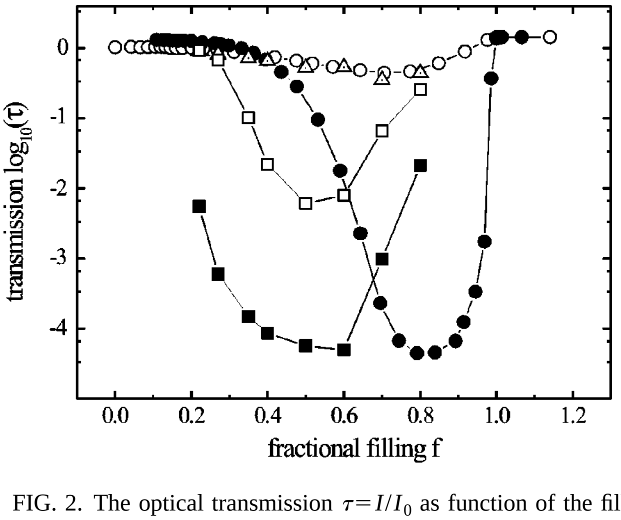

FIG. 2. The optical transmission $\tau=I/I_0$ as function of the filling fraction in various states. Open circles, adsorption at 86 K; closed circles, desorption at 86 K; triangles, at the start of the thermal cycles, $T=86$ K; filled squares, at 50 K, the minimum temperature of the thermal cycles; open squares, at the end of the thermal cycle at 86 K.

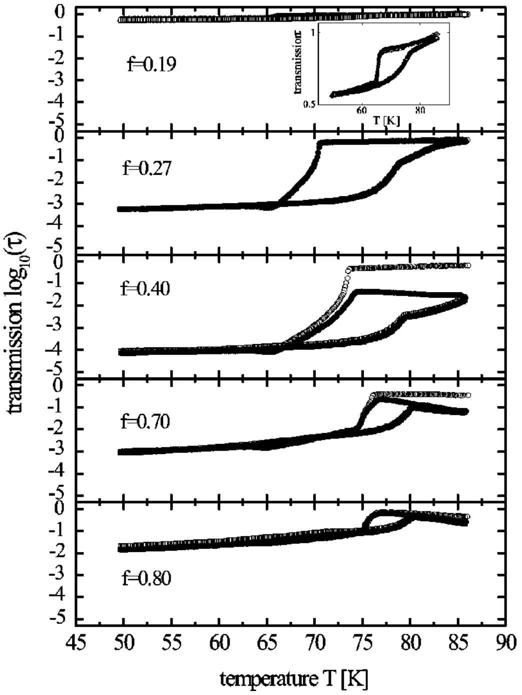

FIG. 3. Transmission during the thermal cycles, from 86 K down to 50 K and back to 86 K, for several fillings. Open symbols refer to the first, closed ones to the second cycle.

At the end of the cycle the vapor pressure is lower than initially and close to the vapor pressure of the desorption branch of the 86-K isotherm at the chosen f. For each nominal f, the cycle has been repeated once starting from the final state of the first cycle. The transmission τ as a function of T is shown in Figs. 3–5.

τ values at the start, at the end of the thermal cycle, and at the minimum temperature of 50 K of the thermal cycle are included in Fig. 2. Here and elsewhere the nominal values of f, as determined from the adsorption/desorption isotherm at 86 K, are used. In one case a partial filling, namely f

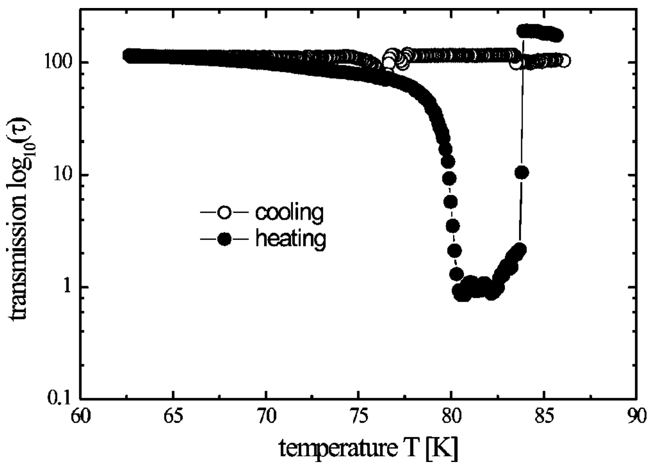

FIG. 4. Transmission during a cooling/heating cycle of an overfilled sample.

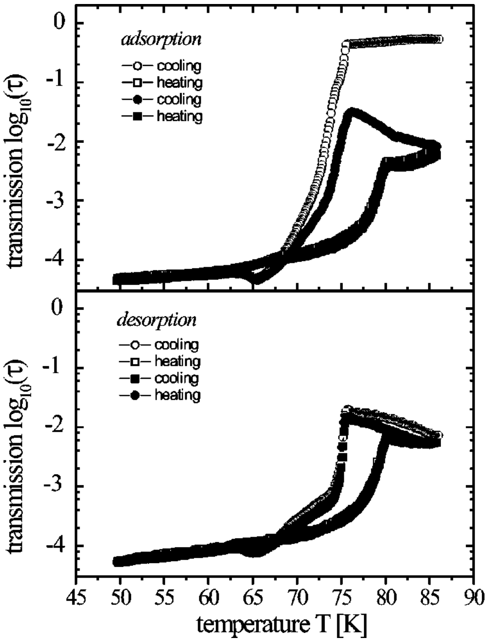

FIG. 5. Transmission during a cooling/heating cycle of samples with $f=0.60$ prepared by adsorption and by desorption at 86 K.

$=0.60$, has been prepared by desorption at 86 K, starting from completely filled pores, rather than by adsorption, see Fig. 5.

Figure 6 shows the liquid fraction x_{liq} of the capillary condensate as a function of temperature. This quantity is obtained by integrating the anomalous part of the heat-capacity data of Ref. 6 as obtained for the first and second coolings, and the intermediate heating. Results are shown for four filling fractions. Note that in this experiment the variation of f with T was negligible, because of a more favorable ratio of the pore volume and the dead volume. The information on $x_{\mathrm{liq}}(T)$ will be helpful for the discussion of the transmission data.

III. DISCUSSION

A. Vapor pressure 86-K isotherm

In order to arrive at an at least qualitative understanding of the behavior of the transmission of the cooling-heating cycles the isothermal adsorption-desorption behavior is discussed first. The f-p isotherm (Fig. 1) is of the type usually observed for simple liquids in Vycor. The initial reversible part at lower p up to a filling $f_c \approx 0.35$ is due to the formation of a film on the pore walls. The value of f_c corresponds to a coverage of about three monolayers. For $f > f_c$ the pores fill via capillary condensation, a process that is hysteretic with respect to filling and draining. According to the theoretical models of Everett[8] and of Saam and Cole[9] for a cylindrical pore of uniform cross section the filling branch at $p=p_a$ and the draining branch of the isotherm at $p=p_d$, $p_d < p_a$, should be vertical in the regime of capillary condensation. For the pore network of Vycor both branches, the adsorption branch in particular, have a finite slope. This is due to the distribution of pore radii. For pore networks the single-pore hysteresis is usually ignored and the observed filling-draining hysteresis is interpreted by referring to the Kelvin equation in combination with "pore blocking." The Kelvin equation relates the reduced vapor pressure p to the curvature of the liquid-vapor interface (with interfacial energy σ and a radius of curvature r), $k_B T \ln(p) = -2\sigma v_m / r$, v_m is the molar volume of the liquid. Assuming that the liquid wets the pore walls completely, the radius of curvature of the concave meniscus of the liquid is equal to the pore radius (or more exactly to the pore radius reduced by the thickness of the preadsorbed layer). In a pore network characterized by a distribution of pore radii, one therefore expects that at a given pressure p all pores up to a radius r are filled, where r and p are related via the Kelvin equation. It is assumed that this is so on adsorption. On desorption, however, pore blocking comes into play.[10] Larger pores that are ready to empty according to the Kelvin equation can do so only if they have a connection to the vapor phase outside the porous matrix. Thus liquid in pores with small diameters blocks the evaporation of larger pores behind. This model leads to a percolation-type invasion of the vapor into the pore network upon desorption at $p=p_d$. The onset of desorption is therefore sharp, phase-transition-like, in agreement with the ex-

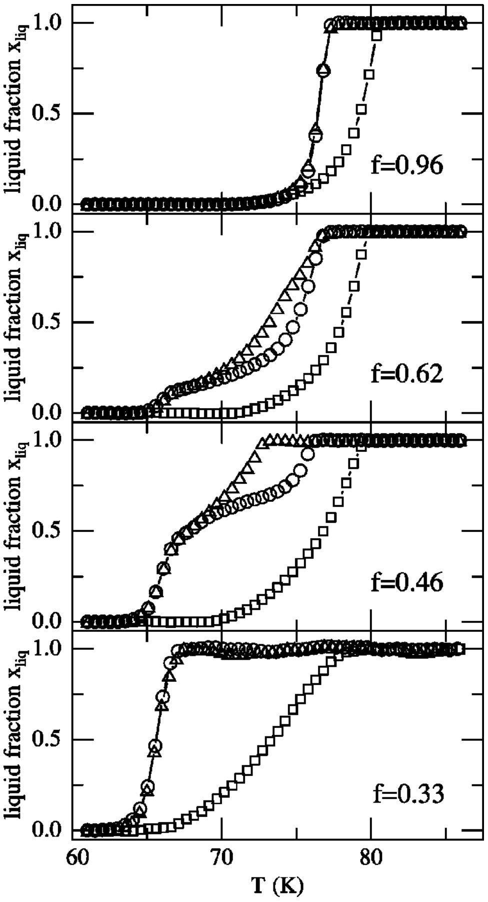

FIG. 6. The temperature dependence of the liquid fraction of the pore filling, as derived from an integration of the freezing and melting peaks of a heat-capacity experiment on Ar in a Vycor glass with the same pore diameter. The data shown are for the first (△) and second (○) cooling runs and the intermediate heating run (□).

perimental result of Fig. 1(a). Page *et al.* have complemented their transmission data by a light-scattering experiment just at the onset of desorption.[7] They observed a dependence of the intensity as function of the scattering angle which is compatible with a fractal exponent. This is what is expected for a percolation process. All this points towards pore blocking but on the other hand simulations have shown that blocked pores can empty via fluctuations in the bottle necks.[11]

B. Transmission at 86 K

As can be seen from Figs. 2–5, there are changes of the transmission by several orders of magnitude, both as function of f at 86 K and as function of T for a constant amount of gas in the cell. Because of these enormous changes of the transmission it is difficult, if not impossible, to compare the results with a model covering the entire τ range, but nevertheless some qualitative statements can be made. We refer to the dependence of the transmission on f and p at 86 K first. Empty Vycor glass, Vycor glass with an Ar coating on the pore walls $(0<f<f_c)$, and also Vycor completely filled with a nonabsorbing optical medium such as Ar are pretty transparent. For these limiting cases, with τ values around 0.8, the attenuation of the laser beam is to the larger part due to reflection losses from the windows and from the sample, leaving little for scattering losses within the sample. This is not unexpected since the variation of the refractive index n within the sample between the fused silica matrix $(n_m=1.45)$ and the pore filling $(n_p=1,\ 1.23,\ 1.28$, for Ar vapor, liquid Ar, and solid Ar, respectively) takes place on a characteristic length L_0 that is small compared to the wavelength of light $(\lambda_{vac}=632.8\ \text{nm})$. L_0 is of the order of 20–25 nm, as suggested by the appearance of a peak of the neutron or x-ray intensity as function of the momentum transfer in small-angle-scattering experiments.[12] L_0 has been interpreted as the average distance of adjacent pores. Empty and completely filled Vycor can be, therefore, approximately regarded as a homogeneous optical medium, the refractive indices of which can be estimated on the basis of effective-medium expressions. One arrives at a refractive index for empty Vycor of about $n_e=1.32$, and at about $n_f=1.39$ and 1.40 for Vycor filled completely with liquid or solid Ar. The strong attenuation of the laser beam that is observed for the desorption branch of the isotherm $(f_c<f<1)$ is therefore not due to the mismatch between the matrix and the medium in the pores, but is rather due to the fact that the empty and filled regions, with indices n_e and n_f, separate on a length scale comparable to λ. Page *et al.* speak of long-range correlations in the pore space. In situations with τ less than 10^{-2} the outgoing laser beam can hardly be identified anymore, the sample is illuminated as a whole. This calls for multiple scattering within the sample. The energy transport can then be described by a random-walk process with a mean free path L^*. Assuming that there is no interference between the various trajectories of the scattered beam and that the coherence length of the radiation is larger than the sample dimension L_s, this leads to a relation analogous to Ohm's law, $\tau\sim L^*/L_s$.[13] Note that an interpretation of the results in terms of a single Mie scattering event is no longer meaningful for $\tau<0.8$. The lowest transmission observed in this study is about 10^{-4}, suggesting L^* values of the order of some hundred nanometers. The largely different transmission of the adsorption and the desorption branch of the capillary condensation regime $(f_c<f<1)$ are in qualitative agreement with the pore blocking concept. On adsorption the pore liquid resides in those pores that have a radius smaller than that given by the Kelvin equation for the chosen vapor pressure p. The average distance between such liquid plugs for f slightly larger than f_c (and correspondingly between vapor bubbles for f approaching unity) is therefore of the order of the characteristic length L_0 of the pore network. Since L_0 is considerably smaller than λ there is little attenuation of the light beam by scattering processes. However, the situation is different for desorption. Compare a given filling f prepared by adsorption and by desorption. For adsorption this filling consists of many small pieces of condensate in the narrowest sections of the pore network, whereas on desorption—because of pore blocking—some of the condensate resides in pores with larger diameters (with terminating menisci in narrow sections). Therefore the average diameter of the filled sections of the pore network is larger than for adsorption. The filled regions are bigger in size and fewer in number. The average distance between them is larger and can approach λ. This causes strong scattering and hence low transmission. In a complementary view, one may refer to the fractal nature of the invading vapor cluster[10] at and slightly above the percolation threshold, that is, for $p\leqslant p_d$. The distribution of material in the pores is much more coarse grained on desorption than on adsorption.

C. Freezing-melting cycles

These ideas are transferred to the temperature cycles. For the lowest filling, $f=0.05<f_c$, the transmission is close to unity and does not depend on T. Changes of τ occur only for partially filled samples with $f>f_c$ that contain some capillary condensate (in addition to the adsorbed layers on the pore walls). Cooling leads to a drop of the transmission. This drop occurs at well-defined temperatures T_f that coincide with the temperature of the freezing anomaly of the heat-capacity experiment and correspondingly with the drop of the liquid fraction x_{liq} of the capillary condensate (Fig. 6), derived from the heat-capacity results. In Fig. 7, we show the values of T_f as function of f. T_f decreases somewhat with decreasing f. It is well known that the depression of the melting and freezing temperature in completely filled pores with respect to the bulk triple-point temperature T_3 scales roughly with $1/r$. This suggests that low fractional fillings should have lower transition temperatures than large fillings, since—at least for samples prepared by adsorption—low fillings occupy the sections of the pore network with smaller diameters.

Most remarkable are the low transmission values obtained after solidification (Fig. 3), which—as far as the magnitude of this effect is concerned—are comparable to those obtained on the desorption branch of the 86 K isotherm. We therefore suggest that freezing triggers a rearrangement of the pore

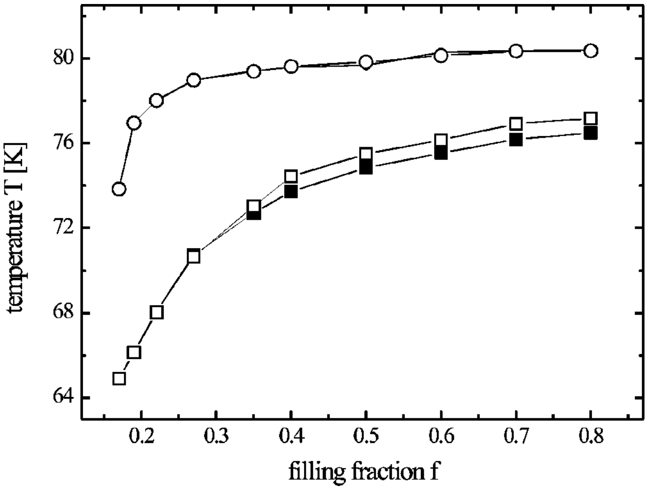

FIG. 7. The freezing (□) and melting temperatures (○) of the first (open symbols) and the second (closed symbols) cooling/heating cycle. The bulk triple temperature of Ar, $T_3 = 83.8$ K.

filling leading to a coarser distribution similar to that obtained by desorption. Figure 2 collects data on $\tau(f)$ obtained by isothermal desorption at 86 K and by cooling down to 50 K. The two sets of data can be almost superimposed by shifting the latter to higher *f* by about 0.3 *f*-units. Some of this shift may be due to the condensation of vapor out of the dead volume into the pores which has been mentioned above. Nevertheless, it appears that the minimum of τ is located at a lower *f* than for isothermal desorption. This view is supported by the *f* dependence of the transmission at the end of the cycle (Fig. 2). Here the transmission is minimal for *f* about 0.5. This corresponds to a situation where about $(0.5 - f_c)/(1 - f_c) = 30\%$ of the pores are filled with the capillary condensate.

In the subsequent heating run, τ increases with increasing temperature (Fig. 3). Below 63 K the heating branch retraces the cooling branch. At higher *T*, a kink of $\tau(T)$ can be observed, the temperature of which coincides with the temperature T_m of the melting anomaly of the heat-capacity experiment, that is, with the kink of $x_{liq}(T)$. Results on $T_m(f)$ are shown in Fig. 7. In the liquid state at and slightly above T_m the transmission is lower than at the start of the cycle. For the lowest fillings ($f = 0.22, 0.27$) further heating, back up to 86 K, restores the initial value of τ, whereas for higher fillings a difference with respect to the initial state remains. The transmission values at the end of the cycle, $T = 86\,K$, are included in Fig. 2. Thus, there are examples that the cooling-heating cycle leads to a remanent change of the transmission at and slightly above T_m. As mentioned already above the vapor pressure at the end of the cycle, p_f, is lower than the adsorption pressure p_a at which the samples have been prepared, $p_d < p_f < p_a$, $p_f - p_d < 0.02$. It appears that even the melted pore filling keeps some memory of the arrangement of the solid state.

The variation of T_m with *f* is in fact weaker than that of T_f. Referring to the scaling of transition temperatures with the pore radius this means that the dependence of the average diameter of the occupied pores on *f* after solidification is weaker than initially. Obviously some material has been transferred from smaller to larger pores.

Altogether the $\tau(T)$ traces (Fig. 3) are reminiscent of the $x_{liq}(T)$-hysteresis loops of the heat-capacity experiment (Fig. 6), apart from the fact that the former do not close at the end of the cycle, after melting.

In the following, secondary features of the transmission data will be discussed that are related to the 66 K anomaly of the heat-capacity experiment and the corresponding step of $x_{liq}(T)$, $f = 0.33$, 0.46, and 0.62, of Fig. 6. Based on the observation that the onset value f_c of capillary sublimation is somewhat lower than for capillary condensation, the 66 K anomaly has been interpreted by a delayering of the third liquid layer on the pore walls in the "empty" part of the pore network. (The first and second monolayers adsorbed on the walls do not participate in phase changes and can therefore be ignored in this context). Upon this process, material is removed from the walls and solidifies in very much the same way as the capillary condensate does at T_f. On heating, the third layer is restored not at 66 K but only later, at T_m. For lower fillings, represented in Fig. 6 by the data on $f = 0.33$, all the crystalline material that is eventually formed stems from this process. For larger fillings, see $f = 0.46$ and 0.62 of Fig. 6, crystallization occurs in two steps, the first one represents the freezing of the capillary condensate that exists already in the liquid regime and the second one the delayering and freezing of the third monolayer. Thus there is a *T* range on cooling, $66\text{ K} < T < T_f$, in which the solidified capillary condensate coexists with the top layer of the wall coating still being liquid. For even higher fillings the empty fraction of the pore network is of course small and the 66 K anomaly could no longer be detected in the heat-capacity experiment (see $f = 0.93$, Fig. 6). The present transmission results confirm the existence and the hysteretic behavior of the delayering process: the heating and cooling branches finally merge below 66 K, that is, after termination of delayering. For the $f = 0.19$ sample of the transmission study (see inset in Fig. 3) and for the $f = 0.33$ sample of the heat-capacity study, almost all the freezing occurs at about 66 K. Obviously these samples started out at 86 K with no capillary condensate in the pores. For larger *f*, the transmission is already lowered by the freezing of the capillary condensate, here the 66 K process leads to a small dip of the cooling trace with the transmission being lower on cooling than on heating. The hysteresis due to the 66 K process can be followed up to the largest fractional filling, $f = 0.80$, of the transmission study.

For all fillings a second cooling-heating cycle has been performed, starting from the final state of the first cycle (Fig. 3). In cases for which the transmission was restored after the first cycle, the second cycle is practically identical to the first one, see, e.g., $f = 0.27$. For the other fillings, the solidification temperature T_f of the second cycle is somewhat larger than that of the first cycle, typically by $\Delta T_f = 0.8$ K (Fig. 7). Referring to the scaling relation $T_3 - T_i \sim 1/r$, $i = s,m$, this observation is consistent with a transfer of pore material from smaller to larger pores during the first cycle. A much stronger increase of T_f has been observed in the heat-capacity experiment for $f = 0.46$ (Fig. 6). Presumably the difference of the two experiments is related to the refilling of the smallest pores due to the condensation of vapor out of the dead volume on cooling down from 86 K in the second cycle of the transmission experiment. This effect was negligible in the heat-capacity study.

We also tried temperature cycles on a completely filled sample. Since the pore filling contracts on cooling and undergoes a volume change at freezing and melting,[14] the only way that guarantees complete filling during the entire cycle is to start from a sufficiently overfilled state, $f>1.2$. In the present study the additional problem arises that the transmission is sensitive to the formation of bulk material on the faces of the sample and on the windows. The pertinent results are shown in Fig. 4. A small increase of τ at about T_3 signals the solidification of the bulk material. Pore freezing leads to a small dip for $75\ \mathrm{K}<T<77\ \mathrm{K}$. Thereafter the transmission of the solidified filling is identical to that of the liquid state suggesting that the sample remains indeed completely filled on cooling. On heating the transmission decreases, this effect culminates at 80 K. Based on photographs we relate this behavior to the thermal expansion of pore filling and to the jump of the molar volume upon melting. Material pushed out of the pores forms solid aggregates (“snow”) on the external faces of the Vycor sample. This leads to increased light scattering and lower transmission. At T_3 this bulk solid melts into a smooth liquid film and the transmission increases. Apart from the interference of the bulk material outside the pores this behavior is in agreement with the extrapolation of the $\tau(T)$ cycles of the partially filled cases to $f=1$. The high transmission of the completely filled sample is a further support for the idea that the low τ of solidified partially filled samples is due to a rearrangement of the material in the pores since this can happen for partial pore occupation, only.

Figure 5 shows results on cooling-heating cycles of samples with $f=0.60$ prepared alternatively by adsorption and by desorption at 86 K. The first thermal cycle of the sample prepared by desorption is close to the second cycle of the sample prepared by adsorption. This confirms that the arrangement of the material in the pore network induced by solidification is similar to what is obtained by isothermal desorption.

IV. CONCLUSIONS

The present results strongly suggest that the initial configuration of the pore liquid for which the liquid occupies all pores up to a certain diameter is changed upon freezing. Material moves, presumably by distillation inside the pore network, from smaller to larger pores and the arrangement turns from fine to coarse. Why is this so? As far as we understand, equilibrium thermodynamics cannot give an answer. The present and previous experiments on Ar in nanometer-size pores in silica matrices leave no doubt that both the liquid and solid pore condensates are stable with respect to the bulk condensate. The reduced vapor pressure p of the pore condensate is less than unity and accordingly the chemical potential difference $\Delta\mu=kT\ln(p)$ with respect to the bulk is negative for both states. According to Saam and Cole, p increases monotonously with the pore radius r and with the ratio of the intermolecular and the (attractive) molecule-substrate interaction. On the basis of this model, condensation in small pores is always favored with respect to large pores (as long as capillary condensation occurs at all). It is hard to see how this situation can be reversed without suppressing capillary condensation completely. Introducing extra energy contributions such as an interfacial energy between the pore solid and the dead layer on the pore walls or an elastic energy of the strained pore solid may modify the dependence of p on the pore radius r, but a situation with a nonmonotonous r dependence of $\Delta\mu$, that is, with a minimum with respect to r appears unlikely.

The rearrangement and coarsening in the solid state is more likely due to metastable states, states that are metastable with respect to competing arrangements in the pores, but stable with respect to the bulk state outside. No doubt such states can exist. The hysteresis of the vapor pressure isotherms and of thermal cycles provides direct evidence.

We have recently proposed a simple thermodynamic model[6] that explains not only the depression of T_f and T_m in pores but also the hysteresis of solidification and melting, including the r dependence of the equilibrium melting temperature T_0 and of the temperatures of the upper and lower ends of the freezing-melting hysteresis, T_+ and T_-. The model refers to a completely filled uniform cylindrical pore and postulates a liquid matching layer between the solid in the pore center and the walls. On cooling solidification occurs first in the center of the largest pores, at $T_-(r=r_\mathrm{max})$. In order to explain the different T widths of the freezing and the melting anomaly of the heat-capacity experiment, we have argued that the pores are actually coupled in the sense that the first solid formed at $T_-(r_\mathrm{max})$ in the largest pore acts as nucleus for solidification and eliminates metastable supercooled states in the centers of all smaller pores for which $T_0(r)$ is larger than $T_-(r_\mathrm{max})$. It is this migration of material from smaller to larger pores that explains qualitatively the results of the present study.

In the following, we try to relate the freezing-melting hysteresis of partially filled pores to the adsorption-desorption hysteresis. Translating the reduced vapor pressures of the solid (s) and the liquid (l) capillary condensate on adsorption (a) and desorption (d) yields four chemical potential differences $\Delta\mu$ of the pore filling with respect to the bulk system. The individual quantities show approximately a linear T dependence, the slopes (or entropies) being close to the bulk reference states.[4] The lines $\Delta\mu_\mathrm{a}^\mathrm{l}(T)$ and $\Delta\mu_\mathrm{a}^\mathrm{s}(T)$ and the lines $\Delta\mu_\mathrm{d}^\mathrm{l}(T)$ and $\Delta\mu_\mathrm{d}^\mathrm{s}(T)$ intersect at temperatures that agree well with the T_f and T_m, respectively. Previously we have argued that this is so because on cooling the system is brought onto the adsorption branch due to condensation of vapor out of the dead volume whereas on heating some pore filling evaporates into the dead volume, hence the system is on the desorption branch.[4] The present results show that this view is too naive, but that it is the rearrangement of the material upon freezing that produces a state with a vapor pressure and a partition of the pore material that is similar to what is obtained by isothermal desorption. Thus the coincidence of T_m and T_f with the intersections of the mentioned coexistence lines of the μ-T diagram is by no means accidental.

Our thermodynamic model offers an explanation of the thermal freezing/melting hysteresis in a completely filled uniform pore. The previous heat-capacity and the present transmission studies have shown that network effects have to be considered in addition. The pores are coupled and nucleation in one part of the network is of importance for the other parts of the network, even to the extent that material transport takes place. The situation is quite similar to the liquid-vapor transition in pores. Here, too, both single-pore and network effects are thought to contribute to the hysteresis of adsorption-desorption isotherms. The liquid-solid as well as the liquid-vapor transition in porous samples are unfortunately ‘‘inverse problems’’: the amount of experimental information that can be extracted is little compared to the complex geometry of pore space.

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