Continuous Freezing of Argon in Completely Filled Mesopores

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We have studied the phase transition of argon in completely filled mesopores. Our effective medium analysis of ultrasonic measurements clearly indicates a continuous phase transition of argon in completely filled pores over a broad temperature range of about 45 K. With decreasing temperature, the amount of frozen argon increases and below about 30 K all adsorbed argon (including the first few layers near the pore wall) is frozen with a shear modulus about equal to the bulk shear modulus. It is remarkable, that in a system showing such a pronounced confinement effect—a continuous phase transition over 45 K—the bulk properties are preserved. A comparison with temperature cycles with one and two adsorbed layers shows, that due to the presence of solid argon in the center of the pores the first few layers are already frozen at a higher temperature (30 K) compared to single layers (20 K). The transfer of our technique from the simple model system that we present in this Letter to other more complex adsorbates and different porous samples should help to enlighten the phase behavior under confinement in further studies.

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Confinement in geometries in the range of nanometers changes phase transitions [1–35]. The liquid-solid phase transition in restricted geometries, like mesopores, is considerably influenced and complicated, in particular by the increased surface to volume ratio in comparison to bulk, the curvature, and the structure of the pore walls. One of the well-known effects is the shift of the melting and freezing points to mostly lower temperatures in mesopores [1]. This shift is usually described with the Gibbs-Thomson equation, which relates the shift of the melting point ΔT to the inverse pore radius r_P, i.e., $\Delta T \propto 1/r_P$ [1]. The derivation of this equation requires the existence of a liquid, nonfreezing layer between the (solid) core in the center and the pore wall [1]. A great number of experiments with various adsorbates in different porous systems show an agreement with this equation [1,24–27,36]; however, there are also some instances, like krypton in hexagonally shaped crystalline carbon pores, that do not follow this equation, probably due to the crystalline surface of the pore walls and the related change of interaction energies in comparison to an amorphous structure [30].

The wetting of the solid in the pore by its own melt, i.e., surface layers near the pore wall that do not freeze, has often been observed [2,10,22,23]. The thickness of this liquid layer increases with increasing temperature [10], a phenomenon that is related to premelting and interfacial melting [15,16,20,25]. The fraction of liquid argon (the number of liquid argon layers) in pores increases with the temperature as a result of the change of the free energy of the filled pore [10]. The first two layers, that coat the pore wall are, however, also in the model in Ref. [10], regarded as "dead" layers, that do not participate in a liquid-solid phase transition.

In a previous paper on the freezing behavior of argon layers in the pores of Vycor [4], we showed, *inter alia*, that both the first and the second layer of argon freeze and melt continuously over a broad temperature range of at least 40 K. The layers are completely frozen at a temperature of about 20 K. In these experiments, the pores were not completely filled; i.e., there were just surface layers but no capillary bridges.

Here, we show that it is possible to calculate the amount of solid adsorbate from ultrasonic measurements during temperature cycles with completely filled pores, a method that might be helpful in further research of phase transitions in confinement. We report on the peculiar freezing behavior of argon being a simple model adsorbate. In addition, the influence of argon in the center of the pores on the phase behavior of the first two surface layers is analyzed.

As a porous sample, we use Vycor glass with an average pore diameter of 8 nm and a porosity ϕ of 0.25. The sample is identical with the one we used for the measurements of temperature cycles with a filling fraction that corresponds to one, two, and three adsorbed surface layers of argon in Ref. [4]. In order to investigate the liquid-solid phase transition during temperature cycles, we used ultrasonic shear waves. Shear waves are a good indicator for liquid-solid phase transitions [33–35] as liquids cannot sustain shear stress; the shear modulus is only increased if there is solid adsorbate. The effective shear modulus is calculated from the effective density of the sample and the experimentally measured transit time of ultrasonic shear waves propagating through the sample. The wavelength of the ultrasonic signal is in the range of 300 μm (carrier frequency $\nu \approx 6.2$ MHz) and is thus much larger than the pore radius. A more detailed description of the experimental setup can be found in Refs. [4,5].

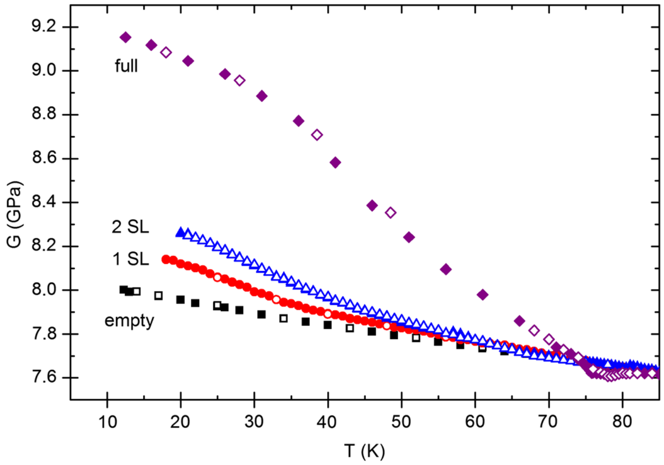

FIG. 1 (color online). Effective shear modulus during temperature cycles for different fillings of the porous sample. During cooling (closed symbols) the first two surface layers (1 SL or 2 SL) are stiffened and the effective shear modulus is higher than for the empty sample. This indicates that the argon layers solidify. Also, the effective shear modulus of the completely filled sample increases markedly on cooling. In this case, the value of the slope of the increase, however, is considerably smaller for temperatures below about 30 K. Between cooling and heating (open symbols), only with complete filling, a small hysteresis is observed (between ca. 76–80 K).

From our previous measurements, we know that it is very time-consuming to reach equilibrium both after each adsorption step during isothermal measurements and after each change of temperature during temperature cycles with constant filling [4,5]. Therefore, not more that one or two measurement points were taken a day, so that a complete cooling and heating cycle between 86 and 12 K took approximately 7 weeks.

The shear modulus of the empty sample shows an almost linear dependence on temperature (see Fig. 1). As the temperature is decreased, a continuous increase of the modulus in comparison to the empty sample is observed for the first and the second surface layer [4]. This is a clear evidence that these layers begin to freeze (for more details, see Ref. [4]).

When the pores are completely filled, we also observe an increase of the effective shear modulus that is related to the process of freezing of the pore condensate (see Fig. 1). Because of the greater amount of adsorbate, the increase is, of course, more pronounced than in the case of single surface layers.

From the increase of the effective shear modulus for one and two adsorbed surface layers (shown in Fig. 1), we were able to calculate the fraction of frozen argon using our effective medium analysis [4]. This analysis is briefly sketched below; for more details please consult Ref. [4].

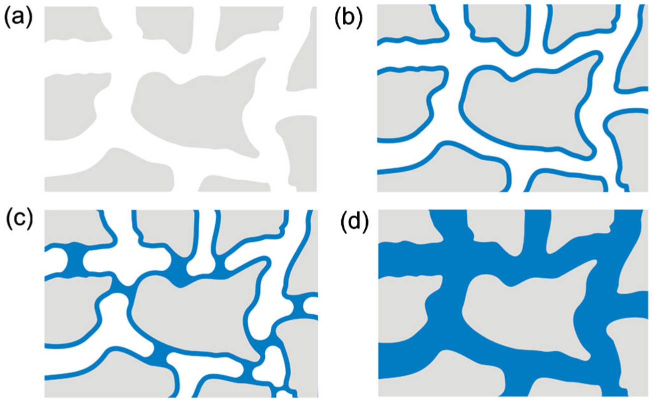

FIG. 2 (color online). (a) Schematic sketch of the spongy structure of the empty porous Vycor glass. (b) At low filling the pore walls are only covered with surface layers of argon. This structure maintains the microstructure of the porous network. (c) At higher fillings capillary bridges are formed and lead therewith to a change of microstructure. (d) In the case of complete filling, the initial microstructure of the network is restored.

The basis of the analysis is the often observed linear dependence between the elastic moduli of porous samples and their porosity (for $\phi \leq 0.25$) [37,38]. Hence, the shear modulus of the empty sample G_0 can be described as a function of the shear modulus of bulk quartz glass, G_Q, that forms the frame of the porous sample and its porosity ϕ:

$$G_0 = G_Q(1 - a\phi). \tag{1}$$

The effective shear modulus depends, of course, on the microstructure of the sample that is accounted for by the factor a. When adsorbate is added, this can result in different structures (see Fig. 2). At low filling fractions f, the adsorbate will form surface layers [Fig. 2(b)], and at higher fillings, capillary bridges are formed [Fig. 2(c)]. Only under the condition that the microstructure of the existing porous network is maintained, could we derive the following equation, describing the dependence of the effective shear modulus G on the shear modulus of the adsorbed solid argon, $G_{\mathrm{Ar,SL}}$ [4]:

$$G = G_0 + \left(1 - \frac{G_0}{G_Q}\right) \tilde{f} G_{\mathrm{Ar,SL}}. \tag{2}$$

In this equation, $\tilde{f}$ represents the filling fraction of frozen adsorbate; only solid argon leads to an increase in G. When the microstructure of the porous network [see Fig. 2(a)] is altered by capillary bridges [see Fig. 2(c)], this equation no longer holds [4].

From our isothermal measurements, we know that the shear modulus of adsorbed solid layers is about equal to the bulk shear modulus [4]. Therewith, as we have shown in Ref. [4], for the first two surface layers, Eq. (2) can be used to calculate the fraction of frozen adsorbate $x = \tilde{f}/f$ during temperature cycles from the measurements of the effective shear modulus. {For the shear modulus of crystalline bulk argon we used the literature values from Ref. [39] (see Ref. [4]).}

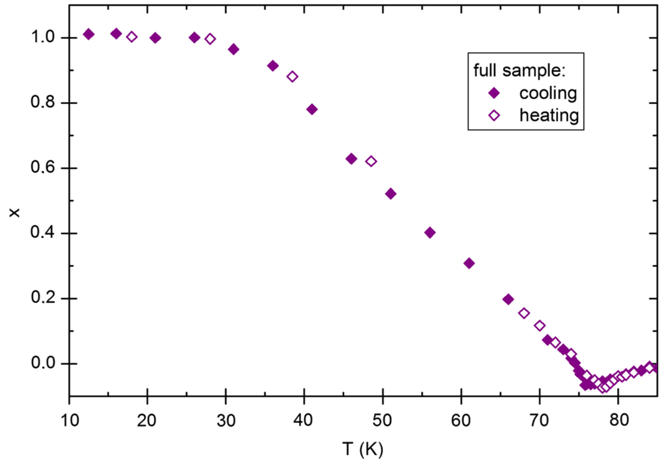

FIG. 3 (color online). The fraction of frozen argon during cooling and heating for completely filled pores. At temperatures below about 30 K the adsorbed argon is completely frozen and no nonfreezing layer remains at these temperatures. The values calculated with Eq. (2) using the ultrasonic data result at low temperatures almost exactly in a fraction of 1. [The slight observed decrease during cooling in the liquid regime (between 85 and 75.8 K) can be contributed to small density changes (see footnote [47]).]

For completely filled pores, the microstructure of the adsorbate is essentially the same as for surface layers [see Fig. 2(b) and 2(d)]. In this case, the microstructure is not a composition of layers and capillary bridges [see Fig. 2(c)], but the adsorbate can be regarded as being composed of single layers. So, the factor a in our effective medium equation should be equal to the factor used for surface layers. Consequently, Eq. (2) can be used to calculate the fraction of frozen argon during cooling and heating for the case of complete filling.

This fraction of frozen argon is shown in Fig. 3. Below 75.8 K the process of freezing starts and the fraction of frozen argon increases continuously over a rather broad temperature range (about 45 K). At a temperature of about 30 K all argon is frozen. Our effective medium analysis yields at temperatures below 30 K a fraction of about 1. This means that, below this temperature, no nonfreezing surface layer of argon remains; then the influence of the surface of the pore walls can no longer prevent a crystallization of the complete adsorbate. The result also further confirms the correctness of the effective medium analysis that we derived in Ref. [4].

With our analysis, we only determine the fraction of frozen argon without resolving the spatial distribution of solid and liquid parts. We know from temperature cycles that the first and second surface layers freeze completely only at very low temperatures ($T \leq 20$ K). So it seems reasonable to assume that the freezing starts in the center of the pores and, with decreasing temperature, the thickness of the liquid layer between the solid core in the center of the pores and the pore walls decreases. This picture essentially corresponds to the thermodynamic model used by Wallacher and Knorr in Ref. [10]. The model mentioned above is related to the well-known effect of surface and interfacial melting [15–17,20,40–45]. In interfacial melting experiments with flat substrates the thickness d of the liquid layer usually follows a power law ($d \propto (\Delta T)^{-1/3}$ with $\Delta T = T_{\mathrm{triple}} - T$, [43]) or a logarithmic dependence ($d \propto |\ln(\Delta T)|$, [43,45]) corresponding to van der Waals forces, respectively, short-range interactions [46]. The peculiar, almost linear, increase of the volume fraction of solid argon over the very broad temperature range (see Fig. 3) does not follow these relations; a reason for this might be nanoconfinement and the related curvature of the substrate (pore surface).

Molz *et al.* (Ref. [33]) interpret the measured increase of the ultrasonic velocity c with decreasing temperature as caused by "the diffusion of thermally activated vacancies" that result in a stress relaxation. But in our isothermal sorption measurements ($T =$ const, increase of the pore filling f), we observe for all temperatures $\{T = 74K - 66K$ in Ref. [4] and now even down to 50 K (not shown)$\}$ a shear modulus of adsorbed argon layers that correspond to the values for bulk argon. This clearly contradicts the argument forwarded in Ref. [33] that, due to a stress relaxation, the full modulus contribution can be observed only at very low temperatures. The isothermal sorption measurements showed also that the amount of solid argon increases with decreasing temperature (at least down to 50 K). We hold these observations to be very convincing evidence for a continuous phase transition of argon in completely filled mesopores (cf. Fig 3).

A comparison of the temperature dependence of the calculated fraction of frozen argon for complete filling and for the first two surface layers further enlightens the complex freezing behavior in mesopores (see Fig. 4). The first and second surface layers of argon are completely frozen around a temperature of 20 K. In the case of completely filled pores, however, at a temperature of 30 K all argon is already frozen. This enables us to conclude that the crystalline structure of solid argon in the pore center influences the surface layers near the wall, and this interaction of the argon atoms is stronger than the interaction of the argon atoms in the first layers with the amorphous pore walls.

In this Letter, we explored the phase transition of argon in the completely filled pores of mesoporous Vycor glass. The simple, globular structure of argon atoms makes this system a sort of model system to study liquid-solid transitions. We conclude that our effective medium analysis of a temperature cycle with a completely filled sample showed that the confined argon undergoes a continuous liquid-solid phase transition over a broad temperature range of 45 K. Below about 30 K all argon is frozen with a shear modulus that corresponds to the bulk shear modulus of argon; i.e., below that temperature the adsorbed

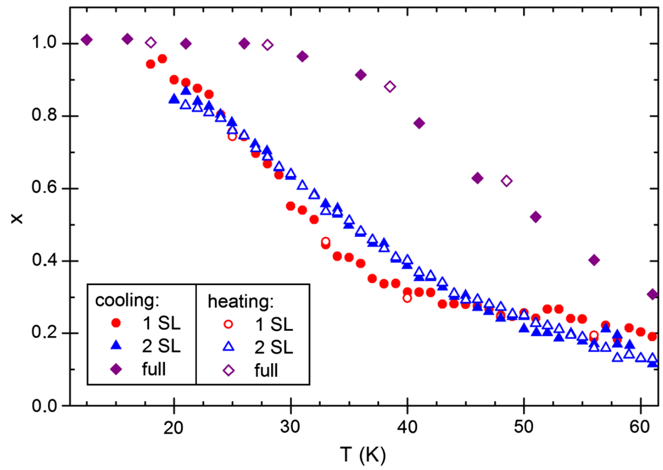

FIG. 4 (color online). A comparison between the temperature-dependent fraction of frozen argon for one or two adsorbed surface layers and completely filled pores. When the pores are completely filled the first few layers already freeze at a higher temperature. The solid argon in the center of the pores obviously impresses its structure on the argon in the surface layers.

argon does not perceive the confinement. We gave evidence that the calculated continuous increase of the fraction of solid adsorbate during cooling corresponds to a continuous liquid-solid phase transition of the adsorbed argon. The method for the analysis of ultrasonic measurements [via Eq. (2)] presented in this Letter for the adsorbate argon could have some impact on forthcoming studies of phase transitions in mesopores, if it can be transferred to other porous systems. For it allows us to determine the state of the phase of the adsorbate in completely filled pores, which is a very common phenomenon in nature, e.g., for water in porous rocks, where the interaction between surface layers and pore walls is different.

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[47] The origin of this decrease can be found in a slight error in the determined effective density of the sample. The density is necessary to calculate the effective shear modulus G from the measured ultrasonic transit time Δt, respective ultrasonic velocity c ($G = c^2 \cdot \rho$), and thereby also to calculate the fraction of frozen argon x. In the liquid regime, a rearrangement of adsorbate is still well possible, and during cooling, additional argon can condense into the pores. In the solid regime, the time necessary for the system to reach equilibrium increases considerably, and consequently, the density can increase only very little. The effect of a minor change in the effective density was already noticed in Ref. [33] for the same system.