Experimental Method for the Determination of the Saturation Vapor Pressure above Supercooled Nanoconfined Liquids

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ABSTRACT: For sorption studies, the saturation vapor pressure $p_0$ above an adsorbate is of great significance. For example, it is needed for the determination of the pore size distribution, the Laplace pressure, and the chemical potential. Above the bulk triple point, $T_3^{\text{bulk}}$, this pressure is identical with the saturation vapor pressure above the bulk liquid. However, below $T_3^{\text{bulk}}$ the correct value of $p_0(T)$ is controversial. Nanoconfined fluids exhibit a shift of the freezing and melting temperatures in comparison to the bulk state. Thus, the adsorbed fluid is supercooled in a certain temperature range below $T_3^{\text{bulk}}$. Here, we show that it is possible to determine the appropriate saturation vapor pressure above the nanoconfined supercooled liquid experimentally. For this purpose, we have performed sorption measurements with liquid argon in nanoporous Vycor glass in the temperature range of the supercooled liquid and at temperatures above the bulk triple point. In order to determine the unknown and temperature-dependent saturation vapor pressure of the supercooled confined adsorbate, $p_0(T)$, we use the Kelvin equation relating this quantity to the pore radius, $r_p$, that is independent of temperature. The knowledge of the absolute values for the liquid—vapor surface tension of the supercooled adsorbate, $\gamma_{lv}(T)$, is not required. However, we presuppose that its dependence on the unknown vapor pressure, $\gamma_v(p_0)$, is bulk-like. Our results indicate that the saturation vapor pressure above the supercooled nanoconfined liquid corresponds to that above supercooled bulk argon (i.e., to the pressure obtained by an extension of the usual vaporization curve to $T < T_3^{\text{bulk}}$). We expect that this method can be used for the determination of $p_0$ above other supercooled adsorbates.

1. INTRODUCTION

The saturation vapor pressure $p_0$ above an adsorbed liquid or solid is of great relevance for sorption studies, and several quantities are influenced by its value. Thus, the calculation of the chemical potential $\Delta \mu$ of pore condensate (in relation to the bulk state) and of the Laplace pressure $p_L$ via the Kelvin equation requires the saturation vapor pressure. The Laplace pressure causes both a deformation of the porous matrix—a phenomenon known as sorption-induced deformation—and a change of the elasticity of the adsorbate. Thus, without the correct value for the saturation vapor pressure, adsorption stress and the extent of deformation cannot be calculated. Also, for the determination of the pore size of a nanoporous material (via standard sorption methods), the knowledge of $p_0$ is indispensable.

The pore size, in turn, influences various properties of adsorbed fluids, for example, its phase transitions, crystalline structure, and elastic properties, as well as the flow of liquids through nanopores. Isothermal sorption measurements with liquid nitrogen or argon are the most common experimental techniques for the determination of pore size distributions.

The saturation vapor pressure above argon (or any other substance) depends significantly on temperature (see the phase diagram of argon, Figure 1). For example, an increase of temperature causes an increase of the vapor pressure above liquid argon (see vaporization curve (red line) in Figure 1). This holds not only for the vapor pressure above the liquid but also for that above the solid (see the sublimation curve (blue line) in Figure 1). The vapor pressure above a supercooled liquid (below the bulk triple point, $T_3^{\text{bulk}}$) is higher than that above the solid at the same temperature. As a result of supercooling, the usual vaporization curve is extended below the bulk triple point (see the red dotted line in Figure 1).

However, for sorption measurements below the triple point of the bulk adsorbate, the value of $p_0$ is not unambiguously defined. In nanopores, the melting and freezing temperatures are lowered, and in a certain temperature range below $T_3^{\text{bulk}}$ the adsorbate can still be liquid, that is, it is supercooled. The
correct value for the saturation vapor pressure above the confined supercooled argon remains controversial as it might deviate both from the sublimation pressure of bulk argon and from the extended vaporization pressure.

Previously, it was argued that argon cannot be used for the determination of the pore size below its triple point because of the unknown value of the saturation vapor pressure. However, Neimark at al. have compared the pore size distributions at 87 and 77 K for MCM-41, that is, for porous materials with an “hexagonal array of quasi-cylindrical pores.” Their results indicate that the pore sizes determined (using nonlocal density functional theory) from the desorption branch are similar at both temperatures, if for $P_{\text{tr}}$ at 77 K, the value of the extended vapor pressure of liquid bulk argon is used (i.e., the vaporization curve is extended below $T_{\text{tr}}^{\text{bulk}}$ using the same analytical expression as for $T > T_{\text{tr}}^{\text{bulk}}$). It remained open, whether this can be generalized to porous materials other than MCM-41.

For bulk substances, it is comparatively simple to determine the saturation vapor pressure above the (supercooled) liquid or solid (i.e., to measure directly the (extended) vaporization or sublimation curve). However, it is generally not straightforward to specify the saturation vapor pressure above a nanoconfined supercooled liquid: in a sorption experiment, below $T_{\text{tr}}^{\text{bulk}}$, it is not possible to increase the vapor pressure up to its saturation value (see Section 3). Nevertheless, it is possible to determine experimentally the appropriate saturation vapor pressure above a nanoconfined supercooled fluid, as we shall show. For this purpose, we have performed an analysis of sorption measurements below and above the bulk triple point. The proposed method is based on the independence of the pore size distribution on temperature and the relation between pore size and saturation vapor pressure. As a simple model system, we use liquid or supercooled argon in nanoporous Vycor glass.

2. METHOD

We have performed several isothermal sorption measurements with liquid and supercooled argon. Our nanoporous sample is a piece of the well-known porous Vycor glass. The sample was placed in a closed metallic container on the cold head of a cryostat, which is connected to a temperature controller. For a schematic drawing and a more detailed description of the experimental setup, please see refs 33 and 34. All measurements were performed with the same sample. Before the measurements, it was cleaned using hydrogen peroxide and washed with distilled water (according to the recommendation of Corning, Inc.). After placing the sample into the sample cell, it was heated to $\approx 30$ °C and evacuated for several hours. A higher temperature was not possible for outgassing because the sample cell is mounted on the cold head of a cryostat (maximum temperature permitted according to the manufacturer (Leybold): 40–50 °C). After measurements at two temperature values (labeled “series 1”), the sample was removed from the sample cell and stored in a desiccator before the other measurements (labeled “series 2”) were performed. The porous sample was filled and drained by changes of pressure in a gas distribution system that is connected to the sample cell via a metallic capillary. The molar amount of the adsorbate in the pores, $n$, at a particular pressure $p$ can be calculated using either the ideal gas equation or the transit time of ultrasonic shear waves (see refs 12, 35, and 36). During every isothermal sorption measurement, the pressure $p$ is successively increased until the pores are completely filled (maximum molar amount: $n$) at the saturation vapor pressure, $P_{\text{tr}}$. Thereafter, the filling fraction of the pores, $f = n/n_0$, is again reduced by a stepwise decrease of the pressure $p$.

Figure 2 shows exemplarily the filling fraction $f$ of a nanoporous Vycor glass sample with liquid argon at 86 K as a function of the vapor pressure $p$ at 86 K during adsorption (closed symbols) and desorption (open symbols). Complete saturation of the pores is reached at the saturation vapor pressure of liquid bulk argon, $p_{\text{tr,measured}} = 884.5$ mbar. The pressure $P_{\text{tr}}$ denotes the steepest point of the desorption branch. This pressure corresponds to the pore radius with the highest occurrence (see analysis). The sketches show schematically the filling of the pores in different pressure ranges.

function of the vapor pressure $p$, that is, at a temperature above $T_{3,\text{tr}}^{\text{bulk}} = 83.8$ K. As it is well known, the adsorption process starts with the formation of adsorbate layers on the pore surface. With increasing pressure $p$, the thickness of these layers increases up to a certain pressure above which capillary bridges form. When all pores are filled with capillary bridges, but the saturation vapor pressure is not yet reached, there still remain curved menisci at the pore ends. Only the increase of $p$ up to the saturation vapor pressure $p_{\text{tr,measured}} = 884.5$ mbar causes a flattening of these menisci (see schematic sketches in Figure 2). During the initial desorption process, the reduction of $p$ again
causes the formation of curved liquid—vapor interfaces at the pore ends. At a certain value for the pressure (that depends in particular on the pore size), the capillary bridges vanish again, and the pores are emptied (the steep part of the desorption branch).

The temperature range of our measurements between ≈76 K and ≈86 K covers the complete liquid regime of argon in our nanoporous Vycor glass sample up to the normal boiling point. Previous measurements have shown that the adsorbed argon starts to freeze near the temperature value of 75.8 K in the nanopores of our Vycor glass samples (i.e., it adsorbed argon begins to freeze near the temperature value of 75.8 K, ref 26). Thus, this result could be supercooled. At the triple point of bulk argon ($T_3^{bulk} = 83.8$ K), both curves have different slopes. In addition, we have determined the pressure values experimentally from two series of sorption experiments [series 1: diamonds (at 80 and 86 K); series 2: squares (at various temperatures)]. During sorption isotherm above $T_3^{bulk}$, the pressure in the sample cell increases until the porous sample is completely saturated with liquid argon at the saturation vapor pressure above liquid bulk argon, $p_0^{bulk,liquid}$ (see red symbols; the red arrow indicates the path $p(t)$ followed during an adsorption isotherm). Below $T_3^{bulk}$, the maximum pressure $p_{max}$ that can be reached in the sample cell is equal to the saturation vapor pressure above solid bulk argon, $p_0^{bulk,solid}$ (see blue symbols; blue arrow: path $p(t)$ followed during an adsorption isotherm), because the vapor sublimates at the walls of the cell. However, as the supercooled adsorbate in the nanopores is liquid-like, it may have a higher saturation vapor pressure (see the dotted blue arrow: part of the adsorption path that is not accessible in the experiment. The question mark indicates that the true saturation vapor pressure, $p_0^{bulk,supercooled}$, is unknown).

Above $T_3^{bulk}$, the nanopores are completely saturated when the vapor pressure $p_0^{bulk,liquid}$ is attained, that is, $f = 1$ holds (see sketch in Figure 5a). Below $T_3^{bulk}$, the pressure in the sample cell can only be increased up to the saturation vapor pressure above solid bulk argon, $p_{max}^{measured} = p_0^{bulk,solid}$, where solid argon starts to sublime at the walls of the measurement cell. However, in contrast to this bulk argon outside the sample, the adsorbate in the pores remains liquid-like in a certain temperature range below the bulk triple point (76 K $\leq T \leq 83.8$ K). As the adsorbate is not solid but liquid-like, we may expect that the saturation vapor pressure for the adsorbate is somewhat higher than that above solid bulk argon, $p_0^{bulk,supercooled} > p_0^{bulk,solid}$. In consequence, it is not possible to achieve a complete saturation of the pores during sorption measurements below the bulk triple point. Nevertheless, for porous Vycor glass, the measurements show that the pores are basically completely filled, as the plateau value ($f = 1$) is already reached (see Figure 3 for $T = 80$ K). Only the menisci at the liquid—vapor interface near the surface of the sample still have a certain curvature (because $p_0^{solid} < p_0^{bulk,supercooled}$), which does not noticeably influence the filling fraction (see the sketch in Figure 5b). These menisci will not flatten by the addition of further argon in the sample cell (as long as there is still vapor in the sample cell). Summarizing, it is not possible to attain the saturation vapor pressure above the nanoconfined supercooled argon below the triple point of bulk argon. This observation raises the question of how to determine the appropriate pressure for the supercooled argon. In the following, we will demonstrate that a pore size analysis offers this possibility.

3. RESULTS AND DISCUSSION

Generally, in sorption experiments on porous media, the pressure in the sample cell can only be increased up to the saturation vapor pressure at the temperature of the isothermal measurement, that is, $p_{max}^{measured} = p_0^{bulk}$. Any further argon added into the sample cell will condense at its walls. Figure 3 displays sorption isotherms with liquid argon in nanoporous Vycor glass at two temperature values, that is, below and above the bulk triple point (80 and 86 K). The reduction of temperature by only 6 K lowers the saturation vapor pressure by more than a factor of two. Figure 4 illustrates the temperature dependence of the saturation vapor pressure above liquid or solid bulk argon for the complete temperature range of our measurements (76 K $\leq T \leq 86$ K). The measured values determined as the maximum pressure reachable during sorption experiments at different temperatures in two series of measurements with the same sample are virtually identical with the literature values for $p_0$, that is, they correspond to the values given by the vaporization and sublimation curves, respectively (cp. with Figure 1; for detailed information on the data used, see ref 26). Thus, this result confirms that

$$p_{max}^{measured} = \begin{cases} p_0^{bulk,liquid} & \text{for } T > T_3^{bulk} \\ p_0^{bulk,solid} & \text{for } T < T_3^{bulk} \end{cases}$$

Figure 3. Filling fraction of the pores of Vycor glass with argon as a function of the vapor pressure $p$ at two temperatures, one below and one above $T_3^{bulk} = 83.8$ K. At the lower temperature (80 K) the filling of the pores is achieved at considerably lower values for the pressure. Both the adsorption and desorption branches are shifted to lower pressure values. The maximum pressure, $p_{max}^{measured}$, decreases from 884.5 mbar at 86 K to 398.3 mbar at 80 K.

Figure 4. Saturation vapor pressure above liquid and solid bulk argon as a function of temperature. The lines show the saturation pressure above liquid and solid bulk argon known from the literature (sublimation and vaporization curves; for information about the data used, see ref 26).
The pore radius $r_k = r_k + t$ is the sum of the Kelvin radius and the thickness $t$ of the remaining layer on the pore surface (see Figure 8). For an approximation of the thickness $t$ of this argon layer, usually, empirical equations are used, such as the Halsey equation. This equation relates the relative pressure $p/p_0$ to the thickness $t$ of the adsorbed layer consisting of $z$ monolayers via

$$t = z u = \frac{-S}{\ln(p/p_0)} u$$

where $u$ denotes the thickness of one argon monolayer. This thickness $u$, in turn, can be estimated from the density $\rho_{\text{liquid}}$ of bulk argon via $u \approx [M/(\rho_{\text{liquid}} N_A)]^{1/3}$ with the molar mass, $M = 39.948$ g/mol, and the Avogadro constant $N_A$. As mentioned above, a reduction of the relative pressure results in a successive emptying of the porous material. The slope of the desorption branch at a particular relative pressure $p/p_0$ can be regarded as a measure of the occurrence of the radius of the pores emptying at that pressure. Thus, the derivative of the filling fraction $f$ with respect to the relative pressure yields the pore size distribution with the aid of the Kelvin and Halsey equations.

As the plateau value of isothermal adsorption is reached also during the measurements done below $T_{3\text{bulk}}$ (see Figure 3 above $\approx 360$ mbar for $T = 80$ K), the pores are filled, even if the actual saturation vapor pressure is not reached. The curved menisci occur at the pore ends and have no impact on the spatial distribution of the pore condensate, that is, they should not alter the desorption process. Consequently, the form of the measured desorption branch is not changed, and an analysis of the pore size distribution will supply the correct values, assuming that the appropriate parameters are used.

The dependence of the filling fraction on the relative pressure contains information about the average pore radius and the pore size distribution. We will utilize this information to deduce the correct saturation vapor pressure above the adsorbed fluid (for $T < T_{3\text{bulk}}$). In the classical method, the desorption branch is used to deduce the pore size distribution. In the steep part, the pores are successively emptied and capillary bridges disappear (see Figures 2 and 8). The Kelvin equation relates the relative pressure $p/p_0$ with the radius of withdrawing menisci (the Kelvin radius $r_k$) via

$$r_k = -\frac{2 V_m \gamma_{lv}}{RT} \cos(\theta) \ln(p/p_0)$$

with the gas constant $R$, the molar volume of the adsorbate, $V_m$, and the liquid–vapor surface tension, $\gamma_{lv}$, at the temperature of the isothermal sorption measurement. For argon, complete wetting of the adsorbed liquid is generally presupposed, that is, a contact angle of $\theta = 0^\circ$ between the curved menisci and the surface layer, so that $\cos(\theta) = 1$ holds.

As mentioned above, a reduction of the relative pressure results in a successive emptying of the porous material. The slope of the desorption branch at a particular relative pressure $p/p_0$ can be regarded as a measure of the occurrence of the radius of the pores emptying at that pressure. Thus, the derivative of the filling fraction $f$ with respect to the relative pressure yields the pore size distribution with the aid of the Kelvin and Halsey equations.

For the analysis, we have to know $V_{m0}$ (see eq 2), and $u$ (see eq 3) at the temperatures studied. Above the triple point of bulk argon, $T_{3\text{bulk}}$, we have used the literature values for the density of bulk liquid argon $\rho_{\text{liquid}}$ to determine the molar volume $V_m = M/\rho_{\text{liquid}}$ (see Figure 6a). For the temperature range below $T_{3\text{bulk}} \approx 83.8$ K, we have used extrapolated values for the density of liquid bulk argon. From a previous study, we know that for supercooled argon, the temperature dependence of the adsorbed argon’s density is similar to that of liquid bulk argon. This finding

$$\rho_{\text{liquid}} = \rho_{0} \exp(b_1 \theta^{0.16} + b_2 \theta^{0.31} + b_3 \theta^{0.6} + b_4 \theta^7),$$

with $\theta = 1 - T/T_c$, $T_c = 150.687$ K, $\rho_{0} = 535.6$ kg/m$^3$, $b_1 = 1.5004262$, $b_2 = -0.31381290$, $b_3 = 0.086461622$, and $b_4 = -0.041477525$. The data below the bulk triple point are extrapolated using the same equation. (b) The thickness of an argon monolayer, $u$, was approximated from the density via the relation $u = [M/(\rho N_A)]^{1/3}$ (see text below eq 3). In the temperature range studied (76 K $\leq T \leq 86$ K), $u$ is almost constant.

Figure 5. Above the triple point of bulk argon, the pores of the porous sample are completely saturated at the vapor pressure of liquid bulk argon, $p_0^{\text{bulk,liquid}}$ (see panel a). However, below $T_{3\text{bulk}}$, complete saturation of the pores cannot be achieved. The maximum pressure that can be reached in the sample cell is the saturation vapor pressure above solid bulk argon, $p_0^{\text{bulk,solid}}$. However, the adsorbed argon remains liquid-like in a certain temperature range. Thus, we can expect that the adsorbate has a higher saturation vapor pressure than solid bulk argon, that is, $p_0^{\text{ads,supercooled}} > p_0^{\text{bulk,solid}}$. In consequence, the adsorbate in the pores exhibits curved liquid–vapor interfaces at the pore ends (see panel b).
supports the use of the extrapolated values of the molar volume of liquid bulk argon below $T_{3}^{\text{bulk}}$ (see Figure 6a).\textsuperscript{45} From the density values, we also calculate the thickness of an argon monolayer, $u$ (see eq 3). The temperature dependence of $u$ is negligible in the temperature range studied ($u \approx 0.36$ nm for 76 K $\leq T \leq 86$ K, see Figure 6b).

The determination of the appropriate surface tension is a more complicated issue. One may argue that the surface tension can be lowered in nanopores.\textsuperscript{46,47} It is known that the surface tension depends on the curvature of the interface.\textsuperscript{48–51} The effect of variation of the surface tension with the curvature becomes noticeable for radii below approximately 10 nm.\textsuperscript{52} However, for liquid argon, the effect on the calculated pore size would be comparatively small for the pore size of Vycor glass and, in particular, the effect would be almost independent of temperature (the Kelvin equation has to be corrected using a multiplier [correction factor] that is almost independent of temperature, see the information in refs 48 and 52). Therefore, above $T_{3}^{\text{bulk}}$, the use of the bulk values for the surface tension will not noticeably affect the temperature dependence of the calculated pore size. From experimental data, Lemmon and Penoncello established the following equation for the liquid–vapor surface tension of bulk argon:\textsuperscript{49} $\gamma_{0} = \gamma_{0}(1 - T/T_{c})^{2}$, with $\gamma_{0} = 37.898063$ mN/m and $x = 1.278$.\textsuperscript{53} Again, we also need the values below the bulk triple point. We will not simply extend the validity range of this relation for the surface tension below the bulk triple point because surface tension is related to the unknown saturation vapor pressure that we want to determine.\textsuperscript{54} It is obvious that a decrease in surface tension results in a lower energy barrier for the atoms to escape into the vapor and hence in a higher saturation vapor pressure.\textsuperscript{54} Indeed, the following empirical relation between the two quantities was proposed (for various liquids)\textsuperscript{44}

$$T \ln(p_{0}) = aRT \left( \frac{M}{\rho_{\text{liquid}} - \rho_{\text{vapor}}} \right)^{2/3} + b$$

(4)

with constants $a$ and $b$ and molecular weight $M$. In the temperature range of our measurements, we can neglect the low density of the argon vapor, $\rho_{\text{vapor}}$, in the denominator, and eq 4 becomes

$$\gamma_{0} = \frac{T \ln(p_{0}) - b}{aV_{m}^{2/3}}$$

(5)

with the molar volume of liquid argon, $V_{m} = M/\rho_{\text{liquid}}$. Although eq 4 is an empirical relation, Pollara deduced eq 5 also via a "semithermodynamical reasoning". Figure 7 shows the validity of this relation for bulk argon in the temperature range 83.8 K $\leq T \leq 100$ K, that is, the linear relation between $T \ln(p_{0})$ and $\gamma_{0}V_{m}^{2/3}$. Assuming that this relation (eq 5) holds both in bulk and nanofluid for liquid and supercooled argon, we may substitute $\gamma_{0}$ in the Kelvin equation (eq 2) by a function of $p_{0}$ using eq 5 with the parameters stated in the legend to Figure 7.

$$r_{k} = -\frac{2V_{m}^{1/3}(T \ln(p_{0}) - b)}{aRT} \cos(\theta) \ln(p/p_{0})$$

(6)

Thus, we do not have to extrapolate absolute values for the liquid–vapor surface tension (equation by Lemmon and Penoncello, see above) to temperatures below the bulk triple point. The analysis via eq 6 (for temperatures below $T_{3}^{\text{bulk}}$) assumes only a bulk-like pressure dependence $\gamma_{0}(p_{0})$ on the possibly altered vapor pressure (see eq 5). (Note that eq 6 is not necessarily universally valid: for other liquids, it may be necessary to combine eq 2 with a different relation $\gamma_{0}(p_{0})$ instead of eq 5.)

With the method described above, we have calculated the pore size distribution of our porous Vycor glass sample at 86 K, that is, in the liquid regime near the normal boiling temperature, where the vapor pressure $p_{0} = p_{0}^{\text{bulk,liquid}}$ is known (see Figure 8). We denote the radius with the highest occurrence as $r_{p} = 3.8$ nm; that is, the value of $r_{p}$ at the steepest point of the desorption branch (see Figure 2 at $p = p^{	ext{D}}$).

![Figure 7](https://dx.doi.org/10.1021/acsomega.9b03565)

**Figure 7.** Relation between $T \ln(p_{0})$ and $\gamma_{0}V_{m}^{2/3}$ for bulk argon for 83.8 K $\leq T \leq 100$ K, that is, above $T_{3}^{\text{bulk}}$. For the calculation, we have used the data of the vaporization curve (for $p_{0}$ in Pa; see ref 26), molar volume $V_{m}$ (in m$^3$/mol; see Figure 6), and the liquid–vapor surface tension $\gamma_{0}$ (in N/m; equation established by Lemmon and Penoncello;\textsuperscript{45} see text). Obviously, the parameters $a$ and $b$ in eq 5 are constant in this temperature range. A fit to the data yields $a = -1.02779 \times 10^8 \pm 4803$ and $b = 221.13 \pm 0.05$.

![Figure 8](https://dx.doi.org/10.1021/acsomega.9b03565)

**Figure 8.** Pore size distribution for the nanoporous Vycor glass sample obtained by the analysis of the desorption branch of a sorption isotherm with liquid argon at 86 K. For its calculation, we have used the Kelvin and Halsey equations (see text).

A variation of temperature in the range of 76 K $\leq T \leq 86$ K should not noticeably alter the pore size distribution or the average pore size. Because of the low value of the thermal expansion coefficient of nanoporous Vycor glass ($\approx 8 \times 10^{-7}$ K$^{-1}$; value from ref 55), we can assume that the pore size of the empty sample does not appreciably differ in this small temperature range. Also, the sorption-induced deformation of the porous glass, which is related to the so-called solvation pressure (that includes the Laplace pressure), has no noticeable effect on the pore size of the sample. The maximum deformation caused by the adsorption of liquid argon is in the range of $\Delta V/V_{0} = 3\Delta l/l_{0} \approx 1 \times 10^{-3}$ (see ref 11). Furthermore, in the temperature range studied (76 K $\leq T \leq 86$ K), the sorption-induced deformation of the sample varies by less than $\Delta V/V_{0} \approx 2.3 \times 10^{-4}$ (see Figure 1 in ref 11; $\Delta l \approx 0.2$ $\mu$m, $l_{0} \approx 2.66$ mm).
To simplify the analysis, we use in the following the requirement that the pore radius with the highest occurrence, \( r_D^p \), is constant. This pore radius is related to the pressure \( P_D \) with the highest value for the slope \( df/d(p/p_D) \) (see above) via the Kelvin and Halsey equations (eqs 3 and 6)

\[
r_D^p = \text{const.} = r_D(p_D/p_0) + f(p_D/p_0) \text{ for all } T
\]

where the constant is the value of \( r_D^p \) evaluated in the temperature range \( T_{\text{bulk}} < T < T_{\text{boiling}} \) (in our case \( r_D^p = 3.8 \) nm see Figure 8). Therefore, we can determine the unknown saturation vapor pressure of the adsorbed liquid by solving this equation numerically for \( p_0 \). The measured values for the steepest point of the desorption isotherm, \( p_D^D \), are shown in Figure 9 as a function of temperature.

![Figure 9. Temperature dependence of the measured pressure of the steepest point of the desorption isotherm, \( p_D^D \). The figure shows that the steep part of the isotherm shifts to lower pressure values with decreasing temperature.](image)

Thus, we can use sorption measurements below the bulk triple point to determine the saturation vapor pressure (above the supercooled liquid) experimentally using eq 7. The result of these calculations is shown in Figure 10. The analysis for \( T < T_{3\text{bulk}} \) reveals that the saturation pressure above the supercooled liquid is indeed higher than the vapor pressure over solid argon (sublimation pressure of bulk argon), and the values are similar to the extrapolated values of the vapor pressure over liquid argon, that is,

\[
P_{0\text{ads, supercooled}} \approx P_{0\text{bulk, supercooled}}
\]

holds for \( T < T_{3\text{bulk}} \). For the extrapolation of the usual saturation vapor pressure (above the bulk liquid) to temperature below \( T_{3\text{bulk}} \), we have used the same analytical expression as above the bulk triple point, that is, we have extended the vaporization curve of bulk argon below \( T_{3\text{bulk}} \) (see the vaporization curve in Figure 1 and ref 26).

Our experimental data thus support the analysis of Neimark et al.\(^{27}\) who have determined the pore size distribution of MCM-41 at 87 and 77 K using nonlocal density functional theory. At the latter temperature, they used the extrapolated values above supercooled bulk argon (the extended vaporization curve) for the saturation vapor pressure above the supercooled liquid. With this procedure, they obtained similar pore size distributions at both temperatures, which indirectly indicated that the saturation vapor pressure above a supercooled nanofluid is similar to that extrapolated value (and differs from the pressure on the sublimation curve). Although for argon in Vycor, we found that relation 8 is valid, this may not be the case for other systems. In particular, for nanoporous systems with smaller pore sizes than that of Vycor, we may expect deviations because of interactions between the adsorbate and pore surface. Deviations may also occur in systems with a stronger interaction between pore surface and adsorbate. When nanocavitation changes the molecular arrangement of the adsorbate (e.g., of alkanes\(^{55}\)), this might also affect the saturation vapor pressure (and the surface tension). In addition, note that this experimental method enables the detection of such deviations because the analysis does not rely on relation 8.

For our porous system, a change of temperature obviously did not cause a change of the desorption mechanism. For other porous systems that empty via cavitation\(^{56-58}\) or exhibit a change of the desorption mechanism with temperature,\(^{59}\) it could be advantageous to use the adsorption branch for the determination of the appropriate saturation vapor pressure. The analysis can be performed in an analogous manner. The only difference is that the Kelvin equation has to be corrected because of the cylindrical menisci (the factor 2 has to be omitted in eq 2). In any case, it is of particular importance to use isotherms reflecting equilibrium transitions (the waiting time after each filling step has to be sufficiently long to allow for a spatial rearrangement of the adsorbate). For example, it took us typically two weeks to measure a complete adsorption and desorption isotherm (see Figure 3). Generally, the analysis may not remain limited to the pore size with the highest occurrence, \( r_D^p \). However, when the form of the pore size distribution is studied as a function of temperature, the adsorption and desorption steps must be narrow (and similar) at all temperatures as they influence the calculated distribution.

Concluding, we would like to emphasize the importance of knowing the correct saturation vapor pressure above the adsorbed fluid. Errors in \( p_0^{\text{ads}} \) can give rise to misleading interpretations, for example, when studying the pore size distribution. If we would use eqs 2 and 3 with the measured values \( p_{\text{measured}} \) (see Figure 4) instead of the correct values for \( p_0 \) (see Figure 10) to evaluate the pore size, we would obtain the results shown in Figure 11. Considering the fact that the pore size does not change with temperature (i.e., \( r_D^p = r_D^p + f_D^p \approx \text{const.} \), these results could be explained by a change in the wetting of the adsorbed argon (see factor \( \cos(\theta) \) in eq 2). Certainly, it is known that temperature influences the contact

![Figure 10. Comparison of the saturation vapor pressure above the adsorbed argon as well as that above bulk argon above and below the bulk triple point, \( T_{3\text{bulk}} \). Above \( T_{3\text{bulk}} \), the saturation pressure above the adsorbed argon is about equal to that above liquid bulk argon (as expected), and below \( T_{3\text{bulk}} \), it is about equal to the saturation vapor pressure above the supercooled liquid bulk argon. The solid lines correspond to the literature values for liquid and solid bulk argon (see Figure 4). For an extrapolation of the saturation vapor pressure above liquid bulk argon below \( T_{3\text{bulk}} \), we have used the same equation as for liquid argon above \( T_{3\text{bulk}} \) (dotted line; extended vaporization curve; see text and Figure 1).](image)
Figure 11. Consequences of an erroneous data analysis using incorrect values for the saturation vapor pressure. (a) Apparent Kelvin radius $r_D^0$, divided by $\cos(\theta)$ and (b) apparent thickness $\tilde{h}$ of the argon layer remaining on the pore surface as a function of temperature calculated using $p_0^{\text{extr}} = p_{\text{max}}^{\text{extr}}$ for both $T > T_{\text{bulk}}^0$ and $T < T_{\text{bulk}}^0$. The pore size $r_D^0 = r_D^0 + \tilde{h}^0$ could be kept constant assuming a significant decrease of $\cos(\theta)$ with decreasing temperature (see panel c), corresponding to an increase of the contact angle from $\theta = 0^\circ$ at 86 K to $\theta \approx 60^\circ$ at 76.5 K.

angle,\textsuperscript{60,61} Thus, complete wetting may be present at higher temperatures, but this could change when decreasing the temperature. The analysis would implicate a considerable change in the wetting; that is, the contact angle would have to change from $\theta = 0^\circ$ at 86 K to $\theta \approx 60^\circ$ at 76.5 K ($\cos(\theta) \approx 0.5$, see Figure 11c). We consider such an increase to be too large for a temperature change of only 9.5 K, particularly because it is not related to any phase transition.\textsuperscript{62}

4. CONCLUSIONS AND OUTLOOK

Summarizing, we have shown that it is possible to determine the saturation vapor pressure above supercooled argon confined in nanoporous Vycor glass. In sorption experiments, this pressure cannot be measured directly because below the triple point of bulk argon, the pressure in the sample cell can only be increased up to the saturation vapor pressure above solid argon (sublimation curve). Now, our analysis shows that the appropriate saturation vapor pressure above the supercooled liquid can be evaluated using sorption experiments. The method relies on the temperature independence of the pore size. Using the Kelvin equation that relates the pore size to the saturation vapor pressure, we determine the appropriate values for $p_0$ below the bulk triple point via a reference measurement above $T_{\text{bulk}}^0$. This analysis requires that a relation $\gamma_s(p_0)$ between surface tension and saturation vapor pressure is known, even though the absolute values of $p_0$ and $\gamma_s$ are unknown. Depending on the liquid under investigation, this may not necessarily be eq 5 we have used for argon but another specific relation, either empirically derived or based on theoretical thermodynamics. Be that as it may, such relations $\gamma_s(p_0)$ can usually be established for the bulk state. Their validity in the supercooled state is an essential assumption in our analysis—but it is less demanding than assuming bulk values for $\gamma_s(T)$.

The results for argon indicate that the vapor pressure is similar to that above supercooled bulk argon. We expect that this experimental method can be generalized to other adsorbates and porous materials with low thermal expansion. Thus, it opens the possibility to determine the saturation vapor pressure above various supercooled adsorbates. Currently, the results indicate that the saturation vapor pressure is the same above supercooled argon in bulk or nanoconfinement. However, further studies (with other adsorbates and also other porous matrices) are necessary before a generalization to other systems. For this purpose, we intend to perform measurements with other supercooled adsorbates (e.g., nitrogen or oxygen) as well as with commonly used porous materials like porous aluminum oxide, porous silicon, or other porous glasses. In general, the proposed method may be used to detect deviations from the (extrapolated) saturation vapor pressure above the bulk liquid (extended vaporization curve). Only the knowledge of the appropriate value for $p_0$ will enable the correct analysis of sorption measurements below the bulk triple point, for example, when interpreting changes in the chemical potential as a result of phase transitions or when studying the effects of the Laplace pressure during sorption-induced deformation.

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Notes
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