Kelvin equation-based scaling model for pore-size estimation in mesoporous materials

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Abstract. In this paper we consider the phase equilibrium state of a fluid confined within a mesoporous controlled cylindrical pore medium. We begin with finding a meniscus shape in the limit of the smoothest curvature variation, for which the curvature radius is the only parameter to define the meniscus dimensions. Then the scaling law is established connecting the meniscus curvature and the pore radius, thus allowing us to create a one-parameter model for finding a pore radius when a meniscus curvature radius is known. Simultaneous use of the model with our previously developed one makes it possible to calculate the pore size on the basis of $P/P_0$ information from the adsorption isotherm.

1. Introduction, formulation of the problem

Fluid in mesoporous materials behaves differently to what we observe in a macroscopic scale. In the latter case the meniscus tends to become spherical. We should question ourselves whether this always happens at the phase equilibrium in mesopores.

![Figure 1](https://via.placeholder.com/150)

Figure 1. The meniscus in the case of the abrupt change of curvature.

Traditionally, the meniscus curvature radius $R$ is considered [1,2] equal to the pore radius reduced by the adsorbed film thickness; hence, the meniscus geometry is tacitly assumed to be hemispherical (figure 1). At the same time the inner surface of the adsorbate is considered cylindrical. This leads to the abrupt mean curvature $H$ change (from $1/R$ to $0.5/R$) with the factor of 2 at the curve where...
condensate-vapor and adsorbate-vapor interfaces join. This can happen if the pore is sufficiently large in diameter or its wall atoms do not strongly attract the fluid molecules until they are close to each other, in other words, if the pore wall attraction would remain almost unchanged (everywhere with possible exclusion of the pore wall proximity) after the wall was replaced by the fluid [3]. Otherwise, the curvature should change smoothly (figure 2) from the meniscus center \((r = 0, z = 0)\) to the adsorbate-vapor interface \((r = r_\infty, z \to \infty)\). (For convenience, the meniscus center curvature radius \(R\) will be chosen as a unit of length for \(r, r_\infty, z, a, h,\) and \(k\). The capitalized letters will be used for the values in SI units everywhere with the single exception: \(r\) is the polar coordinate.) The continuity of the curvature implies that the same should hold near \(r_\infty\), bringing up the first condition: \(h(r_\infty) = 0.5/r_\infty\). The second condition is that the curvature \(h\) at \(r = 0\) should obviously be equal to unity.

\[
h = \frac{r_\infty z_r + z_r (1 + z_r^2)}{2r(1 + z_r^2)^{3/2}} = \frac{\cos r}{2r} + \frac{\sin r}{2r} \tag{1}
\]

is continuous everywhere \((h(r_\infty = \pi/2) = 1/\pi = 0.5/r_\infty)\) with the exclusion of a point \(r = 0\), where it can be easily replaced by its limit value \(h = 1\). Hence, the both conditions are satisfied. (If the curvature changes abruptly, then \(h(r_\infty = 1) = 1/2\).) Decomposing the curvature (1) into power series of \(r\) we obtain:

\[
h = \frac{1}{2} - \frac{r^2}{4} + \frac{r^4}{48} + \ldots + \frac{1}{2} \left( \frac{r^2}{12} + \frac{r^4}{240} + \ldots \right) = 1 - \frac{r^2}{3} + \frac{r^4}{40} + \ldots \tag{2}
\]

Generally speaking, we obtained what we were in search of. At the same time, a positive sign of the 4-th order expansion term seems to be unphysical. The attractive part of the Lennard-Jones interaction between the pore material and a fluid molecule within a cilindrical pore is [4]:

\[
U = -\frac{3\alpha a}{2A} \left( \frac{3}{2} \cdot \frac{5}{2} ; 1 ; \left( \frac{r}{a} \right)^2 \right) \tag{3}
\]

Here \(F\) is a hypergeometric function, \(a = A/R\) is a dimensionless pore radius, \(\alpha\) is the same as in [4]. The series expansion of \(F\) gives:

\[
U \sim -\frac{1}{A^3} \left( \frac{1}{4} + \frac{15}{4} \left( \frac{r}{a} \right)^2 + \frac{525}{64} \left( \frac{r}{a} \right)^4 + \ldots \right) \tag{4}
\]

The zeroth-order term does not drive the curvature change, while the others do. The higher terms of the expansion are of the same sign. The same is believed to hold for the two highest order terms shown.
in the curvature expansion (2). The actual interaction is mediated by the fluid and may fall down steadier (slower than $1/A^3$) when a pore radius increases. The coefficients in the $U$ expansion are expected to be less than they appear in (4). As far as their exact values are unknown, the smoothest possible curvature expression (the limit case) will retain the zeroth and the second order terms:

$$h = 1 - kr^2,$$

where $k$ is a coefficient, which is connected with $r_\infty$ by a condition $h(r_\infty) = 0.5/r_\infty$:

$$1 - kr_\infty^2 = 0.5 / r_\infty.$$  

The numerical solution of the differential equation (5) gives $r_\infty = 1.5$, $k = 8/27$. The simplicity of the result encourages us to look for an analytical solution. The equation for the mean curvature is:

$$h = \frac{rz_{rr} + z_r(1 + z_r^2)}{2r(1 + z_r^2)^{3/2}} = 1 - \frac{8}{27} r^2.$$  

Upon substitution of $\tan u$ for $z_r$ we get:

$$z_r = \frac{r(27 - 4r^2)}{(9 - 4r^2)^{3/2}},$$

$$z(r) = z(\sqrt{9 - r^2}) = 3 - \sqrt{9 - r^2} + \frac{\sqrt{3}}{2} \ln \left( \frac{2\sqrt{3} - 3}{2\sqrt{3}\sqrt{9 - r^2} + 9} \right).$$

3. Meniscus curvature radius scaling

In the previous section we established the law connecting $R$ and $R_\infty$ ($R_\infty/R = 1.5$) in the case of the smooth curvature variation (7). This ratio is independent of the pore radius. The dimensionless second order coefficient $k$ is shown to be constant (compare equations (5) and (7)). If we consider the one in SI units, we’ll see that it is inversely proportional to the curvature radius:

$$K \sim R^{-2}. $$

Alternatively, we can derive this ratio by rewriting (4) in SI units (as a series of $R$):

$$U \sim -\frac{1}{A^2} \left( 1 + \frac{15}{4A^2} R^2 + \frac{525}{64A^4} R^4 + \ldots \right)$$

and dividing the second term coefficient, preceding $R^2$, by the inverse curvature radius:

$$K \sim A^{-3} / R^{-1}. $$

Comparing these relations, we obtain that:

$$R \sim A^{5/3}. $$

Five-thirds is the maximum possible power because the actual interaction, mediated by the fluid, may fall down not so abruptly when a pore radius increases (see the previous section). On the other hand, in the case of the abrupt curvature change, $R \sim A$. Hence, the power should be within the range of $[1; 5/3]$.

Power law should be the same for $R$ and for $R_\infty$ independently of whether there is a smooth or abrupt curvature change. In intermediate situations this shouldn’t always be observed, but the dependencies of both $R$ and $R_\infty$ on the pore diameter are expected to be between these for the aforementioned two types of the curvature change.

To check the model consistency with available predictions, we should use the results of the models where the meniscus curvature radius is estimated at different pore radii but the same temperature. We shouldn’t focus ourselves (at least for now) on the results where the meniscus curvature radius is close to the pore radius (the abrupt curvature change). There is not so much appropriate data available: the isotherms for argon and nitrogen.

The argon adsorption and desorption isotherms [5] were given two interpretations [2,6] concerning the meniscus curvature in possible phase equilibria. In paper [2] the results are shown in the form of the correlation. This is not quite suitable here. We re-calculated the results the same way it had been
done in [2]. Moreover, we added the results for the evaporation branch, not presented in [2]. The same PC-SAFT model [7] (with the same parameter set) was used as an EOS equation and as an equation for the phase equilibria. In the latter case it was accompanied by Young-Laplace equation when needed. The results by the model presented in [2] and by our model [6] are shown in figure 3 by the squares and rounds, respectively. Solid symbols are used for the evaporation branches. Otherwise (for the condensation branches and for the cases with no hysteresis) we used empty symbols. The aforementioned results have been fitted to the function:

\[ R = CA^b. \]  

The fit curves are shown by the solid lines. The fitted \( b \) values are shown in table 1. The dash-dot line will be explained further in the text. For convenience, the dotted and dashed lines in figure 3 show levels \( R = 2A/3 \) and \( R = A \), respectively.

![Figure 3. Effective meniscus curvature radius as a function of the pore radius. Argon. \( T = 87 \text{ K} \).](image)

### Table 1. Fitted values of the \( b \) parameter. Argon.

| Model | Type of the possible equilibrium           | Fitted \( b \) parameter |
|-------|-------------------------------------------|--------------------------|
| [6]   | condensation, no hysteresis               | 1.30±0.04                |
| [2]   | condensation, no hysteresis               | 1.87±0.1                 |
| [6]   | evaporation                               | 0.84±0.04                |
| [2]   | evaporation                               | 1.24±0.05                |

The suitable nitrogen adsorption and desorption isotherms are available in [1]. These data were given the interpretations by the two models [2,6]. Details of the calculations with the model [6] are described in reference [12] of the paper [3]. The calculations results are shown here in figure 4. Symbols and lines have the same meaning as those in figure 3. The fitted \( b \) values are summarized in table 2.

Looking at the both tables, one can find that only two types of the \( b \) values belong to the interval \([1; 5/3]\): those by the model [2] for the evaporation branch and those by the model [6] for the condensation branch (traditionally including the cases without hysteresis). According to the model, if \( R/A \approx 1 \), then \( b \) should be equal to 1. If \( R/A \approx 0 \), then \( b \) should be equal to \( b_{\text{max}} \). Supposing the transition of \( b \) from the pore center to its edge being smooth, we write the lowest (second, due to the function evenness at the pore center) order expansion of \( b \):
\[ b = 1 + (b_{\text{max}} - 1)(1 - (R/A)^2). \] (15)

We have taken the point sets shown in the both figures, for which \( b \) (see table 1, table 2) belongs to the interval of \([1; 5/3]\). For them we have also found \(<R/A>\), the mean values of \( R/A \). We considered the data \(<R/A>, b\) independently of the fluid type but grouped them by the model type. For each model type we have approximated the data with equation (15) to find the \( b_{\text{max}} \) value.

**Figure 4.** Effective meniscus curvature radius as a function of the pore radius. Nitrogen. \( T = 77 \) K.

**Table 2.** Fitted values of the \( b \) parameter. Nitrogen.

| Model | Type of the possible equilibrium | Fitted \( b \) parameter |
|-------|----------------------------------|--------------------------|
| [6]   | condensation, no hysteresis      | 1.39±0.04                |
| [2]   | condensation, no hysteresis      | 2.02±0.13                |
| [6]   | evaporation                      | 0.83±0.19                |
| [2]   | evaporation                      | 1.21±0.27                |

The approximation results are summarized in table 3. The \( b_{\text{max}} \) value by the model [2] is lower than expected. The one by the model [6] is close to the maximum value of 5/3.

**Table 3.** \( b \) as a function of \(<R/A>\). Fitted values of the \( b_{\text{max}} \) parameter.

| Model | Type of the possible equilibrium | \(<R/A>\) | \( b \)        | Fitted \( b_{\text{max}} \) parameter |
|-------|----------------------------------|-----------|---------------|---------------------------------------|
| [2]   | evaporation                      | 0.41      | 1.21±0.27     | 1.27±0.02                             |
|       |                                  | 0.44      | 1.24±0.05     |                                        |
| [6]   | condensation, no hysteresis      | 0.59      | 1.39±0.04     | 1.57±0.04                             |
|       |                                  | 0.66      | 1.30±0.04     |                                        |

Equation (14) can be rewritten as a differential one:
\[ dR/dA = bR/A. \] (16)

If \( b \) is not a constant, then (16) should be used instead of (14) because the former gives correct local validity of (14). Upon substitution of (15) (with \( b_{\text{max}} = 5/3 \)) in (16) we’ll obtain:
\[ dR/dA = \frac{(5 - 2(R/A)^3)R/A}{3}. \] (17)
Its solution is:

\[ R = \frac{A}{\sqrt{1 + (C / A)^{1/3}}}. \]  \hfill (18)

The condensation and no hysteresis data for argon and nitrogen obtained with the model [6] have been approximated by the equation (18) giving the values of the \( C \) parameter 2.69±0.11 nm and 4.03±0.14 nm, respectively. The fit curves are shown in figures 3 and 4 by the dash-dot lines.

Inversely, as soon as we know the parameter \( C \) and the curvature radius \( R \) (the one obtained with the model [6] and capillary condensation \( P/P_0 \) data) we can find the pore radius with almost any nonpolar wetting test fluid, the molecule size of which is much smaller than the expected pore size. The results for \( \text{N}_2 \) and \( \text{Ar} \) are shown in figure 5 in the form suitable for direct use (for controlled cylindrical pore glasses). Dotted and dashed curves are for nitrogen; solid and dashed curves are calculated with the model [6], dotted and dash-dot curves are the results presented in [8].

![Figure 5. Pore diameter as a function \( P/P_0 \). Nitrogen – at \( T = 77 \) K. Argon – at \( T = 87 \) K.](image)

4. Conclusions

In this paper, the model of the meniscus shape has been developed in the limit of the smoothest curvature variation. According to it, the meniscus dimensions are defined only by its curvature radius. The relation has been established between the pore radius and the meniscus curvature one. Its power coefficient has been interpolated for intermediate cases of the curvature variation, thus allowing for a one-parameter model of a pore radius considered as a function of a curvature radius. Combining the model with the model [6] it is possible to calculate the pore diameter on the basis of \( P/P_0 \) information from phase equilibria data concerning non-polar wetting small molecule fluids in mesorous media.

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