Improvement of the Derjaguin−Broekhoff−de Boer Theory for Capillary Condensation/Evaporation of Nitrogen in Mesoporous Systems and Its Implications for Pore Size Analysis of MCM-41 Silicas and Related Materials

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In this work, we propose an improvement of the classical Derjaguin−Broekhoff−de Boer (DBdB) theory for capillary condensation/evaporation in mesoporous systems. The primary idea of this improvement is to employ the Gibbs−Tolman−Koenig−Buff equation to predict the surface tension changes in mesopores. In addition, the statistical film thickness (so-called *t*-curve) evaluated accurately on the basis of the adsorption isotherms measured for the MCM-41 materials is used instead of the originally proposed *t*-curve (to take into account the excess of the chemical potential due to the surface forces). It is shown that the aforementioned modifications of the original DBdB theory have significant implications for the pore size analysis of mesoporous solids. To verify our improvement of the DBdB pore size analysis method (IDBdB), a series of the calcined MCM-41 samples, which are well-defined materials with hexagonally ordered cylindrical mesopores, were used for the evaluation of the pore size distributions. The correlation of the IDBdB method with the empirically calibrated Kruk−Jaroniec−Sayari (KJS) relationship is very good in the range of small mesopores. So, a major advantage of the IDBdB method is its applicability for small mesopores as well as for the mesopore range beyond that established by the KJS calibration, i.e., for mesopore radii greater than ∼4.5 nm. The comparison of the IDBdB results with experimental data reported by Kruk and Jaroniec for capillary condensation/evaporation as well as with the results from nonlocal density functional theory developed by Neimark et al. clearly justifies our approach. Note that the proposed improvement of the classical DBdB method preserves its original simplicity and simultaneously ensures a significant improvement of the pore size analysis, which is confirmed by the independent estimation of the mean pore size by the powder X-ray diffraction method.

Introduction

Gas adsorption, especially adsorption of nitrogen and argon, has been an important tool for characterization of surface and structural properties of nanoporous solids such as adsorbents, catalysts, and other related materials. Numerous adsorption methods have been developed and extensively used for surface area determination, pore size analysis, and surface heterogeneity analysis (see books 1−3 and references therein). Unfortunately, many of those methods produce inconsistent and unreliable results.[4−10]

Experimental verification of the aforementioned methods was hampered by the lack of nanoporous solids with well-defined pore shape, size, and connectivity. Since 1992 this situation changed dramatically due to the discovery of hexagonally ordered mesoporous silica, MCM-41, by Mobil researchers.[11] This discovery was a significant break-through in the design and synthesis of materials of tailored mesoporous structures and pore sizes. These materials were quickly recognized as useful model adsorbents for verification and development of adsorption methods for characterization of mesoporous solids.[4−10] The MCM-41 and other related ordered mesostructures turned out to be essential for testing and further development of the pore size analysis method based on the density functional theory[6] as well as for verification and improvement of the classical characterization methods. In 1997 Kruk et al.[5] used a series of the MCM-41 samples to develop a practical method to calculate the pore size distribution for adsorbents with open-ended cylindrical mesopores. The pore sizes of the MCM-41 samples used were determined on the basis of a geometrical relation that includes the X-ray diffraction interplanar spacing and the volume of ordered mesopores. Subsequently, the experimental relations

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between the capillary condensation/evaporation pressures and the pore size were determined for nitrogen and argon adsorption on silicas and organosilicas (see review 10 and references therein). It was shown that the use of the adsorption branch of the isotherm instead of the desorption branch for the calculation of pore size distribution has several advantages. A simple and accurate method for the pore size analysis was developed by using the well-known Barrett−Joyner−Halenda (BJH) algorithm,[12] which was implemented in a rigorous way without originally proposed approximations.[5] A remarkable improvement of the pore size analysis in the range of small mesopores was achieved by incorporating into the BJH algorithm the statistical film thickness and experimental Kelvin-type relation, both established on the basis of adsorption isotherms measured for a series of well-defined MCM-41 samples.[5] While the relation proposed in the aforementioned work[5] to describe the experimental dependence between the pore radius and the capillary condensation/evaporation pressure is very good in the range of small mesopores (pore radii below 4−4.5 nm), it overestimates the size of larger mesopores.

In this work, we propose a significant improvement of the classical Derjaguin−Broekhoff−de Boer (DBdB) theory for capillary condensation/evaporation in mesoporous systems,[13−17] which is much more advanced than that proposed by Barrett et al.[12] since it takes into account the effects of the pore curvature in the pore size analysis. The incorporation of the surface tension changes in mesopores via the Gibbs−Tolman−Koenig−Buff (GTKB) equation[1,18−20] with the Dubinin and Kadlec[21] (DK) approximation for the displacement of the surface of zero mass density, δ, relative to the surface of tension is a key improvement of the current proposal. Similarly as in the Kruk−Jaroniec−Sayari (KJS) approach,[5] we propose to use in the improved DBdB method the statistical film thickness evaluated accurately on the basis of adsorption isotherms measured for the MCM-41 materials instead of the originally proposed *t*-curve. The current study shows that the aforementioned modifications of the original DBdB theory have significant implications for the pore size analysis of mesoporous solids. To verify the improved DBdB pore size analysis method (IDBdB), a series of the calcined MCM-41 silicas, which are well-defined materials with hexagonally ordered cylindrical mesopores, were used for the evaluation of their pore size distributions. Throughout the entire paper, the results generated by the current proposal are compared with the results obtained by means of the classical DBdB method and nonlocal density functional theory (NDFT) developed by Neimark et al.[22] as well as with the experimental determination of the mean pore sizes by powder X-ray diffraction.

Description of the Model

Neimark et al. pointed out that the macroscopic DBdB theory can be further improved by taking into account the

fluid compressibility and dependences of the surface tension and the disjoining pressure on the pore wall curvature.[23,24] Our proposal partially responds to the ideas introduced by Neimark et al.[23,24]

To begin with, we should point out that the current improved version of the DBdB approach, similarly to the classical DBdB, cannot be applied for the evaluation of the pore size distribution in the micropore range (i.e., pore radii below 1 nm). As commonly known, for the case of small pore radii the classical concepts of phenomenological thermodynamics fail, and the methods of statistical thermodynamics and/or related advanced approaches (e.g., grand canonical Monte Carlo simulations, molecular dynamic simulations, nonlocal density functional theory) should be applied for studying fluids confined in micropores, which according to the IUPAC classification are defined as pores with radii below 1 nm.[1] The presented improved DBdB approach is thermodynamically correct only for pores larger than micropores, where the quantities used for its formulation have clear physical meaning.

The starting equation for the disjoining pressure of the thin film at the free surface of a solid, which is a function of its thickness h, was derived by Derjaguin and Churaev,[25]

$$\Pi(h) = (RT/v_m) \ln(p_0/p) \tag{1}$$

where p/p_0 is the relative pressure of vapor, v_m is the molar volume of liquid, R is the universal gas constant, and T is the temperature. The disjoining pressure isotherm defined by eq 1 provides information about the surface forces acting in the thin films.

By assuming the complete wetting of the surface, Churaev et al. proposed the exponential form for eq 1, which can be written as follows:[26,27]

$$\Pi_1 \exp(-h/\lambda_1) = -(RT/v_m) \ln(p/p_0) \tag{2}$$

Here Π_1 characterizes the strength of the surface force field and the parameter λ_1 is the decay length in the order of a monolayer thickness (i.e., λ_1 characterizes the range of structural forces action). In the case of the hydrophilic surface $\Pi_1 > 0$, and λ_1 is on the order of bulk correlation length.

In some cases, experimental data could be properly described only by using two exponential functions with the adjusted values of parameters:[28]

$$\Pi_1 \exp(-h/\lambda_1) + \Pi_2 \exp(-h/\lambda_2) = -(RT/v_m) \ln(p/p_0) \tag{3}$$

where the first term dominates in the region of thick interlayers and the second term in the range of thin interlayers. Roughly speaking, eq 2 can be applied only for surfaces characterized by weak interactions with the adsorbed medium. For other cases, especially when condensation at high pressures takes place, eq 3 seems to be a more accurate and reliable approximation for the disjoining pressure isotherm.

The disjoining pressure isotherm $\Pi(h)$ for the wetting film formed on a concave surface of the capillary is given

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as follows:[26]

$$\Pi(h) = \Pi_1 \exp(-h/\lambda_1) +$$

$$\Pi_2 \exp(-h/\lambda_2) + \frac{\gamma(r_m)}{r - h} = -(RT/v_m) \ln(p/p_0) \quad (4)$$

In the above equation, we assume that the surface tension of the liquid depends on the meniscus radii $r_m = r - h$, which seems to be particularly important close to the micro−mesopore boundary. This fact is well-known in the basic adsorption literature.

Similarly to Miyahara and co-workers,[29,30] the GTKB equation was used in the current proposal. The GTKB equation for the cylindrical interface (i.e., capillary condensation) can be written as follows:[29,30]

$$\frac{\gamma(r_m)}{\gamma_\infty} = 1 - \frac{\delta}{r_m} \quad (5)$$

In eq 5 γ_∞ denotes the surface tension for the bulk fluid, and δ is the displacement of the surface of zero mass density relative to the surface of tension. Clearly, δ takes a positive value for a droplet and it takes a negative value in the situation considered in the present approach, which is the same situation as the bubble case. At the interface between a single-component liquid and its vapor phase, the absolute magnitude of δ is in the same order as the intermolecular distances in the liquid phase in the case of simple molecules such as argon and nitrogen.

The stability condition for the wetting film was formulated earlier by Derjaguin et al. as $d\Pi(h)dh < 0$. Obviously, both the critical film thickness, h_{cr}, as well as the critical capillary radius, r_{cr}, corresponding to the film collapse can be determined from[31]

$$\frac{d\Pi(h)}{dh}\Big|_{h=h_{cr}, r=r_{cr}} = 0 \quad (6)$$

Clearly, the condition given by eq 6 determines the spontaneous spinodal condensation when the adsorbed film thickness becomes mechanically unstable.

Combination of eqs 4−6 gives the relation between both the critical film thickness and critical capillary radius as a function of the relative pressure for an open-ended cylindrical pore,

$$\begin{cases} \dfrac{\gamma_\infty(r - h - 2\delta)}{(r - h)^3} - \dfrac{\Pi_1}{\lambda_1} \exp(-h/\lambda_1) - \dfrac{\Pi_2}{\lambda_2} \exp(-h/\lambda_2) = 0 \\ \dfrac{\gamma_\infty(r - h - \delta)}{(r - h)^2} + \Pi_1 \exp(-h/\lambda_1) + \Pi_2 \exp(-h/\lambda_2) = -(RT/v_m) \ln(p/p_0) \end{cases} \quad (7)$$

The solution of the above system of algebraic equations can be done by some standard numerical procedures.

For the case of the constant surface tension, i.e., $\delta = 0$, and disjoining pressure isotherm given by eq 2, the system of eqs 7 reduces to the simpler form, developed by Churaev et al.,[26]

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$$\begin{cases} r = h + \sqrt{\dfrac{\gamma_\infty \lambda_1}{\Pi_1 \exp(-h/\lambda_1)}} \\ \dfrac{\gamma_\infty}{(r - h)} + \Pi_1 \exp(-h/\lambda_1) = -(RT/v_m) \ln(p/p_0) \end{cases} \quad (8)$$

Obviously, the simplification of eq 7 to eq 8 can be justified only for nonpolar surfaces where the simple form of the disjoining pressure isotherm can accurately describe the experimental values of the film thickness on the reference flat surface over a wide range of experimental pressures. Moreover, as we will show later the assumption of the constant surface tension can be applied only for sufficiently wide open-ended cylindrical pores.

The desorption from an open-ended cylindrical capillary is determined by the condition for formation of the equilibrium meniscus given by the augmented Kelvin equation, known as the Derjaguin equation,[32]

$$RT \ln(p_0/p) =$$

$$\frac{2v_m\gamma_\infty\left(1 - 2\dfrac{\delta}{r - h_e}\right) + \dfrac{2v_m}{r - h_e}\int_{h_e}^r (r - h)\Pi(h)\, dh}{r - h_e} \quad (9)$$

Similarly to the work of Miyahara and co-workers, we introduced the GTKB equation for the spherical interface into eq 9. The thickness of the adsorbed film being in equilibrium with the meniscus, h_e, is given by[29,30]

$$RT \ln(p_0/p) = \Pi(h_e)v_m + \frac{v_m\gamma_\infty\left(1 - \dfrac{\delta}{r - h_e}\right)}{r - h_e} \quad (10)$$

For the case of the constant surface tension, eqs 9 and 10 reduce to the classical DBdB relations described in the series of papers published by Neimark's group.[33]

On the basis of eqs 9 and 10, we derived analytical formulas for the calculation of the equilibrium transition for open-ended cylindrical pores:

$$\begin{cases} \ln(p_0/p) = [\Pi_1 \exp(-h_e/\lambda_1) + \Pi_2 \exp(-h_e/\lambda_2)]\dfrac{v_m}{RT} + \dfrac{v_m\gamma_\infty\left(1 - \dfrac{\delta}{r - h_e}\right)}{RT(r - h_e)} \\ \ln(p_0/p) = \dfrac{2\dfrac{\gamma_\infty\left(1 - 2\dfrac{\delta}{r - h_e}\right)}{RT} + 2\dfrac{v_m}{RT(r - h_e)}[\zeta_1 + \zeta_2]}{r - h_e} \end{cases} \quad (11)$$

where the coefficients ζ_1 and ζ_2 are expressed as follows:

$$\zeta_1 = \Pi_1\lambda_1\{\exp(-h_e/\lambda_1)[r - \lambda_1 - h_e] + \lambda_1 \exp(-r/\lambda_1)\} \quad (12)$$

$$\zeta_2 = \Pi_2\lambda_2\{\exp(-h_e/\lambda_2)[r - \lambda_2 - h_e] + \lambda_2 \exp(-r/\lambda_2)\} \quad (13)$$

The final systems of eqs 7 and 11 are the classical Kelvin relations corrected for the surface forces and varying surface tension according to the GTKB equations. In fact, the Kelvin equations and standard DBdB relations are the special cases of the current proposal. As we will show later for the case of the constant surface tension, they are

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Table 1. Parameters for the Disjoining Pressure Isotherm of Nitrogen at 77.4 K and Argon at 87.3 K Adsorbed on the Selected Reference Silica Surface

parameter	Ravikovitch−Neimark (nitrogen)	Ravikovitch−Neimark (argon)	LiChrospher Si-1000 (nitrogen)
Π_1, MPa	254.360329	443.060153	355.941071
Π_2, MPa	18.136518	19.165023	114.938853
λ_1, nm	0.172913	0.154058	0.154360
λ_2, nm	0.655448	0.571725	0.339628

equivalent to the DBdB theory developed by Ravikovitch and Neimark.[33]

The solution of the above equations requires the parameters for the disjoining pressure isotherm. Table 1 reports these quantities for the case of nitrogen and argon adsorbed on the reference flat silica surface. Moreover, Figure 1 presents the accuracy of the numerical fitting of the disjoining pressure isotherm, i.e., eq 3, for the aforementioned reference silica surface (note that the surface properties of porous solids can be easily taken into account; experimental adsorption data for a reference solid allow us to take into account the surface properties of the solids studied in pore size analysis).[5] For the case of polymolecular adsorption of nitrogen on the silica surface at 77 K, we adopted the pressure range suggested by Churaev and Zorin (i.e., for $h < 0.5$ nm the macroscopic quantities of liquid used in the current proposal lose physical meaning).[27] According to Dubinin's suggestion, we paid special attention to the fitting of the high-pressure experimental film thickness.[34] In the case of argon adsorption on the silica surface, we adopted the initial relative pressure suggested by Neimark et al.[23]

The displacement of the surface of zero mass density, δ, relative to the surface of tension can be estimated by the various methods proposed in the literature.[8,19,21,35] Figure 1S in the Supporting Information shows the calculation of the capillary condensation curves for the case of different approximations for δ. As one can find from this figure, the numerous approximations used for the representation of δ lead to almost the same results. This is reasonable because all aforementioned approximations generate the absolute value δ of the same order as the intermolecular distances in the liquid phase. Thus, in our calculations we assumed that δ can be estimated by using Dubinin and Kadlec formulas because this approach leads to the results that are in the best agreement with experimental X-ray diffraction (XRD) data.

Here, we should mention the weakness of the current proposal. First, the surface chemistry of the MCM-41 or other type of mesoporous silicas might be slightly different from that of the selected reference nonporous surface. For example, the surface of the mesoporous silica materials may exhibit smaller polarity due to a smaller amount of silanols than that on the reference one. In such case the disjoining pressure isotherm should be substituted by a more suitable one. Clearly, this is very simple since the parameters of the disjoining pressure isotherm given by eq 3 can be found immediately by a simple numerical fitting procedure. Second, similarly to the classical DBdB approach we neglected the problem of enhanced solid−fluid interactions in mesopores due to the curvature effect. In other words, the parameters of the disjoining pressure of the adsorbed film were calibrated for the arbitrary selected reference nonporous silica surface and consequently they were not dependent on the pore radii. For
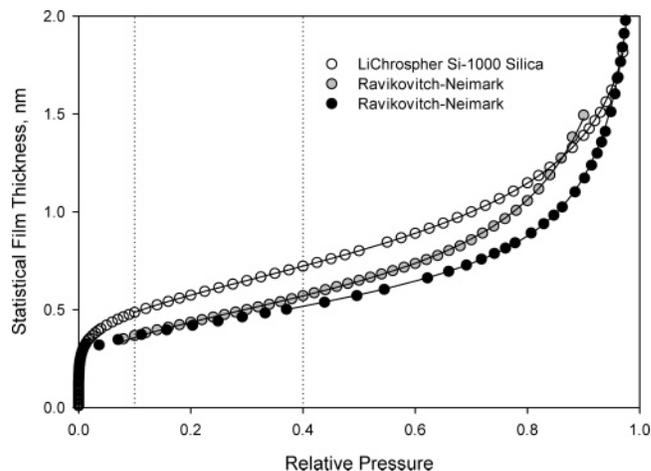

Figure 1. Description of the experimental film thickness curves by eq 3 (solid lines): adsorption of nitrogen at 77.4 K on the reference LiChrospher Si-1000 silica (open circles) and those reported by Ravikovitch and Neimark for nitrogen at 77.4 K (closed gray circles) and argon at 87.3 K (closed black circles) on the silica surface.

the case of microporous materials, this simplification seems to be very far from the reality. However, in the case of the mesoporous silicas under study a very good agreement is observed between the results obtained by the current approach that ignores the curvature effects on the solid−fluid potential and the NDFT theory. Thus, we do not see any reason to introduce the latter effect, which undoubtedly complicates the form of the final system of eqs 7 and 11. However, in the case of extension of the present approach to the micropore range this fact should be taken into account, which will be addressed in our future studies.

At the end of this section, it should be pointed out that our improvement of the classical DBdB theory does not include any additional fitting parameters and it is thermodynamically correct. The current proposal is reduced to the classical Kelvin or DBdB theories under suitable simplifications. In the next section, we will show that in the case of small capillaries the effect of the surface tension variation has a significant influence on the relation of the capillary condensation/evaporation on the relative pressure. Obviously, for larger open-ended cylindrical mesopores the current version of the DBdB theory reduces to the classical one developed by Ravikovitch and Neimark.

Finally, we should point out that the current proposal, which is based on classical thermodynamics, is characterized by macroscopic properties. This means that details of the fluid properties at the molecular level are not considered. Consequently, the proposed method is computationally much simpler than those based on statistical thermodynamics; however, as will be shown later it generates curves for filling/emptying the open-ended cylindrical mesopore geometry that are very close to those obtained by the aforementioned more sophisticated methods. This is not surprising because for simple fluids confined in mesopores phenomenological thermodynamics is applicable.

Results and Discussion

In the preceding section, the general formulas were presented for the improved DBdB theory. Note that the solution of all derived equations is computationally simple

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Table 2. Values of the Capillary Condensation Pressure (p/p_0) and the Corresponding Pore Diameter for Nitrogen on the Silica Surface at 77 K Calculated by the IDBdB Method^a

w_{silica}, nm	p/p_0	w_{silica}, nm	p/p_0	w_{silica}, nm	p/p_0
2.000	0.022	8.102	0.755	14.203	0.891
2.305	0.053	8.407	0.768	14.508	0.894
2.610	0.098	8.712	0.780	14.814	0.897
2.915	0.153	9.017	0.791	15.119	0.900
3.220	0.212	9.322	0.801	15.424	0.903
3.525	0.271	9.627	0.810	15.729	0.905
3.831	0.328	9.932	0.819	16.034	0.908
4.136	0.382	10.237	0.826	16.339	0.910
4.441	0.432	10.542	0.834	16.644	0.912
4.746	0.477	10.847	0.840	16.949	0.914
5.051	0.518	11.153	0.847	17.254	0.916
5.356	0.554	11.458	0.853	17.559	0.918
5.661	0.587	11.763	0.858	17.864	0.920
5.966	0.617	12.068	0.863	18.169	0.922
6.271	0.643	12.373	0.868	18.475	0.924
6.576	0.667	12.678	0.872	18.780	0.925
6.881	0.688	12.983	0.877	19.085	0.927
7.186	0.707	13.288	0.881	19.390	0.928
7.492	0.725	13.593	0.884	19.695	0.930
7.797	0.741	13.898	0.888	20.000	0.931

^{a} Statistical film thickness was estimated from the LiChrospher Si-1000 silica (ref 5).

and very fast in comparison to the NDFT or grand canonical Monte Carlo simulation (GCMC) methods.[36,37]

The model of cylindrical mesopores with both ends open is most often used in the pore size analysis. Since the MCM-41 silicas possess hexagonally ordered cylindrical mesopores, they are the most suitable model materials for verification of the improved DBdB equations proposed in this work.[38] That is why eqs 7 and 11 that describe the capillary condensation/evaporation in the open-ended cylindrical mesopores were solved for the case of low-temperature nitrogen adsorption/desorption by using the following parameters: $\sigma_{ff} = 0.3681$ nm, $\gamma_\infty = 8.88 \times 10^{-3}$ N/m, $V_m = 34.68$ cm^3/mol, and $T = 77$ K.[1,39] Table 2 contains numerical data for the capillary condensation pressure in cylindrical siliceous mesopores expressed as a function of the pore diameter. These data can be used to find the pore diameter corresponding to the capillary condensation pressure estimated from nitrogen adsorption isotherms.

First, Figures 2 and 3 show the comparison of the results obtained by the classical DBdB method refined by Ravikovitch and Neimark[34] and by the currently improved DBdB method with and without assumption of the surface tension variation upon the pore radii. For argon and nitrogen adsorption on the silica surface, the improved DBdB method with assumption of the constant surface tension reproduces data generated by the Ravikovitch−Neimark version of the DBdB theory.[34] It is clear because in this case the same forms of the statistical film thickness for the disjoining pressure isotherm as well as a constant value of the surface tension are used. Oppositely, for the case of the surface tension variation computed according to the GTKB equations implemented in the currently improved DBdB method, both adsorption and desorption capillary curves are considerably different in the range of pore radii $R < 10$ nm. In this range a shift of the dependence of the condensation/evaporation pressure on
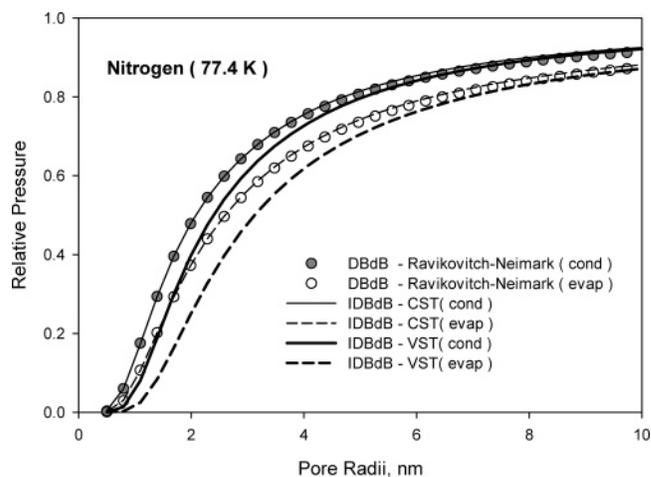

Figure 2. Comparison of the standard DBdB prediction of the capillary condensation/evaporation curves for nitrogen adsorption on silica at 77 K computed via the Ravikovitch−Neimark procedure (closed/open circles) and the proposed improved IDBdB method by assuming the constant (thin solid and dashed lines) and variable surface tension computed from the GTBK equations (bold solid and dashed lines).
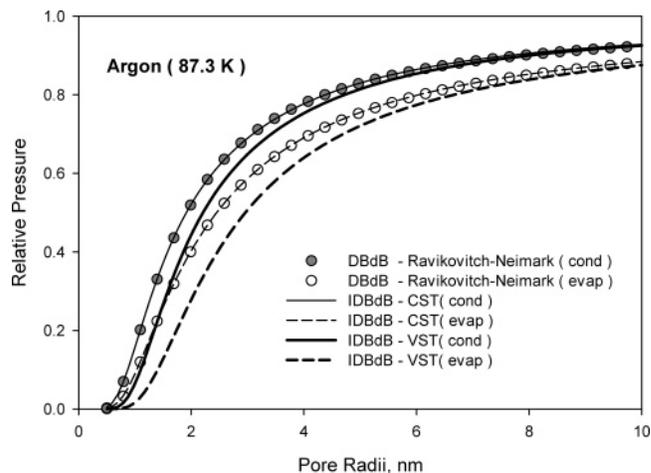

Figure 3. Comparison of the standard DBdB prediction of the capillary condensation/evaporation curves for argon adsorption on silica at 87 K computed via the Ravikovitch−Neimark procedure (closed/open circles) and the proposed improved IDBdB method by assuming the constant (thin solid and dashed lines) and variable surface tension computed from the GTBK equations (bold solid and dashed lines).

the radius of cylindrical open-ended mesopores is observed for both adsorbates studied. This shift is significant in the range of small pore radii due to the variation of the surface tension.

Figure 4 and Supporting Information Figure 2S show the theoretical curves obtained by the IDBdB and ND-FT[17,22,40,41] methods for the capillary condensation/evaporation relative pressure plotted as a function of the pore radius in comparison to the experimental data reported by Kruk and Jaroniec.[10] As can be seen from Figure 4, the proposed improvement of the classical DBdB method significantly shifts both curves, which improves the agreement between theoretical and experimental relationships for the capillary condensation/evaporation

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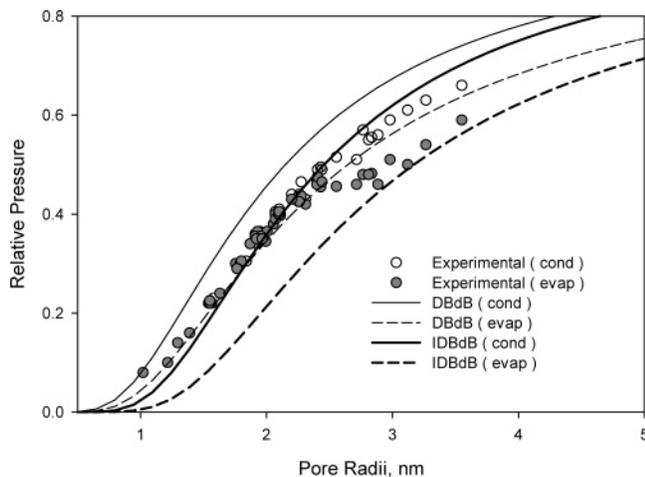
Figure 4. Comparison of the experimental relation between the pore radii and the capillary condensation/evaporation pressure (open/closed circles) with the classical DBdB method (thin solid line, condensation curve; thin dashed line, evaporation curve) and the proposed improved DBdB method (bold solid line, condensation curve; bold dashed line, evaporation curve).

Figure 5. Nitrogen adsorption−desorption isotherms for the calcined MCM-41 silicas.

pressure vs pore radius. Note that the improved DBdB equations predict the capillary condensation in open-ended cylindrical mesopores over the entire mesopore range and the capillary evaporation for mesopores greater than 3 nm. This asymptotic prediction is worthy to be pointed out because the classical DBdB method underestimates the experimental pore radii as reported by Neimark et al.[34]

The comparison of the improved DBdB pressure−radius curves with the NDFT and KJS curves shown in Supporting Information Figure 2S is particularly interesting. First of all, the difference between the capillary condensation curves predicted by NDFT and improved DBdB above pore radii 3−3.5 nm is very small. If we take into account that the improved DBdB is based on the macroscopic quantities, the larger difference between the aforementioned curves in the range of smaller pore radii is fully justified. In the case of the capillary evaporation curve, the asymptotic agreement is also found; however the difference between these two independent approaches is more pronounced. The prediction of the capillary condensation pressure vs pore radius curve by the IDBdB method is fully comparable with NDFT, especially for the most interesting pore radii at the boundary of micro- and mesopores. The proposed improvement of the DBdB theory is particularly valuable because it provides a simple and effective way for inclusion of the surface properties of a solid through an accurate statistical film thickness, the determination of which is currently possible due to the availability of ordered mesoporous materials such as MCM-41.

The agreement of the capillary condensation pressure vs pore radius relationship predicted by the improved DBdB theory with that established experimentally by Kruk et al.[5] is very good especially for pore radii less than ∼3.5 nm. For larger pore radii, the deviation of the KJS approximation from both the NDFT and improved DBdB methods is larger because the KJS calibration was done up to about 3.5 nm pore radii. Therefore, for larger mesopores the KJS method overestimates the pore size in comparison to both the NDFT and IDBdB methods. In the other words, the KJS method gives accurate pore radius estimation in the range of its calibration (i.e., from about 1 to 3.5 nm) and provides a reasonable approxima-
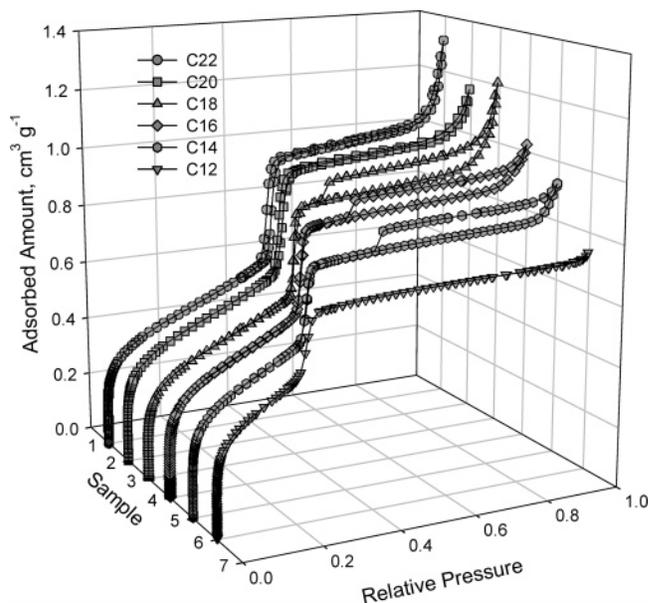
tion for the pore radii ranges of 0.5−1.0 and 3.5−4.5 nm. Since the KJS method is based on the experimentally established empirical relationship, it has limited applicability for pore size analysis in the range beyond that used in the KJS work. Clearly, this fact favors the development of thermodynamically rigorous methods such as that presented here.

Up till now our discussion was focused on the improved DBdB description of the capillary condensation/evaporation curves. Another important problem is to propose an accurate method for evaluation of the pore size distribution (PSD) from a single low-temperature adsorption isotherm. As was pointed out by Jaroniec and co-workers[5] and Morishige and Nakamura[42] and confirmed by the current study, the adsorption branch of the isotherm, which reflects multilayer formation and capillary condensation, seems to be more suitable for the pore size analysis. Consequently, in the next part of our paper, we will illustrate the use of the adsorption branch of the isotherm for pore size analysis.

For the validation of the improved DBdB method, we used a series of nitrogen adsorption isotherms for calcined MCM-41 samples, which are shown in Figure 5. The method of synthesis of these materials as well as their basic characterization are described elsewhere.[43,44] Shown in Figure 6 and Table 3 is the comparison between the KJS, classical DBdB, and improved DBdB methods. Additionally, for the series of MCM-41 silicas studied the pore radii data determined by XRD are attached. Moreover, the mean pore radii estimated from the inflection point of the adsorption branch of the nitrogen isotherm predicted by NDFT spinodal condensation as reported by Neimark et al.[22] are also presented. The Dollimore and Heal (DH) algorithm[45] was used for the calculation of the pore size distributions shown in Figures 6 and 3S. As can be seen from Figure 6, the agreement between two independent approaches, i.e., the KJS and improved DBdB, as well as the XRD predictions is particularly good

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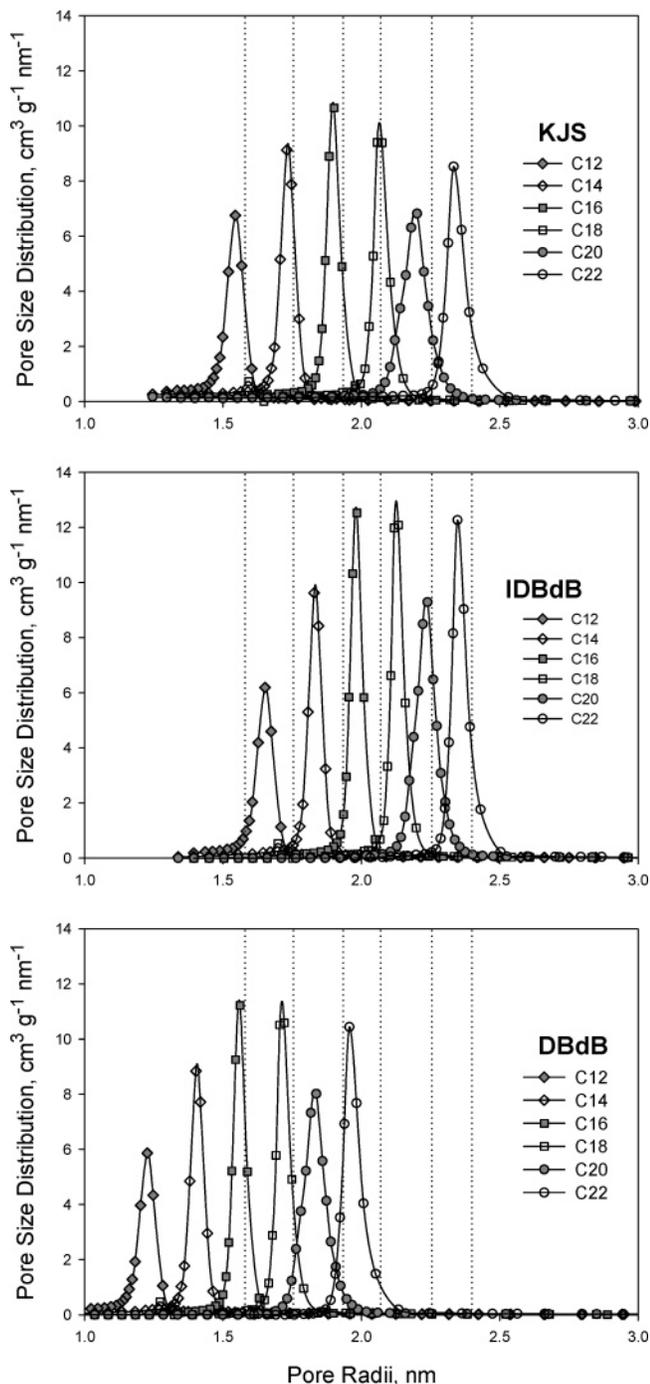(45) Dollimore, D.; Heal, G. R. *J. Appl. Chem.* **1964**, *14*, 109.

Figure 6. The comparison of the pore size distributions calculated by the KJS, DBdB, and improved DBdB (by applying DH algorithm) methods for the calcined MCM-41 samples studied. The dotted lines denote XRD pore radii estimation.

for the MCM-41 silicas studied. The positions and dispersion of all PSDs are very similar. It should be underlined that the pore radii for the considered series of MCM-41 changes from 1.5 to 2.5 nm and obviously the predictions of both methods are very close. Larger differences are expected for larger pore radii due to the reasons mentioned above. Contrary to both mentioned methods, the standard

Table 3. Basic Characteristics of the Calcined MCM-41 Materials Studied Obtained by the Dollimore−Heal (DH) Method[a]

		sample code					
method	parameter	C22	C20	C18	C16	C14	C12
IDBdB (DH)	$\bar{R}$, nm	2.35	2.24	2.13	1.98	1.83	1.65
	V_t, cm^3 g^{-1}	1.17	1.07	1.08	0.98	0.86	0.61
KJS (DH)	$\bar{R}$, nm	2.33	2.20	2.06	1.90	1.73	1.55
	V_t, cm^3 g^{-1}	1.18	1.10	1.13	1.05	0.95	0.70
DBdB (DH)	$\bar{R}$, nm	1.96	1.84	1.72	1.56	1.40	1.23
	V_t, cm^3 g^{-1}	1.00	0.98	0.96	0.90	0.80	0.57
XRD	$\bar{R}$, nm	2.40	2.26	2.07	1.94	1.76	1.58
NDFT	$\bar{R}$, nm	2.20	2.07	1.96	1.84	1.70	1.69

[a] Abbreviations: $\bar{R}$, pore radius at the maximum of PSD; V_t, total pore volume obtained by integration of PSD.

DBdB method underestimates the pore sizes significantly. Clearly, this underestimation is caused partially by the inaccurate *t*-curve and by neglect of the surface tension changes in mesopores.

Figure 3S presents the detailed comparison of PSDs computed by the improved DBdB with different approximations for the displacement of the surface of zero mass density, δ. Additionally, for comparison purposes, the XRD pore radii estimation and mean pore radii values computed from the NDFT spinodal condensation[22] are attached. As can be seen from this figure, the different approximations for the displacement of the surface of zero mass density, δ, generate very similar PSDs. This result is not surprising if one takes into account the curves for the capillary condensation pressure versus pore radii displayed in Figure 1S.

Summing up, we can state that the combination of the current improvement of the classical DBdB theory with the DH algorithm improves significantly the calculation of PSD from the adsorption branch of a single nitrogen isotherm measured at 77 K. The incorporation of the surface tension variation upon pore size as well as the replacement of the statistical film thickness by the recently measured one on LiChrospher Si-1000 silica significantly influence both capillary condensation and evaporation curves especially in the region of small pore radii. This fact is manifested by shifting both mentioned curves in the direction of wider pore sizes as expected on the basis of the NDFT data reported by Neimark et al.[22] The unsolved problem, i.e., divergence of the capillary condensation and evaporation curves in the range of small pore radii, observed in DBdB and NDFT will be addressed in future studies.

Supporting Information Available: Figures showing Kelvin-type relations (2 figures) and pore size distributions (1 figure). This material is available free of charge via the Internet at http://pubs.acs.org.