

REVIEW

Review of Kelvin's Equation and Its Modification in Characterization of Mesoporous Materials

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(Dated: Received on June 14, 2005; Accepted on July 19, 2005)

Physical and mathematical models as well as calculation methods of nitrogen bed on porous media have been introduced to evaluate the structural parameters of mesoporous materials. Kelvin's equation is a link between the relative adsorbate pressure, the mean pore radius, and pore capillarity on the basis of macroscopic capillary condensation. However, Kelvin's equation has been identified that it underestimates the calculated pore size of a material especially in the boundary of pore size which is between 2 and 4 nm. Various modifications on Kelvin's equation were mentioned in order to develop a new model to improve the accuracy of pore size calculation. The problems on conventional mathematical models were analyzed and discussed. A number of calculation methods on physisorption and pore size, especially fundamental theories of physisorption, basis of models and their deficiencies are reviewed. It can provide guidance on developing a modified Kelvin's equation for pore size calculation.

Key words: Kelvin's equation, Physisorption, Adsorption isotherm, Hysteresis loop, Pore size distribution

I. INTRODUCTION

Ordered mesoporous materials have received much attention on its potential applications as catalysts, porous supports, and adsorbents in separation and oxidation processes due to its high access area in porous media. Since both adsorption and oxidation processes happen on the surface in porous media, geometrical configuration of pore and, more importantly, the determination of pore size are main concerns in the material characterization. To date, numerous studies have been focused on developing methods for pore size evaluation. In particular, accuracy of the determined pore size is critically important which can help understanding the geometry of pore network.

Here, three common methods for characterization of porous materials are addressed as follows:

(i) Powder X-ray diffraction analysis (XRD) [1-7]. It is used as a primary source of information about parameters of the crystalline planes formed in a material structure. However, the disadvantage of the XRD analysis is that it cannot measure both pore size and pore wall thickness directly. Thus, XRD method only provides a crystalline plane orientation of the material and the particle size distribution by means of its shape pattern of the peak found in the spectrum.

(ii) Transmission electron microscopy (TEM) [8,9]. It can provide an electronic image of the material usu-

ally with a nano-size scale. In principle, periodicity of pore channels, effective pore diameter, pore wall thickness, and length of pore channels can be measured directly. Due to the limitation of sample preparation, only a small portion of material can be analyzed by TEM.

(iii) Physisorption analysis. Physical adsorption isotherms can be worked out by using nitrogen as adsorbate gas. It has an advantage to evaluate a relative large quantity of sample compared to the TEM analysis [10]. Through this analysis, specific surface area, pore volume, and pore size distribution (PSD) can be calculated [11-24]. However, the calculation of these parameters requires a number of adsorption mathematical models. Therefore, accuracy of these models can significantly affect the estimation of the real material structure.

There are many other methods such as t -plot, α_s -plot, etc. can calculate the external surface area, total surface area, pore volume, and micropore size [12,19,25-29]. These methods are based on the information of adsorption parameters on solid surface to characterize the pore structure, thus its accuracy is enslaved to the adsorption model and reliability of the assumptions.

Physisorption method based on the theoretical background of capillary condensation is a classical method to characterize structural and surface properties of mesoporous materials. In IUPAC classification, Type IV adsorption isotherm characterizes mesoporous adsorption hysteresis and its analysis is the basis of obtaining properties of mesoporous structure. At present, Barrett-Joyner-Halenda (BJH) method [29] and Dollimore-Heal (DH) method [30,31] are generally used on the basis of macroscopic condensation theory. However, these

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methods systematically underestimate actual pore size especially in the boundary from micro- to meso- pores. In addition, absence of uniform mesopore material restricts developing a new adsorption model and modifying the existing calculation method. In 1992, a family of mesoporous molecular sieves, designated as M41S, have been discovered by scientists of Mobil Company [1]. MCM-41 possesses an array of regular channels and is arranged as a two-dimensional hexagonal lattice with a uniform pore size. This provides a long-desired opportunity for testing mathematical models between capillary condensation and experimental data. In addition, utilizing new methods (NLDFT, MS), studying phase equilibrium in the confined space (pore channel), and developing new models and characterization methods can also be realized.

In this work, pore size estimation by Kelvin equation and its various modifications were discussed. Technical problems in characterization of mesoporous materials were analyzed and reviewed in order to propose the feasibility of new model establishment and methodology for characterization.

II. KELVIN'S EQUATION

A. Kelvin-Cohan (KC) equation

Kelvin's equation [10] comprised the correlation between pore critical radius and relative pressure (P/P_0) at capillary condensation. Originally, Kelvin's equation provided the relation of capillary radius and saturated vapor pressure of adsorbate on spherical meniscus without consideration of the adsorbed film thickness. The adsorbed film was firstly formed on the pore wall during the adsorption and then gradually became thick until the films joining together. Thus, formation of the adsorbed films in confined pores greatly affected the capillary condensation, and the calculation of film thickness, t , and pore critical radius, r_c , at capillary condensation was the key problem. Cohan proposed the modified Kelvin's equation considering the film in the open-ended cylindrical pore. According to Cohan, the capillary condensation in an infinite cylindrical pore was described by Kelvin's equation for the cylindrical interface between the adsorbed film and vapor,

$$RT \ln \frac{P_A}{P_0} = -\frac{\gamma V_L}{r_p - t_A} \quad (1)$$

while the evaporation/desorption is associated with the formation of a hemispherical meniscus between the condensed fluid and vapor,

$$RT \ln \frac{P_D}{P_0} = -\frac{2\gamma V_L}{r_p - t_D} \quad (2)$$

Here, P_A/P_0 and P_D/P_0 are relative pressures of adsorption and desorption, respectively; γ and V_L are sur-

face tension and molar volume of bulk liquid; t_A and t_D are adsorption film thickness at the relative pressures of P_A/P_0 and P_D/P_0 , respectively. When the difference between the film thickness t_A and t_D is small compared to pore radius, the width of the hysteresis is given by

$$\frac{P_D}{P_0} = \left(\frac{P_A}{P_0} \right)^2 \quad (3)$$

The KC Eq.(2) constitutes the basis of the conventional BJH method for pore size calculation. In this method, the Harkin-Jura equation [32,33] and the Halsey equation [30] semiempirical equation are used to predict the thickness, t , of adsorption layer formed on the surface of nonporous silica at a given relative pressure, as shown below:

$$t = \frac{1}{10} \left[\frac{13.99 \ln 10}{0.34 \ln 10 - \ln(P/P_0)} \right]^{1/2} \quad (4)$$

$$t = 0.354 \left[\frac{-5}{\ln(P/P_0)} \right]^{1/3} \quad (5)$$

This two equation may be considered as a special case of the Frenkel- Halsey-Hill (FHH) equation,

$$t = \left(\frac{-RT}{a} \ln \frac{P}{P_0} \right)^{-1/s} \quad (6)$$

Halsey equation is used to obtain the multi-layer thickness by the DH method, the thickness, t , of the adsorption layer obtained from Eq.(1) and Eq.(2) is approximately 0.1 nm larger than the value actually measured by Sing *et al.* in all regions of relative pressure [34]. In the Harkins-Jura equation, the thickness is well matched with the measured value when relative pressure is smaller than 0.3; however, it became unsatisfying when P/P_0 is greater than 0.5. The interface between the multi-molecular adsorption layer formed within the pore of silica with a diameter of several nanometers and the gas phase has a greater curvature than that formed on the surface of the nonporous silica. A large curvature of such interface is thought to have a considerable effect on the multi-layer film thickness within the pore. Thus many works have been carried out to modify these methods.

B. Broekhoff-de Boer (BdB) theory

The BdB theory leads to capillary condensation and desorption pressures, which differs substantially from those of Cohan's equations, even in relative larger pores. The BdB theory takes into account the influence of surface forces on the equilibrium and stability adsorption films and introduces the concept of disjoining pressure which is proposed by Derjaguin(DBdB) [35]. For cylindrical pores, the equilibrium thickness of the adsorbed

film is determined by the balance of capillary and disjoining pressure and is given by,

$$\Pi(t)V_L + \frac{\gamma V_L}{r_p - t} = RT \ln \frac{P_0}{P} \quad (7)$$

The disjoining pressure accounts for the sum of fluid-solid intermolecular interaction and is considered to be independent of pore wall curvature in BdB approach. Thus, the disjoining pressure of adsorption film on the flat surface is used in Eq.(7) and is better described by the power law $\Pi(t) \propto t^{-m}$ known as the FHH equation. For the adsorption of nitrogen at 77.4 K on various substrates, the exponent m is between 2.2 and 2.8. In the DBdB theory it is assumed that, as vapor pressure increases and the limit of stability of the adsorption film is achieved, condensation will occur. The limit of stability corresponds to the critical film thickness $t=t_{cr}$, given by the algebraic equation,

$$-\left[\frac{d\Pi(t)}{dt}\right]_{t=t_{cr}} = \frac{\gamma}{(r_p - t_{cr})^2} \quad (8)$$

Thus, the conditions of capillary condensation in a cylindrical pore are determined by Eqs.(7) and (8). Desorption from the cylindrical capillary is determined by the condition of formation of the equilibrium meniscus based on Kelvin's equation, which is known as the Derjaguin equation:

$$RT \ln \frac{P_0}{P} = \frac{2\gamma V_L}{r_p - t_e} + \frac{2V_L}{(r_p - t_e)^2} \int_{t_e}^{r_p} (r_p - t)\Pi(t)dt \quad (9)$$

Here, t_e is the thickness of the adsorbed film in equilibrium with the meniscus. The conditions of desorption are determined by Eqs.(7) and (9). However, DBdB method did not receive as widespread acceptance as the BJH method. Recently, a variant of the DBdB method under the nickname "BdB-FHH" (with the FHHF exponent $m=3$) was applied to calculation of pore size distributions in MMS with cylindrical and spherical pores [10]. There were many attempts to modify the DBdB theory in order to account for the effect of pore wall curvature, which are expected to be appreciable in sufficient narrow pores. It is well understood that capillary fluid and the adsorbed films in nanopores are experienced the effective tensile pressure (hundreds of atmospheres in the nanometer size pores) which enhances the instability of the liquid-like matter [37]. Although the above mentioned effects have attracted a lot of attention, a systematic approach to this complex problem has yet to be developed. Broekhoff and de Boer introduced a relationship between t and P/P_0 , taking into account the interfacial curvature effect [32-34], shown as follows:

$$-RT \ln \frac{P_0}{P} - F(t) = -\frac{\gamma_\infty V_m}{r_p - t} \quad (10)$$

Here, $F(t)=\mu_L-\mu_c$; μ_c and μ_L represent chemical potentials of the multi-molecular adsorption layer with

thickness t and the bulk liquid condition, respectively. Assuming that $\mu_L-\mu_c$ depends only on the thickness t of the multi-molecular adsorption layer, that is, the chemical potential μ_c of multi-molecular adsorption layer is constant irrespective of the surface curvature on which adsorbed form multimolecular layer. Using the Harkins and Jura equation, Broekhoff and de Boer gave $F(t)$ as follows which is the thickness of nitrogen molecule adsorption layer on the surface of the nonporous silica:

$$F(t) = RT \left[\frac{13.99}{(10t)^2} - 0.034 \right] \ln 10 \quad (11)$$

If Eq.(11) is substituted into Eq.(10) and the constants of individual physical properties are further substituted, the following equation will be obtained concerning the thickness t of the nitrogen multi-molecular layer formed within cylindrical pore:

$$-RT \ln \frac{P}{P_0} = \left[\frac{2.0409}{10(r_p - t)} + \frac{13.99}{(10t)^2} - 0.034 \right] \ln 10 \quad (12)$$

Originally, Broekhoff and de Boer employed the constant interfacial tension that is not affected by the interfacial curvature. When the effect on the multi-layer thickness of the interface curvature between multi-molecular adsorption layer and gas phase within the cylindrical pore is considered, the effect of the curvature on the interfacial tension should be considered as one possibility.

In BdB method the relation between pore diameter and relative pressure is shown as follows:

$$r_p - t = \frac{-2\gamma_\infty V_m}{RT \ln(P/P_0)} - \frac{\int_t^{r_p} 2(r_p - t)F(t)dt}{(r_p - t)RT \ln(P/P_0)} \quad (13)$$

Simultaneous solution of Eqs.(10) and (13) yields the multi-layer thickness t and the critical radius $r_c (= r_p - t)$ where capillary condensation occurs. In the case of nitrogen adsorption in silica pores, the following equation, which can be obtained by substituting the values of individual physical properties into Eq.(13), is shown:

$$10(r_p - t) = -\frac{4.0819 \ln 10}{\ln(P/P_0)} - \frac{\ln 10}{10(r_p - t) \ln(P/P_0)} \times \left\{ 27.98 \left(\frac{1}{r_p} - 1 - \ln \frac{r_p}{t} \right) - 0.034 [10(r_p - t)]^2 \right\} \quad (14)$$

The values of t and r_c can be obtained by solving Eqs.(14) and (12), and well match the values which were measured by Naono *et al.*.

Although both values of t and r_c are more accurate than that in KC equation, the application of BdB method is made difficult by the initial choice of Eq.(11). Lukens *et al.* [36] introducing the Hill's approximation [10] made it easier:

$$F(t) = \frac{\alpha}{t^3} \quad (15)$$

Here, α is empirical constant relating to adsorbate and adsorbent, for nitrogen adsorption in silica pores at 77 K, $\alpha=5 \times (3.54)^3$. If Eq.(15) is used, the forms of Eqs.(10)-(13) become fairly simple:

$$\ln \frac{P_0}{P} - \frac{\alpha}{t^3} = \frac{f\gamma_\infty V_m}{RT(r_p - t)} \quad (16)$$

$$\frac{3\alpha}{t^4} = \frac{f\gamma_\infty V_m}{RT(r_p - t)^2} \quad (17)$$

$$\ln \frac{P_0}{P} - \frac{\alpha}{r_p t^2} = \frac{2\gamma_\infty V_m}{RT(r_p - t)} \quad (18)$$

The relation between the pore size t and condensation pressure can be found by solving Eqs.(16) and (17). An analogous relation for desorption branch of the isotherm can be obtained by solving Eqs.(16) and (18). The pore diameter of SBA-15 obtained by LS-BdB method, 7.8 nm, is in excellent agreement with the pore size of 7.82 nm determined from the TEM image. A useful feature of LS-BdB method is the ability to easily differentiate between different pore structures. But for materials with spherical pores and large windows, the results determined by LS-BdB method are in doubt. Also, for samples, showing adsorption isotherms with hysteresis, the pore size obtained by LS-BdB method are inaccurate [38]; this method does not allow to calculate the entire PSD for small porous materials (approximately 2 nm) and may give inconsistent results.

Bhatia and Snowane [40,41] related $f(t)$ to the incremental fluid-solid interaction potential $\tilde{\phi}(t, r)$ at the multi-layer surface and considered the effect of curvature on surface tension to obtain:

$$RT \ln \frac{P_0}{P} + \tilde{\phi}(t, r) = \frac{V_1 \gamma_\infty (r - t)}{(r - t - \lambda/2)^2} \quad (19)$$

for the multilayer isotherm, where γ_∞ is the surface tension at a flat interface and for its stability

$$\left. \frac{\partial \tilde{\phi}}{\partial t} \right|_{t=t_c} = \frac{V_1 \gamma_\infty (r - t_c + \lambda/2)}{(r - t_c + \lambda/2)^3} \quad (20)$$

boundary. Here, t_c is the critical adsorption film thickness when capillary condensation occurs, λ is the inter-layer spacing, and the fluid- solid interaction potential is based on Lennard-Jones centers in the fluid and solid phases. For low pressures where the multi-layer did not exist, Snowane and Bhatia used heterogeneous Unilan model, following their approach to construct hybrid models applicable over a wide pressure range. Pore size distribution obtained by Bhatia and Snowane for their various MCM-41 samples based on nitrogen adsorption at 77 K cannot be obtained from analysis of argon adsorption. Other modifications of the BdB model have been also proposed for the characterization of materials. Zhu *et al.* [42] used empirical formulation

$$\mu_a - \mu_g = RT \ln \frac{P_0}{P} + C_1 + \frac{C_2}{r^n} - \frac{C_3}{t^2} \quad (21)$$

in which C_1 , C_2 , C_3 and n are constants obtained by fitting the multi-layer region of the isotherm. For the onset of capillary condensation, they used the classical Cohan relation for a cylindrical meniscus, which, however, is not consistent with the stability criterion obtained from the application of Eq.(22) to this model.

$$\frac{d^2(\Delta G)}{dN^2} = 0 \quad (22)$$

Kruk *et al.* [21] applied an empirical adjusted form of Kelvin's equation:

$$r = \frac{2\gamma_\infty v_1}{RT \ln(P/P_0)} + t + C \quad (23)$$

where C is a constant, taking the values of 3 Å for nitrogen and 4.38 Å for argon. However, in this case, it is not clear whether Kelvin's equation, representing equilibrium on a hemispherical meniscus, is applicable to the adsorption branch.

In small mesopore, the effect of interface curvature on interface tension should be considered. Tolman, Kirkwood, and Buff stated that the interface tension in the condensation phase-gas phase interface depends on the interfacial curvature. The greater its curvature, the greater its effect on the interfacial tension. At present, this relationship is known as the Gibbs-Tolman-Koenig-Buff equation (GTKB equation) [39]. The corresponding GTKB equations for the spherical and cylindrical interfaces are:

$$\frac{\gamma(\rho)}{\gamma_\infty} = 1 - 2\frac{\delta}{\rho} \quad (24)$$

$$\frac{\gamma(\rho)}{\gamma_\infty} = 1 - \frac{\delta}{\rho} \quad (25)$$

Here, $\gamma(\rho)$ is the interfacial tension on the interface with curvature radius ρ , and δ is the displacement of the surface of zero mass density relative to the surface of tension. δ takes a positive value for a droplet and it takes a negative value for a bubble. Note that δ takes a negative value in this situation, because the phase is located within the interface between the multi-molecular adsorption layer and the gas phase in cylindrical pore, which is the same situation as the bubble case. It is well investigated that, at the interface between the single-component liquid phase and its vapor phase, the absolute magnitude of δ is in the same order as the intermolecular distance in the liquid phase in the case of simple molecules such as argon and nitrogen. $|\delta|$ takes the value 0.3 ± 0.1 nm. Considering this effect, Miyahara *et al.* [43,44] proposed the theoretical equation for the multilayer thickness t within the cylindrical pore,

$$RT \ln \frac{P}{P_0} = N_A \Delta\psi(r_c, r_p) - V_m \frac{\gamma(r_c)}{r_c} \quad (26)$$

where N_A is the Avogadro's constant and $\Delta\psi$ represents the potential energy of attractive interaction between

the adsorbate and the solid surfaces, as shown in the equation

$$\Delta\psi(r_c, r_p) = -\frac{3C}{2}K_3(r_c, r_p) \quad (27)$$

where C is a constant and $K_3(r_c, r_p)$ is giving by the following equation:

$$K_3(r_c, r_p) = r_p^{-3} \int_0^\pi \left\{ -\frac{r_c}{r_p} \cos \theta + \left[1 - \left(\frac{r_c}{r_p} \right)^2 \sin^2 \theta \right]^{1/2} \right\}^{-3} d\theta \quad (28)$$

Eq.(26) has a form similar to that of the BdB Eq.(10). The difference between these two equations is only that the value of the surface tension in the adsorbate bulk liquid condition in Eq.(10) is used as the value of interfacial tension without any further modification, while Eq.(26) uses a predicted value obtained from the GTKB equation to indicate the effect of the interfacial curvature on the interfacial tension. When the interfacial curvature is r_c , replacing γ_∞ in Eq.(1) with γ , which is predicted by Eqs.(24) and (25), yields the GTKB-Kelvin-spherical equation and GTKB-Kelvin-cylindrical equation, respectively [45]:

$$r_c = \frac{\gamma_\infty V_m + \sqrt{(\gamma_\infty V_m)^2 + 4\gamma_\infty V_m \delta RT \ln(P/P_0)}}{-RT \ln(P/P_0)} \quad (29)$$

$$r_c = \frac{\gamma_\infty V_m + \sqrt{(\gamma_\infty V_m)^2 + 2\gamma_\infty V_m \delta RT \ln(P/P_0)}}{-RT \ln(P/P_0)} \quad (30)$$

Miyahara *et al.*[44] proposed the following revised Kelvin's equation:

$$1 = \int_0^{r_c} \frac{1}{\gamma[\rho(r)]} \left\{ \frac{1}{V_m} \left[N_A \Delta\psi(r, r_p) - RT \ln \frac{P}{P_0} \right] - \frac{\gamma[\rho(r)]}{\rho_2(r)} \right\} dr \quad (31)$$

where r is a distance from the center of the cylindrical pore toward the radius direction.

$$\frac{1}{\rho(r)} = \frac{1}{\rho_1(r)} + \frac{1}{\rho_2(r)} \quad (32)$$

where $\rho_1(r)$ and $\rho_2(r)$ are the curvature radius of the condensation phase-gas phase interface indication in Fig.1, having the relationship as following:

$$\rho_2(r) = r \left[\int_0^r \frac{1}{\rho_1(r)} dr \right]^{-1} \quad (33)$$

Miyahara *et al.* gave interfacial tension γ based on the GTKB equation:

$$\frac{\gamma[\rho(r)]}{\gamma_\infty} = 1 - \frac{\delta}{\rho(r)} \quad (34)$$

By solving Eqs.(21), (26), (27), (28), and (29), values of r_p and t can be obtained. Predicted values of t and r_c based on the Miyahara *et al.* are 0.1 to 0.2 nm smaller and 0.5 to 0.8 nm larger, respectively, than the values actually measured by Naono *et al.* and are rather closer to the values measured by Sing *et al.* on nonporous silica.

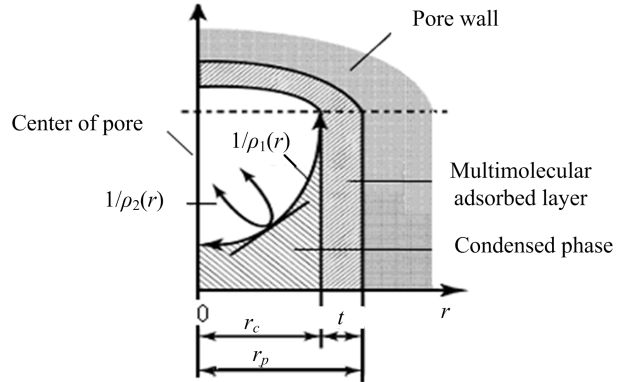


FIG. 1 Schematic representation of the condensed phase in the cylindrical pore suggested in Miyahara's model.

To sum up, when the adsorption isotherm is related to the pore size in the gas adsorption method, adsorption and desorption phenomena are divided into (i) the formation of a multi-molecular adsorption layer on the solid surface and (ii) capillary condensation or evaporation, with each category being analyzed by a separate theoretical equation or empirical equation. Pore radius r_p can be obtained by the sum of (i) accurate thickness t of the multi-molecular adsorption layer and (ii) the critical radius r_c , where capillary condensation or evaporation occurs. Recent research has shown that the foregoing methods is not suit for interpreting adsorption and calculating pore size in pores which diameter smaller than 100 Å. Because the continuum model used in the classical methods is not fit for the small pores only containing a few molecule diameters. This model can not accurately predict the critical conditions, such as the critical pore diameter of applying to surface layering and condensation mechanism. Kim *et al.* proposed super-critical continuum model in micropores [56], however, the existing of phase transition make the adsorption of sub-critical fluid is very complexity, and it is not correct using small length scale bulk properties in such small pores. Molecule Simulation and DFT calculation proved that the overlap of potential from the surrounding pore wall leads to substitute continuum pore filling adsorption for surface mechanism without condensation transition. Classical Kelvin equation and its modifications can not correctly predict critical pore diameter relating to the disappearance of phase transition, and thus can not give the capillary coexistence curve. Although further modified BdB method can correctly predict the relationship between adsorption film thickness t and pore radius, and the capillary coexis-

tence curve [13], this method can not obtain the critical pore radius where phase transition occurs because it is considered that the adsorbate potential in pores is equal to the potential on nonporous adsorbent and then neglected the relation between pore radius and potential field. Further research introduced the relationship mentioned above and considered the effect of curvature on interface tension using single pore model, such as cylindrical pore model, which did not allow the investigation of pore structure networking effects and surface heterogeneous effects. When such effects are ignored, surface area, pore radius, and PSD predicted from these methods are inaccurate. In addition, in theoretical research the network structure causes a shift of the desorption branch of the hysteresis loop towards smaller pore sizes due to restricted accessibility toward pore segments located at interior positions in the pore structure network.

From the foregoing discussion the key to interpret adsorption behavior and accurately calculate parameters of pore structure is to modify the adsorption model in the boundary region of micro-mesopores. In such small pores, the different adsorption models to describe sub-monolayer and multilayer-condensation adsorption should be established, considering the potential of adsorbate-adsorbate and adsorbate-adsorbent, and then the correct relationship between potential and pore size and the effect of curvature on interface tension can be obtained.

III. CONCLUSION

Numerous researches were carried out to investigate adsorption nature in the boundary between micro- and meso-porous regions to obtain a comprehensive and accurate pore size characteristics from the analysis of sorption isotherms. Significant progress was achieved regarding to the understanding of sorption phenomena in narrow pores. The main thrust of recent research in this field is commonly dealt with the following problems: (i) To what extent can notions of bulk phase equilibrium be employed in confined systems? (ii) What is the microscopic structure of a confined gas or liquid and how does this dependence upon the geometry of the pore and the nature of confining substrate? When does the quasi-two- or one-dimensional ordering occur? That is what the effect of packing constraints and substrate forces on the statistical arrangements of molecules in the fluid? (iii) How are the transport properties such as diffusion and viscosity affected by confinement? Unfortunately, the developed theoretical models till now are still finding the answers to the above questions. The following aspects are the research emphases and development trends in this field in the future:

(1) Phase behavior in the confined space should be further investigated. In narrow pores especially mesopores and in the boundary of porous region, the properties of adsorbate phase are much different from that the bulk liquid because of the potential between adsorbate-

adsorbate molecules and adsorbate molecules-adsorbent atoms. This potential leads to the enhanced adsorption in narrow pores which makes the pore structure parameters obtained by classical methods are not correct. Thus, the microscopic interacted potential is the key to study the confined fluid. At present, LJ potential is widely used to describe the microscopic interaction. In theoretical research, the determination of LJ parameters is the main problem. Therefore, the choice of the LJ potential parameters and the choice which kind of LJ potential forms should be applied the primary task in this field.

(2) A satisfying verification of theoretical models for pore size analysis of mesoporous materials could be achieved. So far only for highly ordered materials (such as mesoporous molecular sieves) can develop models within the framework of an independent pore model. It is found that methods and theories based on a single pore model are in some cases applicable (to some extent) to describe the sorption and phase behavior of fluids in porous materials consisting of the ordered three-dimensional pore networks. However, the phase and hysteresis behavior of fluids in the disordered porous systems is still not well understood and more theoretical and experimental work is clearly required to understand the combined effects of confinement, pore geometry, connectivity, etc. on the origin pore condensation and hysteresis. Furthermore, more work is necessary to evaluate to which extent pore size analysis in terms of a pore size distribution curve (which is essentially based on the single pore model) is appropriate for characterizing materials with complex and disordered pore networks. Therefore, it is important to develop more realistic adsorption models, which attempt to describe the microstructure of porous materials at length scales beyond that of a single pore model.

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