A New Approach to Describe High-Pressure Adsorption Isotherms in Subcritical and Supercritical Conditions

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In this article, we present a new approach to describe adsorption equilibrium of pure gases in a wide range of pressure. This approach is based on a simple statistical mechanics treatment combining the potential theory and lattice fluid models. The obtained equation for the calculation of the excess adsorption can predict the curve progression of isotherms defined by the IUPAC I classification, and for those at supercritical conditions. Notwithstanding that the basic idea of the developed equation is to adapt to the adsorption equilibrium in supercritical conditions at high pressure, the model correlates very well experimental data at low pressure in subcritical conditions. It is applicable to a wide range of pressures and fits satisfactorily the experimental data in a broad range of pressures and temperatures. In particular, the model predicts the maximum of excess adsorption and its minimum. A comparison between this approach and two others is given. © 2009 American Institute of Chemical Engineers *AIChE J,* 55: 1793–1802, 2009

Keywords: high-pressure adsorption, supercritical conditions, thermodynamic analysis, excess adsorption, adsorption equilibrium

Introduction

The knowledge of physical adsorption phenomena of gases is a key issue for the gas separation industry as well as for the storage of some gases.[1,2] Adsorption equilibrium data over a large range of pressure and temperature are required for the modeling of the dynamic of adsorption for gas storage and purification processes. Among them, adsorption at very high pressure is actually applied for the natural gas and hydrogen storage. In this range of pressures the gases are usually in supercritical state.

While the adsorption equilibrium isotherms are well defined by the standard IUPAC classification for the subcritical fluids, the behavior of supercritical fluids is fundamentally different.[3,4] This difference relies in the existence of a maximum of the Gibbs excess adsorption (plotted as surface mass excess vs. pressure or fugacity) at very high pressure, observed by many authors.[5–15]

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The difference between excess and absolute adsorption is usually very small in the case of subcritical adsorption due to the low bulk density. In the supercritical region and at high pressure this difference becomes significant[7,14,15] as shown by J. Keller; all experimental measure the excess adsorption.[16] There is a large number of theoretical studies about the prediction of the absolute adsorbed amount in subcritical conditions, but only few studies concerning the amount of excess adsorption in super critical conditions are available. To determine the absolute adsorbed amount it is necessary to know the exact volume of the adsorbed phase, which is difficult to specify accurately.[17] In the case of micro porous adsorbent materials, one can consider that the volume of pores and the volume of the adsorbed phase are identical. However, the volume of the adsorbed phase is usually smaller than the volume of the pores. One approach proposed by DD. Do consists in using classical equilibrium models like Langmuir, Freundlich or Toth applied to the absolute adsorbed amount and then find the excess adsorption, defined as the difference between absolute amount in the adsorbed volume and the amount of the molecules in the bulk density. The author obtained the volume of the adsorbed phase as one of the parameters for the fitting procedure.[17] Ono et al. and Aranovich et al.[18–22] propose a more rigorous theoretical approach. This approach is based on the conception of the lattice theory. An other approach based on the thermodynamic description of excess mass of adsorption is the 3-Parameter-Isotherm equation (3PIG equation). This was initially proposed by Honinberg[23] and later developed by Harting and coworkers.[23–26] The obtained equation is very simple and gives good correlations with experimental data. Subramanian and collaborators[27–29] developed the simplified local density (SLD) model to describe the adsorption behavior in super critical conditions. The use of the potential theory proposed initially by Polannyi[30] and developed later by Dubinin and coworkers[31–33] for supercritical fluid has been considered in a number of papers.[12,34–36] However, in its original form, Dubinin–Radushkevich and Dubinin–Astachov equations contain the parameter "saturated pressure" which cannot be defined in a supercritical region. To avoid this contradiction, some authors postulated that the adsorbate phase is in quasiliquid state in supercritical conditions.[34,35] This approach has no physical basis for the computation of the pseudovapor pressure in a supercritical gas. Therefore, another empirical relation for the saturated pressure was introduced by replacing it with limited pressure. Similarly, the saturated adsorption is replaced by the term of limited adsorption.[36]

The more adequate description of high-pressure adsorption can be obtained by grand canonical Monte Carlo (GCMC) simulations.[5,37–40] However, these methods can be time-consuming and they cannot give the analytical expression for the adsorbed amount that may by used in dynamic models for adsorption processes.

We must note that adsorption isotherms in supercritical conditions show a maximum, and also a minimum at very high pressure (Menon[41,42] and Malbrunot et al.[43]). These physical attributes are alike obtained by Monte Carlo simulations for excess adsorption with experimental validation.[5] Up to now this behavior cannot be predicted by the existing equilibrium models.

The topic of this article is to develop a model to describe equilibrium of pure gases in supercritical conditions based on a simple statistical mechanics treatment combined with lattice fluid models and the potential theory of adsorption to predict the excess adsorption in supercritical conditions up to very high pressures.

Theory

We started from the potential theory[30] assuming a simplified exponential distribution of the adsorption potential in the pore volume:

$$\theta = f(A/E) = \exp\left[-\left(\frac{A}{E}\right)\right] \tag{1}$$

whereas E is the characteristic energy of adsorption and θ is the degree of filling which can further be defined as[33]:

$$\theta = \frac{W}{W_0} = \frac{\Gamma}{\Gamma_{\max}}.$$

The quantity A is the differential molar work of adsorption during the adsorption process in the micropore. W_0 is the maximum volume that the adsorbate can occupy and W is the volume of the adsorbate in the micropore. In this case, we assume that $\Gamma_{\max}$ is the maximum of adsorption and equal to W_0. In our case, the adsorption potential is defined as the difference between the chemical potential of the adsorbed phase and the chemical potential of the bulk at the same temperature.

$$A = \mu^{s} - \mu^{g} \tag{2}$$

We use a lattice thermodynamic approach to describe the bulk and adsorbed phases.[44,45] The thermodynamic description assumes spherical molecules in a square lattice. Each cell of the lattice may be occupied by only one molecule. To obtain a thermodynamic model as function of the pressure, not all the lattices are considered as full: some cells contain molecules whereas others are empty. The degree of occupancy x of the gas phase lattice is defined by $x = N/M$ where N is the total number of cells occupied by molecules and M the total number of cells in the lattice. The relation between x and the gas phase density $\hat{\rho}$ is given by Hocker, Aranovich, and Donohue[46]:

$$x = \frac{\hat{\rho}}{\rho^{\max}} \frac{N_A}{M_m} \tag{3}$$

Here $\rho^{\max}$ is the maximal number density. Considering that the molecules behave like hard spheres we obtain[44]:

$$\rho^{\max} = \sqrt{2}/\sigma^3$$

where σ is the molecule radius and $\hat{\rho}$ is the ordinary mass density expressed in g/cm^3.

A simplified statistical mechanics theory is used to provide an expression of the chemical potential in both bulk gas and adsorbed gas phases,[47,48] given by partial derivation of the Helmholtz free energy with respect to the molecule number at a constant temperature (see Appendix). Thus, the adsorption potential A for the excess adsorption in Eq. 2 becomes:

$$A = -kT\ln b - kT\ln\frac{x}{1-x} + kTax \tag{4}$$

where the parameter b is defined as $b = V^s/V^g$.

The combination of Eqs. 1 and 4 leads to the following relation between the amount of excess adsorption and the gas phase density:

$$\Gamma = \Gamma_{\max}\left[\frac{bx}{1-x}e^{-\frac{c}{T}x}\right]^{sT} \tag{5}$$

In Eq. 5 the characteristic energy E and the parameter b are independent from the temperature.

The parameter s is defined as:

$$s = \frac{k}{E} \tag{6}$$

This parameter is not related to the temperature.

For parameter c we have:

$$c = -\frac{\delta E_{\mathrm{m-m}}}{M_g k} \tag{7}$$

The maximum adsorption capacity $\Gamma_{\max}$ corresponds to the maximum volume $V^s_{\max}$ of the adsorbed phase. Assuming that the maximum volume $V^s_{\max}$ is independent of the temperature and the molar volume is in function of the coefficient of expansion ℓ, then the maximum loading[30] is expressed following next equation:

$$\Gamma_{\max} = \Gamma^0_{\max}\exp\left[-l\left(T - T^0\right)\right] \tag{8}$$

where $\Gamma^0_{\max}$ is the maximal adsorption capacity at a reference temperature T^0. By replacing $\Gamma_{\max}$ in Eq. 5 we obtain:

$$\Gamma = \Gamma^0_{\max}\exp\left[-l\left(T - T^0\right)\right]\left[\frac{bx}{1-x}e^{-\frac{c}{T}x}\right]^{sT} \tag{9}$$

The Eq. 9 can be used to fit adsorption equilibrium data at different temperatures. The following parameters are involved $\Gamma^0_{\max}$, ℓ, b, c and s. Those can be estimated by nonlinear fitting of the experimental data.

In summary, we can thus present the algorithm of calculating the excess adsorption as below:

1. Total adsorption is calculated by setting the values of temperature and pressure. With these values, the mass density of the bulk phase is deduced by the equation of state for the gas phase.
2. From the bulk mass density, one estimates the degree of occupancy on for the adsorbed phase lattice $x = N^g/M^g$ using Eq. 2.
3. Excess adsorption can be then deduced by a non-linear fitting from Eq. 9.

The adsorption behavior predicted by the new equation

To simplify the analysis of the behavior of Eq. 9 we introduce following new parameters:

$$t = \frac{kT}{E} = sT \tag{10}$$

$$a = \frac{c}{T} \tag{11}$$

$$K = \Gamma_{\max}\exp\left(\frac{kT}{E}\ln b\right) \tag{12}$$

Thus the Eq. 9 becomes:

$$\Gamma = K\left[\frac{x}{1-x}e^{-ax}\right]^{t} \tag{13}$$

Analyzing Eq. 13 we can conclude that the shape of the adsorption isotherms depends on the sign of parameter $t = kT/E$ and the function in the parenthesis:

$$f(x) = \frac{x}{1-x}e^{-ax} \tag{14}$$

When the value of t is positive the maximum of this function corresponds to the maximum of the adsorbed amount. From a physical point of view E is always positive,[31–33] the maximum of this function coincide with the maximum of the adsorbed amount. Provided that $a^2 - 4a > 0$, function[14,15] has two optima:
a maximum for

$$x = a - \sqrt{a^2 - 4a}/2a$$

and the minimum for

$$x = a + \sqrt{a^2 - 4a}/2a$$

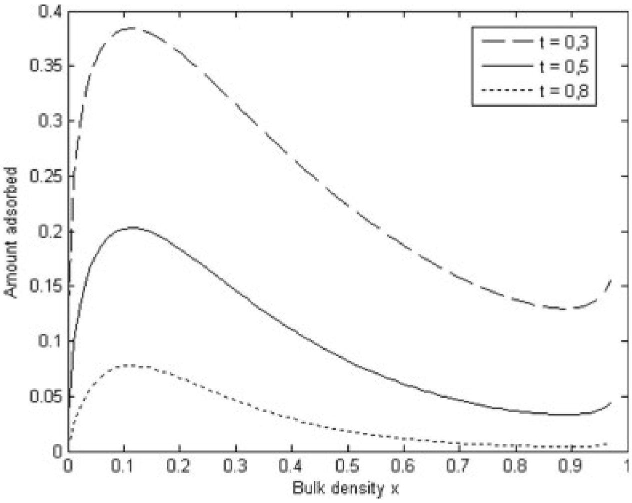

Figure 1. Isotherms of supercritical fluid adsorption for $K = 1$, $a = 10$ and different values of kT/E.

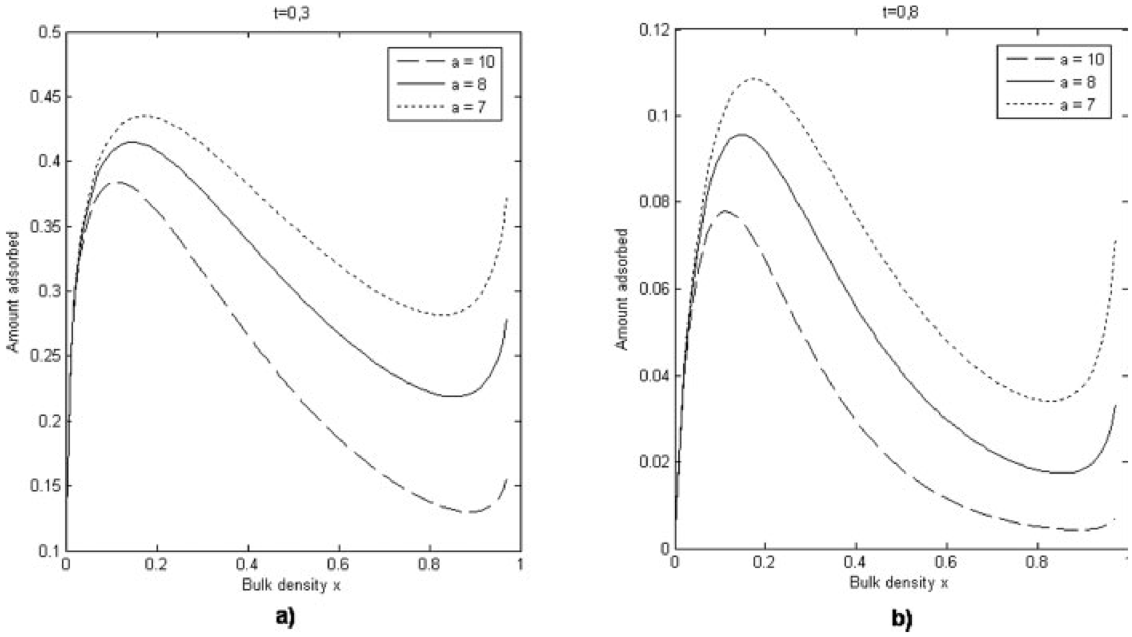

Figure 2. Isotherms of supercritical fluid adsorption for $K = 1$ and different values of a and t.

This relation is obtained by annulment of the derivate of this function with respect to x.

This isotherm behavior is also observed experimentally although in the literature only the maximum is generally reported. But the minimum occurs at very high pressures.[10,41–43]

Some numerical experiments with Eq. 15 are presented here. Figure 1 gives the amount of Gibbs adsorption calculated from Eq. 13 for $K = 1$, $a = 10$ and different values of $t = kT/E$. We can see that with these values the adsorption isotherms have a maximum with increasing x and a minimum at higher pressures followed by a light re-increase. Independently of the value of parameter t both extrema are located approximately at the same value of the bulk density for either, maximum and minimum. It is showed that the influence of this parameter on the value of the adsorbed amount is related to the values of the characteristic energy E. Thus, the value of adsorbed amount at both maximum and minimum grows symmetrically with the increasing of the characteristic energy. On the other hand, the

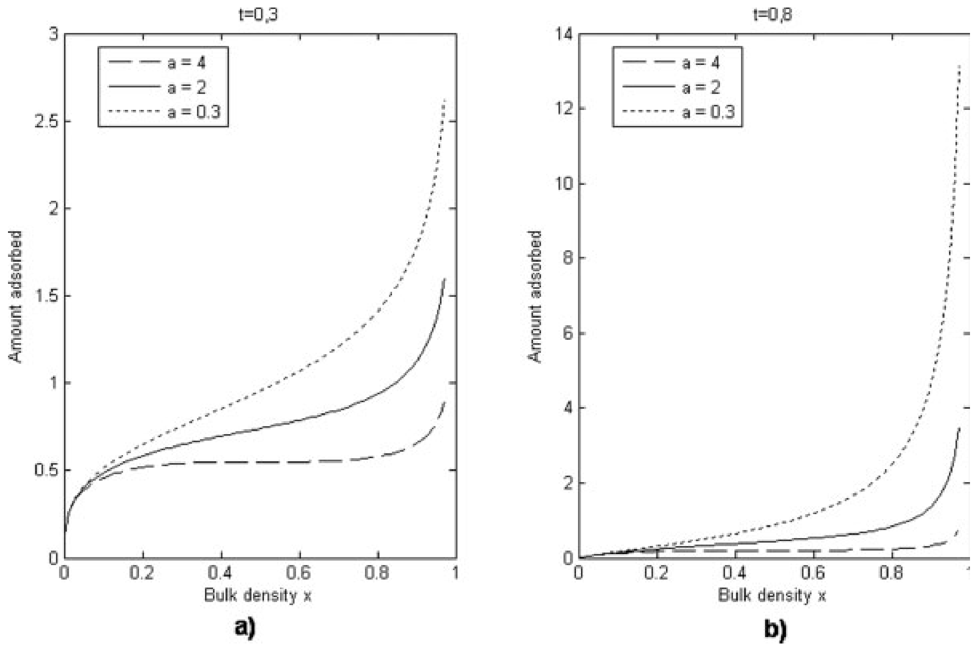

Figure 3. Isotherms of supercritical fluid adsorption for $K = 1$, $t = 0{,}3$ and $t = 0{,}8$ and different value of a.

characteristic energy influences the slope of decrease to the isotherm after the maximum. For small values of kT/E (large values of E, $t = 0{,}3$), the slope of diminution after the maximum and the slope of re-increase after the minimum are greater than these at small values of E ($t = 0{,}8$). Because it is situated in exponent of the Eq. 13 the parameter t influence strongly the value of the adsorbed amount which changes considerably with small changes of the value of t.

Figure 2 represents the adsorption isotherms behavior predicted by the presented equation using two values for the characteristic energy and three values for the coefficient. For example, when the value of a decreases, the position of the maximum increases and occurs at higher bulk density. In the same manner the position of the minimum decreases and moves toward smaller bulk density values. Alike the re-increase after the minimum is related to the value of a. We can also see that the impact of a to the position the maximum and minimum depends on the value of parameter t. With the diminishment of a, the difference between the values of the minimum and the maximum decreases.

If $a = 4$ there are no extrema and the isotherm increases monotonously with the raise of x (Figure 3a). Thus, by the model one can describe the II and III type isotherms according to the standard IUPAC classification.[3,4]

We can conclude from aforementioned discussion that the model is adjustable for the fitting of adsorption isotherms in a wide range of pressures but we may notice that unfortunately Henry's low is not followed at very low pressures. However, this is not of main importance for most industrial applications.

Model Validation

Experimental data at low pressure

To carry out the results obtained by the model at low pressures, the data reported by Reich et al.[49] were used. Figures 4–6 show the adsorption equilibrium isotherm of CH_4, C_2H_4, and C_2H_6 on activated carbon respectively at 301.4, 260.2, 212.7 K and a pressure up to 3.5 MPa. In these conditions CH_4, C_2H_4, and C_2H_6 are in subcritical state. To optimize the parameters, the model is fitted to the experimental data of all temperatures simultaneously. In this work, the MatLab code "nlinfit" is used for the fitting of multiple isotherms data at various temperatures. The parameter values are given in Table 1. The reference temperature is $T_0 = 273.15\text{K}$.

One can observe that at this range of pressures and temperatures the calculated results are in good concordance with the experimental data. The root mean square error is respectively for CH_4, 0.7265; C_2H_4, 0.4635; and C_2H_6, 0.4039. Notwithstanding that the basic idea of this approach is to adapt to the adsorption equilibrium at supercritical conditions at high pressure, the model correlate satisfactorily experimental data at low pressure in subcritical conditions.

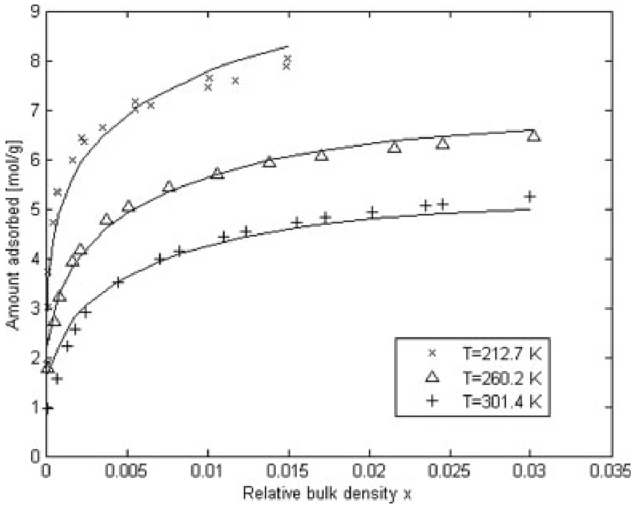

Figure 5. Adsorption isotherms for ethylene on activated carbon at different temperatures.

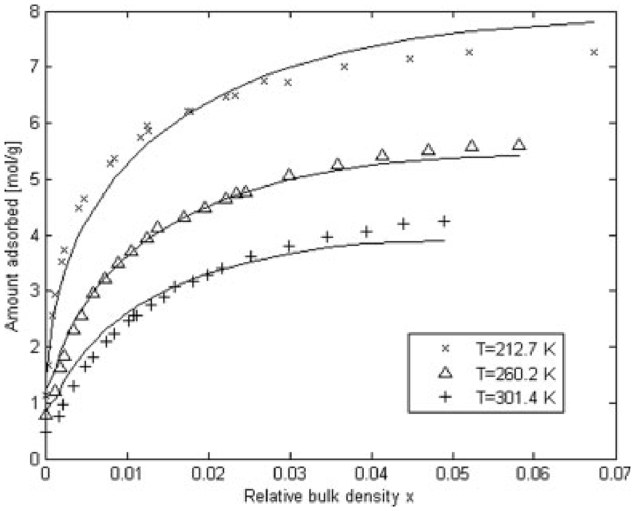

Figure 4. Adsorption isotherms for methane on activated carbon at different temperatures.

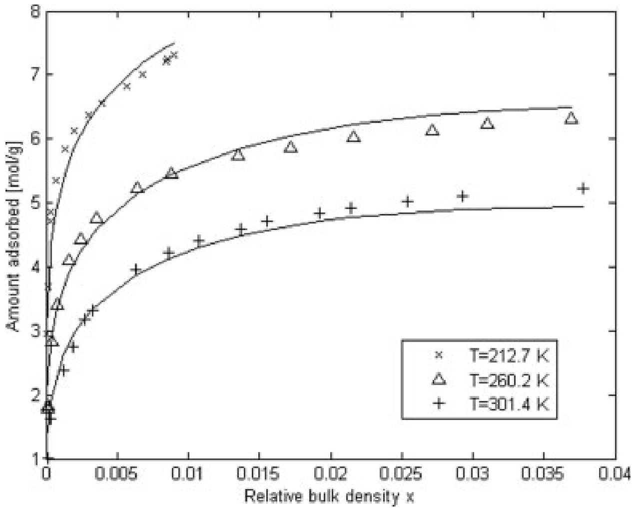

Figure 6. Adsorption isotherms for ethane on activated carbon at different temperatures.

Table 1. Values of the Adjusted Parameters

Gases/Parameters	Γ^0_{max} (mol/g)	b	ℓ	c	s	Square Deviation
Methane	12.95	6.0421	4.0952×10^{-3}	4.6661×10^{-3}	1.7311×10^{-3}	0.0569
Ethylene	11.3455	8.5298	4.1611×10^{-3}	9.6246×10^{-3}	1.0135×10^{-3}	0.2545
Ethane	11.7884	4.3490	3.6695×10^{-3}	8.3668×10^{-3}	8.8360×10^{-4}	0.3653

Experimental data at moderate pressure

Figures 7–9 represents the adsorption isotherms calculated by Eq. 9 and experimental data taken from F. Dreisbach and HW Lösch.[50] In this range of pressure (up to 50 MPa) one can observe the typical isotherms of supercritical fluids with maximum for the adsorbed amount. The predictions by the proposed model, which has three parameters at a given temperature (see Eq. 13), are compared with the results of two models: the Ono-Kondo approach[18–22] using four parameters and 3-Parameter-Isotherm equation.[23–26]

Figures 7 and 8 represents the experimental results for adsorption of Argon and Nitrogen compared with the predictions obtained by the three models. It shows that in present conditions there is a satisfactory agreement between the predictions and the experimental results. The best prediction is obtained with Eq. 9, where the mean square deviation is minimal.

Figure 9 represents the experimental data for adsorption of Methane on activated carbon and the predictions of the three approaches. We can note that the proposed equilibrium equation gives the most satisfying prediction. Further, one can see that the Ono-Kondo approach has a more important difference with experimental data. The results obtained using the 3-PIG equation is also less predictive. The root mean square errors are respectively in case of adsorption of methane 0.1011 for present equation, 0.5742 for Ono-Kondo equation and 0.1562 for 3 PIG model. In case of nitrogen they are 0.0815 for present equation, 0.0801 for Ono-Kondo equation and 0.4447 for 3 PIG model. In the case of argon the root mean square errors are 0.0655 for present equation, 0.1144 for Ono-Kondo equation and 0.1562 for 3 PIG model. We can see that in the exception of adsorption of nitrogen when the equation of Ono-Kondo has a smallest root mean square error, the present equation provides the best prediction and its root mean square errors are less than the others.

Experimental data at very high pressure

Figures 10 and 11 presents experimental data for the adsorption isotherm of supercritical methane and nitrogen at $T = 298.15$ K. We use the experimental data obtained by P Malbrunot et al..[43] These results are compared with the calculated values by the Eq. 9 and the Ono-Kondo equation. As seen in Figure 10, the Ono-Kondo equation is in significant difference with the experimental data. This is due to the fact that this model is able to predict only the maximum of adsorption isotherms and monotonic decrease of the adsorbed amount thereafter. The advantage of the proposed model is its capability to describe the maximum and minimum in the considered pressure range.

Figure 11 presents experimental data by P. Malbrunot et al.[42] for the adsorption of methane on activated carbon at $T = 298.15$ K compared with the present equation and the Ono-Kondo equation. In this case, the minimum of excess adsorption is clearer than in the case of the nitrogen. One observed the good agreement between the experimental data and the amount calculated using the proposed model. The Ono-Kondo equation cannot predict this minimum. The root mean square errors are in case of adsorption of methane 0.1704 for the present equation, and 0.4339 for Ono-Kondo

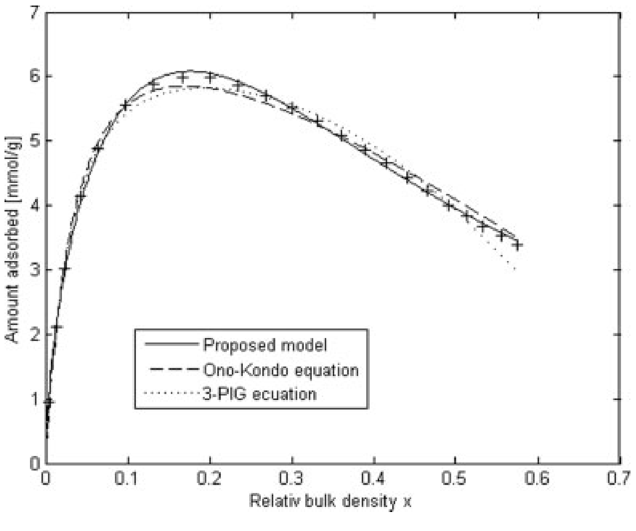

Figure 7. Adsorption isotherms for argon at 298.15 K.

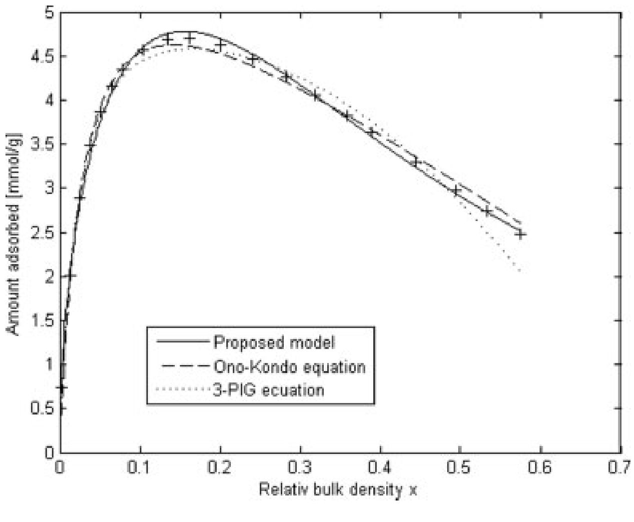

Figure 8. Adsorption isotherms for nitrogen at 298.15 K.

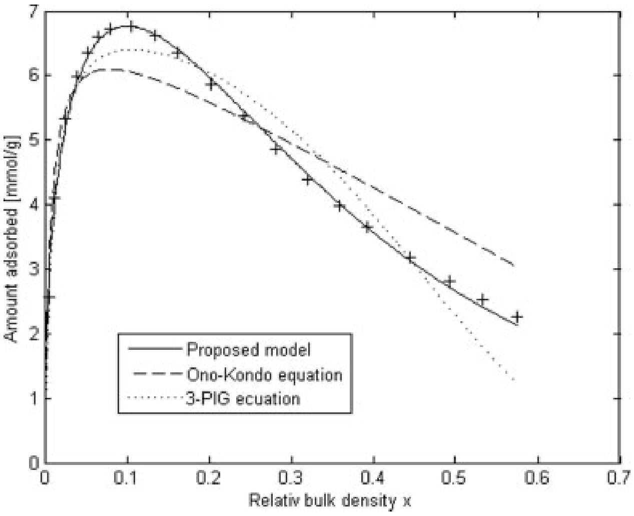

Figure 9. Adsorption isotherms for methane at 298.15 K.

equation. In case of nitrogen they are 0.2021 for present equation and 0.5858 for Ono Kondo equation.

Conclusion

In this article, we present a new equation to predict gas adsorption isotherms up to very high pressure 650 MPa.

The approach is based on the potential theory and the conception of a lattice fluid model. The statistic mechanical description of this system gives a new equation for the calculation of the adsorbed mass excess. Finally, we propose a five parametric model, where the parameters can be obtained by the fitting of the experimental data. The results of the equilibrium equation are compared to experimental data at different temperatures. The agreement between the isotherms obtained with our equilibrium equation and the experimental data is satisfactory. The comparison of the proposed method and two other approaches is also given. The proposed model shows the best prediction in the range of high and very high pressures. The adsorption isotherms predicted by the new approach exhibit a maximum at moderate pressure and a minimum at very high pressure followed by a slight re-increase of the gas excess adsorption. The model has a great adjustability according to the experimental data. In this equation, the parameters for the description of the isotherms have a complex relationship between themselves and this affect to the minimum, maximum and the curvatures of the isotherms. By using this new model, one can describe the isotherms of the gases in subcritical and supercritical conditions up to very high range of pressure. Future works could be extended to supercritical gas adsorption on porous materials at both high pressure and low temperature conditions (Weinberger, Submitted).

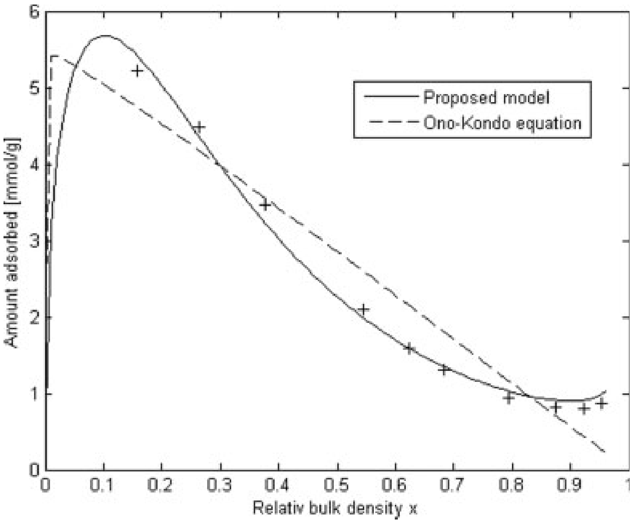

Figure 10. Adsorption isotherm for methane on activated carbon at T = 298 K.

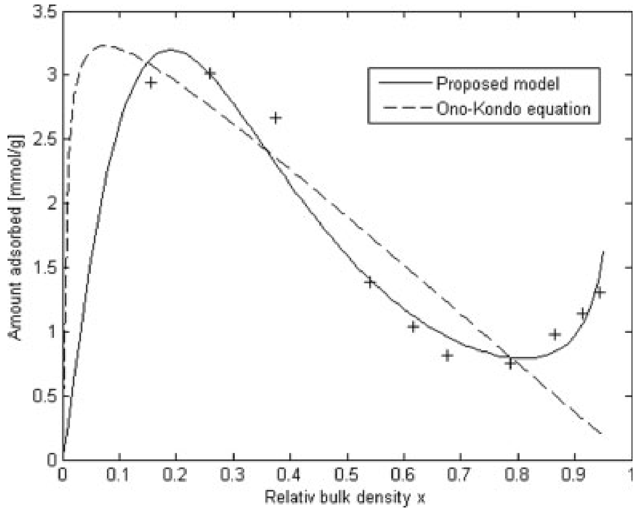

Figure 11. Adsorption isotherm for nitrogen on activated carbon at T = 298 K.

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Notation

A = differential molar work of adsorption, J/mol
a = parameter of the proposed model
b = parameter of the proposed model
E = characteristic energy of adsorption, J
$E_{\mathrm{m-m}}$ = energy of interaction per molecule between two molecules, J
$E_{\mathrm{m-s}}$ = energy of interaction per molecule between the molecules and the solid surface, J
h = constant of Plank, J/s
K = parameter of the model proposed
k = constant of Boltzmann, $m^2 kg/(Ks^2)$
M = total number of cells in the lattice
M_{m} = molar mass, g/mol
m = mass of the molecule, g

N = total number of cells occupied by molecules
N_A = number of Avogadro
r = molecule radius, m
T = temperature, K
t = parameter of the proposed model
W = volume filled by the fluid molecules, cm^3
W_0 = total volume of the adsorbed phase, cm^3
x = degree of occupation of the gas lattice
Z = partition function
z = partition function per molecule

Greek letters

λ = de Broglie's thermal wave length
Γ = excess adsorption, g/mol
Γ_{max} = maximum of excess adsorption, g/mol
δ = coordination number of the lattice
ℓ = coefficient of expansion
θ = degree of filling of adsorption space
Λ = energy of the level, J
μ = chemical potential
Ω = degeneracy number
$\hat{\rho}$ = mass density of the bulk, g/cm^3
ρ^{max} = maximum density, number of molecules per volume unit

Superscripts

g = gas phase
o = referent state
s = adsorbed phase

Subscripts

int = internal part of the partition function
j = number of energy level
total = total partition function
trans = translational part of the partition function

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Appendix

The partition function for a system of N molecules in a lattice may be written in a quantum mechanical form as[46,47]:

$$Z = \sum_j \Omega_j e^{-E/kT} \tag{A1}$$

The summation includes all energetic levels. As usual, β stands for $1/kT$. Equation (A1) is rewritten for gas and adsorbed phases retaining only the maximum term[46]:

$$Z^{\mathrm{g}}_{\mathrm{total}} = \Omega^{\mathrm{g}} \left(z^{\mathrm{g}}_{\mathrm{trans}} z^{\mathrm{g}}_{\mathrm{int}} \right)^{N^{\mathrm{g}}} \tag{A2}$$

$$Z^{\mathrm{s}}_{\mathrm{total}} = \Omega^{\mathrm{s}} \left(z^{\mathrm{s}}_{\mathrm{trans}} z^{\mathrm{s}}_{\mathrm{int}} \right)^{N^{\mathrm{g}}} \tag{A3}$$

If the molecules of the both phases are confined respectively in volumes V^{g} and V^{s} one may write the following expression for the translational partition functions per molecule[46]:

$$z^{\mathrm{g}}_{\mathrm{trans}} = V^{\mathrm{g}} \Lambda^{-3} \tag{A4}$$

$$z^{\mathrm{s}}_{\mathrm{trans}} = V^{\mathrm{s}} \Lambda^{-3} \tag{A5}$$

De Broglie's thermal wavelength is defined by $\Lambda^2 = h^2/2\pi mkT$. Thus, for an isothermal adsorption we have $(z^{\mathrm{g}}_{\mathrm{trans}})_T = const.$ and $(z^{\mathrm{s}}_{\mathrm{trans}})_T = const.$ From this point, gas and adsorbed phase are treated in different manners. Using standard arguments, degeneracy number of the gas is calculated assuming a perfect mixture between occupied and unoccupied cells[46,47]:

$$\Omega^{\mathrm{g}} = M^{\mathrm{g}}!/N^{\mathrm{g}}!(M^{\mathrm{g}} - N^{\mathrm{g}})! \tag{A6}$$

The configurational partition function per molecule of the gas phase ($z^{\mathrm{g}}_{\mathrm{int}}$) is written[43,47]:

$$z^{\mathrm{g}}_{\mathrm{int}} = \exp\left[-\frac{\delta E_{\mathrm{m-m}}}{2kTM^{\mathrm{g}}} N^{\mathrm{g}} \right] \exp(ax^{\mathrm{g}}) \tag{A7}$$

In the equation (A7) $E_{\mathrm{m-m}}$ is the intermolecular energy between two molecules. The expression $N^{\mathrm{g}}\delta/(2M^{\mathrm{g}})$ represents the total number of interaction pairs and the coefficient $a = -\delta E_{\mathrm{m-m}}/2KTM^{\mathrm{g}}$ is a constant for an isothermal adsorption.

At low pressure, the density of the adsorbed phase is significantly greater than that of the gas phase. At low and at high pressure (10–650 MPa), the adsorbed phase lattice is almost full.[50] In these conditions, all quantities related to the adsorbed phase should vary slowly with pressure. Indeed, as shown by Aranovich et al.[51] using the Ono Kondo model, if $x^{\mathrm{g}} > 0.1$ then x^{s} becomes a slowly varying function of x^{g}, i.e., of pressure (see Figure 4, in reference 51). Furthermore, if one assumes that the adsorbed phase lattice is almost full, the degeneracy number Ω^{s} is a decreasing function of N_{s} (total number of adsorbed molecules) i.e., pressure. Whereas the interaction partitions function per molecule:

$$Z^{\mathrm{s}}_{\mathrm{int}} = \exp\left[-\left(\frac{N^{\mathrm{s}} E_{\mathrm{m-s}}}{kT} + \frac{zN^{\mathrm{s}} E_{\mathrm{m-m}}}{2M^{\mathrm{s}} kT} \right) \right] \tag{A8}$$

is obviously an increasing function of N^{s}.[46] Indeed, the interaction energy per molecule between adsorbed molecules $E_{\mathrm{m-m}}$ and the interaction energy per molecule between the molecules and the solid surface $E_{\mathrm{m-s}}$ are negative. This led us to consider that the product $\Omega^{\mathrm{s}}(z^{\mathrm{s}}_{\mathrm{int}})^{N^{\mathrm{s}}}$ is constant as a first approximation. From the discussion above, this approximation is expected to be reasonable when $x_{\mathrm{g}} > 0.1$, allowing thus the model to reproduce the two optima observed in the adsorption curve. For $x_{\mathrm{g}} \ll 0{,}05$, the solid lattice is only partially filled (see Figure 4, reference 51). This may explain why at very low pressure (very low x_{g}) our model does not predict the Henry's law. But, this has no consequences on the general trend of the adsorption curve, as shown on Figures 4–11.

From the discussion follows that:

$$Z^{\mathrm{s}}_{\mathrm{total}} \approx \mathrm{cons}\tan t \left(V^{s} \Lambda^{-3} \right)^{N^{\mathrm{s}}} \tag{A9}$$

Respectively for the gas phase:

$$Z^{\mathrm{g}}_{\mathrm{total}} = \frac{M^{g}!}{N^{g}!(M^{\mathrm{g}} - N^{\mathrm{g}})!} \left[V^{\mathrm{g}} \Lambda^{-3} \exp(ax) \right]^{N^{\mathrm{g}}} \tag{A10}$$

The Helmholtz free energy of both phases is obtained through the standard relation $A = kT\ln Z_{\mathrm{total}}$. Using Eqs. A9 and A10 and applying Stirling's approximation of the factorial one obtains the Helmholtz free energy of both phases.

The relation between the Helmholtz free energy and chemical potential is given by:

$$\mu = \left(\frac{\partial A}{\partial N}\right)_T$$

Thus, for the chemical potential of both phases we obtained:

$$\mu^{\mathrm{g}} = \left(\frac{\partial A_{\mathrm{H}}^{\mathrm{g}}}{\partial N^{\mathrm{g}}}\right)_T = kT\ln\frac{x}{1-x} - kT\ln\left[V^{\mathrm{g}}\Lambda^{-3}\exp(ax)\right] \quad \text{(A11)}$$

$$\mu^{\mathrm{s}} = \left(\frac{\partial A_{\mathrm{H}}^{\mathrm{s}}}{\partial N^{\mathrm{s}}}\right)_T = kT\ln\left[V^{\mathrm{s}}\Lambda^{-3}\right] \quad \text{(A12)}$$

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