Percolation Model of Adsorption-Desorption Equilibria with Hysteresis*

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The problem of equilibrium for adsorption-desorption of condensable vapours in porous media was studied experimentally and theoretically. Algorithms for random generation of square lattices of spherical pore sites and cylindrical pore connections as well as for adsorption and desorption in such networks were developed. Percolation properties of the model were discussed and the model predictions were compared to experimental data for the system Vycor glass—nitrogen.

The effective design and understanding of porous adsorbents or catalyst supports nature depends upon the ability to measure and evaluate experimentally both, the pore size distribution and the topology of the pore network. Recently, new methods based on the use of percolation theory to analyze adsorption-desorption hysteresis were proposed for determination of the pore size distribution and connectivity of porous solids [1—5]. For adsorption and desorption of condensable vapours, the adsorptive in the adsorbent exists as adsorbed molecules on the solid surface, condensate in fine pores and as vapour in the voids. During desorption, as the relative pressure is reduced, systems in which capillary condensation occurs, generally show hysteresis, that is, in a particular pressure range more vapour remains adsorbed than during the initial adsorption process. Classical theories of hysteresis based on single pore adsorption [6, 7] cannot satisfactorily explain some important experimental observations, such as the higher-order adsorption-desorption scanning curves. Models that treat the pore system as an interconnected network have been developed more recently. These models attribute hysteresis to pore blocking where the emptying of a large pore filled with capillary liquid has to be preceded by the emptying of its smaller neighbours [1, 2, 4, 5, 8—10]. Hence, the primary desorption is a connectivity-related phenomenon. Such phenomena can be described best by percolation theory [11].

This contribution presents basic properties of a percolation model based on square lattice structure and compares numerical solutions of the model with experimental equilibrium data for the adsorption-desorption equilibria of nitrogen on Vycor glass.

THEORETICAL

Basic Models of Adsorption-Desorption Hysteresis

The master equation for any model of adsorption-desorption hysteresis is the macroscopic Kelvin equation for capillary condensation

$$\ln \frac{P}{P^0} = \frac{-2\gamma V_{\mathrm{L}}}{RT} \frac{1}{r} \qquad (1)$$

which relates the vapour (condensation) pressure P to the characteristic dimension of the pore connection or the pore site, r.

The hysteresis of capillary condensable vapour has several possible origins. A classical hysteresis theory, the 'independent pore model' [6], regards the difference between the relative vapour pressures at which ink-bottle pores fill and empty as the prime factor causing hysteresis. There is a single relative vapour pressure corresponding to the filling of the pore site with radius, R_{A}. On the other hand, there is a different single relative vapour pressure corresponding to the emptying of the pore throat with radius R_{D}.

More elusive is the 'pore-blocking model' [1, 4, 5, 12], which assumes that the pore cannot empty until at least one of its neighbours has emptied as a consequence of smaller dimension of the neighbours

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or corresponding connections. The incorporation of the pore-blocking effect extends the independent pore theory. There is still a single pressure for filling but several for emptying, one for each connection to the neighbouring pores. The pore-blocking effect depends crucially on the interconnections and the interconnectedness of the pore space of the porous material. In this work the idea of pore-blocking model is used for modelling the sorption processes using the percolation theory.

Percolation Theory of Adsorption-Desorption with Hysteresis

Percolation theory is the theory of connected structures formed by random links on a lattice or tree. The classical percolation theory is focused on two problems, the bond percolation problem, and the site percolation problem. The bond problem of percolation theory is closely related to the desorption process for systems with hysteresis. At some value of the relative vapour pressure, x, there is an associated probability, p, that condensate can evaporate from the bond (connection) and so empty the site (cavity) of the pore. The condition for such bond emptying must also include the probability that the bond is connected via conductive bonds to the edge of the network. During the desorption from ideal (infinite) system, the probability for initially filled system, p, is progressively reduced until, at some critical (threshold) probability, p^T, the system starts to empty. Thereafter, the pores continue to empty as they become connected and more and more windows are conductive. The position of the percolation threshold is affected by the connectivity C, which is defined as the average number of windows per pore site. The explanation for the sharp knee on the desorption isotherm where desorption commences is that at this point (see Fig. 2) the connection-making process proceeds in a cascade-like manner into the bulk of the material and empty pores are no longer restricted to the surface of the adsorbent. Obviously, the size of the sample has impact on the sharpness of the desorption knee and, if the sample consists of small groups of pores (e.g. micro-particles of bi-disperse adsorbent), the knee can be significantly rounded, as presented in Fig. 1.

During adsorption, the probability that a pore site fills at some value of x is q, and is unaffected by interconnectivity effects. The primary adsorption process in the capillary condensation region can be treated as a classic site percolation problem. Pores with different dimensions are randomly distributed in the pore space. All pores are equally accessible and connectivity of the pores plays no role since for geometric and thermodynamic reasons all of the windows to a given pore site may fill with condensate before the site fills. However, even if the pore site becomes isolated from the bulk vapour, it can still fill by condensing vapour
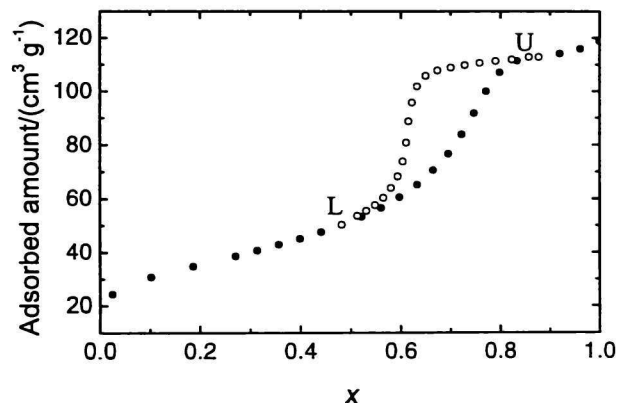

Fig. 1. Experimental adsorption-desorption equilibrium data for the system Vycor glass—nitrogen at 77 K. ● Experimental adsorption, ○ experimental desorption. L and U are limiting points of the hysteresis loop.
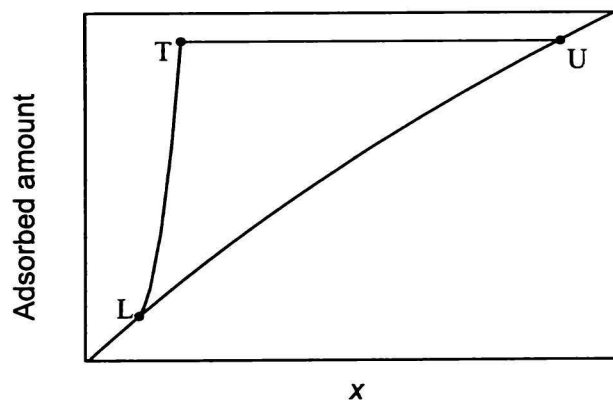

Fig. 2. Theoretical hysteresis-dependent adsorption-desorption equilibria for infinite system. The points L, U have the same meaning as in Fig. 1, T signs the percolation threshold position.

from adjacent pores that can then refill from the bulk vapour. All that matters is the effective size of the pore sites. Percolation properties of the primary adsorption are of particular interest for the kinetic behaviour of the process [13, 14].

A disagreement between the theory and experiment exists for the case of real primary desorption, since the real desorption isotherm is not horizontal and desorption does occur. Most of the theoretical and experimental studies indicate that the finite size of the porous material micro-particles and corresponding desorption from the surface of the micro-particles is the main reason of this discrepancy. Different explanations (decompression or nucleation) for this fact were discussed in literature [4, 5]. Empirical correction functions were proposed for computation of the real amount adsorbed during primary desorption, as well as during higher-order desorption processes. More sophisticated model to explain and unify equilibrium and kinetics of vaporization from surface of micro-

particles based on 'shell and core' approach was developed in our recent study [13].

For the modelling of processes inside the pore structure different types of lattice models can be used. In our previous papers [4, 5, 13—15] the Bethe tree structure for modelling the pore sites interconnectedness was used. The main attraction of Bethe tree structure is that the description of its behaviour when it is randomly filled or emptied can be carried out analytically. Bethe tree can give simplified expressions for several properties of the porous medium, while retaining most features of the percolation theory [16, 17]. However, these models can be used only for the simplest cases, e.g. for one-component isothermal system, otherwise the analytical solutions (if obtainable) would be too 'awkward'. The main theoretical drawback of the Bethe lattice is that it does not allow for reconnections among the pores.

A more realistic network is obtained if the pores are distributed on a lattice with reconnections, such as square (2-D) or cubic (3-D) lattices. In our percolation model, the alternative for 2-D lattice was used in which spherical pore sites are connected to each other by cylindrical connections. The pore sites are placed at the nodes, and the connections along the bonds of the lattice. The pore site volume was calculated following its characteristic radius and it was assumed that the pore volume resides entirely in the pore sites. Negligible volume of each connection was supposed. First, the ideal lattices (without defects, every internal pore having four connections) were treated. The radius of each pore site was generated first, using subroutine RNWIB from IMSL library, which generates pseudo-random numbers from a Weibull distribution. Once the pore sites were generated, four pore connections for each pore site were generated using subroutine RNSTA, which generates pseudo-random numbers from a stable distribution. A lattice with a connectivity of three could be obtained by removing at random 25 % of the bonds. The important constraint for the pore connections generation was that the radius associated with the pore site must be greater than the radius of any of its connections. The generation of the pore sites for any experimental adsorption-desorption systems is simpler and is associated with the experimental primary adsorption isotherm. On the other hand, the generation of the pore connections is more complicated and is associated with the primary desorption branch of the main hysteresis loop.

Modelling of Adsorption-Desorption in 2-D Square Lattices

Two basic models of hysteresis were tested using the 2-D lattices and compared to experimental data: *independent pore model* and *pore-blocking model*. For both models the primary adsorption process is the same. The amount adsorbed increases with increasing

relative pressure. Before the capillary condensation occurs the amount adsorbed is related to the thickness of adsorbed film on the pore surface. The film thickness is determined from the relative pressure value using an empirical relation [7, p. 135]

$$t = 0.31377 \left(\frac{-5}{\ln(x)} \right)^{1/3} \qquad (2)$$

At the lower limiting point – the starting point for hysteresis loop, L (see Figs. 1 and 2), the capillary condensation commences in finest pores. For these pores the sum of thickness of adsorbed film and inner core must be lower than the radius calculated from eqn (1). The amount adsorbed in such pores is computed from the volume of entire pore site assuming that the site is completely filled with capillary condensate. As the pressure is progressively increased, wider and wider pores are filled until the relative pressure x^U corresponding to the upper limiting point U is reached. It is presumed that at U all pores are already filled with capillary condensate and any adsorption beyond this pressure is associated only with the change of menisci freely accessible to the vapour.

The primary desorption process is the reversal of the above. The situation for adsorbed film on the surface of the pore is the same for desorption as for adsorption. For the independent pore model, we use basically the same algorithm as for primary adsorption. After the evaporation of the liquid from the pore, there still remains an adsorbed film that is equivalent to the value of relative pressure [7]. Size distribution of pore connections is irrelevant and cannot be evaluated for the independent pore model.

The primary desorption modelled with the pore-blocking approach needs a more complicated algorithm. The pore-blocking effect depends on both, radius of a pore and connection of the individual pore with the vapour phase (existence of connection between the pore and the adsorbent outer surface). Whether a pore remains full or empty depends upon the outer surface accessibility to the condensed vapours contained in the pore. After the liquid evaporation from the originally filled pore site, there still remains an adsorbed film in both, the pore site and the pore connections, corresponding to the value of relative pressure [7].

EXPERIMENTAL

Adsorption-desorption equilibria for systems with condensable vapours are useful for more sophisticated determination of the pore size distribution and connectivity of the porous medium. Vapour of liquid nitrogen at its boiling temperature of 77 K is normally used in such experiments although other vapours, e.g. water vapour can also be used. Vycor glass, a porous

glass, which has been widely used as a model material in studies of properties of fluids and molecules in highly confined geometries, was used as adsorbent for experimental study with nitrogen vapour, while the large pore volume effectively adsorbs bulk fluids by capillary condensation at higher ambient vapour pressures [18]. Sorption data were obtained using an Erba Sorptomatic 1900 apparatus (Milan, Italy). Equilibrium results show significant hysteresis loop of Type-H2 (IUPAC classification), as seen in Fig. 1.

RESULTS AND DISCUSSION

The basic qualitative properties of the square lattice percolation model and its capability to predict adsorption-desorption hysteresis were studied prior to its application to experimental data. First, the test of the model capability to predict hysteresis qualitatively was carried out. The visualization of both, the primary adsorption (Figs. 3a and c) and the primary desorption (Figs. 3b and d) process is presented. The distributions of pores filled with capillary condensate were compared for relative pressures inside the main hysteresis, above and below the percolation threshold. Results for the square lattice 50 × 50 are shown. Several interesting features and differences can be emphasized. First, unlike the random distribution of filled pore sites for adsorption (*cf.* Fig. 3a *vs.* 3c) the distribution for desorption (*cf.* Fig. 3b *vs.* 3d) is significantly more
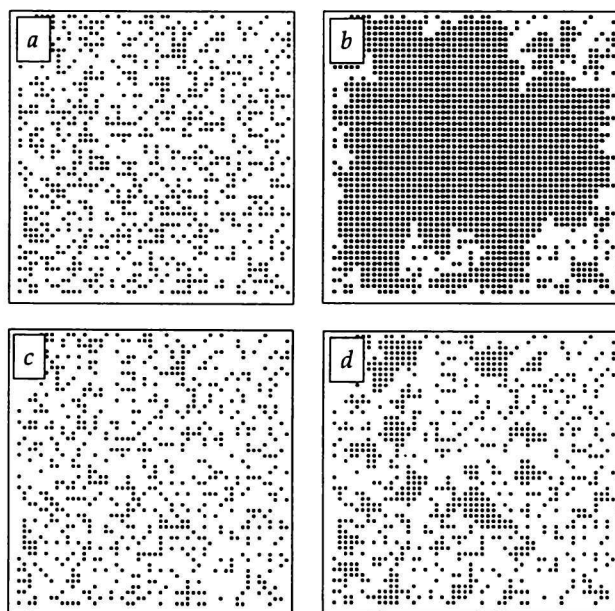

Fig. 4. Impact of lattice size on the shape of equilibrium isotherms. Lattice dimensions: 10 × 10 (———), 30 × 30 (– – –), 50 × 50 (· · ·), 100 × 100 (– · –).

Fig. 3. Distribution of pores filled with capillary condensation for the same relative pressure inside the main hysteresis loop. 2-D lattice with 50 × 50 pore sites and connectivity $C = 4$. a) Primary adsorption, $x = 0.58$; b) primary desorption, $x = 0.58$; c) primary adsorption, $x = 0.553$; d) primary desorption, $x = 0.553$.
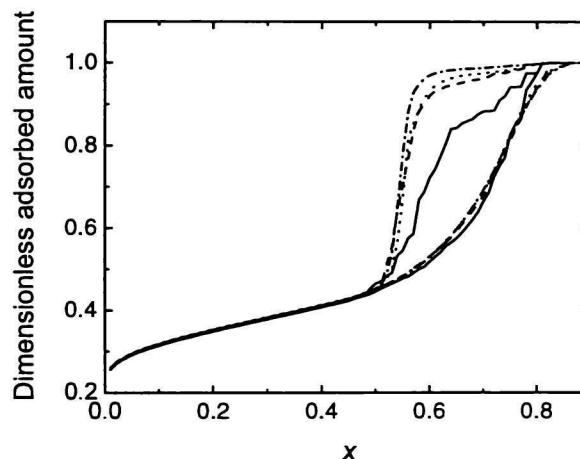
"organized". During desorption for relative pressure above the percolation threshold, $x = 0.58$ (Fig. 3b), there are small clusters of empty sites at the edges of the lattice and a compact core of the filled sites. For relative pressure below the threshold, $x = 0.553$ (Fig. 3d), one can still observe small clusters of filled pores in the network, however, there are several chains of empty (connecting) pores in both directions. Fractions of filled sites for desorption, significantly higher than for adsorption, exhibit the adsorption-desorption hysteresis.

Then, as the second, the test of the impact of the lattice size on the equilibrium isotherms shape was investigated. The square lattices with different lattice sizes (10 × 10, 30 × 30, 50 × 50, 100 × 100) were tested. Fig. 4 shows that results for the lattice 100 × 100 pores are still different from those for the lattice 50 × 50. As expected [3, 19], the lattice size increase extends the horizontal part of the theoretical primary desorption branch of the hysteresis loop between upper limiting point and the percolation threshold. Simultaneously, the percolation threshold (the rounded knee) of the primary desorption is moving to lower relative pressures. Moreover, the rounded knee is sharper for bigger lattices. The optimum size of lattice, applicable to various experimental systems can still be limited by the computer capacity. Unlike the infinite Bethe tree structures, the finite size of the square lattice reflects the finite size of microparticles in real porous materials better.

The third test of the 2-D model was aimed at its capability to predict experimentally observed secondary processes. In Fig. 5 the comparison of predicted scanning curves with the independent pore and the pore-blocking model is shown. The solution with the independent pore model (Fig. 5a) is qualitatively different from the experimental results published elsewhere [1, 5, 12]. On the other hand, pore-blocking model
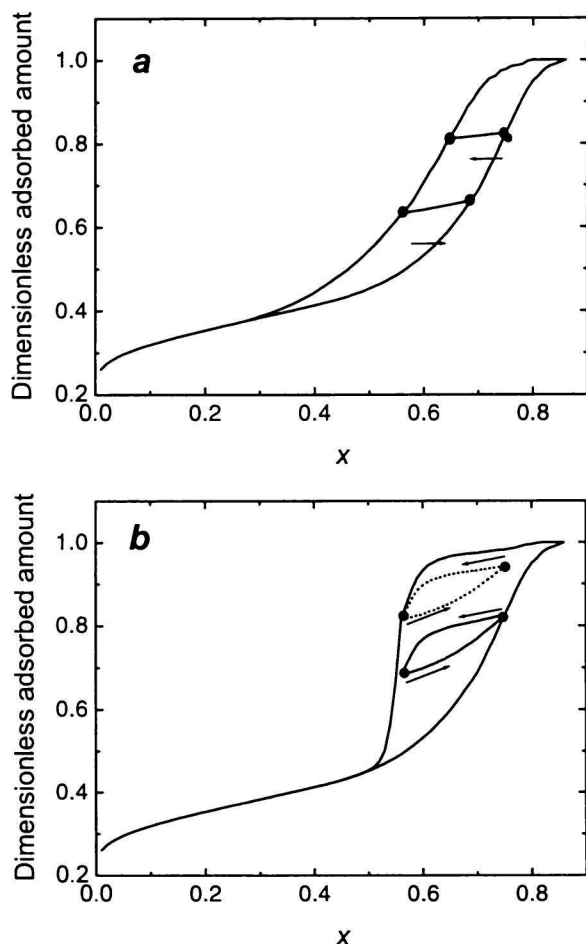
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Fig. 5. Adsorption-desorption scanning curves (arrows) for the system Vycor glass—N$_2$. *a*) Independent pore model, *b*) pore-blocking model.

Fig. 6. Comparison of experimental data for the system Vycor glass—N$_2$ at 77 K with mathematical solutions using independent pore (– – –) and pore-blocking (———) models for a square lattice with the connectivity $C = 4$. ● Experimental adsorption, ○ experimental desorption.

Fig. 7. Size distribution of *a*) pore sites (adsorption). *b*) pore connections (desorption).

(Fig. 5*b*) successfully predicts the shape and the position of different scanning curves. All the tests proved that this simple network model could be used to compute the theoretical adsorption-desorption equilibria for systems with hysteresis.

The experimental system Vycor glass—nitrogen was chosen for comparison with theoretical predictions of the square lattice model (Fig. 6). The independent pore model gives a wrong shape of the hysteresis loop. Better agreement with experimental data was obtained for the pore-blocking model, which fairly predicts both, the adsorption and the desorption isotherm. The model exhibits a slow decrease of adsorbed amount between the upper limiting point and the percolation threshold and rapid decrease of adsorbed amount below the percolation threshold. However, the position of theoretical percolation threshold is at a lower relative pressure than the one experimentally observed. It suggests that the connectivity of the real network can be higher than four, the maximum value for the selected 2-D network.

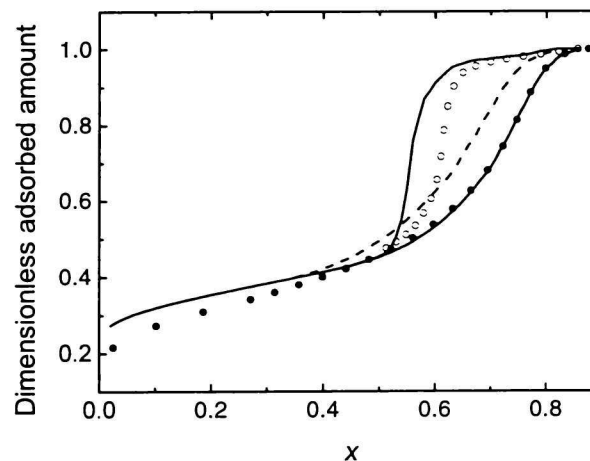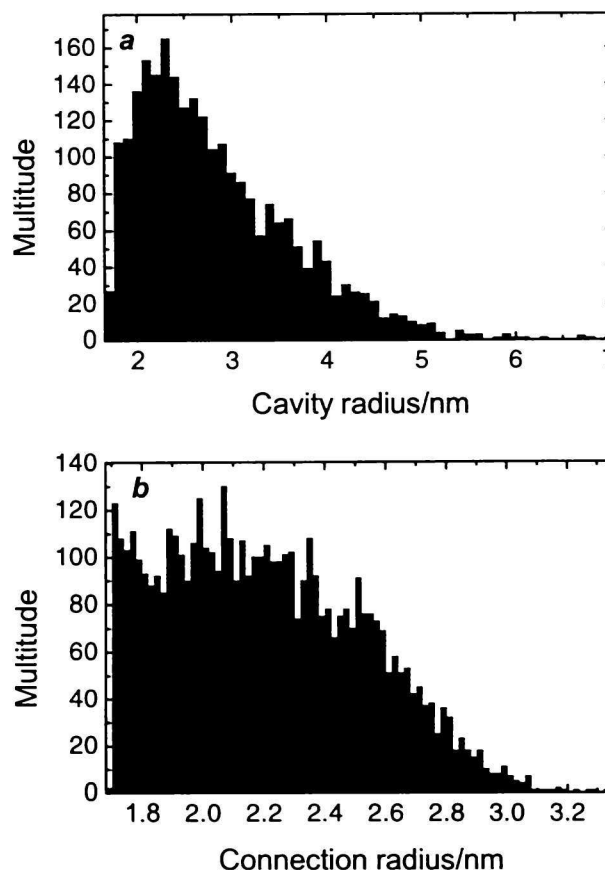Another possible reason of the quantitative differ-

ences between the experiment and the model simulation is the shape of a priori chosen distribution functions for the pore sites and the pore connections. Various a priori chosen explicit distribution functions were

tested and used for pore cavities and pore connections (2-parameter Weibull distribution for the sites and a stable distribution for the connections, both from IMSL library). Evaluated size distributions of the pore cavities and the pore connections are plotted in Fig. 7. More sophisticated method for evaluation of the size distribution functions will be reported in our coming paper [20].

CONCLUSION

A percolation square lattice model for modelling the adsorption-desorption equilibria for systems with hysteresis was developed. Satisfactory agreement with experimental data for the system Vycor glass—nitrogen was obtained by incorporating the pore-blocking assumption into the percolation model. Parametric study of the lattice size was performed showing that the lattice size 30 × 30 is sufficient to get satisfactorily smooth fits of the primary adsorption and desorption equilibrium curves. The percolation square lattice model containing the pore-blocking assumption was also successful for modelling the equilibrium scanning curves inside the hysteresis loop. Generally, improvement of the experimental data fit could be obtained by simultaneous optimization of the lattice size and the lattice connectivity as well as the testing of different distribution functions for the pore sites and the pore connections. Higher flexibility of the model can be expected by employing cubic (3-D) lattices. Evaluated connectivity and size distributions for both, the pore sites and the pore connections can be subsequently used also for modelling of other important processes in porous materials, e.g. adsorption-desorption kinetics, pore plugging, deactivation of catalyst, solid-fluid reactions, etc.

SYMBOLS

C	connectivity	
p	probability that the bond is filled by capillary condensate	
q	probability that the site is filled by capillary condensate	
r	bond or site radius of curvature	nm
P	vapour pressure	Pa
P^0	saturation vapour pressure	Pa
R	gas constant	J mol^{-1} K^{-1}
T	temperature	K
t	adsorbed film thickness	nm
V_L	molar volume of the liquid adsorbate	m^3 mol^{-1}
x	relative pressure	
γ	surface tension	N m^{-1}
L	lower limiting point	
U	upper limiting point	
T	percolation threshold	

Subscripts

A	adsorption
D	desorption

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