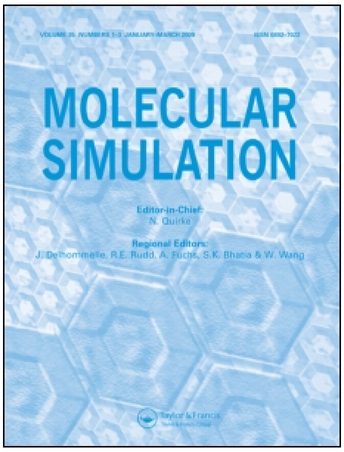
This article was downloaded by:
On: *14 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Simulation

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

Connectivity effects for slit pores linked by a channel

V. V. Sizov[a]; E. M. Piotrovskaya[a]; E. N. Brodskaya[a]
[a] St. Petersburg State University, St. Petersburg, Russia

To cite this Article Sizov, V. V. , Piotrovskaya, E. M. and Brodskaya, E. N.(2005) 'Connectivity effects for slit pores linked by a channel', Molecular Simulation, 31: 11, 759 — 763
To link to this Article: DOI: 10.1080/08927020500262630
URL: http://dx.doi.org/10.1080/08927020500262630

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Molecular Simulation, Vol. 31, No. 11, 15 September 2005, 759–763

Taylor & Francis
Taylor & Francis Group

Connectivity effects for slit pores linked by a channel

V. V. SIZOV*, E. M. PIOTROVSKAYA§ and E. N. BRODSKAYA||

St. Petersburg State University, Universitetskii pr. 26, 198504 St. Petersburg, Russia

(Received June 2005; in final form July 2005)

This paper describes a Monte Carlo computer simulation study of connectivity effects in a system of two parallel slit pores and a quasi-one-dimensional joint. A numerical method for evaluation of accessible volume in computer simulation studies of adsorption in pores is presented and applied to simple slit pores and systems of interconnected pores. A local version of the grand canonical ensemble Monte Carlo method is used to study adsorption under conditions mimicking mass transfer limitations.

Keywords: Monte Carlo simulation; Adsorption; Pore connectivity; Accessible volume

1. Introduction

The influence of pore space connectivity on the properties of adsorbed fluid is recognized as one of the most significant effects determining the course of adsorption in pores [1]. Computer simulation studies provide a convenient way for elucidating the possible molecular mechanisms of this influence. However, many popular models of carbonaceous and siliceous adsorbents are based on the isolated pore concept, which renders them as useless for studying the effects of connectivity. On the other hand, for more realistic models of carbonaceous and siliceous adsorbents, the effects of connectivity can be concealed by other important factors, thus hindering the ability to study selectively the desired property of porous systems by means of computer simulations. One possible way of solving this problem is to construct a model of interconnected pores from simple blocks, such as slit and cylindrical pores. Apart from being computationally inexpensive, this approach also presents a good choice of well-studied reference (i.e. non-interconnected) systems.

While discussing connectivity effects one should distinguish two types of interactions between different regions of the pore network: (a) direct through-space interactions, i.e. interactions, primarily, long-range of molecules adsorbed in one pore with the molecules in the adjacent pore (this type of interactions can be observed even for porous systems without topological connectivity); (b) through-fluid interactions, i.e. interactions between molecules adsorbed in two non-interacting pores with molecules adsorbed in the region connecting both pores. For non-polar fluids the typical range of the first type of interactions does not exceed 1.0–1.5 nm, while their strength is rarely sufficient to have qualitative impact on the properties of the porous system. The distinctive feature of the latter type is the explicit connectivity of the system provided by "windows" between spatially separated pores.

The goal of this work is to study the effects of pore space connectivity separately from direct through-space interactions. For this purpose, we have developed a simple model of connected pores, consisting of two parallel slit pores linked by a quasi-onedimensional channel in the z direction (figure 1). The slit pore width of 3.4σ was chosen allowing a maximum of three adsorbed fluid layers in either pore. Periodic boundary conditions were applied in x and y directions, leading to a periodically interconnected system with one connecting channel per unit cell area of the solid wall between the slit pore. We considered two model systems, differing in the effective diameter of the connecting channel: ca. 2.5σ for system **I** and 3.5σ for system **II** (where σ is the geometrical parameter of Lennard–Jones potential used for fluid–fluid interactions). Apart from the outermost layers of the solid, which were described by the 10-4-3 potential [2], the structure of the adsorbent was modeled following the explicit atom approach. The connecting channel was

---

*Corresponding author. Tel.: +7-812-428-4066. Fax: +7-812-428-6939. E-mail: sizovvv@mail.ru
§Tel.: + 7-812-428-4066. Fax: +7-812-428-6939. E-mail: elena@nonel.pu.ru
||Tel.: + 7-812-428-4093. Fax: +7-812-428-6939. E-mail: brodsky@chem.spbu.ru

Molecular Simulation
ISSN 0892-7022 print/ISSN 1029-0435 online © 2005 Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/08927020500262630

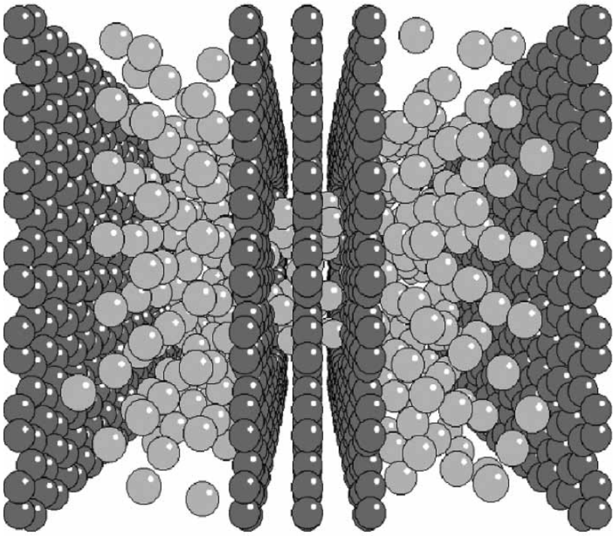


Figure 1. The connected pores model with adsorbed Lennard–Jones fluid particles.

created by removing solid atoms from the graphite-like wall between the pores and replacing the carbon atoms on the edges of the resulting vacancy by united-atom CH(arom.) groups. The shape of the connecting channel cannot be readily described as cylindrical, though the estimate of its average width presented above was obtained basing on this assumption.

In order to exclude the direct pore–pore interaction, the length of the connecting channel was chosen to be approximately equal to the radius of effective intermolecular interactions. We considered a simple Lennard–Jones fluid with the cutoff radius equal to 3.5σ. Therefore, the length of the connecting channel of approximately 1.8σ together with the typical fluid–wall distance of 0.95σ results in a minimum distance of about 3.7σ between molecules adsorbed in two different slit pore regions. Since this distance is greater than the cut-off radius chosen, the direct interaction of fluid molecules in adjacent pores is completely omitted in our model.

2. Methodology

An obvious choice of the reference system for the study of connectivity effects is an isolated slit pore, identical to those appearing in the connected system. Any difference occurring between adsorption isotherms for an isolated slit pore and the interconnected system should be treated as a connectivity effect. However, all isotherms should be calculated using an identical technique. If the density vs. chemical potential isotherms are chosen for analysis, the estimation of density of the adsorbed fluid $\rho = N/V$, where N is the number of adsorbed molecules and V is the pore volume, can be hindered by the complexity of the pore shape when interconnected systems are considered.

2.1 Accessible volume evaluation

The technique used here to estimate the actual volume which can be accessed by fluid particles is different from the traditional *effective pore width* approach, which is frequently used to evaluate the volume of idealized slit-like pores. This is mostly due to the fact that the definition of the effective pore width for a complex porous system fails to produce the effective pore volume since one has to take into account the volume of the region (or regions) connecting the simple-shaped pores. Thus, we chose the accessible volume estimation method based on the closest-contact surface for fluid–solid interactions. We define the closest contact distance from a statistical point of view, i.e. as the minimum distance between fluid particles and adsorbent surface observed in a preliminary test simulation with temperature and fluid density similar to those used in the production run. Taking into account the possible heterogeneity of the solid surface, we consider the fluid–solid interaction energy associated with the closest contact distance, rather than the distance itself.

The minimum distance from the fluid particle to the solid wall observed in our test simulations was 0.76σ, though the probability of such configurations was extremely low; a more reasonable estimate of the closest contact distance is $0.84/0.88\sigma$. In our preliminary simulations the maximum interaction energy rarely exceeded $+15\varepsilon$, which was chosen as the closest contact energy criterion E_0 for accessible volume evaluation. However, lower interaction energy values, such as $E_0 = 0$, can hardly result in a significantly different value of the accessible volume. This is due to the fact that repulsion energy for Lennard–Jones-like potentials rises very fast for distances below 0.95σ. The effect of varying the contact energy on the resulting accessible volume will be illustrated below.

Using the contact energy $E_0 = 0$ as input we are now able to build the limiting surface accessible for the centers of mass of the fluid particles. This is not, however, our ultimate goal, since the accessible volume should include those regions of the pore space, which can be accessed by any part of the fluid particle. Therefore, we introduce the effective diameter of fluid particles, d_{eff}, which allows us to treat fluid particles as bodies of finite size rather than point masses. For a Lennard–Jones fluid below the reduced temperature $2.0/2.5\,\varepsilon/k_{\mathrm{B}}$ (where k_{B} is the Boltzmann constant) our simulations suggest d_{eff} equal to 0.87σ.

The calculation of the accessible volume is performed via a two-step numerical procedure on a 3D grid covering the entire simulation cell (figure 2). The first step includes the evaluation of fluid–solid interaction energy over the simulation cell and the determination of the closest contact surface and the volume accessible to the fluid particle center of mass, as suggested by the E_0 criterion.

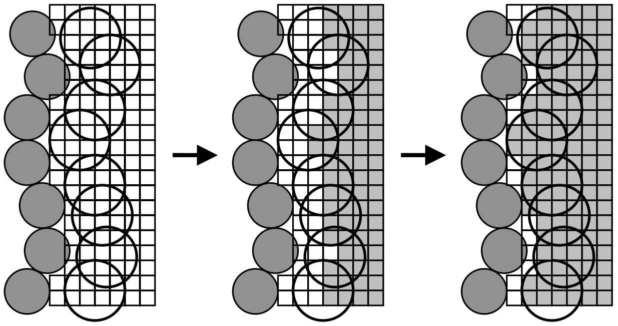


Figure 2. Two-step algorithm for accessible volume calculation. Dark circles represent atoms of the solid, open circles are the possible positions of fluid particles.

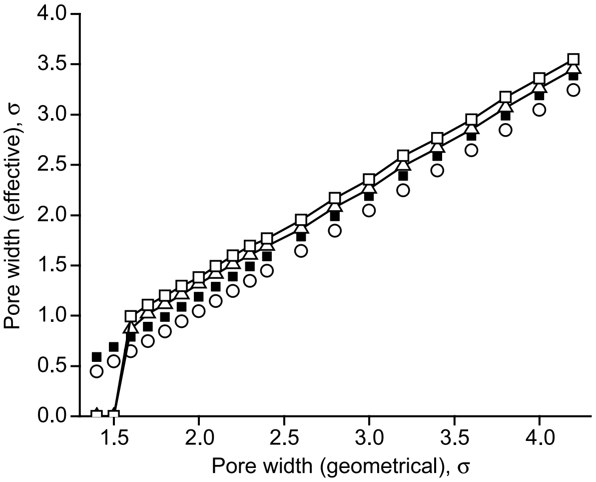


Figure 3. Effective pore width for an ideal graphite slit pore evaluated using different techniques. Filled rectangles: $H_{\mathrm{eff}} = H - 0.813\sigma$; open circles: $H_{\mathrm{eff}} = H - 0.956\sigma$; open triangles: accessible pore width for $E_0 = 0$; open rectangles: accessible pore width for $E_0 = +15\varepsilon$.

The second step covers the estimation of the volume accessible to the part of a fluid molecule other than the center of mass, which is performed by applying the d_{eff} criterion to the closest contact surface. In this work, the second step integration is carried out using the same spatial grid as in the first step; however, a finer grid may be used for this purpose. The grid scale was chosen to reproduce the volume of a sphere with the diameter equal to d_{eff}: 0.043σ was considered a reasonable choice in terms of both accuracy and the number of grid points. The proposed algorithm can be readily implemented in parallel with near-absolute scalability.

As the first system for the testing of the proposed accessible volume evaluation method we have chosen the isolated carbonaceous slit pore with solid walls composed of carbon atoms ($\varepsilon/k_{\mathrm{B}} = 28\,\mathrm{K}$ and $\sigma_{\mathrm{solid}} = 0.340\,\mathrm{nm}$). This system has received a lot of attention, and many empirical approaches to estimating the pore volume have been proposed; so, the isolated graphitic carbon pore is a perfect reference for evaluating the performance of our numerical procedure. In terms of effective pore width one can use the general expression

$$H_{\mathrm{eff}} = H - C,$$

where H is the geometrical pore width (i.e. normal distance between centers-of-solid-atoms planes), C—inaccessible pore space correction. The common choices for C are: σ_{solid} and $\sigma_{\mathrm{SF}} = 0.5(\sigma_{\mathrm{fluid}} + \sigma_{\mathrm{solid}})$, as well as $0.85\sigma_{\mathrm{SF}}$ [3]. For the case of methane adsorption in carbon pores ($\varepsilon/k_{\mathrm{B}} = 148.1\,\mathrm{K}$, $\sigma_{\mathrm{fluid}} \equiv \sigma = 0.373\,\mathrm{nm}$) this leads to inaccessible region widths of 0.912σ (0.340 nm), 0.956σ (0.356 nm) and 0.813σ (0.303 nm), respectively. The plots of effective vs. geometrical pore width calculated using different methods are presented in figure 3. The effective pore width was calculated using two of the empirical approaches with $C = 0.956$ and 0.813σ, as well as the accessible volume evaluation technique with $E_0 = 0$ and $+15\varepsilon$ (ca. 2200 K). To obtain the accessible pore width the accessible volume was divided by the area of the simulation cell. The agreement between different methods used for evaluating the pore width is reasonable, though for $H = 1.7$ the difference between empirical formulas and the numerical approach exceeds 15% for $E_0 = 0$ and 25% for $E_0 = +15\varepsilon$. This might be due to the fact that some empirical approaches neglect the chance of fluid molecules approaching the solid wall close enough to reach positive solid–fluid interaction energy values. A noteworthy feature of the numerical method is zero H_{eff} obtained for all pore widths H below 1.6σ: the concept of the minimum pore width for which adsorption is possible cannot be incorporated into most empirical expressions for effective pore width.

For an isolated slit pore with heterogeneous walls, such as the one studied in [4,5], we can obtain a similar dependence, using the $\sigma_{\mathrm{SF}} = 0.716\sigma$ value averaged over all atoms and united-atom groups forming the pore walls (figure 4). The agreement between the empirical formula and the numerical estimate of the effective pore width is

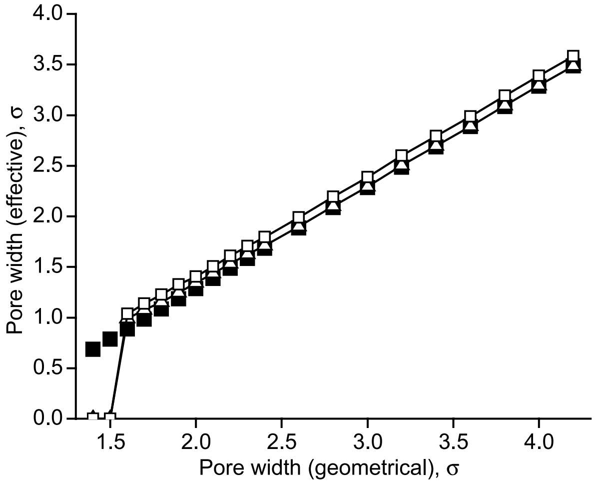


Figure 4. Effective pore width for an activated carbon slit pore evaluated using different techniques. Filled rectangles: $H_{\mathrm{eff}} = H - 0.716\sigma$; open triangles: accessible pore width for $E_0 = 0$; open rectangles: accessible pore width for $E_0 = +15\varepsilon$.

better than for a graphite-like slit pore. The numerical approach should have an additional advantage when describing a strongly heterogeneous surface, e.g. one with "pits" and "cracks".

For the two models of porous systems considered in this work (**I** and **II**), the accessible volumes calculated using $E_0 = +15\varepsilon$ and $d_{\text{eff}} = 0.87\sigma$ were 404.3 and $419.9\sigma^3$, respectively. This is a definite improvement over the $606.5\sigma^3$ ($L_x = 8.97\sigma$, $L_y = 7.77\sigma$, $L_z = 8.70\sigma$) volume of the simulation cell, since the latter figure cannot be used for estimating the total fluid density. As compared to the $192.7\sigma^3$ volume of a single isolated slit pore, the interconnected double-slit-pore system has only 5 to 9 percent greater volume provided by the availability of the connecting channel. In fact, an asymmetrical isolated slit pore with one "solid" wall and one "holed" wall should have an accessible volume of nearly $200\sigma^3$. Thus, both the 2.5 and 3.5σ connecting channels are responsible for only a small fraction of the total accessible volume.

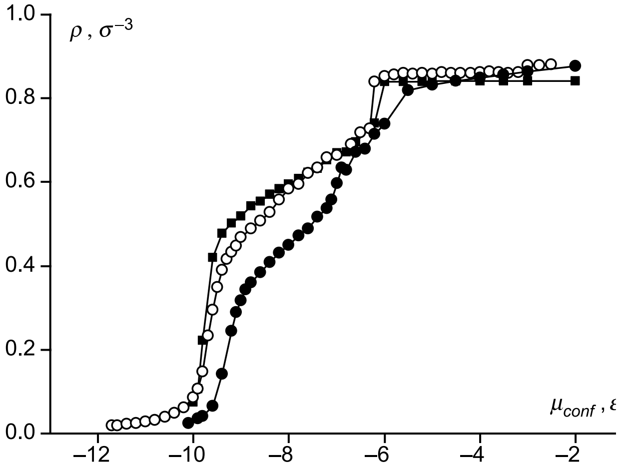


Figure 5. Methane adsorption isotherms for systems **I** and **II** and the reference isolated slit pore calculated at 111 K using the conventional GCMC method (filled rectangles—reference slit pore; open circles—system **I**, filled circles—system **II**).

2.2 *Local GCMC technique*

The primary approach to computer simulation of adsorption used in this work is the grand canonical ensemble Monte Carlo (GCMC) method [6]. An alternative "local" [7] Monte Carlo technique was also used to evaluate the reliability of GCMC simulations results. In this approach, the slit pore regions were used as "control volumes" in a traditional GCMC way, while the molecules adsorbed in the connecting region were treated in the framework of the canonical ensemble Monte Carlo. Unlike most simulations employing control volumes (see, for example [8–10]), we used the dual ensemble technique to ensure the ergodicity and proper sampling for a given set of μ (chemical potential), V (cell volume) and T (temperature).

The simulations were carried out using our own Monte Carlo code for systems **I** and **II** containing up to 355 fluid molecules. The length of MC runs was 60–150 million steps (conventional GCMC) or 10–30 million steps (local GCMC). The averages were typically computed over the last 30% of the MC trajectory. The energy grid constructed for accessible volume evaluation was used to accelerate the MC simulations by prohibiting attempts of particle insertion into inaccessible regions of the simulation cell.

3. Simulation results

Methane adsorption isotherms obtained from GCMC simulations at 111 K for model pores **I** and **II** are presented in figure 5. Both isotherms show significant deviations from the isotherm calculated for an isolated slit pore under the same conditions. For system **II** at low pressure the fluid molecules are adsorbed mostly over graphite-like surface regions away from the connecting channel. The reason for this is the weakening of the adsorption field at the channel/pore junction. The number of molecules adsorbed in the connecting channel increases slowly with the chemical potential, the adsorbed particles retaining relatively high mobility even at high pressure. Thus, the availability of the connecting channel leads to a noticeable differences in adsorption energies between various parts of the porous system and, consequently, to a different pore filling mechanism as compared to an isolated slit pore.

Judging from the calculated isotherms, system **II** can be described as having strong connectivity, i.e. no effective isolation of slit pore regions occurs even at high pressure. On the contrary, system **I** has weak connectivity. So, one can expect to observe the filling of the channel at low pressure, which effectively isolates the slit pores from each other. Since, the differences between **I** and **II** at 298 K were far less obvious due to lower fluid densities, we chose not to investigate the behavior of model pores at high temperature in detail. The adsorption isotherm for system **I** (figure 5) has a peculiar feature—the low-pressure branch, corresponding to the filling of the connecting channel with both slit pores remaining empty. This unphysical result was treated as an artifact related to the deficiency of the GCMC when applied to systems, where exchange between the pore space and the bulk phase is hindered (e.g. by diffusion limitations). The local GCMC technique was used to correct the unphysical behavior observed for system **I**. The calculated adsorption isotherm was in excellent agreement with the one obtained via the traditional GCMC approach, with the absence of the low-density branch being the only exception (figure 6). Thus, the local GCMC technique with two control volumes appears to be the appropriate way of studying adsorption in porous systems with restricted pore/bulk exchange. Furthermore, this technique was more

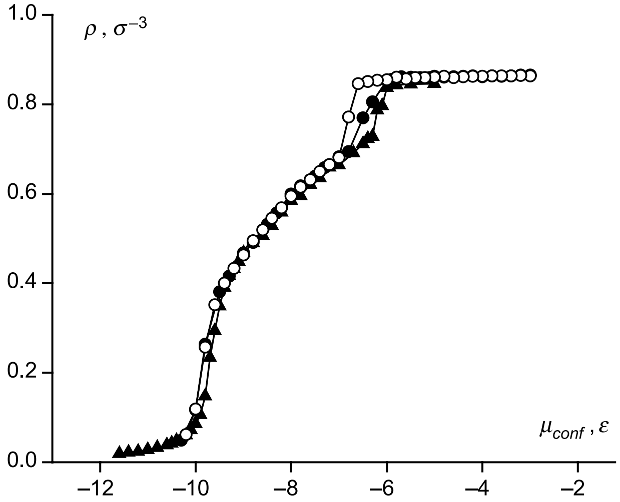


Figure 6. Methane adsorption and desorption isotherms for system I calculated using the conventional and modified GCMC methods (triangles—conventional GCMC, adsorption; filled circles—modified GCMC, adsorption; open circles—modified GCMC, desorption).

efficient than the traditional one, especially in resolving the hysteresis loop at $\mu_{\text{conf}} = -7/-6\varepsilon$.

4. Conclusions

In this paper we have demonstrated the effects of pore connectivity by comparing the calculated adsorption isotherms for an isolated slit pore and a set of two parallel slit pores connected by a channel. This comparison was facilitated by the accessible volume evaluation technique proposed in this work. While giving results similar to various empirical approaches for simple slit pores, this technique can be readily applied to more complex porous systems, thus providing the necessary basis for direct comparison of the total fluid density in isolated and connected pores.

Apart from the traditional GCMC method, for the simulation of adsorption in slit–channel–slit channel–slit systems we employed a modified MC simulation technique by restricting the insertion/deletion attempts to the slit pore regions. This modification to the GCMC method proved to be successful in terms of both accuracy and speed of Markov chain convergence. However, the most significant advantage of the local technique is the ability to closely match the conditions of adsorption under mass transfer limitations arising due to the various strength of coupling between certain regions of the pore and the bulk phase.

Acknowledgements

This work was supported by the “Universities of Russia” program of the Ministry of Education of the Russian Federation (grant No. UR.05.01.310) and the Ministry of Industry and Science (grant No. NSh-676.2003.3)

References

[1] J. Rouquerol, D. Avnir, C.W. Fairbridge, D.H. Everett, J.H. Haynes, N. Pernicone, J.D.F. Ramsay, K.S.W. Sing, K.K. Unger. International union of pure and applied chemistry: Recommendations for the characterization of porous solids. *Pure Appl. Chem.*, **66**, 1739 (1994).

[2] W.A. Steele. The physical interaction of gases with crystalline solids. *Surf. Sci.*, **36**, 317 (1973).

[3] J.P.R.B. Walton, N. Quirke. Capillary condensation: A molecular simulation study. *Mol. Simulat.*, **2**, 361 (1989).

[4] A.M. Vishnyakov, E.M. Piotrovskaya, E.N. Brodskaya. Capillary condensation and melting/freezing transitions for methane in slit coal pores. *Adsorption*, **4**, 207 (1998).

[5] V.V. Sizov, E.M. Piotrovskaya, E.N. Brodskaya. Modeling of methane adsorption in slitlike pores with structural and energetic nonuniformity. *Russ. J. Phys. Chem.*, **75**(Suppl. 1), S61 (2001).

[6] M.P. Allen, D.J. Tildesley. *Computer Simulation of Liquids*, Oxford University Press, New York (1987).

[7] A. Papadopoulou, E.D. Becker, M. Lupkowski, F. van Swol. Molecular dynamics and Monte Carlo simulation in the grand canonical ensemble: Local versus global control. *J. Chem. Phys.*, **98**, 4897 (1993).

[8] G.S. Heffelfinger, F. van Swol. Diffusion in Lennard–Jones fluids using dual control volume grand canonical molecular dynamics simulation (DCV-GCMD). *J. Chem. Phys.*, **100**, 7548 (1994).

[9] S. Furukawa, T. Shigeta, T. Nitta. Non-equilibrium molecular dynamics for simulating permeation of gas mixtures through nanoporous carbon membrane. *J. Chem. Eng. Japan*, **29**, 725 (1996).

[10] A.P. Thompson, D.M. Ford, G.S. Heffelfinger. Direct molecular simulation of gradient driven diffusion. *J. Chem. Phys.*, **109**, 6406 (1998).