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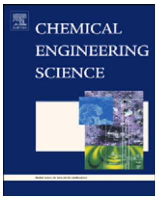

Shorter Communication

# Investigating the validity of the Bosanquet formula for estimation of diffusivities in mesopores

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ABSTRACT

Molecular Dynamics (MD) simulations were performed to determine the self-diffusivity, $D_{i,self}$, of $H_2$, $CO_2$, Ar, Kr, $CH_4$, $C_2H_6$, $C_3H_8$, and $nC_4H_{10}$ for a variety of pore concentrations within one-dimensional mesopores of 2 nm, 3 nm, 3.4 nm, 4 nm, 5.8 nm, 7.6 nm and 10 nm sizes. The MD simulated values of $D_{i,self}$ are compared with estimations of the commonly used Bosanquet formula $1/D_{i,self} = 1/D_{i,Kn} + 1/Đ_{ii,fl}$, that combines molecule–wall and molecule–molecule interactions:, where $D_{i,Kn}$ is the Knudsen diffusivity, and $Đ_{ii,fl}$ is the self-diffusivity of species $i$ in the fluid phase at the same molar concentration, $c_i$, as within the mesopores. For components with poor adsorption strength, such as $H_2$, the MD simulated $D_{i,self}$ values are in good agreement with the estimations using the Bosanquet formula for the whole range of pore concentrations. For components with strong adsorption at the pore walls, the MD simulated values are significantly lower than the Bosanquet estimations when molecule–wall interactions are dominant. These deviations are traceable to the failure of the Knudsen prescription of diffuse reflectance on molecule–wall collisions, because adsorption at the pore walls introduces a bias in the molecular hops. For any given molecule, the Bosanquet estimations tend to be increasingly accurate when the pore diameters are increased.

## 1. Introduction

The Bosanquet equation for self-diffusivity of species $i$ for combining molecule–wall and molecule–molecule interactions

$$1/D_{i,self} = 1/D_{i,Kn} + 1/Đ_{ii,fl} \tag{1}$$

was developed in a classified report dated September 27, 1944, and this interpolation formula only became known when it was later cited by Pollard and Present (1948) in a classic paper providing a rigorous foundation to Eq. (1) using arguments based on the kinetic theory of gases.

The molecule–wall interactions are quantified by the formula that was first put forward by Knudsen (1909), and subsequently refined by Smoluchowski (1910):

$$D_{i,Kn} = \frac{d_p}{3}\sqrt{\frac{8RT}{\pi M_i}} \tag{2}$$

The molecule–molecule interactions are characterized by the self-diffusivity in the *fluid* phase, $Đ_{ii,fl}$. For fluids with low molar densities, $c_i$, the $Đ_{ii,fl}$ can be estimated using a variety of methods (Poling et al., 2001). One commonly used estimation method is that of Fuller, Schettler and Giddings (FSG) (Fuller et al., 1966), developed for *binary* mixtures; $Đ_{ii,fl}$ can be determined by taking both species to be the identical to each other.

The Bosanquet formula is firmly entrenched in the chemical engineering literature and is widely used in practice to calculate $D_{i,self}$ in meso- and macro-porous materials (Spiegler, 1966; Youngquist, 1970), most notably in the calculation of catalyst effectiveness factors (Froment and Bischoff, 1979). The Bosanquet equation (1) can also be derived as a limiting case of Dusty Gas Model (Mason and Malinauskas, 1983) for binary mixture diffusion by taking the species in the mixture to be the identical to each other.

Our primary objective in this communication is to investigate the validity of Eq. (1) by carrying out Molecular Dynamics (MD) simulations of diffusivities in one-dimensional *meso*porous channels with well-defined sizes. Specifically, MD simulations were performed to determine $D_{i,self}$ of $H_2$, $CO_2$, Ar, Kr, $CH_4$, $C_2H_6$, $C_3H_8$, and $nC_4H_{10}$ for a variety of pore concentrations within one-dimensional mesopores of 2 nm, 3 nm, 3.4 nm, 4 nm, 5.8 nm, 7.6 nm and 10 nm sizes. We aim to demonstrate that the Bosanquet formula severely over-estimates the self-diffusivities when the species $i$ has a strong adsorption strength, and molecule–wall interactions are dominant.

For convenience and easy reference, the molecular simulation methodology, specification of force fields, and simulation data on

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diffusivities are provided in the Supplementary Material accompanying this publication.

## 2. Results and discussion

Firstly, consider the MD simulations of the self-diffusivity of a variety of species in the *fluid* phase, $Đ_{ii,fl}$, for a range of molar concentrations, $c_i$ (see Figs. 1a and b). The fluid phase diffusivities decrease with increasing $c_i$. The decrease of $Đ_{ii,fl}$ with increasing $c_i$ is linear at low concentrations, and the MD simulated values are in excellent agreement with estimations using the FSG method (Fuller et al., 1966), also plotted in Fig. 1as continuous solid lines. For values of $c_i > 10$ kmol m$^{-3}$, the $Đ_{ii,fl}$ predictions of the FSG method are not reliable. Similar agreement is obtained for the MD simulations of the fluid phase Maxwell–Stefan diffusivity for *binary* mixtures, $Đ_{12,fl}$, and the estimations of the FSG method (see Figs. 1c and d).

Let us now consider self-diffusivities $D_{i,self}$ within the 3.4 nm channels of the covalent organic framework BTP-COF (Krishna and van Baten, 2011a); the MD simulated diffusivities of a variety of guest molecules are shown in Fig. 2. For the Bosanquet calculations presented in Fig. 2 we use the MD simulated $Đ_{ii,fl}$, at the same molar concentrations as within the pores, rather than the FSG calculated ones, in order to ensure applicability for the entire range of pore concentrations. For $H_2$, that has poor adsorption strength, the MD simulated values of $D_{i,self}$ are in reasonably good agreement with the calculations using Eq. (1) for the entire range of pore concentrations. For $CO_2$, Ar, $CH_4$, $C_2H_6$, and $C_3H_8$ the Bosanquet formula severely over-estimates the self-diffusivities, when molecule–wall interactions are dominant, i.e. at low pore concentrations. The reasons for this departure must be attributed to the failure of the Knudsen formula for molecules with strong adsorption strength; this failure has been highlighted in several recent publications (Bhatia et al., 2011; Krishna, 2009; Krishna and van Baten, 2009a, 2009b, 2011a, 2011b, 2011c). Adsorption causes the molecules to bind to the wall, and perhaps hop to a neighboring adsorption site, rather than return to the bulk after collision; this introduces a *bias* in the molecular hops. This bias increases with increasing adsorption strength, causing a violation of the diffuse reflectance assumption that is invoked in deriving Eq. (2) (Bhatia et al., 2011; Krishna, 2009; Krishna and van Baten, 2011c). It has been demonstrated that the departures from the Knudsen formula correlates with the binding energy for

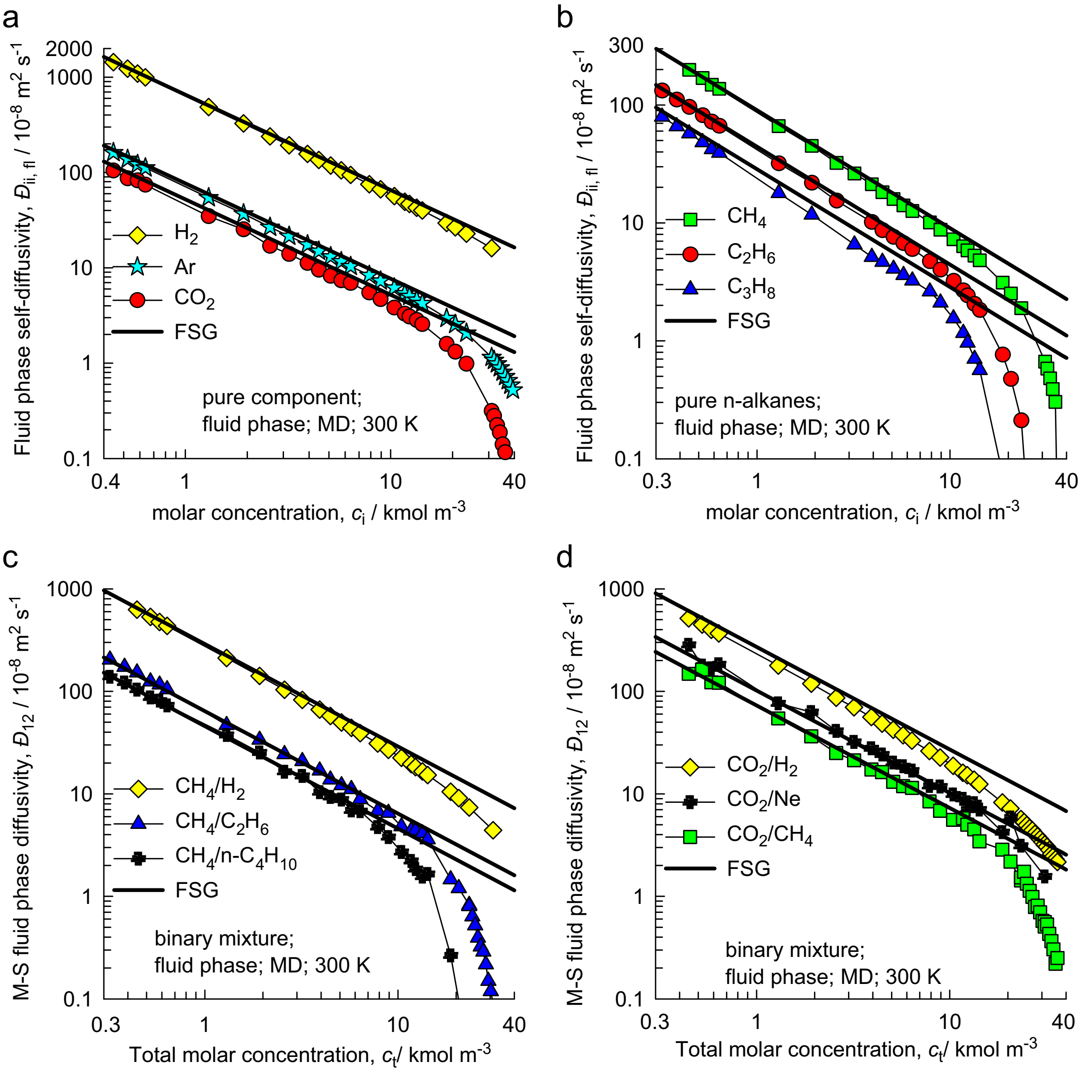

**Fig. 1.** (a, b) MD simulations of fluid phase unary self-diffusivities $Đ_{ii,fl}$ of (a) $H_2$, $CO_2$, Ar, and (b) $CH_4$, $C_2H_6$, $C_3H_8$ at 300 K as a function of the fluids concentration $c_i$. (c, d) MD simulations of fluid phase binary Maxwell–Stefan diffusivities $Đ_{12,fl}$ of (c) $CH_4/H_2$, $CH_4/C_2H_6$, $CH_4/C_3H_8$, and (d) $CO_2/H_2$, $CO_2/CH_4$, $CO_2/Ne$ mixtures at 300 K as a function of the total fluids concentration $c_t$. The solid continuous lines are the estimations of $Đ_{ii,fl}$ and $Đ_{12,fl}$ using the correlation of Fuller, Schettler and Giddings (Fuller et al., 1966).

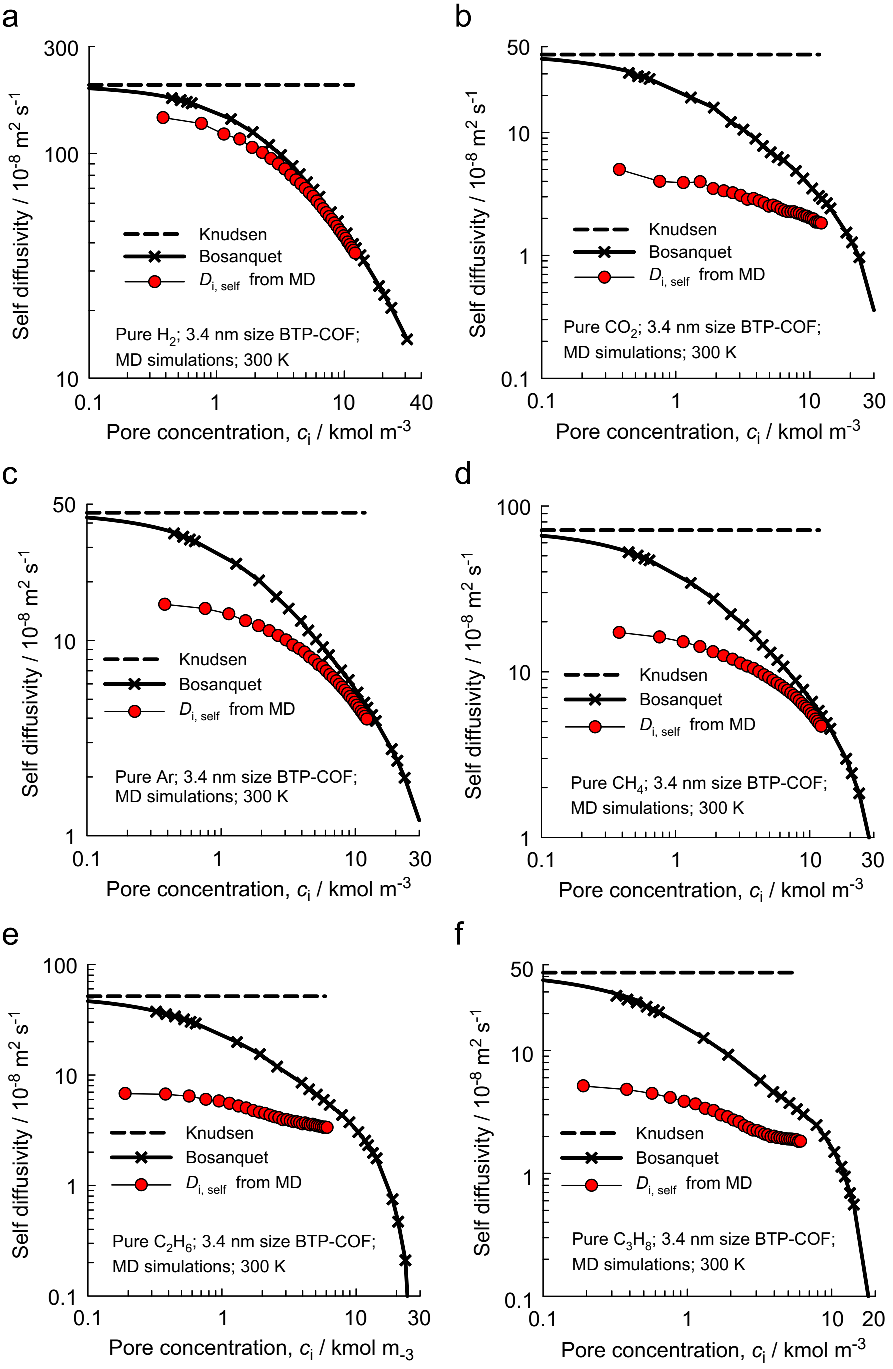

**Fig. 2.** MD simulations of self-diffusivities $D_{i,self}$ of (a) $H_2$, (b) $CO_2$, (c) Ar, (d) $CH_4$, (e) $C_2H_6$, and (f) $C_3H_8$ at 300 K in BTP-COF, a covalent organic framework with 3.4 nm pore size, as a function of the pore concentration $c_i$. The MD simulations (circles) are compared with the estimations using the Bosanquet and Knudsen formulae.

adsorption of the molecules at the pore walls (Krishna and van Baten, 2011a).

Results analogous to those presented in Fig. 2 apply to all guest–host combinations investigated; the data are available in the Supplementary Material accompanying this publication.

The curvature of the surfaces of the pore walls should be expected to have an influence on the failure of the diffuse reflectance prescription of Knudsen. We should anticipate that with increasing pore diameters, i.e. with decreasing curvature of the walls, the bias in the hops introduced by adsorption would be lessened. In order to confirm this expectation, let us compare the self-diffusivities of $CH_4$ in cylindrical silica pores of increasing diameters (see Fig. 3). We note that the degree of over-estimation of the self-diffusivities using the Bosanquet formula decreases as the pore diameter increases. For quantification of this finding, we collected the data on the self-diffusivities of Ar and $CH_4$ at a fixed loading of $c_i = 0.1$ kmol m$^{-3}$ in pores of different diameters. Fig. 4 presents a plot of the ratio of the self-diffusivities $D_{i,self}$ for Ar and $CH_4$ obtained from MD to that calculated by the Bosanquet formula plotted as a function of the pore diameter. As anticipated in the foregoing discussions, we observe that the departures of the Bosanquet formula from MD simulation results tends to decrease with increasing pore diameters. Since it has already been established that the molecule–molecule interaction term in

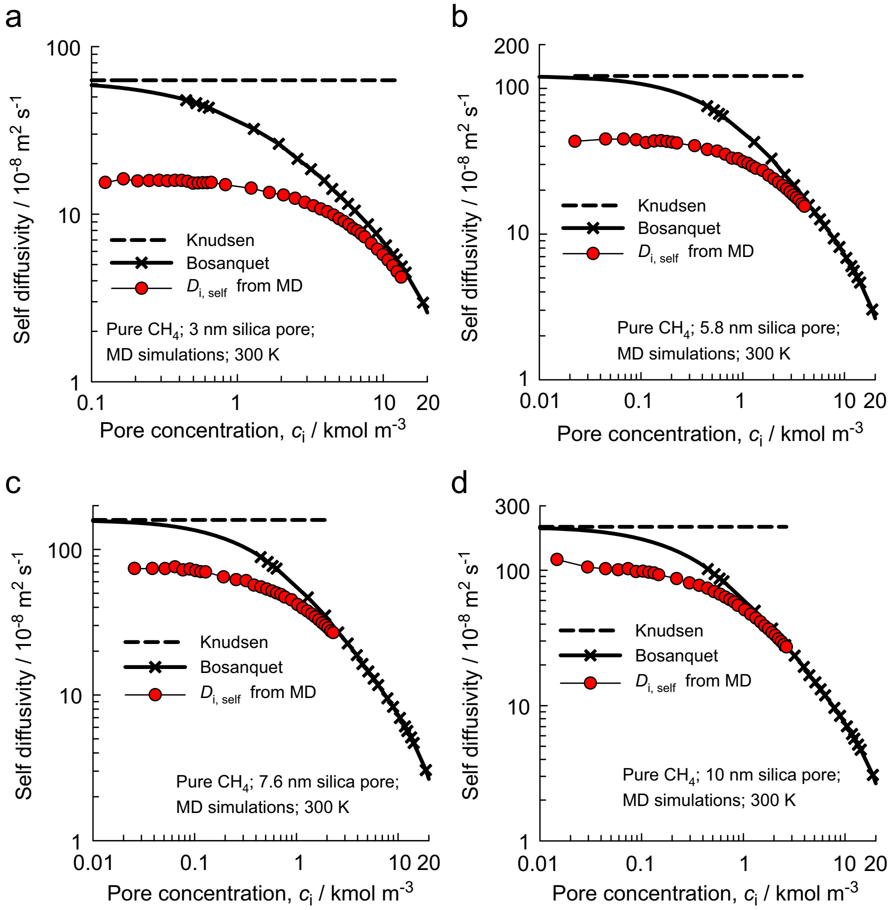

**Fig. 3.** MD simulations of self-diffusivities $D_{i,self}$ of $CH_4$ at 300 K in cylindrical silica pores of (a) 3 nm, (b) 5.8 nm, (c) 7.6 nm, and (d) 10 nm sizes, as a function of the pore concentration $c_i$. The MD simulations (circles) are compared with the estimations using the Bosanquet and Knudsen formulae .

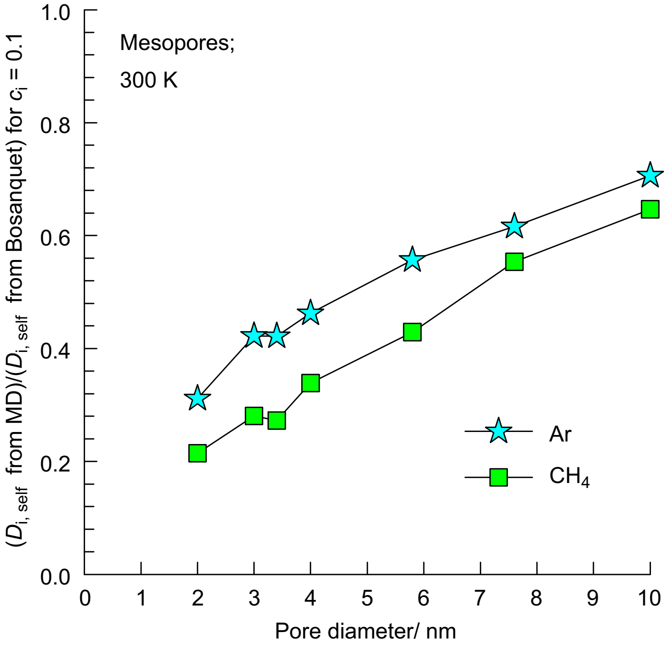

**Fig. 4.** Ratio of the self-diffusivities $D_{i,self}$ for Ar and $CH_4$ (at $c_i$=0.1 kmol $m^{-3}$) in mesopores obtained from MD to that calculated by the Bosanquet formula plotted as a function of the pore diameter.

Eq. (1), is correctly estimated (cf. Fig. 1), the observed deviations in the Bosanquet formula are solely attributable to the shortcomings of the Knudsen prescription.

Bhatia and co-workers (Bhatia, 2010; Bhatia and Nicholson, 2011) have re-analyzed a variety of experimental data for diffusion in mesopores that confirm the conclusions drawn in the foregoing. Further experimental confirmation is provided below.

Gruener and Huber (2008) have conducted careful experiments to determine the diffusivities of poorly adsorbing gases He and Ar in silicon nanochannels. As anticipated, the experimental data are in good agreement with the estimations using Knudsen prescription.

Huang et al. (2011) have reported the diffusivities of n-heptane and toluene in SBA-15 materials of two different pore sizes. The molar masses of the two species are nearly equal, 0.1 and 0.092 kg $mol^{-1}$, respectively. However, the diffusivities of toluene are found to be significantly lower than that of n-heptane, because of its significantly higher adsorption strength (Krishna and van Baten, 2011b).

In the experimental study of Katsanos et al. (2005), the measured diffusivities of nC5, nC6 and nC7 in α-alumina ($d_p$=21.6 nm) and γ-alumina ($d_p$=10.6 nm) were found to be in the range of 10–27% of the values anticipated by the Knudsen formula.

Goguet et al. (2011) have found that the interpretation of their TAP pulse response experiments, designed to be conducted within the Knudsen diffusion regime, required the inclusion of the influence of adsorption on molecule–wall interactions.

In his re-analysis of the diffusivity data of Reyes et al. (1997), Ruthven (2010) has concluded that the Knudsen formula holds with good accuracy. This conclusion is however based on the assumption of a uniform pore diameter of 7 nm for the silica sample used in the Reyes experiments. It remains to be ascertained whether the existence of a distribution of pore sizes of the silica sample will have a bearing on the conclusions drawn by Ruthven.

## 3. Conclusions

Molecular Dynamics simulations have been used to investigate the validity of the Bosanquet formula for calculation of the self-diffusivities of a variety of guest molecules within one-dimensional channels in the 2 nm–10 nm range. For molecules, such as $H_2$, that adsorb poorly, the Bosanquet formula is of reasonable accuracy for a wide range of pore concentrations. Significant departures of the Bosanquet formula are found with strongly adsorbing molecules at pore concentrations where molecule–wall collisions are dominant, already underlined in several recent investigations (Bhatia et al., 2011; Krishna and van Baten, 2009a, 2009b, 2011a, 2011b, 2011c). An important new finding pertains to the influence of the pore diameter. With increasing pore diameter, the bias in the molecular hops introduced by adsorption has a decreasing influence. As a consequence, the Bosanquet formula becomes increasingly accurate as the pore diameter increases.

The results of the current investigation also cast doubts on the validity of the Dusty Gas Model, when applied to mixtures in which at least one of the species has strong adsorption characteristics. As an example, the recent work on the modeling of intra-particle diffusion and reaction for steam reforming and methanol synthesis processes (Rout et al., 2008; Solsvik and Jakobsen, 2008) requires further scrutiny to examine the extent to which the failure of the Knudsen prescription influences the overall reactor performance.

## Nomenclature

| | |
|---|---|
| $c_i$ | concentration of species $i$, mol $m^{-3}$ |
| $d_p$ | pore diameter, m |
| $D_{i,self}$ | self-diffusivity of species $i$ within the pore, $m^2\ s^{-1}$ |
| $Đ_{ii,fl}$ | self-diffusivity of species $i$ in fluid phase, $m^2\ s^{-1}$ |
| $Đ_{12,fl}$ | Maxwell–Stefan diffusivity for binary mixture in fluid phase, $m^2\ s^{-1}$ |
| $D_{i,Kn}$ | Knudsen diffusivity of species $i$, $m^2\ s^{-1}$ |
| $M_i$ | molar mass of species $i$, kg $mol^{-1}$ |
| $R$ | gas constant, 8.314 J $mol^{-1}$ $K^{-1}$ |
| $T$ | temperature, K |

*Subscripts*

| | |
|---|---|
| $i$ | referring to component $i$ |
| $fl$ | referring to fluid phase |
| $Kn$ | referring to Knudsen |

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## Appendix A. Supplementary Information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.ces.2011.11.026.

## References

Bhatia, S.K., 2010. Modeling pure gas permeation in nanoporous materials and membranes. Langmuir 26, 8373–8385.

Bhatia, S.K., Bonilla, M.R., Nicholson, D., 2011. Molecular transport in nanopores: a theoretical perspective. Phys. Chem. Chem. Phys. 13, 15350–15383.

Bhatia, S.K., Nicholson, D., 2011. Some pitfalls in the use of the Knudsen equation in modelling diffusion in nanoporous materials. Chem. Eng. Sci. 66, 284–293.

Froment, G.F., Bischoff, K.B., 1979. Chemical Reactor—Analysis and Design. John Wiley & Sons, New York.

Fuller, E.N., Schettler, P.D., Giddings, J.C., 1966. A new method for prediction of binary gas-phase diffusion coefficients. Ind. Eng. Chem. 58, 19–27.

Goguet, A., Hardacre, C., Inceesungvorn, B., Morgan, K., Shekhtman, S.O., 2011. Correction for a possible reversible adsorption over an “inert” material. Catal. Sci. Technol. 1, 760–767.

Gruener, S., Huber, P., 2008. Knudsen diffusion in silicon nanochannels. Phys. Rev. Lett. 100, 064502.

Huang, Q., Qamar, R.A., Eić, M., 2011. Single component and binary diffusion of n-heptane and toluene in SBA-15 materials. Adsorpt.—J. Int. Adsorpt. Soc. 17, 27–38.

Katsanos, N.A., Bakaoukas, N., Koliadima, A., Karaiskakis, G., 2005. Diffusion and adsorption measurements in porous solids by inverse gas chromatography. J. Phys. Chem. B 109, 11240–11246.

Knudsen, M., 1909. Die Gesetze der Molekularströmung und der inneren Reibungsströmung der Gase durch Röhren. Ann. Phys. 333, 75–130.

Krishna, R., 2009. Describing the diffusion of guest molecules inside porous structures. J. Phys. Chem. C 113, 19756–19781.

Krishna, R., van Baten, J.M., 2009a. An investigation of the characteristics of Maxwell–Stefan diffusivities of binary mixtures in silica nanopores. Chem. Eng. Sci. 64, 870–882.

Krishna, R., van Baten, J.M., 2009b. Unified Maxwell–Stefan description of binary mixture diffusion in micro- and meso-porous materials. Chem. Eng. Sci. 64, 3159–3178.

Krishna, R., van Baten, J.M., 2011a. Investigating the validity of the Knudsen prescription for diffusivities in a mesoporous covalent organic framework. Ind. Eng. Chem. Res. 50, 7083–7087.

Krishna, R., van Baten, J.M., 2011b. Influence of adsorption on the diffusion selectivity for mixture permeation across mesoporous membranes. J. Membr. Sci. 369, 545–549.

Krishna, R., van Baten, J.M., 2011c. A molecular dynamics investigation of the unusual concentration dependencies of Fick diffusivities in silica mesopores. Microporous Mesoporous Mater. 138, 228–234.

Mason, E.A., Malinauskas, A.P., 1983. Gas Transport in Porous Media: The Dusty-Gas Model. Elsevier, Amsterdam.

Poling, B.E., Prausnitz, J.M., O’Connell, J.P., 2001. The Properties of Gases and Liquids, 5th edition McGraw-Hill, New York.

Pollard, W.G., Present, R.D., 1948. On gaseous self-diffusion in long capillary tubes. Phys. Rev. 73, 762–774.

Reyes, S.C., Sinfelt, J.H., DeMartin, G.J., Ernst, R.H., Iglesia, E., 1997. Frequency modulation methods for diffusion and adsorption measurements in porous solids. J. Phys. Chem. B 101, 614–622.

Rout, K.R., Solsvik, J., Nayak, A.K., Jakobsen, H.A., 2008. A numerical study of multicomponent mass diffusion and convection in porous pellets for the sorption-enhanced steam methane reforming and desorption processes. Chem. Eng. Sci. 66, 4111–4126.

Ruthven, D.M., 2010. Letter to the Editor. Response to Comments from S.K. Bhatia and D. Nicholson. Chem. Eng. Sci. 65, 4521–4522.

Smoluchowski, M., 1910. Zur Kinetischen Theorie der Transpiration und Diffusion verdünnter Gase. Ann. Phys. 338, 1559–1570.

Solsvik, J., Jakobsen, H.A., 2008. Modeling of multicomponent mass diffusion in porous spherical pellets: application to steam methane reforming and methanol synthesis. Chem. Eng. Sci. 66, 1986–2000.

Spiegler, K.S., 1966. Diffusion of gases across porous media. Ind. Eng. Chem. Fundam. 5, 529–532.

Youngquist, G.R., 1970. Diffusion and flow of gases in porous solids. Ind. Eng. Chem. 62, 52–63.