

비겹침 구형 모델을 이용한 세공 박막 내 수소 기체의 분산 및 확산 특성

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Partitioning and Diffusion Properties of Hydrogen Gases in Porous Membranes Using the Nonoverlapping Sphere Model

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Abstract

The modified statistical-mechanical theory for dense fluid mixtures of rigid spheres has been applied to rigid sphere fluids in the nonoverlapping pore model. The resulting expressions for the partition coefficient and diffusivity illustrate the influence of steric hindrance on the thermodynamic and transport properties in such systems. The open membrane model without the size-exclusion and shielding effects shows considerable overestimation of the diffusion flux when the effective mean pore radii of the order of 20Å or less are involved. Theoretical predictions investigated here were also compared with experimental data for hydrogen gases in inorganic porous membranes and it was observed a qualitative agreement in the low pressure limit.

1. Introduction

The thermodynamic and transport properties of hydrogen gases in porous media are of considerable interests in experimental and industrial applications such areas as membrane gas separation, heterogeneous catalysis, and fuel gas storage in zeolite cavities. In many situations, and particularly when the size of pores is commensurate with that of diffusing molecules into microporous membranes, a controversial picture frequently emerges from the available experimental data on the equilibrium partitioning and hindered diffusivity. Consequently, the ability of theoretical calculations to clarify these issues has been limited in these smaller porous structure.^{1,2)}

By introducing the concept of the pore size distribution with a proper choice of porous medium structure factors, reasonably accurate models may be obtained to predict the steric and dynamic properties in the pore phase. For most practical porous materials, however, there is a spatial variation of pore sizes. Experimental methods are based on the assumption that the absolute size of the pore size distribution can reliably be obtained so that the pore cross-sectional shape is known. In fact, the experimental extraction of an absolute pore distribution is not straightforward and this assumption may be seriously in error and leads to large uncertainties.³⁾

In the present work, the influence of membrane density and the molecular size

of nonadsorbing gases have been investigated by applying the dusty gas concept⁴⁾ to the rigid sphere model of dense fluid mixtures. We consider the special case of the rigid sphere fluid and then employ the modified kinetic theory⁵⁾ to evaluate corrections to the dusty gas model arising from statistical correlations to the size-exclusion hindrance. In the following two sections, the diffusion fluxes based on the statistical-mechanical theory and their application to the multicomponent diffusion for rigid gases in the nonoverlapping sphere model are described in details. The results obtained from theoretical predictions are also compared with the available experimental data obtained from the hydrogen separation processes using the inorganic porous membranes.

2. Statistical-Mechanical Theory for Diffusion Flux

As expressed in Stefan-Maxwell form for species α in a multicomponent mixture of rigid spheres, the diffusion flux J_α confined to isothermal conditions can be represented as

$$\sum_{\lambda=1}^s \frac{n_\lambda J_\alpha - n_\alpha J_\lambda}{n D_{\alpha\lambda}} = - \sum_{\lambda=1}^s \frac{n_\lambda}{n_\alpha} \left(\delta_{\alpha\lambda} + \left(\frac{\partial \ln(\gamma_\alpha)}{\partial \ln(n_\lambda)} \right)_{T, n, n_{\neq \alpha}} \right) \nabla n_\lambda \quad (1)$$

in which n_α and γ_α are the number density and the activity coefficient for species α ; $\delta_{\alpha\lambda}$, the Kronecker delta notation; $D_{\alpha\lambda}$, the mutual diffusion coefficient of component α with respect

to component λ in the membrane. This equation is the general form based on the statistical-mechanical theory of transport.

When the kinetic theory of dilute gases through porous media is used to evaluate the parameters in Eq. (1), the resulting equation can be reduced to the dusty gas model, in which the membrane itself is treated as one component of the gas mixture, consisting of motionless giant molecules held fixed in the pore space.⁴⁾ Using the additional conditions for membrane component m such as

$$\nabla n_m = 0 \quad (2)$$

$$\frac{m_a}{m_m} \rightarrow 0 \quad (3)$$

one may have

$$\frac{J_a}{D_{aM}} + \sum_{\lambda=1}^{K-1} \frac{n_\lambda J_a - n_a J_\lambda}{n D_{a\lambda}} = \quad (4)$$

$$- \sum_{\lambda=1}^{K-1} \frac{n_a}{n_\lambda} \left(\delta_{a\lambda} + \left(\frac{\partial \ln(\gamma_a)}{\partial \ln(n_a)} \right)_{T, n_1, \dots, n_a} \right) \nabla n_\lambda$$

where

$$D_{a\lambda} = \frac{3}{8n\sigma_{a\lambda}^2} \left(\frac{kT(m_a + m_\lambda)}{2\pi m_a m_\lambda} \right)^{1/2} \frac{1}{g_{a\lambda}(\sigma_{a\lambda})} \quad (5)$$

and

$$D_{aM} = \frac{n}{n_m} D_{am} \quad (6)$$

To complete the specification of the diffusion flux, theoretical expressions for

$g_{a\lambda}(\sigma_{a\lambda})$ and γ_a can be obtained from the scaled particle approximation,⁶⁾ i.e.,

$$g_{a\lambda}(\sigma_{a\lambda}) = \frac{1}{1-\xi_3} + \frac{6\xi_2}{(1-\xi_3)^2} \left(\frac{R_a R_\lambda}{R_a + R_\lambda} \right) + \frac{12\xi_2^2}{(1-\xi_3)^3} \left(\frac{R_a R_\lambda}{R_a + R_\lambda} \right)^2 \quad (7)$$

$$\ln \gamma_a = -\ln(1-\xi_3) + \frac{6\xi_2 R_a + 12\xi_1 R_a^2 + 8\xi_a R_a^3}{(1-\xi_3)} + \frac{18\xi_2^2 R_a^2 + 24\xi_1 \xi_2 R_a^3}{(1-\xi_3)^2} + \frac{24\xi_2^3 R_a^3}{(1-\xi_3)^3} \quad (8)$$

where

$$\sigma_{a\lambda} = \frac{\sigma_a + \sigma_\lambda}{2} = R_a + R_\lambda \quad (9)$$

and

$$\xi_i = \frac{\pi}{6} \sum_{j=1}^K n_j (\sigma_j)^i \quad (10)$$

3. Application to Rigid Sphere Fluids in the Nonoverlapping Sphere Model

In specializing to diffusion of nonadsorbing gases, the nonoverlapping sphere model is chosen here as a representation of porous membranes. In terms of membrane properties, we make use of the following relationships for the porosity, ψ , and the effective mean pore radius, R_{eff} ,

$$\frac{\pi}{6} n_m \sigma_m^3 = 1 - \psi \quad (11)$$

and

$$R_{eff} = \frac{2\psi}{n_m S} = \frac{\sigma_m}{3} \frac{\psi}{1 - \psi} \quad (12)$$

The contact radial distribution function in Eq. (7) and the activity coefficient in Eq. (8) may then be rearranged, respectively,

$$g_{al}(\sigma_{al}) = \frac{1}{\psi} \left[1 + 3 \left(\frac{1 - \psi}{\psi} \right) \frac{\delta_m}{1 + \delta_\lambda} + 3 \left(\frac{1 - \psi}{\psi} \right)^2 \left(\frac{\delta_m}{1 + \delta_\lambda} \right)^2 \right] \quad (13)$$

$$\gamma_a = \frac{1}{\psi} \exp \left[\left(\frac{1 - \psi}{\psi} \right) (3\delta_m + 3\delta_m^2 + \delta_m^3) + \left(\frac{1 - \psi}{\psi} \right)^2 (4.5\delta_m^2 + 3\delta_m^3) + 3 \left(\frac{1 - \psi}{\psi} \right)^3 \delta_m^3 \right] \quad (14)$$

where

$$\delta_m = \frac{\sigma_a}{\sigma_m} = \frac{R_a}{R_m} \quad (15)$$

We will assume that diffusion is taking place unidirectionally across a membrane with bulk gas/membrane interfaces at $z = 0$ and $z = L$. It is necessary to specify boundary conditions at $z = 0$ and $z = L$ relating the membrane fluid number densities to the bulk fluid number densities on both sides of the membrane. Under these conditions,

we have

$$\begin{aligned} \mu_{am} &= \mu_a^o + kT \ln(\gamma_a n_a) \\ &= \mu_a^o + kT \ln(n_{af}) \\ &= \mu_{af} \end{aligned} \quad (16)$$

This equation gives the simple relationship of $\gamma_a n_a = n_{af}$, and the partition coefficient, K_a , is expressed by the inverse of the activity coefficient for the rigid sphere model

$$K_a = \frac{1}{\gamma_a} = \frac{n_a}{n_{af}} \quad (17)$$

A reduced partition coefficient and diffusivity can be obtained by incorporating the influence of steric exclusion on the free molecule transport of the gas

$$\begin{aligned} \frac{K_a}{K_a^o} &= \exp \left[- \left(\frac{1 - \psi}{\psi} \right) (3\delta_m + 3\delta_m^2 + \delta_m^3) \right. \\ &\quad \left. - \left(\frac{1 - \psi}{\psi} \right)^2 (4.5\delta_m^2 + 3\delta_m^3) \right. \\ &\quad \left. - 3 \left(\frac{1 - \psi}{\psi} \right)^3 \delta_m^3 \right] \end{aligned} \quad (18)$$

and

$$\begin{aligned} \frac{D_{aM}}{D_{aM}^o} &= \left[(1 + \delta_m)^2 + 3 \left(\frac{1 - \psi}{\psi} \right) \delta_m (1 + \delta_m) \right. \\ &\quad \left. + 3 \left(\frac{1 - \psi}{\psi} \right)^2 \delta_m^2 \right]^{-1} \end{aligned} \quad (19)$$

In those equations the open membrane quantities for K_a^o and D_{aM}^o are defined as

$$K_{\alpha}^o = \psi \quad (20)$$

and

$$D_{\alpha M}^o = \frac{1}{\tau} \left(\frac{2}{3} R_{eff} \langle \bar{v}_{\alpha} \rangle \right) \quad (21)$$

where $\langle \bar{v}_{\alpha} \rangle$ denotes the molecular mean speed of component α , i.e., $\sqrt{8kT/\pi m_{\alpha}}$.

In Figs. 1 and 2 we illustrate the reduced partition coefficient in Eq. (18) and the reduced diffusivity in Eq. (19) for hydrogen gases in the porous membrane phase as a function of the membrane particle size over a given range of the porosity, $0.4 < \psi < 0.8$. A rigid diameter for hydrogen molecule ($\sigma = 2.928 \text{ \AA}$) was taken as equal to the length parameter in the Lennard-Jones potential, which was calculated from extrapolations to high temperature in conjunction with the quantum mechanical correction.⁷⁾ It is clear from the results shown in these figures that the open membrane dusty gas model in Eqs. (20) and (21) cannot be used with confidence to predict diffusion fluxes in microporous media, particularly when the effective mean pore radii of the order of 20 \AA or less are involved.

Recently, Morooka and his co-workers⁸⁻¹⁰⁾ have reported the experimental results for gas separations using membrane technologies. Among them, hydrogen gases were separated from other gases through the silica-based porous membranes, in which tetraethoxysilane (TEOS), phenyltriethoxysilane (PTES), and

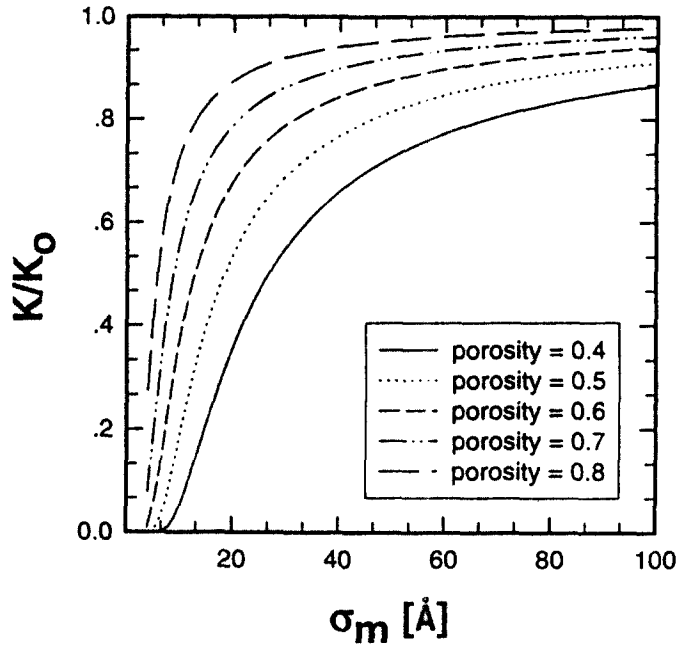


Fig. 1 Reduced partition coefficients, K/K_0 , for hydrogen gases in the nonoverlapping sphere model having a membrane particle size of σ_m .

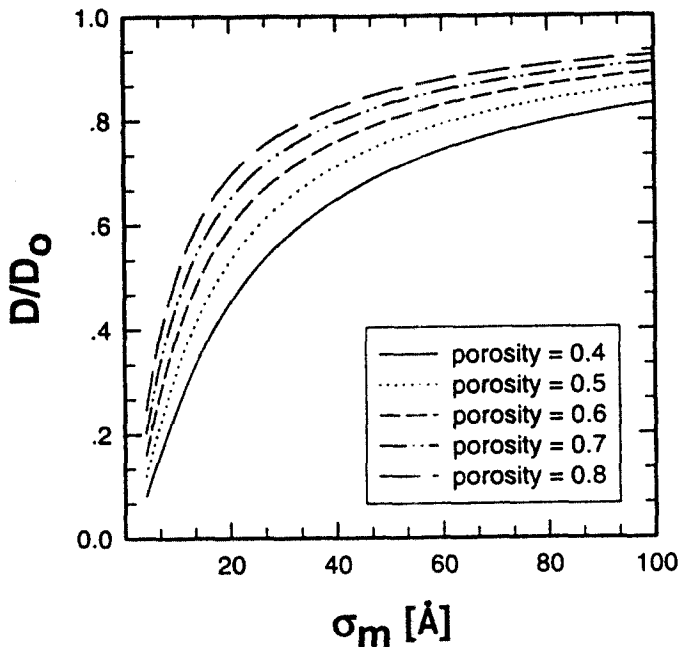


Fig. 2 Reduced diffusion coefficients, D/D_0 , for hydrogen gases in the nonoverlapping sphere model having a membrane particle size of σ_m .

diphenyldiethoxysilane (DPDES) were used as the Si source by the chemical vapor deposition method. The experimental values for hydrogen permeance in their work was reported to be greatly dependent on the pore size control. As indicated in these figures, the resulting hindrance effect is sensitive to a given pore size, and, in the lower pressure region, their experimental results for TEOS- and PTES-derived membranes were shown to be in a qualitative agreement with the theoretical predictions employed in this work.

The deviations were greater for the systems of the DPDES-derived membranes. In this case, the higher values of hydrogen permeances exhibited for the diffusion fluxes indicate that these membranes possessed two types of micropores: abundant pores through which hydrogen permeated and a small number of pores where nitrogen molecules were permeable but not able to pass one another. This trend may be due to differences in the pore structure and the increasing influence of steric hindrance in smaller pores. Although it is known that surface flow can contribute significantly to transport in micropores, theoretical results obtained here suggest that the contribution of size-exclusion steric hindrance may be much larger and the hindered diffusive flow play a major role in the transport process.

4. Conclusions

In this work the modified statistical-mechanical theory for dense fluid mixtures of rigid spheres has been applied to rigid sphere fluids in the nonoverlapping pore model. It is shown that the dense fluid kinetic theory can be used to predict diffusional transport of gases through porous membranes, which considers volume exclusion and shielding due to the molecular size effects. The resulting expressions for the partition coefficient and diffusivity illustrate the influence of steric hindrance on the thermodynamic and transport properties in such systems. In the low pressure limit, it was observed a qualitative agreement between theoretical predictions and the available experimental data for the system of hydrogen gases separated by the inorganic porous membranes.

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