A Statistical Mechanical Model for Adsorption and Flow of Pure and Mixed Gases in Porous Media with Homogeneous Surfaces

Part I: Theoretical Development

A unified statistical mechanical treatment is developed for adsorption and surface diffusion on homogeneous surfaces. Using molecular parameters, the model accounts for all physical effects of adsorbent-adsorbate, adsorbate-adsorbate, and adsorbate-gas interactions at submonolayer coverages.

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SCOPE

The adsorption and surface mobility of substances on solids is relevant in such diverse processes as catalysis, some proposed separations, and olfactory reception by insects. As is well known, there is an attractive potential for fluid molecules toward the surface. This potential varies along the surface because the arrangement of adsorbent atoms causes the adsorbate molecules to suffer varying momentum changes as they move. In fact, if the local variation is large enough, admolecules may become localized, the amount being a function of temperature and surface coverage. In addition, the admolecules vibrate normal to the surface; this is a momentum exchange mechanism with the surface as well as an equilibrium energy effect, which was ignored in an earlier treatment (Lee and O'Connell, 1972). Further, the admolecules interact with each other, the quantitative effects depending upon whether they are mobile or not and upon their location in the structured potential. Finally, there may be important interaction between the gaseous and adsorbed molecules which affect the total flux.

There are several important physical cases to be considered. The bulk gas phase may be pure or mixed, with the amount adsorbed ranging from negligible to a significant fraction of a monolayer. The solid can be packed in a porous bed, with the flux being due to different pressures at the inlet and outlet for a pure component, or to different partial pressures of the components in a mixture while the total pressure is constant throughout the system. A special case of the latter is tracer flow of one isotope present at very low concentrations in another isotope. Each of the above cases results in slightly different macroscopic relations, although the molecular phenomena are the same.

A number of treatments of adsorption and surface diffusion exist. However, these theories often treat only equilibrium or transport, rather than both. Surface equilibrium and transport should be amenable to a unified potential model and statistical mechanical treatment such as second virial coefficients and ideal gas transport properties are. Part I of the present study gives the development of the expressions for all of the physical situations of adsorption and flux of gases through a porous beds of homogeneous adsorbents with submonolayer coverage. In Part II the expressions are applied to several cases of pure and mixed gases with graphitized carbon black.

CONCLUSIONS AND SIGNIFICANCE

Expressions have been developed from statistical mechanics to model the equilibrium isotherms and all of the transport properties for an important class of adsorption systems. Specifically, these include pure and mixed gases, which can be localized or mobile when adsorbed at submonolayer coverage on homogeneous surfaces in porous beds where the gas phase is in the Knudsen regime. The important physical effects rigorously or approximately included are gas-adsorbate interactions, including enhanced fluxes due to convective bulk phase flow, molecular scattering mechanisms that control the surface flow due to both the structured adsorption potential and the vibrations normal to the surface (including anharmonicity, which becomes important at high temperatures), and interactions between mobile and localized species at finite coverages. Most of these phenomena are well

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defined in physical and nondissociative chemical adsorption, so the emphasis is oriented toward them. However, to the extent that molelcular flow and interactions are the same in dissociative systems, the theory will apply.

The relations are complex because of the generality attempted; the equations and parameters are explicitly discussed. The input information includes appropriate physical properties of the adsorbent and the bed and intermolecular potential energy parameters for adsorbate-adsorbate and adsorbate-adsorbent interactions. Numerical results, a strategy for parameter fitting, and comparisons with data for physical adsorption are given in Part II. The present work on homogeneous surfaces also provides a basis for describing static and dynamic properties of heterogeneous systems.

INTRODUCTION

Previously, we published work describing the adsorption and surface diffusion of pure gases (Lee and O'Connell, 1972, 1975) and the adsorption of binary gases (Lee and O'Connell, 1974) on homogeneous solid surfaces based on a single model for partially mobile adsorption using the methods of statistical mechanics. This approach is physically realistic and can be extended to mixed gases and heterogeneous surfaces. With extension, it is also capable of describing the bulk and surface flow in the presence of interactions between the two phases. For example, the model for the momentum exchange between the bulk molecules and admolecules proposed by Thakur et al. (1980) is readily applicable for this purpose. The concept of partially mobile adsorption is a natural consequence of the admolecular potential energy, whose calculated values are available in a number of references (e.g., Steele, 1973). The calculated results clearly show that the surface potential is structured with energy peaks and valleys. Steele and Ross (1961) showed that the adsorption can be considered mobile or localized for practical purposes only in extreme cases of the ratio of potential to kinetic energies, $\epsilon_i/kT < 0.5$ or $\epsilon_i/kT > 5$, respectively, where ϵ_i is the difference between the maxima and the minima of the periodic potential.

Despite this understanding, adsorption has usually been modeled by a Langmuir localized adsorption or by Hill–de Boer mobile adsorption (Ross and Olivier, 1964), probably because the effect of partially mobile adsorption is not readily discernible in equilibrium adsorption. However, the structure of the adsorption potential is essential in describing the limitations on the rate of surface flow. Both admolecule-admolecule and admolecule-surface interactions are important in the mechanism of surface diffusion (Ash and Barrer, 1967). The latter involves the thermal oscillation of surface atoms, the periodic structure of the surface potential that directly affects the movement of admolecules parallel to the surfaces, and vertical vibrations of admolecules that also cause energy and momentum exchange with the surface atoms. This last effect was neglected in our previous treatment (Lee and O'Connell, 1972, 1975). As shown in Part II, proper treatment of this effect results in improved description of the temperature variation of the properties of these systems with physically realistic potential parameters.

In addition to the above extension of our model, this work describes its formulation for mixtures and gives a theoretical framework for the interaction of bulk and surface flow in homogeneous surfaces. This report describes the theory; Part II gives the calculational methods and comparisons with experimental data.

POTENTIAL MODEL

The potential energy of an admolecule varies with its distance from the surface, depending on its position relative to the lattice surface atoms (Steele, 1973; Steele and Ross, 1961). The vertical potential has a short-range repulsive part and a long-range attractive part. For submonolayer adsorption, we define a two-dimensional adsorbed layer along the time-averaged position of admolecules normal to the surface. In this layer we model the local horizontal variation of the admolecule-surface potential of component i at position r_k as

$$\begin{aligned} U_{si}(r_{ks}) &= -U_{oi} & r_{si} > \sigma_{Si}/2 \\ &= -U_{oi} - \epsilon_i & r_{si} < \sigma_{Si}/2 \end{aligned} \tag{1}$$

where r_{si} is the separation between center of the molecule and the center of a site. This means that the site has a cylindrical energy well of diameter σ_{Si} and depth ϵ_i whose values depend on the component adsorbed. Steele and Ross's (1961) calculation shows that the horizontal variation is more like a conical well, but scattering from a cylindrical well is much simpler to evaluate. The surface will have many sites associated with the surface atoms. In the present case, the surface is considered homogeneous, so every site on the whole surface is characterized by Eq. 1.

The potential energy of an admolecule is also affected by other admolecules. Sinanoglu and Pitzer (1980) discuss this interaction; it is more like hard spheres than is the bulk potential for the same species. Thus, we model this potential by a hard-disk repulsion plus a weak, long-range attractive force similar to the Sutherland potential model (Hirschfelder et al., 1954).

$$\begin{aligned} U_{ij}(r_{ij}) &= \infty & r_{ij} < \sigma_{Hij} \\ &= -\epsilon_{Gij}\left[\frac{\sigma_{Hij}}{r_{ij}}\right]^6 & r_{ij} > \sigma_{Hij} \end{aligned} \tag{2}$$

where r_{ij} is the separation of the centers of the admolecules projected to the surface. Thus, the interaction potential between two admolecules of components i and j is determined by the attractive potential parameter ϵ_{Gij} and the hard-disk diameter σ_{Hij}. The total potential of a molecule i located at r_k, $U_i(r_k)$, is the sum of its surface and admolecule contributions

$$U_i = U_{si}(r_{si}) + \Sigma\, U_{ij}(r_{ij}) \tag{3}$$

EQUILIBRIUM STATISTICAL MECHANICS

For equilibrium properties, the partition function approach is adopted as previously (Lee and O'Connell, 1972, 1974, 1975). The admolecule-surface potential leads to the zero coverage Henry's constant and to the fraction of adsorbed molecules in the mobile and localized states accessible to them. The fraction in each state can be calculated from admolecule-surface interactions if the number of sites is significantly greater than the number of admolecules. This is true on graphitized carbon black at coverages fairly close to a monolayer, for example. Here, then, the fractions can be assumed to be independent of the amount adsorbed, leading to an "indistinguishable mixture" of mobile and localized species. However, for strongly localized chemisorption systems with few sites, this analysis would be inappropriate. The admolecule interactions with the Van der Waals fluid approximation lead to a coverage dependence with separate contributions from the attractive and repulsive parts. Standard statistical mechanical methods of analysis (e.g., Hill, 1960) can readily be applied to this model (as long as proper modifications are made to account for partial localization).

The molecular partition function for a single admolecule of component *i* is written as

$$q_i = q_i^{tr}\, q_i^{rot}\, q_i^{vib}\, q_i^{z} e^{U_{si}/kT} \qquad (4)$$

where q_i^{rot} and q_i^{vib} denote the rotational and vibrational partition functions, q_i^z is the partition function for the normal motions, and q_i^{tr} is the partition function for the translational motion along the two-dimensional plane. In the harmonic oscillator assumption with the frequency ν_i, q_i^z is

$$q_i^z = e^{-h\nu_i/2kT} / (1 - e^{-h\nu_i/kT}) \qquad (5)$$

The frequency ν_i should depend on whether the admolecule is on a site or not, but we assume a single average value for simplicity. For anharmonic vibrations, ν_i can be made a function of T (see below). The expression for q_i^{tr} for admolecules not on the sites (mobile-off site) is

$$q_{imo}^{tr} = \Lambda_i^{-2} A(- \Theta_{Si}) \qquad (6)$$

where

$$\Theta_{Si} = \pi\, p_s\, \sigma_{Si}^2/4 \qquad (7)$$

$\Lambda_i^{-1} = (2\,\pi\, m_i\, kT/h^2)^{1/2}$ and p_s is the number of sites per unit surface area. The admolecules on sites have extra potential energy ϵ_i and this potential energy is combined with the translational part. If the radial component of the kinetic energy is less than ϵ_i at the point of the contact with the site, the admolecules are localized. Thus, the expressions for localized admolecules, q_{il}, and mobile-on site molecules, q_{ims}, are

$$q_{il}^{tr} = \Lambda_i^{-2}(\Theta_{Si}/\varrho_s)e^{\epsilon_i/kT}\,\mathrm{erf}\,(\epsilon_1/kT) \qquad (8)$$

$$q_{ims}^{tr} = \Lambda_i^{-2} A\, \Theta_{Si} e^{\epsilon_i/kT}\, \mathrm{erfc}(\epsilon_i/kT) \qquad (9)$$

where erf (ϵ_i/kT) and erfc (ϵ_i/kT) are defined as

$$\mathrm{erf}\,(\epsilon_i/kT) = \frac{2}{\sqrt{\pi}} \int_0^{\sqrt{\epsilon_i/kT}} z^{-x^2}\, dx \qquad (10)$$

$$\mathrm{erfc}\,(\epsilon_i/kT) = \frac{2}{\sqrt{\pi}} \int_{\sqrt{\epsilon_i/kT}}^{\infty} e^{-x^2}\, dx = 1 - \mathrm{erf}\,(\epsilon_i/kT) \qquad (11)$$

They reflect the restrictions on the components of momentum distribution. This leads to

$$\begin{aligned} q_{im}^{tr} &= q_{imo}^{tr} + q_{ims}^{tr} \\ &= \Lambda_i^{-2} A[1 - \Theta_{Si} \\ &\quad + \Theta_{Si} e^{\epsilon_i/kT}\mathrm{erfc}(\epsilon_i/kT)] \end{aligned} \qquad (12)$$

It is to be noted that in writing q_{il}^{tr} the usual horizontal vibration mode is replaced by a restricted translational mode, a result of the assumption of cylindrical sites. The fractions of the various types of admolecules are then written as

$$f_{imo} = (1 - \Theta_{Si})/(1 - \Theta_{Si} + \Theta_{Si} e^{\epsilon_i/kT}) \qquad (13)$$

$$f_{il} = \Theta_{Si} e^{\epsilon_i/kT} erf(\epsilon_i/kT)/(1 - \Theta_{Si} + \Theta_{Si} e^{\epsilon_i/kT}) \qquad (14)$$

$$f_{ims} = \Theta_{Si} e^{\epsilon_i/kT}\, \mathrm{erfc}(\epsilon_i/kT)/(1 - \Theta_{Si} + \Theta_{Si} e^{\epsilon_i/kT}) \qquad (15)$$

$$\begin{aligned} f_{im} = f_{imo} + f_{ims} &= [1 - \Theta_{Si} \\ &\quad + \Theta_{Si} e^{\epsilon_i/kT}\mathrm{erfc}(\epsilon_i/kT)]/(1 - \Theta_{Si} + \Theta_{Si} e^{\epsilon_i/kT}) \end{aligned} \qquad (16)$$

The partition function for adsorbed mixtures is then

$$Q = \left[\prod_j \frac{N!}{(N_j f_{jm})!(N_j f_{jl})!} \frac{q_{im}^{N_j f_{jm}} q_{jl}^{N_j f_{jl}}}{(N_j f_{jm})!(N_j f_{jl})!}\right] \frac{M_s!}{(M_s - \sum_j N_j f_{jl})\,!} \frac{Z_N}{A^N} \qquad (17)$$

where

$$Z_N = \left[\prod_j (A_f f_{jm})^{N_j f_{jm}} (A_f f_{jl})^{N_j f_{jl}}\right] \exp \left\{ - \sum_j \sum_i (\varphi_{mij} f_{jm} + \varphi_{lij} f_{jl}) N_i/kT \right\} \qquad (18)$$

and

$$\begin{aligned} \vartheta_{mij} &= - \int_{\sigma_{Hij}}^{\infty} \epsilon_{Gij} \left(\frac{\sigma_{Hij}}{\tau}\right)^6 (f_{im} + 2 f_{il}) \left(\frac{N_i}{A}\right) 2\pi r dr \\ &= -2\epsilon_{Gij}\ \Theta_i (f_{im} + 2 f_{il}) \end{aligned} \qquad (19)$$

$$\begin{aligned} \vartheta_{lij} &= - \int_{\sigma_{Mij}}^{\infty} \epsilon_{Gij} \left(\frac{\sigma_{Hij}}{\tau}\right)^6 f_{il} \left(\frac{N_i}{A}\right) 2\pi r dr \\ &= -2\epsilon_{Gij}\ \Theta_i f_{il} \left(\frac{\sigma_{Hij}}{\sigma_{Mij}}\right)^4 \end{aligned} \qquad (20)$$

In addition, σ_{Mij} is defined by the following expression

$$\sigma_N\, \eta < \sigma_{Hij} < \sigma_N(\eta + 1) = \sigma_{Mij} \quad \eta = 1,2,3, \ldots\ldots \qquad (21)$$

where σ_N is the nearest distance of the surface lattice and η is an integer. Also σ_{Hij} and ϵ_{Gij} are given by

$$\sigma_{Hij} = (\sigma_{Hi} + \sigma_{Hj})^{/2} \qquad (22)$$

$$\epsilon_{Gij} = (\epsilon_{Gi} \bullet \epsilon_{Gj})^{1/2} \qquad (23)$$

The free area A_f is calculated from the relation

$$\partial \ln(A_f/A)^N/\partial A = \sum_i \sum_j (\pi\sigma_{Hij}^2/2)(N_i N_j/A^2)\ R_{Aij} g_{ij}(\sigma_{Hij}) \qquad (24)$$

where $g_{ij}(\sigma_{Hij})$ is the hard disk radial distribution function and R_{Aij} corrects it for the decrease of contact probability between localized molecules. The hard disk radial distribution function at contact is obtained from the two-dimensional scaled particle theory (Lebowitz et al., 1965)

$$g_{ij}(\sigma_{Hij}) = 1/(1 - \Theta) + (\sigma_{Hi}\sigma_{Hj}/2\sigma_{Hij}^2)\,\Theta/(1 - \Theta)^2 \qquad (25)$$

$$\Theta = \sum_i \Theta_i \qquad (26)$$

$$\Theta_i = \frac{\pi}{4}\, \rho_i \sigma_{Hi}^{\ 2} \qquad (27)$$

The localized admolecules may not contact one another if the distance between boundaries of occupied sites is less than σ_{Hij}. Otherwise they can contact freely. This discontinuity results from the cylindrical well assumption. This undesirable variation can be avoided by assuming that the contact probability for localized admolecules is one-half of that for mobile-mobile and localized-mobile admolecules. Thus, we assume the correction factor to be

$$R_{Aij} = 1 - \frac{1}{2} f_{il} f_{jl} \qquad (28)$$

The free area A_f then becomes

$$A_f = A(1 - \Theta)^{S_2}[- S_1\, \Theta/(1 - \Theta)] \qquad (29)$$

where

$$S_1 = \sum_i \sum_j \frac{N_i}{N} \frac{\Theta_i}{\Theta} \frac{\sigma_{Hi}}{\sigma_{Hj}} R_{Aij} \tag{30}$$

$$S_2 = \sum_i \sum_j \frac{N_i}{N} \frac{\Theta_j}{\Theta} \frac{\sigma_{Hi}}{\sigma_{Hj}} R_{Aij} \left[\frac{1}{2} \frac{(\sigma_{Hi} + \sigma_{Hj})^2}{\sigma_{Hi}\sigma_{Hj}} - 1 \right] \tag{31}$$

The adsorption isotherm follows from the equality of the chemical potential in both phases. Assuming ideal gas for the bulk phase, we have

$$\frac{\overline{G}_i}{kT} = - \left(\frac{\partial \ln Q_G}{\partial N_G} \right)_{V,T} = \frac{G_i^0}{kT} + \ln y_i P = - \left(\frac{\partial \ln \Theta}{\partial N} \right)_{A,T} \tag{32}$$

Then

$$P_i \equiv y_i P = H_i \frac{\rho_i}{\left[1 - \sum_j \Theta_j (1 - f_{jm}) / \Theta_{Hj} \right]^{(1-f_{jm})} (1 - \Theta)^{R_{1i}}} \exp\left[\frac{R_{2i} - R_{3i}\Theta^2 + R_{4i}\Theta}{(1-\Theta)^2} - 2 \sum_j \frac{\Theta_j}{kT} \epsilon_{Gij} \left(\frac{\sigma_{Hij}}{\sigma_{Hj}} \right)^2 R_{Bij} \right] \tag{33}$$

where

$$R_{Bij} = 1 + f_{il} f_{jl} \left[\left(\frac{\sigma_{Hij}}{\sigma_{Mij}} \right)^4 - 1 \right] \tag{34}$$

$$R_{1i} = 2\sigma_{Hi}^2 \left[\sum_k \frac{\Theta_k}{\Theta} \frac{R_{Aik}}{\sigma_{Hi}\sigma_{Hk}} - \sum_l \sum_k \frac{\Theta_l \Theta_k}{\Theta^2} \frac{R_{Alk}}{\sigma_{Hl}\sigma_{Hk}} \right] \tag{35}$$

$$R_{2i} = \Theta_i (S_1 + S_2) \tag{36}$$

$$R_{3i} = 2\sigma_{Hi}^2 \left[\sum_k \frac{\Theta_k}{\Theta} \frac{\sigma_{Hi}^2 + \sigma_{Hk}^2}{\sigma_{Hi}^2 \sigma_{Hk}^2} R_{Aik} - \sum_l \sum_k \frac{\Theta_l \Theta_k}{\Theta^2} \frac{\sigma_{Hl}^2 + \sigma_{Hk}^2}{\sigma_{Hl}^2 \sigma_{Hk}^2} R_{Aik} \right] \tag{37}$$

$$R_{4i} = R_{3i} - \Theta_i S_2 \tag{38}$$

$$H_i = \Lambda^{-1} \frac{kT f_{im}^{fim} f_{il}^{fil}}{(1 - \Theta_{Si} + \Theta_{Si} e^{\epsilon_i/kT})} \left[1 - \exp\left(\frac{-h\nu_i}{kT} \right) \right] \exp\left[- \left(U_{io} - \frac{1}{2} h\nu_i \right) / kT \right] \tag{39}$$

and

$$\Theta_{Hi} \equiv \Theta_{Si} \; (\sigma_{Hi}/\sigma_{Si})^2 \tag{40}$$

For a pure component Eq. 33 reduces to

$$P = H_i \frac{\rho_i}{(1 - \Theta f_{jl}/\Theta_{Hi})^{fil} (1 - \Theta)^{R_{Aii}}} \exp\left[R_{Aii} \frac{3\Theta - 2\Theta^2}{(1-\Theta)^2} - R_{Bii} \frac{2\epsilon_{Gi}}{kT} \Theta \right] \tag{41}$$

Other thermodynamic properties can be calculated from the partition function or adsorption isotherm. For example the isosteric heat of adsorption, q_{st}, is

$$\begin{aligned} \frac{q_{st}}{RT} &= \left(T \frac{\partial \ln P_i}{\partial T} \right)_{\Theta_i} \\ &= T \left(\frac{d \ln H_i}{dT} \right) + T \left(\frac{\partial R_{Aii}}{\partial T} \right)_\Theta \frac{3\Theta - 2\Theta^2}{(1-\Theta)^2} - T \left(\frac{\partial R_{Bii}}{\partial T} \right) \frac{2\epsilon G_i}{kT} \Theta + R_{Bii} \frac{2\epsilon_{Gi}}{kT} \Theta \\ &\quad - T \left(\frac{\partial R_{Aii}}{\partial T} \right)_\Theta \ln(1 - \Theta) - T \left(\frac{\partial f_{il}}{\partial T} \right) \ln\left(1 - \frac{\Theta}{\Theta_{Hi}} f_{il} \right) + \frac{f_{il}\Theta/\Theta_{Hi}}{(1 - \Theta f_{il}/\Theta_{Hi})} T \left(\frac{\partial f_{il}}{\partial T} \right)_\Theta \end{aligned} \tag{42}$$

TRANSPORT THROUGH POROUS MEDIA WITH ADSORPTION

To be directly compared with experimental data, both macroscopic expressions and microscopic modeling must be given. Macroscopically the total flow through a porous plug J_i^T is the sum of surface flux J_i^S and bulk flux J_i^G:

$$J_i^T = J_i^S + J_i^G \tag{43}$$

In general, J_i^S and J_i^G are not independent, and the presence of other components affects their values. Lumping the effect of such interactions into interaction factors Γ_i^S and Γ_i^G, we rewrite Eq. 43 as

$$J_i^T = \Gamma_i^S J_i^{SO} + \Gamma_i^G J_i^{GO} = J_i^S + J_i^G \tag{44}$$

where J_i^{SO} and J_i^{GO} are fluxes in the absence of interactions

$$J_i^{S0} = -D_i^{Se} \frac{dC_i}{dl} \tag{45}$$

$$J_i^{G0} = \frac{-D_i^{Ke}}{RT} \frac{dP_i}{dl} \tag{46}$$

where C_i is concentration of admolecules of component *i* per unit bed volume. If we assume the bulk flow is in the Knudsen regime, the effective bulk diffusion coefficient is

$$D_i^{Ke} = (2/3) r_{av} (8kT/\pi m_i)^{1/2} \; (\epsilon/\tau) \tag{47}$$

where r_{av} is the mean pore radius, R is the gas constant, T is the temperature, m_i is the molecular mass, ϵ is the void fraction, and τ is the tortuosity factor.

For the determination of surface flux, a reference flux of nonadsorbed gas is experimentally determined. Then, by the molecular weight correction of Eq. 47, the bulk flux of adsorbable gases, J_i^{GO}, is calculated. The difference between the measured total flux J_i^T and the calculated bulk flux is then attributed to surface flux. The surface flux determined by this method is related to J_i^{SO} using an interaction factor Γ_i^M:

$$J_i^T - J_i^{GO} = \Gamma_i^M J_i^{SO} \tag{48}$$

where Γ_i^M is obtained from Eq. 44, 45, and 46.

$$\Gamma_i^M = \Gamma_i^S + \frac{D_i^{Ke}}{D_i^{Se}} \frac{\Gamma_i^G - 1}{RT} \frac{dP_i}{dC_i} \tag{49}$$

Other than total fluxes or surface fluxes, experimental data are often reported as local quantities. They can be total permeability, K_i^T, surface permeability, K_i^S, total diffusion coefficient, D_i^T, and surface diffusion coefficient, D_i^S. These quantities are defined by the following equations.

$$J_i^T = -K_i^T \frac{dP_i}{dl} = -D_i^T \frac{dC_i}{dl} \tag{50}$$

$$J_i^T - J_i^{G0} = -K_i^S \frac{dP_i}{dl} = -D_i^S \frac{dC_i}{dl} \tag{51}$$

The present theory allows their calculation from the following:

$$K_i^T = \Gamma_i^M D_i^{Se} \frac{dC_i}{dP_i} + \frac{D_i^{Ke}}{RT} \tag{52}$$

$$D_i^T = \Gamma_i^M D_i^{Se} + \frac{D_i^{Ke}}{RT} \frac{dP_i}{dC_i} \tag{53}$$

$$K_i^S = \Gamma_i^M D_i^{Se} \frac{dC_i}{dP_i} \tag{54}$$

$$D_i^S = \Gamma_i^M D_i^{Se} \tag{55}$$

Knudsen flow occurs when the mean free path is much larger than the pore diameter. If the ratio of the mean free path to the pore diameter is not greater than unity, the usual method of calculating the gas phase flux from the helium flux by the molecular weight correction becomes unreliable. Such problems related with these porous media are discussed by Barrer and Gabor (1960), for example.

For the calculation of Γ_i's, it is convenient to use a matrix form.

$$-\begin{bmatrix} \frac{dP_1}{dl} & \frac{D_1^{Ke}}{RT} \\ \frac{dC1}{dl} & D_1^{Se} \\ & \\ \frac{dP_c}{dl} & \frac{D_c^{Ke}}{RT} \\ \frac{dC_c}{dl} & D_c^{Se} \end{bmatrix} = \begin{bmatrix} \alpha_{11} & - - - - - - - & \alpha_{1.2c} \\ \alpha_{21} & - - - - - - - & \alpha_{2.2c} \\ & & \\ \alpha_{2c-1,1} & - - - - - - - & \alpha_{2c-1,2c} \\ \alpha_{2c,1} & - - - - - - - & \alpha_{2c,2c} \end{bmatrix} \begin{bmatrix} J_1^G \\ J_1^S \\ \\ J_c^G \\ J_c^S \end{bmatrix}$$

where c is the number of components. If a component k does not adsorb, the elements D_k^{Se} and J_k^S are zero so they should be omitted from Eq. 56. Inversion of Eq. 56 gives a coefficient matrix $(\boldsymbol{b})_{ij} = (\boldsymbol{a}^{-1})_{ij}$

$$\begin{bmatrix} J_1^G \\ J_1^S \\ \\ J_c^G \\ J_c^S \end{bmatrix} = - \begin{bmatrix} b_{11} & - - - - - - - & b_{1.2c} \\ b_{21} & - - - - - - - & b_{2c.2c} \\ & & \\ b_{2c-1,1} & - - - - - - - & b_{2c-1,2c} \\ b_{2c,1} & - - - - - - - & b_{2c,2c} \end{bmatrix} \begin{bmatrix} \frac{D_1^{Ke}}{RT} & \frac{dP_1}{dl} \\ D_1^{Se} & \frac{dC1}{dl} \\ \frac{D_c^{Ke}}{RT} & \frac{dP_c}{dl} \\ D_1^{Se} & \frac{dC_c}{dl} \end{bmatrix}$$

where the quantities Γ_i^G and Γ_i^S are then

$$\Gamma_i^G = \sum_j b_{2(i-1)+1,2(j-1)+1} \quad \frac{D_j^{Ke}}{D_i^{Ke}} \frac{dP_j}{dP_i} + \sum_j b_{2(i-1)+1,2j} \quad \frac{D_j^{Se}}{D_i^{Ke}} \frac{dC_j}{dP_i} RT \tag{58}$$

$$\Gamma_i^S = \sum_j b_{2i,2(j-1)+1} \quad \frac{D_j^{Ke}}{D_i^{Se}} \frac{dP_j}{dC_i} \frac{1}{RT} + \sum_j b_{2i,2j} \frac{D_j^{Se}}{D_i^{Se}} \frac{dC_j}{dC_i} \tag{59}$$

Model expressions for the coefficients a and diffusion coefficient D_i^{Se} are given below. In addition to them, an expression for dP_i/dC_i is needed. For a pure component, this derivative can be evaluated from differentiating the experimental adsorption isotherm or from the above theory and its parameters. For mixtures, however, dP_i/dC_j cannot be directly evaluated from equilibrium adsorption. Rather, the following relation must be used.

$$\frac{dP_i}{dl} = \sum_j \left(\frac{\partial P_i}{\partial C_j}\right)_{T,C_{k\neq j}} \left(\frac{dC_j}{dl}\right) \tag{60}$$

where $\partial P_i/\partial C_j$ is the isotherm derivative. Equation 60 could be evaluated experimentally only if profiles for the P_i's or C_i's are known. Normally, however, the theoretical expression for these quantities, Eq. 33, would be used.

STATISTICAL MECHANICS OF SURFACE DIFFUSION

For transport, we use the Chapman-Enskog method as before. A Boltzmann equation is written for the admolecule distribution function with collision operators for the various scattering mechanisms. In addition to those of the structured potential and the admolecules, we now include effects from normal vibrations, adsorbed molecules of other components, and interactions with bulk gas molecules.

In the above expressions, the surface diffusion coefficient contains the information about the field of the adsorbed molecules which must be mobile. In the absence of interactions with the bulk phase, three types of effects are considered: admolecule-site interactions, normal vibrations, and admolecule-admolecule interactions. When a mobile molecule collides with a site, it changes its energy state. Depending on its momentum, it may leave the site or not. Even if it leaves the site, it loses part of its momentum in the direction of flow. There are also vertical collisions of admolecules with the surface due to normal vibrations, which result in partial loss of the momentum in the direction of flow. As the amount adsorbed increases, the mobile molecules collide with localized molecules as well. When there are other components adsorbed on surfaces, the collisional effects should also include those with localized and mobile species of the other components.

To make the statistical mechanical analysis less complicated, we consider a steady state problem for homogeneous media in the presence of an external force X_i (which turns out to be the chemical potential gradient) acting on species *i* as presented by Rice and Gray (1967) for liquid diffusion. The Boltzmann equation for mobile species of component *i* can be written as

$$X_i \bullet \nabla_{p_i} F_{im} = \sum_j J_2(F_{im},F_{jl}) + J_2(F_{im},F_s) + J_2(F_{im},z) + \sum_{i \neq j} J_2(F_{im},F_{jm}) \tag{61}$$

where the righthand side indicates the four binary collision operators due to interactions with localized admolecules, interactions with sites, normal vibrations, and interactions with the mobile species of other components, respectively. The *F*'s are the momentum distribution functions for various species. When normalized, they are given by following equations at equilibrium.

$$F_{il}^{(o)} = \frac{\rho_i f_{il}}{2\pi m_i kT} \exp\left(-\frac{p_i^2}{2m_i kT}\right) / \operatorname{erf}(\epsilon_i/kT) \qquad \frac{p_{ix}^2}{2m_i} < \epsilon_i \tag{62}$$

$$F_{im}^{(o)} = F_{ims}^{(o)} + F_{imo}^{(o)} \tag{63}$$

$$F_{imo}^{(o)} = \frac{\rho_i f_{imo}}{2\pi m_i kT} \exp\left(-\frac{p_i^2}{2m_i kT}\right) \tag{64}$$

$$F_{ims}^{(o)} = \frac{\rho_i f_{ims}}{2\pi m_i kT} \exp\left(-\frac{p_i^2}{2m_i kT}\right) / \operatorname{erfc}(\epsilon_i/kT) \qquad \frac{p_{ix}^2}{2m_i} > \epsilon_i \tag{65}$$

$$F_s^{(o)} = \frac{\rho_s}{2\pi m_s kT} \exp\left(-\frac{p_s^2}{2m_s kT}\right) \tag{66}$$

In the above equations for $F_{il}^{(0)}$ and $F_{ims}^{(0)}$, p_{ix} is a component of the momentum and reflects the assumption that admolecules on sites that move perpendicular to the circumference but have kinetic energy less than ϵ_i are localized, as in the equilibrium property calculations.

Consistent with the theory of the Van der Waals fluid (Dymond and Alder, 1966), $J_2(F_{im},F_{jl})$ and $J_2(F_{im},F_{jm})$ involve only hard-disk interactions and are written as

$$J_2(F_{im},F_{jl}) = g_{ij}(\sigma_{\mathrm{Hij}})\sigma_{Hij} \iint_{g\cdot k>0} (F'_{im}F'_{jl} - F_{im}F_{jl})\,(\mathbf{g} \bullet \mathbf{k})d\mathbf{k}d\mathbf{p}_j \tag{67}$$

$$J_2(F_{im},F_{jm}) = g_{ij}(\sigma_{Hij})\sigma_{Hij} \iint_{g\cdot k>0} (F'_{im}F'_{jm} - F_{im}F_{jm})\,(\mathbf{g} \bullet \mathbf{k})d\mathbf{k}d\mathbf{p}_j \tag{68}$$

where **g** is the reduced relative velocity and ***k*** is the unit vector in the center to center direction. Primed quantities refer to the states after collision.

$J_2(F_{im},F_s)$ is formulated similar to that in the square well theory of bulk transport (McLaughin and Davis, 1966), but without the hard-sphere collision effects. The incoming and outgoing collisions are assumed uncorrelated because of the rapid vibration of surface atoms. This collision operator consists of two parts; one for incoming collisions and the other for outgoing collisions.

$$J_2(F_{im},F_s) = J_2(F_{imo},F_s) + J_2(F_{ims},F_s) \tag{69}$$

$$J_2(F_{imo},F_s) = \frac{\sigma_{si}}{2} \iint_{g\cdot k>0} (F'_{imo}F'_s - F_{imo}F_s)\,(\mathbf{g} \bullet \mathbf{k})d\mathbf{k}d\mathbf{p}_s \bullet g_{is}(+\sigma_{Si}/2) \tag{70}$$

$$J_2(F_{ims},F_s) = \frac{\sigma_{Si}}{2} \int \int_{g\cdot k<-\left(\frac{\epsilon_i}{kT}\right)^{1/2}} (F'_{ims}F'_s - F_{ims}F_s)\,(\mathbf{g} \bullet \mathbf{k})d\mathbf{k}d\mathbf{p}_s \bullet g_{is}(-\sigma_{Si}/2) \tag{71}$$

where $g_{is}(+\sigma_{Si}/2)$ and $g_{is}(-\sigma_{Si}/2)$ are the radial distribution functions at contact of sites and admolecules at the outside and inside of the cylindrical wall, respectively. They are assumed to be 1 and $e^{\epsilon_i/kT}$, respectively, so that their ratio is consistent with that of the square well theory. The quantity $J_2(F_{im},z)$ is the effect of normal vibrations on the surface plane. The normal motion of admolecules would not affect the motion in the surface plane for elastic collisions, but here they are inelastic. We formulate this effect using the basic equation of Markovian processes (Rice and Gray, 1965).

$$J_2(F_{im},z) = \int [F_{im}(\mathbf{p}'_i)K(\mathbf{p}'_i,\mathbf{p}_i) - F_{im}(\mathbf{p}_i)K(\mathbf{p}_i,\mathbf{p}'_i)]d\mathbf{p}'_i \tag{72}$$

where $K(\mathbf{p}_i,\mathbf{p}_i')$ is the rate of transition from $\mathbf{p}_i'$ *to* $\mathbf{p}_i'$. In this particular case, $\mathbf{p}_i'$ is in the equilibrium distribution whereas $\mathbf{p}_i$ is not. Therefore $K(\mathbf{p}_i',\mathbf{p}_i)$ should be zero and $J_2(F_{im},z)$ can be rewritten as

$$J_2(F_{im},z) = -\int F_{im}(\mathbf{p}_i)K(\mathbf{p}_i,\mathbf{p}'_i)d\mathbf{p}'_i = -F_{im}(\mathbf{p}_i)\zeta_i \tag{73}$$

Now the solution for the distribution can be obtained in the usual linear approximation (Lee and O'Connell, 1972) by assuming

$$F_{im} = F_{im}^{(o)}(1 + \Phi_i) \tag{74}$$

and multiplying both sides of Eq. 61 by $\psi_i^{(0)}$

$$\psi_i^{(s)} \equiv \frac{q_i}{(2m_i kT)^{1/2}} S_{3/2}^{(s)}\left(\frac{p_i^2}{2m_i kT}\right) \tag{75}$$

where $S_{3/2}^{(s)}$ is a Kihara function (Kihara, 1953) for bulk transport and q_i is the component of momentum in the direction of flow. Finally we integrate over $\mathbf{p}_i$. In the solution we assume

$$F_{il} = F_{il}^{(o)} \tag{76}$$

$$F_s = F_s^{(o)} \tag{77}$$

because localized molecules and sites do not flow. We also assume the mass of the sites is very large. Then $\mu_{is} = m_i$ and $p_{ix}/\sqrt{2m_i kT}$ is very close to **g**. Therefore the limit of integration on the relative velocity frame in Eq. 68 becomes consistent with the equation on the absolute velocity frame in Eq. 65. Furthermore, in the evaluation of $J_2(F_{im},F_{jm})$ it is convenient to assume that F_{jm} is in equilibrium in the frame of motion with the average velocity $<v_j>$ for component *j*. This means that $F_{jm}^{(o)}$ and $\Phi_i - <v_j>$ replaces F_{jm} and Φ_i. Finally we identify X_i as the chemical potential gradient of admolecules, which is equal to the chemical potential gradient of bulk molecules.

$$X_i = -\Delta \overline{G_i} \tag{78}$$

Using the above development in Eq. 61, the desired effective surface diffusivity is

$$D_i^{Se} = \frac{1}{\delta \xi_{ii}} \left(\frac{\partial \ln P_i}{\partial \ln_{\rho_i}} \right) \tag{79}$$

where δ is the effectiveness factor for surface diffusion, $(\delta \ln P_i/\partial \ln p_i)$ is the isotherm derivative, and ξ_{ii} is given below. The number density per unit surface area, ρ_i is related to C_i by

$$C_i = \rho_i \sigma / N_{av} \tag{80}$$

where N_{av} is the Avogadro's number and σ is the surface area per unit bed volume. The quantity ξ_{ii} is calculated from

$$\begin{aligned} \xi_{ii} = (4\pi m_i/kT)^{1/2} \Big[& \sum_j \rho_i g_{ij} (\sigma_{Hij}) E_{Pij} (2\mu_{ij}/m_i)^{1/2} \\ & + \rho_s A_f \sigma_{Si} E_{Si} + \zeta_i E_{Ki} \\ & + \sum_{j \neq i} \rho_i g_{ij} (\sigma_{Hij}) E_{Mij} (2\mu_{ij}/m_i)^{1/2} / f_{im} \Big] \end{aligned} \tag{81}$$

$$\xi_{ij} = (8\pi \mu_{ij}/kT)^{1/2} \rho_i g_{ij} (\sigma_{Hij}) E_{Mij} / f_{jm} \tag{82}$$

$$E_{Ki} = (m_i/4\pi kT)^{1/2} / f_{im} \tag{83}$$

$$\begin{aligned} E_{Si} = G_c(\epsilon_i/kT)/[2\sqrt{2} f_{im} \{ 1 - & \Theta_{Si} \\ & + \Theta_{Si} (e^{\epsilon_i/kT} \operatorname{erfc}(\epsilon_i/kT) \\ & + (\epsilon_i/kT)^{1/2}/\sqrt{\pi} \}] \end{aligned} \tag{84}$$

$$\begin{aligned} E_{Pij} = \Big[& G_a(2\epsilon_j/kT) / \operatorname{erf}(\epsilon_j/kT) \\ & + (f_{ims}/f_{imo}) \left\{ G_a\left(\frac{2\epsilon_i + 2\epsilon_i}{kT} \right) \right. \\ & \left. - G_a\left(\frac{2\epsilon_i}{kT} \right) \right\} / \{ \operatorname{erfc}(\epsilon_i/kT) \operatorname{erf}(\epsilon_j/kT) \} \Big] \\ & f_{il}(1 - \Theta_{St}) / [2 f_{im} \{ 1 - \Theta_{Si} + \Theta_{St} (e^{\epsilon_i/kT} \operatorname{erfc}(\epsilon_i/kT) \\ & + (\epsilon_i/kT)^{1/2}/\sqrt{\pi}) \}] \end{aligned} \tag{85}$$

$$\begin{aligned} E_{Mij} = \Big[& f_{imo} f_{imo} + f_{imo} f_{ims} \{ 1 - G_a(2\epsilon_j/kT) \} \\ & / \operatorname{erfc}(\epsilon_j/kT) + f_{ims} f_{jmo} \{ 1 - G_a(2\epsilon_i/kT) \} / \\ & \operatorname{erfc}(\epsilon_i/kT) + f_{ims} f_{jms} \left\{ 1 - G_a\left(\frac{2\epsilon_i + 2\epsilon_j}{kT} \right) \right\} / \\ & \{ \operatorname{erfc}(\epsilon_i/kT) \operatorname{erfc}(\epsilon_j/kT) \} \Big] \\ & (1 - \Theta_{St}) / [2 f_{imo} \{ 1 - \Theta_{St} + \Theta_{Si} (e^{\epsilon_i/kT} \operatorname{erfc}(\epsilon_i/kT) \\ & + (\epsilon_i/kT)^{1/2}/\sqrt{\pi} \}] \end{aligned} \tag{86}$$

Also

$$\begin{aligned} & G_a(\epsilon_i/kT) = \frac{2}{\pi^{1.5}} \int e^{-x^2 - y^2 - X^2 Y^2} x^3 \, dx \, dy \, dX \, dY \\ & x^3 + y^2 + X^2 + Y^2 \leq \epsilon_i/kT \quad x > 0 \end{aligned} \tag{87}$$

and

$$G_c(\epsilon_i/kT) = 1 + \epsilon_i/2kT - 2G_b(\epsilon_i/kT) \tag{88}$$

where

$$G_b(\epsilon_i/kT) = \int_{z \geq 0} e^{-z^2} z^2 (z^2 + \epsilon_i/kT)^{1/2} \, dz \tag{89}$$

The functions G_a and G_b are tabulated in Lee and O'Connell (1972). The function erfc(ϵ_i/kT) defined by Eq. 11 often appears in denominators in our expressions. Accurate values for it may be obtained from the tabulated function G_d (Table 1) for small values of ϵ_i/kT.

$$\begin{aligned} G_d(\epsilon_i/kT) & = e^{\epsilon_i/kT} \operatorname{erfc}(\epsilon_i/kT) \\ & = \frac{2}{\sqrt{\pi}} \int_0^\infty e^{-z^2} z (z^2 + \epsilon_i/kT)^{-1/2} \, dz \end{aligned} \tag{90}$$

The friction coefficient ζ_i is calculated as a product of the vertical vibrational frequency ν_i and the average momentum accommodation coefficient γ_i in each collision. The accommodation coefficient, γ_i, is implicitly a dyadic quantity in the direction of the velocity of colliding molecules; it must be transformed to an effective accommodation in the direction of the average flow leading to

$$\zeta_i = \nu_i \gamma_i \int \cos^2 \vartheta d\vartheta \int d\vartheta = 1/2 \nu_i \gamma_i \tag{91}$$

For the case of surface diffusion of a tracer (component t) which is negligible in concentration in component i but with the same intermolecular forces,

$$J_t^S = -D_t^{Se} \frac{\partial C_t}{\partial l} \tag{92}$$

GAS-SURFACE FLUX INTERACTION

To account for effects of molecular collisions between the bulk and adsorbed phases, we extend the momentum balance equation developed by Thakur et al. (1980) for the partial pressure gradient of species i in a mixture flowing through a porous medium. Here,

$$-\frac{dP_i}{dl} = \frac{\tau}{\epsilon} \left(M_i^W + M_i^S + \sum_{j \neq i} M_{ij}^G \right) \tag{93}$$

where the quantities M_i^W, M_i^S, and M_{ij}^G are the rate of momentum lost per unit pore volume due to collisions of i with the wall, with admolecules of i and other components j, and with bulk phase j molecules, respectively. For a pure component, M_{ij}^G vanishes and only the effect of collisions with wall and admolecules remains. Therefore this equation is valid in the Knudsen regime. For mixtures, when convective flow is absent in the bulk phase Eq. 93 is probably valid even at high pressures. In particular, convective flow can be neglected if the total pressure is constant even though the mole fractions differ across the bed. In Eq. 93 the wall momentum loss is

$$M_i^W = \frac{\epsilon}{\tau} \frac{RT}{D_i^{Ke}} \left(1 - \sum_j \Theta_{ij} \right) J_i^G \tag{94}$$

where J_i^G is the bulk phase flux for component i, and D_i^{Ke} is the Knudson diffusion coefficient of component i given in Eq. 47. Finally Θ_{ij} is the fraction of surface covered by admolecules of component j that collide with bulk phase component i. Thakur et al. (1980) obtained the following equation for M_i^s:

TABLE 1. TABULATED VALUES OF FUNCTIONS

ϵ/kT	$G_a(\epsilon/kT)$	$G_c(\epsilon/kT)$	$G_d(\epsilon/kT)$	ϵ/kT	$G_a(\epsilon/kT)$	$G_c(\epsilon/kT)$	$G_d(\epsilon kT)$
0.0	0.0	0.0	1.0	5.0	0.922	1.250	0.252
0.2	0.039	0.012	0.643	5.2	0.932	1.316	0.228
0.4	0.098	0.034	0.553	5.4	0.941	1.380	0.225
0.6	0.163	0.062	0.498	5.6	0.948	1.446	0.221
0.8	0.228	0.096	0.458	5.8	0.955	1.514	0.218
1.0	0.291	0.134	0.427	6.0	0.961	1.580	0.215
1.2	0.351	0.176	0.403	6.2	0.966	1.648	0.211
1.4	0.407	0.220	0.382	6.4	0.971	1.716	0.209
1.6	0.460	0.266	0.365	6.6	0.975	1.784	0.206
1.8	0.510	0.314	0.349	6.8	0.979	1.854	0.203
2.0	0.556	0.364	0.336	7.0	0.982	1.920	0.200
2.2	0.598	0.416	0.324	7.2	0.985	1.992	0.198
2.4	0.637	0.468	0.314	7.4	0.987	2.062	0.195
2.6	0.674	0.522	0.304	7.6	0.989	2.138	0.193
2.8	0.707	0.578	0.295	7.8	0.991	2.202	0.191
3.0	0.737	0.636	0.287	8.0	0.993	2.274	0.189
3.2	0.765	0.694	0.280	8.2	0.994	2.344	0.187
3.4	0.791	0.752	0.273	8.4	0.995	2.416	0.185
3.6	0.814	0.812	0.267	8.6	0.996	2.488	0.183
3.8	0.835	0.872	0.261	8.8	0.997	2.560	0.181
4.0	0.853	0.934	0.255	9.0	0.998	2.632	0.179
4.2	0.870	1.016	0.250	9.2	0.999	2.706	0.177
4.4	0.886	1.058	0.245	9.4	1.000	2.778	0.175
4.6	0.899	1.122	0.241	9.6	1.000	2.852	0.174
4.8	0.912	1.186	0.236	9.8	1.000	2.924	0.172

$$M_i^S = \frac{\epsilon}{\tau}\left\{\frac{RT}{D_i^{Ke}}\sum_j \Theta_{ij}(1 - f_{jm})\, J_i^G + \frac{RT}{D_i^{Ke}}\sum_j \Theta_{ij} f_{jm}\frac{\mu_{ij}}{m_j}\left(J_i^G - J_i^S\frac{8N_i}{3\pi C_j f_{jm}}\right)\right\} \tag{95}$$

On the righthand side of Eq. 95 the first term is due to inelastic collisions with the localized *i* admolecules while the second term is due to elastic collisions with mobile *i* admolecules. An expression for Θ_{ij} can be developed assuming that the collisions of bulk *i* molecules with localized *j* admolecules are diffusive, while those with mobile *j* admolecules are elastic. Thakur et al. gave such an expression for Θ_{ji} for interphase collisions and our extension to the multicomponent case is

$$\Theta_{ij} = \left[1 - \left(1 - \sum_k \Theta_{Tik}\right)\right.$$
$$\left.\exp\left\{-5\sum_k \Theta_{Tik}\Big/\left(1 - \sum_k \Theta_{Tik}\right)\right\}\right]\Theta_{Tij}\Big/\sum_k \Theta_{Tik} \tag{96}$$

where

$$\Theta_{Tik} = \frac{\pi}{4}\rho_k\sigma^2{}_{Hik} \tag{97}$$

ρ_k is the number density of component *k* per unit surface area and σ_{Hij} is the arithmetic average of σ_{Hi} and σ_{Hj}. $M_{ij}{}^G$ is written from the kinetic theory of gases:

$$M_{ij}^G = \frac{RT}{D_{ij}}\left(y_j J_i^G - y_i J_j^G\right) \tag{98}$$

where y_i is the mole fraction of *i* in the bulk phase and D_{ij} is the mutual diffusion coefficient.

For the calculation of surface fluxes in the presence of interphase collisions, the momentum transfered to the mobile species of component *i* from the bulk phase is a driving force for surface flow. For a mole of mobile admolecule *i*, this effect is obtained from the second term of the righthand side of Eq. 95 multiplied by τ/ϵ and divided by the moles of mobile admolecule in a unit volume of bed ($=$ $C_i f_{im}$). This term is added to the chemical potential gradient to give an effective driving force $X_i{}^e$ for component *i*.

$$X_i^e = RT\sum_j \frac{\Theta_{ji}}{D_j^{Ke}}\frac{\mu_{ij}}{m_j}\left(J_j^G - J_i^G\frac{8N_j}{3\pi C_i f_{im}}\right)\frac{1}{C_i} - \frac{RT}{\delta C_i}\frac{\partial \ln P_i}{\partial \ln \rho_i}\frac{dC_i}{dl} \tag{99}$$

This is now substituted for X_i in the modified Boltzmann equation given in Eq. 61, and the general flux equation is obtained. Lee et al. (1983) give the derivation for pure components.

For a pure component flow, the above analysis indicates that the interaction increases the bulk phase flow. This is analogous to replacing the fixed-wall inelastic collision by an elastic collision against a wall moving in the same direction, where the bulk phase flow would certainly be enhanced. The surface flow is also increased by bulk flowing in the same direction, as our numerical results always show.

Use of Eq. 93–99 yields expressions for the matrix **a** of Eq. 56. This matrix is numerically inverted to given matrix **b** which is needed in evaluating $\Gamma_i{}^G$ and $\Gamma_i{}^S$ of Eqs.58 and 59.

$$a_{2(i-1)+1,2(j-1)+1} = \left[1 - \sum_k \Theta_{ik} f_{km}(1 - \mu_{ik}/m_i)\right](1 - \delta_{uj}) + y_i\frac{D_i^{Ke}}{D_{ij}}\left(\frac{\tau}{\epsilon}\right) \tag{100}$$

$$a_{2(i-1)+i1,2j} = -\Theta_{ij}\frac{\mu_{ij}}{m_i}\frac{8}{3\pi}\frac{N_i}{C_j} \tag{101}$$

$$a_{2i,2(j-1)+1} = \frac{\Theta_{ji}}{D_j^{Ke}\xi_{ii}}\frac{\mu_{ij}}{m_j} \tag{102}$$

$$a_{2i,2j} = 1 + \frac{1}{\delta}\sum_k \frac{\Theta_{Kt}}{D_k^{Ke}\xi_{tt}} \frac{\mu_{ik}}{m_k} \frac{8}{3\pi} \frac{N_k}{C_i f_{tm}} \qquad (i = j)$$

$$= -\frac{\xi_{tt}}{\zeta_{tt}} \qquad (i \neq j) \quad (103)$$

Finally, to completely relate the theory to experiment, equations must be given for the reduction of pore volume due to adsorption, for the momentum accommodation coefficients X_i in Eq. 91 and for a method to correct vibrations normal to the surface for the effect of anharmonicity. We define the effective void fraction ϵ^e for bulk flow

$$\epsilon^e = \epsilon - \sigma\sum_i \Theta_i\sigma_{Hi} \qquad (104)$$

where Θ_i is the fractional surface coverage by component i as defined by Eq. 27, σ is the surface area per unit bed volume, and σ_{Hi} is the hard-disk diameter of component i. In writing Eq. 104 to account for pore size reduction we assume the admolecules are hard spheres.

For the momentum accommodation coefficient of a single collision of an admolecule with a surface atom, the classical expression due to Baule (Loeb, 1961, for example) is used with a proportionality factor α_i.

$$\gamma_i = \alpha_i m_s/(m_i + m_s) \qquad (105)$$

where m_s and m_i are the molecular weight of surface atoms and adsorbed components, respectively. Goodman (1969) assumed that α_i depends on the incident angle and the structure of solid surface. When his results for point molecules colliding with hard-sphere surface atoms are angle-averaged, $\alpha_i = 0.5$ for the tangential momentum accommodation. We assert that this is adequate for real collisions on the surfaces of interest here.

For the normal vibration anharmonicity, which is important for modeling over wide temperature ranges, we follow the method of Pitzer (1953) for equilibrium and transport properties. An effective vibrational frequency, ν^e, for use in the partition function of Eq. 5 and the friction coefficient of Eq. 91 can be calculated as

$$\nu^e = \frac{kT}{h}\left[1 - \left\{1 - \exp\left(\frac{h\nu}{kT}\right)\right\}/ \left\{1 + \frac{2h\nu x}{kT}/\left(\exp\left(\frac{h\nu}{kT}\right) - 1\right)^2\right\}\right] \qquad (106)$$

where x is a parameter. This effective frequency is used for the adsorption isotherm of Eq. 39 when x is nonzero.

Anharmonicity also effects transport. The potential energy normal to the surface is flattened relative to the harmonic form because the vibrational frequency is proportional to the square root of the second derivative of the potential with respect to the distance. This in turn implies that the effective distance of the potential minimum from the surface is increased, while the minimum adsorption potential energy remains constant. In a structured surface potential (whether homogeneous or not), the differences in energy between sites and surroundings are reduced as the average adsorbate-adsorbent separation is increased. As a result, the potential appears more uniform and the effective value of the site energy, ϵ_i, becomes smaller as the temperature increases. Inspection of Steele's (1973) calculation for argon and krypton indicates that a relation for the effective activation energy, ϵ_i^e might be

$$\epsilon_i^e = \epsilon_i(\nu_i^e/\nu_i) \qquad (107)$$

This ϵ_i^e is used in Eq. 84–90 when the anharmonicity parameter x is nonzero.

CONCLUSIONS

A complete theory has been developed for equilibrium and transport for porous media with submonolayer adsorption on homogeneous surfaces. Equations 33 to 40 (with Eqs. 106 and 107 for systems varying over wide temperature ranges) are used to describe equilibrium adsorption for highly mobile to highly localized adsorbates. Depending on the desired transport property chosen from Eqs. 44–55, the model expressions are Eqs. 58, 59, 60, 79, 80–91, 96, 97, and 100–107. The model quantities are the physical parameters of the mean adsorption energy U_{oi}, the low temperature vibration frequency ν_i and its anharmonicity χ, the surface potential energy ϵ_i and site diameter σ_{Si}, the admolecule interaction energy ϵ_{Gi} and diameter σ_{Hi}, and the surface tortuosity factor δ. Also needed are the experimentally accessible bulk void fraction ϵ, the site density p_s and nearest neighbor site separation σ_N, the total surface area A, the surface area per unit volume σ, the Knudsen diffusion coefficient D_i^{Ke}, and the gas phase mutual diffusion coefficients D_{ij}. While this appears to be a large amount of information, the application of the model to real systems is fairly straightforward. Part II applies the model to all of the data we are aware of.

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NOTATION

A = surface area per unit mass of adsorbent, $m^2 \cdot kg^{-1}$
A_f = free area, Eq. 29
a = element of matrix defined by Eq. 56
b = element of matrix defined by Eq. 57
C = molar concentration of admolecules per unit bed volume, $mol \cdot m^{-3}$
D^{Ke} = effective Knudsen diffusion coefficient, Eq. 47 $m^2 \cdot s^{-1}$
D^S = surface diffusion coefficient, Eqs. 45–59, 79, $m^2 \cdot s^{-1}$
D^T = total diffusion coefficient, Eq. 53, $m^2 \cdot s^{-1}$
E_K = factor for surface diffusion coefficient, Eqs. 81 and 83
E_M = factor for surface diffusion coefficient, Eqs. 81 and 86
E_P = factor for surface diffusion coefficient, Eqs. 81 and 85
E_S = factor for surface diffusion coefficient, Eqs. 81 and 84
F = momentum distribution function, Eqs. 61–77
f = fraction of admolecules in state
$\overline{G_i}$ = chemical potential, J/mol^{-1}
G_a = function defined by Eq. 87 for use in Eqs. 85 and 86
G_b = function defined by Eq. 89 for use in Eq. 88
G_c = function defined by Eq. 88 for use in Eq. 84
G_d = function defined by Eq. 90 for estimating $\mathrm{erfc}(\epsilon_i/kT)$ at small values of ϵ_i/kT
g = relative velocity of colliding molecules along the mass center, $m \cdot s^{-1}$
g = radial distribution function
H = Henry's constant for adsorption, Eqs. 33 and 39, Pa/m^2
h = Planck's constant, 6.625×10^{-34} $J \cdot s$
J = molar flux, $mol \cdot m^{-2} \cdot s^{-1}$
J_2 = collision operators
K = permeability, Eqs. 50–54, $mol \cdot m^{-1} \cdot Pa^{-1} \cdot s^{-1}$

k = Boltzmann constant, $1.38 \times 10^{-23} J \cdot K^{-1}$
$\mathbf{k}$ = unit vector between spaces centers
l = coordinate along the axis of flow, m
M_s = number of surface sites
M = rate of momentum loss due to collisions, Eqs. 93–98
m = atomic or molecular mass
N = number of molecules
N_{av} = Avogadro's number, 6.023×10^{23} molecules·mol^{-1}
P = pressure, Pa
P_i = partial pressure of component i = y_iP, Pa
p = momentum
Q = system partition function, Eq. 17
q = molecular partition function, Eqs. 4–12
q_{st} = isosteric heat of adsorption, Eq. 42, J·ml^{-1}
R = universal gas constant, 8.314 J·mol^{-1}·K^{-1}
R_A = correction factor defined by Eq. 28
R_B = correction factor defined by Eq. 34
R_1 = defined by Eq. 35
R_2 = defined by Eq. 36
R_3 = defined by Eq. 37
R_4 = defined by Eq. 38
r = separation between species centers, m
r_{av} = mean pore radius, m
S_1 = expression defined by Eq. 30 used in Eq. 29
S_2 = expression defined by Eq. 31 used in Eq. 29
T = temperature, K
U = potential energy of admolecules, Eqs. 1–3, J·mol^{-1}
$<v_j>$ = average velocity of component j, M·s^{-1}
X_i = force acting on an admolecule, Eq. 61
x = anharmonicity parameter Eq. 106
y = gas phase mole fraction
Z_N = configurational part of the partition function, Eq. 18

Greek Letters

α = proportionality factor for accommodation, Eq. 105
γ = momentum accommodation coefficient, Eq. 91
Γ = gas-adsorbate interaction coefficient factor, Eqs. 44–59
δ = effectiveness factor for surface diffusion, Eq. 79
δ_{ij} = Kronecker delta
ϵ = bed void fraction
ϵ_i = admolecule-site interaction energy, J·mol^{-1}
ϵ_G = admolecule-admolecule interaction energy, J·mol^{-1}
ζ = friction coefficient defined by Eq. 91 for use in Eq. 81
θ = total surface coverage, Eq. 26
θ_i = surface coverage by component i, Eq. 27
θ_{ij} = surface coverage for interphase interaction defined in Eq. 96 for use in Eqs. 94 and 95
θ_s = fractional coverage of surface (dimensionless), Eq. 7
θ_T = fractional coverage of surface defined by Eq. 97
θ_H = surface coverage defined by Eq. 40, for use in Eqs. 33, 41, and 42
Λ = inverse de Broglie wave length = $(2\pi m_ikT/h^2)^{-1/2}$, m^{-1}
μ = reduced mass, kg
ν = frequency of normal vibration, s^{-1}
ξ = terms defined by Eqs. 81 and 82
ρ = moles adsorbed per unit surface area, m^{-2}
ρ_s = number density of sites per unit surface area, m^{-2}
σ = surface area per unit bed volume, m^{-1}
σ_H = hard-disk size for admolecule-admolecule interaction, m
σ_S = site size, m
σ_M = nearest distance between localized admolecules, m, Eq. 21
σ_N = nearest distance between surface sites, m
$\varphi_m \varphi$ = quantities defined in Eqs. 19 and 20 for Eq. 18
Φ = linear perturbation term in the momentum distribution function, Eq. 74
τ = bed tortuosity factor for Knudsen flow
$\psi_i^{(s)}$ = factor defined by Eq. 75

Superscripts

o = standard state
O = absence of interphase interactions, Eqs. 45 and 46
(o) = equilibrium distribution
e = effective properties
G = bulk gas phase
K = Knudsen flow
rot = rotational mode
S = adsorbed phase
Se = effective surface flow
T = total
tr = transational mode
vib = intramolecular vibrational mode
W = unadsorbed surface
z = normal vibrational mode

Subscripts

i = component i
ij = interactions between components i and j
im = mobile state of component i
imo = mobile state of component i off sites
ims = mobile state of component i on sites
il = localized state of component i
j = running index for components
k = running index for components
oi = potential off sites relative to bulk phase
s = surface site
Si = interactions between component i and surface sites
t = tracer component
x = normal to site circumference

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