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SURFACE DIFFUSION ON ENERGETICALLY HETEROGENEOUS SURFACES—AN EFFECTIVE MEDIUM APPROXIMATION APPROACH

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Abstract—A model based on the effective medium approximation is presented which describes surface diffusivity on an energetically heterogeneous surface as a function of overall surface coverage and a heterogeneity parameter. The heterogeneity parameter is obtained independently from the equilibrium adsorption data. The effect of heterogeneity on surface diffusion depends on the relationship between the activation energy of surface diffusion and the energy of adsorption. The effect of the coordination number is discussed. On comparison with other models for both heterogeneous and homogeneous surfaces, it is shown that the model proposed in this work gives a better representation of the experimental data.

INTRODUCTION

Surface diffusion is the transport of a substance within an adsorbed phase. Under certain conditions, it contributes significantly towards intraparticle mass transfer. Several models have been suggested in the literature to describe surface diffusion. These models can be grouped under three categories: (1) mechanistic models in which the migrating molecule is viewed as "hopping" from one adsorption site to another (Higashi *et al.*, 1963; Smith and Metzner, 1964; Weaver and Metzner, 1966; Yang *et al.*, 1973; Thakur *et al.*, 1980; Thakur and Brown, 1983), (2) a two-dimensional Fick's law in which surface flow is caused by a gradient in the surface concentration (Carman, 1956; Kammermyer, 1958; Aris, 1983; Rieckert, 1985), and (3) hydrodynamic models in which surface diffusion is treated as a two-dimensional fluid flow on the solid surface (Flood, 1955; Flood and Huber, 1955; Gilliland *et al.*, 1958; Suzuki *et al.*, 1984). Monte Carlo simulations have also been used to describe surface diffusion. This approach, though very instructive requires intensive computation. These models have been recently reviewed by Kapoor *et al.* (1989b). It has been shown that surface diffusivity increases with an increase in adsorbed-phase concentration and temperature, and follows an Arrhenius-type temperature dependence (Ross and Good, 1956; Sladek *et al.*, 1974; Okazaki *et al.*, 1981; Tamon *et al.*, 1981). Also it has been suggested that the activation energy for surface diffusion is related to and is a fraction of the energy of adsorption (Robell *et al.*, 1964; Gilliland *et al.*, 1974; Sladek *et al.*, 1974).

All the studies on surface diffusion so far were on homogeneous surfaces, except those of Seidel and Carl (1989), Marchese and co-workers (Horas *et al.*, 1988; Zgrablich *et al.*, 1986) and Kapoor and Yang (1989). Seidel and Carl (1989) assumed that surface diffusivity is related to the adsorption isotherm through the adsorption energy distribution. They calculated different adsorption energy distributions by correlating the equilibrium adsorption data to different isotherms (e.g. Freundlich, Dubinin–Radushkevich and Toth isotherms). By using these energy distributions they developed the functional forms of concentration-dependent surface diffusivity. They suggested that surface diffusivity is independent of the adsorbed-phase concentration on a homogeneous surface, and that the concentration dependence arose due to the surface heterogeneity. Their results showed that surface diffusivity increases with an increase in adsorbed-phase concentration, which is consistent with the results reported in the literature. However, in the limit of zero adsorbed-phase concentration, surface diffusivity becomes zero in their model which is in contrast to the results reported in the literature (Carman and Raal, 1951; Higashi *et al.*, 1963; Yang *et al.*, 1973; Gilliland *et al.*, 1974; Tamon *et al.*, 1981).

Horas *et al.* (1988) and Zgrablich *et al.* (1986) developed models for surface diffusion on an energetically heterogeneous surface based on the percolation concepts. They assumed that the adsorption sites are connected by resistances with randomly distributed values. Their models showed that the surface diffusivity increases with an increase in adsorbed-phase concentration, and it approaches a finite value in the limit of zero adsorbed-phase concentration. Their models, though informative, result in rather complex expressions for the effective surface diffusivity.

Kapoor and Yang (1989) developed a parallel-path model (PPM) to describe surface diffusivity on an energetically heterogeneous surface. They assumed that the surface consists of a series of parallel paths such that each path has a uniform but different en-

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ergy, and the surface flow is in the direction of these parallel paths. By using the HIO model (Higashi *et al.*, 1963) to describe surface diffusion on a homogeneous surface and a uniform distribution of energies, they developed analytic expressions for the relative surface diffusivity in terms of the adsorbed-phase concentration and the heterogeneity parameter. The heterogeneity parameter could be obtained independently from the equilibrium adsorption data.

In this paper, we present relationships based on the effective medium approximation (EMA) (Landauer, 1952; Kirkpatrick, 1973; Odagaki and Lax, 1981) to describe surface diffusivity on an energetically heterogeneous surface. Simple analytic expressions are derived for one- and two-dimensional EMA. The effect of the coordination number on the surface diffusivity is discussed, and finally comparisons are given between the theoretical predictions and the experimental data taken from the literature.

THEORY

The effective medium or self-consistent approximation assumes that a typical basic element of a heterogeneous system can be regarded as being embedded in an equivalent homogeneous medium whose properties are to be calculated (Torquato, 1987). EMA theories have been discussed by Kirkpatrick (1973) and Sahimi *et al.* (1983). Recently, EMA has been used to describe diffusivity in a pore network (Benzoni and Chang, 1984; Mo and Wei, 1986; Burganos and Sotirchos, 1987; Yeh and Yang, 1989) and in disordered media (Haus *et al.*, 1983; Odagaki and Lax, 1981; Sahimi *et al.*, 1983), and for calculating electrical conductivity and electromagnetic properties of composites (Hashin, 1968; Milton, 1984). In this study, we use EMA to describe surface diffusion on an energetically heterogeneous surface.

The effective medium theory can be used to describe effective transport properties far from the percolation threshold. Percolation processes can be described as a site percolation, bond percolation, or correlated bond percolation problem (Kirkpatrick, 1973). The percolation threshold is then defined as the fraction of blocked sites (or bonds) at which the transport is discontinued. The problem considered here can be modeled as a site percolation problem, in which the surface diffusivity value is different for different sites. A blocked site in this case then corresponds to a site on which the surface diffusivity is zero, i.e. the activation energy of surface diffusion on that site is infinity. Physically, however, the activation energy of surface diffusion on any site can not be infinity, so the process of surface diffusion on a heterogeneous surface is far from the percolation threshold.

Consider a surface consisting of small patches of N different energies. The surface diffusivity on each of these patches is constant. However, it varies among the patches with different energies. We now consider surface diffusion due to an adsorbed-phase concentration gradient. There exist concentration gradients on the surface due to both a uniform "external gradient" and a fluctuating "local gradient." The EMA stipulates that the average of these fluctuating gradients over any sufficiently large region of the surface is zero (Kirkpatrick, 1973).

One-dimensional diffusion

First we consider surface diffusion in one dimension. The mean mass flux due to the uniform external concentration gradient (ΔC_m) is given by

$$J_m = -bD_s^{\text{Het}}\,\Delta C_m \tag{1}$$

where D_s^{Het} is the mean surface diffusivity on the heterogeneous surface, and b is the proportionality constant. The local concentration gradient caused by patch i with diffusivity $D_{s,i}^{\text{Hom}}$ is

$$\Delta C_i = \frac{J_m}{-bD_{s,i}^{\text{Hom}}}. \tag{2}$$

The concentration gradient, ΔC_i, includes the uniform external gradient and the fluctuating local gradient. As the average of the fluctuating local gradients must vanish, the following relation should hold:

$$\sum_{i=1}^{N} x_i(\Delta C_i - \Delta C_m) = 0 \tag{3}$$

where x_i is the fraction of the ith kind of patch of surface, such that

$$\sum_{i=1}^{N} x_i = 1. \tag{4}$$

Combining eqs (1)–(4) we get

$$\frac{1}{D_s^{\text{Het}}} = \sum_{i=1}^{N} \frac{x_i}{D_{s,i}^{\text{Hom}}}. \tag{5}$$

Equation (5) is similar to that suggested by Yeh and Yang (1989) for effective diffusivity in a zeolite containing pores of different sizes, and reported by Torquato (1987) in the review on the thermal conductivity of disordered heterogeneous media. Physically, eq. (5) corresponds to a surface consisting of parallel patches of uniform but varying energies and the flow is perpendicular to the direction of these patches.

Equation (5) was derived considering patches with discrete energy distribution of energies. We extend eq. (5) by assuming a continuous distribution of energy, so that the summation can be replaced by an integral to give

$$\frac{1}{D_s^{\text{Het}}} = \int_{\varepsilon_{\min}}^{\varepsilon_{\max}} \frac{f(\varepsilon)\,\mathrm{d}\varepsilon}{D_s^{\text{Hom}}(\varepsilon)} \tag{6}$$

where $f(\varepsilon)\,\mathrm{d}\varepsilon$ is the fraction of patches with energies between ε and $\varepsilon + \mathrm{d}\varepsilon$, $D_s^{\text{Hom}}(\varepsilon)$ is the value of surface diffusivity on a patch with energy ε, and $\varepsilon_{\min}$ and $\varepsilon_{\max}$ are the minimum and maximum values of energy. The normalized energy distribution, $f(\varepsilon)$, then follows

$$\int_{\varepsilon_{\min}}^{\varepsilon_{\max}} f(\varepsilon)\,\mathrm{d}\varepsilon = 1. \tag{7}$$

The functional form of $D_s^{\text{Hom}}(\varepsilon)$ is given as [see Kapoor and Yang (1989)]

$$D_s^{\text{Hom}}(\varepsilon) = \frac{D_{so}}{1-\theta}\exp(-a\varepsilon/RT) \tag{8}$$

where D_{so} is the frequency factor, $a\varepsilon$ is the activation energy for surface diffusion, θ is the fractional surface coverage, and ε is the energy of adsorption. The activation energy of surface diffusion has been suggested as a fraction of the energy of adsorption (Robell *et al.*, 1964; Gilliland *et al.*, 1974; Sladek *et al.*, 1974). Sladek *et al.* (1974) correlated surface diffusivity data of various physisorbed species and found that the value of a was 1.0 and 0.5, depending on the nature of the gas–solid system.

Assuming that the equilibrium adsorption can be described by the Langmuir isotherm, we get

$$\theta = \frac{P\bar{b}}{1 + P\bar{b}} \tag{9a}$$

where

$$\bar{b} = b_o \exp(\bar{\varepsilon}/RT). \tag{9b}$$

Equation (9a) gives the fractional surface coverage, θ, as a function of the pressure P and temperature T. The parameter $\bar{b}$ is related to the energy of adsorption.

Substituting eqs (8) and (9a) in eq. (6) for $a = 1$, and noting that $\varepsilon = \bar{\varepsilon}$ for the homogeneous patch, we have

$$\frac{1}{D_{s,\theta}^{\text{Het}}} = \int_{\varepsilon_{\min}}^{\varepsilon_{\max}} \frac{f(\varepsilon)\mathrm{d}\varepsilon}{D_{so}\exp(-\varepsilon/RT) + D_{so}Pb_o}. \tag{10}$$

We introduce the subscript θ for the surface diffusivity on the heterogeneous surface to suggest the adsorbed-phase concentration dependence. Equation (10) can be solved by substituting an energy distribution function, $f(\varepsilon)$. In principle, any suitable distribution function can be used; however, for mathematical simplicity a uniform distribution is used here. The uniform distribution is given as

$$f(\varepsilon) = \frac{1}{\varepsilon_{\max} - \varepsilon_{\min}} \quad \text{for } \varepsilon_{\min} \leqslant \varepsilon \leqslant \varepsilon_{\max}$$

and

$$f(\varepsilon) = 0 \quad \text{for } \varepsilon < \varepsilon_{\min},\ \varepsilon > \varepsilon_{\max}. \tag{11}$$

The mean ($\bar{\varepsilon}$) and square root of variance (σ) of the uniform distribution are given as

$$\bar{\varepsilon} = (\varepsilon_{\max} + \varepsilon_{\min})/2 \tag{12a}$$

and

$$\sigma = (\varepsilon_{\max} - \varepsilon_{\min})/(2\sqrt{3}). \tag{12b}$$

Substituting eq. (11) in eq. (10), and on integration and simplification, gives

$$D_{s,\theta}^{\text{Het}} = \frac{D_{\theta=0}^{\text{Hom}}(e^{2s\theta} - 1)}{\theta(e^s - e^{2s\theta - s})} \tag{13}$$

where $D_{s,\theta}^{\text{Het}}$ is the surface diffusivity on a heterogeneous surface at fractional coverage, θ, and $D_{\theta=0}^{\text{Hom}}$ is the surface diffusivity on a homogeneous surface (with energy equal to the mean energy $\bar{\varepsilon}$) in the limit $\theta \to 0$. The parameter $D_{\theta=0}^{\text{Hom}}$ is a constant. Parameter s in eq. (13) is the heterogeneity parameter, and is related to the spread of the energy distribution. The parameter s is given by

$$s = \sqrt{3}\sigma/RT = \frac{\varepsilon_{\max} - \varepsilon_{\min}}{2RT}. \tag{14}$$

Similarly, an expression was derived for surface diffusivity for $a = 0.5$, which is given as

$$D_{s,\theta}^{\text{Het}} = \frac{D_{\theta=0}^{\text{Hom}} s\sqrt{P\bar{b}}}{\tan^{-1}(\sqrt{P\bar{b}e^{s}}) - \tan^{-1}(\sqrt{P\bar{b}e^{-s}})} \tag{15a}$$

where

$$P\bar{b} = \frac{e^{2s\theta} - 1}{e^s - e^{2s\theta - s}} \tag{15b}$$

Two-dimensional diffusion

The effective diffusivity in two dimensions using EMA is given by (Kirkpatrick, 1973)

$$\int_{D_{\min}}^{D_{\max}} \frac{D - D_{s,\theta}^{\text{Het}}}{D + \left(\frac{z}{2} - 1\right)D_{s,\theta}^{\text{Het}}} f(D)\,\mathrm{d}D = 0 \tag{16}$$

where z is the coordination number, and $f(D)$ is the probability distribution function of surface diffusion. The value of δ is 3, 4 and 6 for honeycomb, square and triangular lattices, respectively. A similar expression is also given by Torquato (1987) for the effective conductivity of two-phase media.

Assuming a uniform distribution of energies [eq. (11)], and substituting eqs (8) and (9a) in eq. (16), for $a = 1$ we get

$$\beta \int_{\varepsilon_{\max}}^{\varepsilon_{\min}} \frac{\exp(-\varepsilon/RT) + \alpha_1}{\exp(-\varepsilon/RT) + \alpha_2} \exp(-\varepsilon/RT)\,\mathrm{d}\varepsilon = 0 \tag{17a}$$

where

$$\beta = \frac{1}{RT[\exp(-\varepsilon_{\max}/RT) - \exp(-\varepsilon_{\min}/RT)]} \tag{17b}$$

$$\alpha_1 = Pb_o - \frac{D_{s,\theta}^{\text{Het}}}{D_{so}} \tag{17c}$$

and

$$\alpha_2 = Pb_o + \left(\frac{z}{2} - 1\right)\frac{D_{s,\theta}^{\text{Het}}}{D_{s\theta}}. \tag{17d}$$

Equation (17a) on integration and simplification gives

$$\frac{e^{+s} + P\bar{b} + \left(\frac{z}{2} - 1\right)D_{s,\theta}^{\text{Het}}/D_{\theta=0}^{\text{Hom}}}{e^{-s} + P\bar{b} + \left(\frac{z}{2} - 1\right)D_{s,\theta}^{\text{Het}}/D_{\theta=0}^{\text{Hom}}} = \exp\frac{\mathrm{e}^{s} - \mathrm{e}^{-s}}{\frac{z}{2}D_{s,\theta}^{\text{Het}}/D_{\theta=0}^{\text{Hom}}} \tag{18}$$

where $P\bar{b}$ is given by eq. (15b). Equation (18) describes the ratio of the surface diffusivity on a heterogeneous surface at fractional coverage, θ, to the surface diffusivity on a homogeneous surface (with energy equal to $\bar{\varepsilon}$) at $\theta \rightarrow 0$ (i.e. relative surface diffusivity) as a function of θ and s. As mentioned earlier, the parameter s is a measure of the extent of heterogeneity and is given by eq. (14).

Similarly, for $a = 0.5$ an expression was derived for surface diffusivity which is given by

$$\frac{e^{-s/2} + P\bar{b}e^{s/2} + \left(\frac{z}{2} - 1\right)D^{\mathrm{Het}}_{s,\theta}/D^{\mathrm{Hom}}_{\theta=0}}{e^{s/2} + P\bar{b}e^{-s/2} + \left(\frac{z}{2} - 1\right)D^{\mathrm{Het}}_{s,\theta}/D^{\mathrm{Hom}}_{\theta=0}} = \exp\left[-\frac{e^{s/2} - e^{-s/2} + P\bar{b}(e^{-s/2} - e^{s/2})}{\frac{z}{2}D^{\mathrm{Het}}_{s,\theta}/D^{\mathrm{Hom}}_{\theta=0}}\right] \quad (19)$$

where $P\bar{b}$ is again given by eq. (15b).

Parallel-path model

In our earlier work (Kapoor and Yang, 1989) we presented a PPM to describe surface diffusivity on a heterogeneous surface. Expressions were developed for $D^{\mathrm{Het}}_{s,\theta}/D^{\mathrm{Het}}_{s,\theta=0}$ as a function of θ and s, for $a = 1$ and 0.5, respectively. For a comparison between the expressions developed here for $D^{\mathrm{Het}}_{s,\theta}/D^{\mathrm{Hom}}_{\theta=0}$, the PPM is presented in a modified form for $a = 1$:

$$D^{\mathrm{Het}}_{s,\theta}/D^{\mathrm{Hom}}_{\theta=0} = \frac{e^{s} - e^{-s}}{2s} + \frac{e^{2s\theta} - 1}{e^{s} - e^{2s\theta - s}} \quad (20)$$

and for $a = 0.5$:

$$D^{\mathrm{Het}}_{s,\theta}/D^{\mathrm{Hom}}_{\theta=0} = \frac{e^{s/2} - e^{-s/2}}{s}\left[1 + \left(\frac{e^{2s\theta} - 1}{e^{s} - e^{2s\theta - s}}\right)\right]. \quad (21)$$

RESULTS AND DISCUSSION

The surface diffusivity on a heterogeneous surface is a function of $D^{\mathrm{Hom}}_{\theta=0}$, s and θ [see eqs (13), (15) and (18)–(21)]. The parameter $D^{\mathrm{Hom}}_{\theta=0}$ is generally not known. The heterogeneity parameter is, however, obtained directly from the equilibrium adsorption data according to the LUD isotherm (Myers, 1984; Kapoor *et al.*, 1989a), which is given as

$$n(T, P) = \frac{q_m}{2s}\ln\frac{1 + P\bar{b}e^{s}}{1 + P\bar{b}e^{-s}} \quad (22)$$

where n is the amount adsorbed at pressure P and temperature T, q_m is the amount adsorbed corresponding to the monolayer coverage, and $\bar{b}$ and s are the parameters related to energy of adsorption and the energetic heterogeneity, respectively. The LUD isotherm is derived by assuming that adsorption on a homogeneous surface can be described by the Langmuir isotherm, and the adsorption energy distribution can be approximated by a uniform distribution. The experimental equilibrium adsorption data (n vs P at a given temperature) can be correlated well by taking q_m, $\bar{b}$ and s as three parameters (Kapoor *et al.*, 1989a). The behaviour of the LUD isotherm has been discussed recently by Ritter *et al.* (1990).

The effect of heterogeneity on surface diffusion was studied in terms of $D^{\mathrm{Het}}_{s,\theta}/D^{\mathrm{Hom}}_{\theta=0}$ (relative surface diffusivity) as a function of θ, at various values of s. The results for $a = 1$ and $a = 0.5$ are shown in Figs 1 and 3, respectively. Figures 1 and 3 show a comparison between the predictions from the three models: one-dimensional EMA (EMA-1D), two-dimensional EMA (EMA-2D) and PPM. The curve for $s = 0$ corresponds to the HIO model which describes the behavior on a homogeneous surface. It is seen that qualitatively all models show that surface diffusivity increases with θ. This trend is consistent with the results reported in the literature (Kapoor *et al.*, 1989a). From Figs 1 and 3, it can be seen that the value of the relative surface diffusivity ($D^{\mathrm{Het}}_{s,\theta}/D^{\mathrm{Hom}}_{\theta=0}$) at a given θ and s is different depending on the value of a, i.e. the relationship between the activation energy for surface diffusion and the energy of adsorption. It should be noted, however, that for a given homogenous surface (with the same $\bar{\varepsilon}$) the value of the diffusivity, $D^{\mathrm{Hom}}_{\theta=0}$, is greater for the case of $a = 0.5$ compared to the case of $a = 1$ (assuming that the value of D_{s0} is the same in both cases).

Figure 1 shows the relationship between the relative surface diffusivity and θ, at various values of s, as predicted by the two models (EMA-1D and EMA-2D) for $a = 1$. Also, shown are the predictions of HIO and PPM for comparison. It is seen that the EMA-1D model predicts the relative surface diffusivity on a heterogeneous surface to be lower than that on the homogeneous surface (with the same $\bar{\varepsilon}$) for low surface

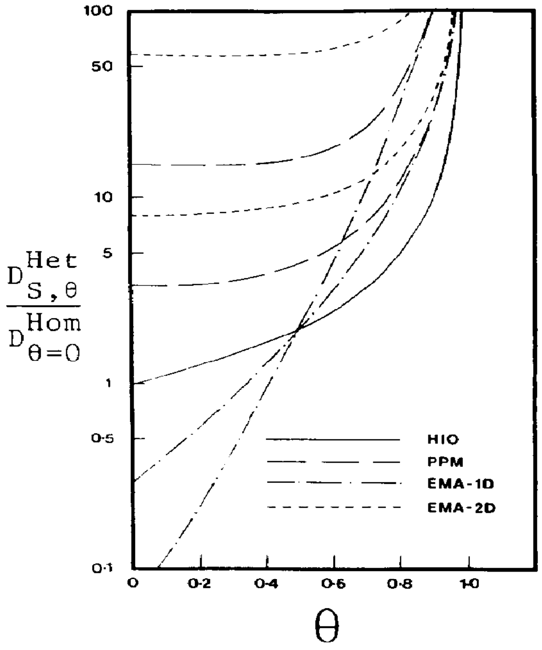

Fig. 1. Comparison of HIO, PPM, EMA-1D and EMA-2D models (for $a = 1$). The solid curve is for $s = 0$; the other two curves are for $s = 3$ and 5, with larger deviations for $s = 5$.

coverages, and higher at higher coverages, i.e. as the value of s increases, the relative surface diffusivity vs θ curve sharpens. This observation can be explained as follows. The EMA-1D model corresponds to the case of resistances in series. Thus, the effective resistance (inverse of diffusion) is controlled by the largest resistance. At low values of θ, adsorption occurs mostly on the high-energy patches (with $\varepsilon > \bar{\varepsilon}$) and the adsorbate molecules are held more strongly on the surface. This results in a lower overall diffusivity compared to the diffusivity on a homogeneous surface (with $\varepsilon = \bar{\varepsilon}$). However, as θ increases, the high-energy patches become saturated, and more adsorption occurs on the lower-energy patches. So at high surface coverages (high values of θ) surface diffusivity on the high-energy patches increases due to the concentration dependence and the contribution from the lower-energy patches increases due to more adsorption, thus resulting in an increase in overall relative surface diffusivity.

The predictions from the PPM show that the relative surface diffusivity on a heterogeneous surface is larger than that on the homogeneous surface (with $\varepsilon = \bar{\varepsilon}$) for a given value of θ, and it increases with an increase in the extent of heterogeneity (s). The PPM corresponds to the case of resistances (patches) in parallel. Thus, the total flux is the sum of fluxes from each patch. In this case, there is no possibility of flow from a patch of one energy to one of different energy. It is seen from Fig. 1 that the curves corresponding to the PPM are rather flat for low values of θ, compared to the HIO model predictions. At low values of θ, adsorption occurs mainly on the high-energy patches and, as the diffusivity is low on the high-energy patches, there is little effect on the overall diffusivity with increase in θ. At much higher values of θ, however, more adsorption occurs on the low energy-patches, which increases the overall diffusivity significantly. Thus, the curves corresponding to PPM are steeper compared to that of the HIO model.

The EMA-2D model assumes the surface consists of patches of different energies arranged randomly, and it allows for the flow from a patch of one energy to one of different energy. In this case, molecules adsorbed on one patch are allowed to diffuse to its neighboring patches, which results in molecules finding the path of minimum resistance. Based on the above discussion, it is expected that the surface diffusivity predicted by the EMA-2D model will be higher than that predicted by the other models. This is clearly shown in Fig. 1. As the value of s increases, the relative surface diffusivity also increases. The curves shown in Fig. 1 for the EMA-2D model correspond to the case of a two-dimensional square lattice, i.e. the coordination number (z) is 4. For a two-dimensional case there exist other lattices such as triangular ($z = 6$) and honeycomb ($z = 3$). The coordination number represents the number of nearest neighbors of the adsorption site. As the coordination number increases, the possibilities for a molecule on a particular patch to move to another patch increases. This further means that the probability of a molecule finding a patch with lower energy increases, which should result in a higher value of diffusivity. The effect of coordination number for three lattices ($z = 3$, 4 and 6) is shown in Fig. 2. As discussed above, the effective diffusivity on a heterogeneous surface increases with an increase in coordination number, although this increase in surface diffusivity is small.

For $a = 0.5$, the relationships between the relative surface diffusivity and θ as predicted by the models

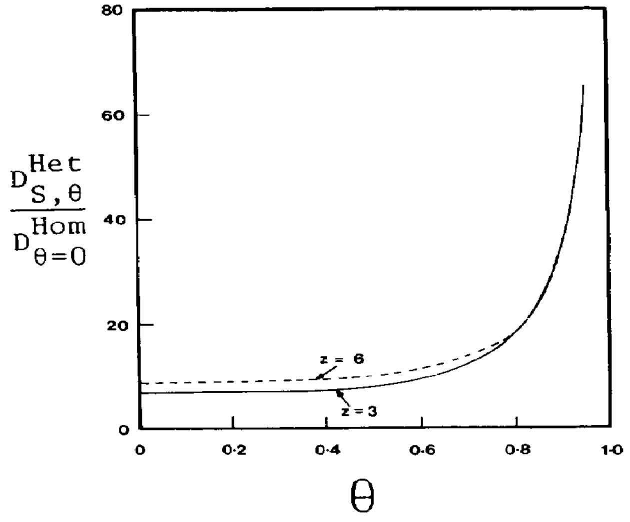

Fig. 2. Effect of coordination number on the surface diffusion on an energetically heterogeneous surface (EMA-2D results).

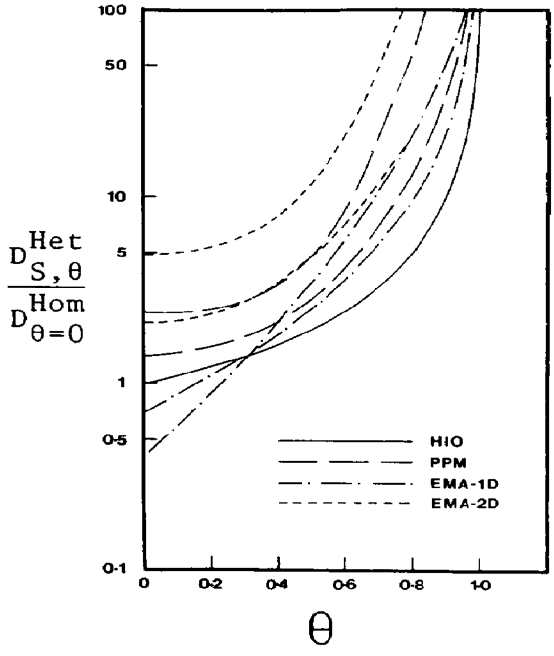

Fig. 3. Comparison of HIO, PPM, EMA-1D and EMA-2D models (for $a = 0.5$). See Fig. 1 caption for s values.

are shown in Fig. 3. Comparison between Figs 1 and 3 shows that the effect of heterogeneity on the relative surface diffusivity is less strong in the case of $a = 0.5$. As mentioned earlier, the value of $D_{\theta=0}^{\mathrm{Hom}}$ is different for the two cases ($a = 1$ and 0.5), so it is difficult to compare the effect of heterogeneity on the absolute surface diffusivity in the two cases. Qualitatively, however, the trends predicted by the models for $a = 0.5$ are similar to those predicted for $a = 1$. The effect of coordination number for $a = 0.5$ was also similar to that shown in Fig. 2 for $a = 1$, e.g. the relative surface diffusivity increased (only slightly) with an increase in z at a given θ.

COMPARISON WITH EXPERIMENTAL DATA

Experimental data on the equilibrium adsorption and surface diffusivity for various gas–solid systems were used to compare various models for surface diffusion on heterogeneous surfaces. These gas–solid systems consisted of 17 systems corresponding to $a = 1$ and four systems corresponding to $a = 0.5$. Also, these systems included a range of temperatures on six different adsorbents.

The equilibrium adsorption data on 18 systems were correlated to the LUD isotherm [eq. (22)] by nonlinear regression, and the three parameters q_m, $\bar{b}$ and s were calculated. The parameter values are listed in Table 1. The parameter s is related to the spread of the energy distribution, and thus is a measure of the extent of heterogeneity. The value of $s = 0$ corresponds to a homogeneous surface, and as the value of s increases the surface becomes increasingly heterogeneous. It is seen from Table 1 that the extent of heterogeneity is a function of various factors such as temperature, and type of adsorbent and adsorbate. The following systems showed weak heterogeneity, CF_2Cl_2 on Linde Silica at 251.5 K, and C_4H_{10} on Spheron 6 Carbon Black at 303 and 314.7 K, whereas C_3H_6 on Vycor Glass at 303 K was the most heterogeneous among all the systems tested. The parameters for the three systems consisting of C_2H_5COOH on activated carbon could not be calculated due to the lack of experimental adsorption data. The values of s, however, for these three systems were calculated by correlating the surface diffusivity data using $D_{\theta=0}^{\mathrm{Hom}}$ and s as two parameters (this point will become clear later).

The four models, HIO, PPM, EMA-1D and EMA-2D, were compared using experimental data taken from the literature. The experimental data were generally available in the form of surface diffusivity vs the amount adsorbed, or vs the fractional coverage (θ). In the case of data with amount adsorbed, the value of q_m from Table 1 was used to convert it to the fractional coverage. The data were then correlated by the four surface diffusion models. The HIO model has only one parameter, $D_{\theta=0}^{\mathrm{Hom}}$, whereas the other three models require $D_{\theta=0}^{\mathrm{Hom}}$ and s. The value of s obtained from correlating the equilibrium adsorption data were used

Table 1. Regression parameters for the LUD isotherm [eq. (22)]

System	T (K)	q_m (mol/kg)	$\bar{b}$ (1/atm)	s
$NH_3^{\dagger}$	298.0	2.51	5.26	2.50
$SO_2^{\dagger}$	303.0	1.09	7.59	0.72
$CO_2^{\dagger}$	195.0	2.99	4.19	1.11
$C_3H_6^{\ddagger}$	273.0	0.81	3.92	1.00
$C_3H_6^{\ddagger}$	298.0	0.60	2.81	1.28
$CF_2Cl_2^{\S}$	251.5	1.59	6.11	0.10
$SO_2^{\S}$	273.0	3.27	6.81	1.32
$SO_2^{\S}$	263.0	4.04	2.43	1.57
$CF_2Cl_2^{\|}$	251.5	4.90	100.75	3.02
$CF_2Cl_2^{\|}$	239.9	6.13	32.30	1.50
$C_4H_{10}^{\P}$	303.0	0.47	0.45	0.50
$C_3H_6^{\P}$	303.0	0.30	3.31	3.10
$C_4H_{10}^{\dagger\dagger}$	314.7	0.43	11.83	0.02
$C_4H_{10}^{\dagger\dagger}$	303.0	0.42	21.21	0.01
$C_2H_5COOH^{\dagger\dagger}$	313.0	—	—	0.50
$C_2H_5COOH^{\ddagger\ddagger}$	303.0	—	—	0.60
$C_2H_5COOH^{\ddagger\ddagger}$	293.0	—	—	1.00
$SO_2^{\S\S}$	273.0	6.33	4.20	1.41
$SO_2^{\S\S}$	263.0	7.40	4.87	1.69
$SO_2^{\S\S}$	252.3	7.39	8.29	1.95
$SO_2^{\S\S}$	239.4	12.52	3.61	2.95

† Vycor Glass (Gilliland *et al.*, 1974).
‡ Vycor Glass (Gilliland *et al.*, 1958).
§ Linde Silica (Carman and Raal, 1951).
‖ Carbolac (Carman and Raal, 1951).
¶ Vycor Glass (Okazaki *et al.*, 1981).
†† Spheron 6 Carbon Black (Ross and Good, 1956).
‡‡ Activated carbon (Suzuki and Fujii, 1982).
§§ Carbon (Ash *et al.*, 1963).

Table 2. Comparison of the predictions from the HIO, PPM, EMA-1D and EMA-2D surface diffusion models for the systems corresponding to $a = 1$

		HIO		PPM		EMA-1D		EMA-2D	
System	T (K)	$D^{\mathrm{Hom}}_{\theta=0}$ (cm^2/s)	Avg. rel. err. (%)	$D^{\mathrm{Hom}}_{\theta=0}$ (cm^2/s)	Avg. rel. err. (%)	$D^{\mathrm{Hom}}_{\theta=0}$ (cm^2/s)	Avg. rel. err. (%)	$D^{\mathrm{Hom}}_{\theta=0}$ (cm^2/s)	Avg. rel. err. (%)
NH_3†	298.0	7.71×10^{-6}	34.93	3.50×10^{-6}	32.96	1.11×10^{-5}	40.36	3.16×10^{-6}	31.06
SO_2†	303.0	2.09×10^{-5}	38.10	2.09×10^{-5}	38.02	8.78×10^{-5}	50.53	1.93×10^{-5}	36.99
CO_2†	195.0	5.00×10^{-5}	21.54	4.55×10^{-5}	20.28	7.90×10^{-5}	39.75	4.14×10^{-5}	20.13
C_3H_6‡	273.0	9.14×10^{-5}	22.97	8.13×10^{-5}	23.26	2.01×10^{-4}	48.81	7.68×10^{-5}	22.64
C_3H_6‡	298.0	1.06×10^{-4}	14.92	9.08×10^{-5}	14.31	1.52×10^{-4}	16.68	7.72×10^{-5}	14.78
CF_2Cl_2§	251.5	1.84×10^{-5}	9.55	1.84×10^{-5}	9.55	1.84×10^{-5}	9.55	1.84×10^{-5}	9.55
SO_2§	273.0	2.20×10^{-5}	20.72	1.82×10^{-5}	20.83	3.34×10^{-5}	21.05	1.56×10^{-5}	20.32
SO_2§	263.0	1.89×10^{-5}	26.78	1.55×10^{-5}	26.15	2.83×10^{-5}	27.36	1.32×10^{-5}	26.03
CF_2Cl_2∥	251.5	1.03×10^{-5}	25.23	3.67×10^{-6}	33.83	8.87×10^{-6}	24.64	2.95×10^{-6}	21.21
CF_2Cl_2∥	239.9	1.73×10^{-5}	29.75	1.38×10^{-5}	28.51	2.59×10^{-5}	41.82	1.10×10^{-5}	28.85
C_4H_{10}¶	303.0	2.96×10^{-5}	9.87	2.88×10^{-5}	9.86	4.01×10^{-5}	20.53	2.79×10^{-5}	9.67
C_3H_6¶	303.0	1.60×10^{-5}	32.17	6.26×10^{-6}	30.16	1.04×10^{-5}	57.98	4.14×10^{-6}	22.45
C_4H_{10}††	314.7	8.53×10^{-5}	34.76	8.53×10^{-5}	34.76	8.53×10^{-5}	34.76	8.53×10^{-5}	34.76
C_4H_{10}††	303.0	5.28×10^{-5}	20.98	5.28×10^{-5}	20.98	5.28×10^{-5}	20.98	5.28×10^{-5}	20.98
C_2H_5COOH‡‡	313.0	1.23×10^{-6}	38.29	9.90×10^{-7}	34.64	1.73×10^{-6}	51.78	8.29×10^{-7}	34.19
C_2H_5COOH‡‡	303.0	7.08×10^{-7}	46.68	6.83×10^{-7}	46.49	1.26×10^{-6}	83.65	6.61×10^{-7}	46.21
C_2H_5COOH‡‡	293.0	4.29×10^{-7}	41.56	3.89×10^{-7}	40.93	6.93×10^{-7}	73.23	3.56×10^{-7}	40.19

† Vycor Glass (Gilliland *et al.*, 1974).

‡ Vycor Glass (Gilliland *et al.*, 1958).

§ Linde Silica (Carman and Raal, 1951).

∥ Carbolac (Carman and Raal, 1951).

¶ Vycor Glass (Okazaki *et al.*, 1981).

†† Spheron 6 Carbon Black (Ross and Good, 1956).

‡‡ Activated carbon (Suzuki and Fujii, 1982).

for this purpose. Thus all the models had only one parameter, so that a fair comparison could be made. The comparison was made based on the average relative error (avg. rel. err.), which is defined as

$$\text{avg. rel. err.} = \frac{100}{N} \sum_{j=1}^{N} \text{abs}[(D_{s,\theta}^{\text{Het}})_{j,\text{cal}} - (D_{s,\theta}^{\text{Het}})_{j,\text{exp}}]/(D_{s,\theta}^{\text{Het}})_{j,\text{exp}} \quad (22)$$

where N is the number of data points, and $(D_{s,\theta}^{\text{Het}})_{\text{cal}}$ and $(D_{s,\theta}^{\text{Het}})_{\text{exp}}$ are the calculated and experimental values of surface diffusivity.

The comparison of the predictions from the four models, for all the systems corresponding to $a = 1$, is shown in Table 2. Table 2 lists the values of $D_{\theta=0}^{\text{Hom}}$ and the avg. rel. err. for each model for all 17 systems. The PPM, EMA-1D and EMA-2D models are given by eqs (20), (13) and (18), respectively. The HIO model for a homogeneous surface is given as

$$D_{s,\theta}^{\text{Hom}} = \frac{D_{\theta=0}^{\text{Hom}}}{1-\theta}. \quad (23)$$

It is interesting to note that for the three systems, CF_2Cl_2 on Linde Silica at 251.5 K and C_4H_{10} on Spheron 6 Carbon Black the parameter $D_{\theta=0}^{\text{Hom}}$ and the avg. rel. err. for all four models were similar. These systems showed small values of s, which corresponds to a homogeneous surface. Thus, it shows that the three models derived for the heterogeneous surface reduce to the HIO model, in the limit of small value of s. In fact, all three models for heterogeneous surface (PPM, EMA-1D and EMA-2D) reduce identically to the HIO model as $s \rightarrow 0$. The system, C_3H_6 on Vycor Glass at 303 K, which showed the maximum value of s, also showed a large difference in the values of the avg. rel. err. for the three heterogeneous surface diffusion models compared to those for the HIO model. An overall comparison of the four models showed that the EMA-2D model correlated the experimental data the best, followed by the PPM, and the HIO and EMA-1D models. The EMA-1D model corresponds to the case of molecules diffusing on patches of surface normal to the direction of the flux. Thus the EMA-1D model represents a lower bound for surface diffusion on a heterogeneous surface. The PPM, on the other hand, allows molecules on a patch of a given energy to diffuse only on the patches with the same energy and the patches are parallel to the flux. Thus, the PPM represents a first-order upper bound, as also reported by Torquato (1987). The EMA-2D model allows molecules to diffuse from a patch of one energy to a patch of different energy, thus representing a more realistic case.

A comparison between the PPM and the EMA-2D model [equations (18) and (20), respectively] shows that both models are analytic in form. The PPM gives an explicit value of diffusivity as a function of θ and s, whereas the EMA-2D model gives an implicit function. Thus, the PPM can be used to obtain an estimate, whereas the EMA-2D model should be used as a more rigorous model.

Table 3. Comparison of the predictions from the HIO, PPM, EMA-1D and EMA-2D surface diffusion models for the systems corresponding to $a = 0.5$

System	T (k)	HIO		PPM		EMA-1D		EMA-2D	
		$D_{\theta=0}^{\text{Hom}}$ (cm^2/s)	Avg. rel. err. (%)	$D_{\theta=0}^{\text{Hom}}$ (cm^2/s)	Avg. rel. err. (%)	$D_{\theta=0}^{\text{Hom}}$ (cm^2/s)	Avg. rel. err. (%)	$D_{\theta=0}^{\text{Hom}}$ (cm^2/s)	Avg. rel. err. (%)
$SO_2^{\dagger}$	273.0	2.15×10^{-4}	23.17	1.78×10^{-4}	22.44	1.93×10^{-4}	24.74	1.63×10^{-4}	21.10
$SO_2^{\dagger}$	263.0	2.14×10^{-4}	17.55	1.68×10^{-4}	16.62	1.78×10^{-4}	18.80	1.39×10^{-4}	15.82
$SO_2^{\dagger}$	253.3	2.02×10^{-4}	17.33	1.65×10^{-4}	16.78	1.74×10^{-4}	18.87	1.43×10^{-4}	15.90
$SO_2^{\dagger}$	239.4	1.08×10^{-4}	12.41	8.87×10^{-5}	11.76	9.39×10^{-5}	12.81	7.99×10^{-5}	11.14

† Carbon (Ash *et al.*, 1963).

Ash *et al.* (1963) reported surface diffusion data of SO_2 on carbon at four temperatures. For the SO_2–carbon system the value of $a = 0.5$. The comparison of the predictions from the four models for these four systems is given in Table 3. Similar to Table 2, Table 3 lists the values of $D_{\theta=0}^{\mathrm{Hom}}$ and the avg. rel. err. for each model for all four systems. For $a = 0.5$, the four models (HIO, PPM, EMA-1D and EMA-2D) are given by eqs (23), (21), (15) and (19), respectively. The results given in Table 3 show trends similar to those seen in Table 2, i.e. the EMA-2D model showed the least deviation from the experimental results, followed by the PPM, and the HIO and EMA-1D models. Also, all models are analytical and explicit in form, except the EMA-2D model which gives an implicit relationship between $D_{s,\theta}^{\mathrm{Het}}$ and the parameters θ and s.

CONCLUSIONS

(1) Simple analytic expressions were presented for surface diffusivity on an energetically heterogeneous surface. These expressions were derived using EMA in one and two dimensions.

(2) On comparison with other models, it was shown that the EMA-2D model gave a better representation of the experimental data.

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NOTATION

a	ratio of activation energy of surface diffusion and energy of adsorption
b	constant in the Langmuir isotherm, 1/kPa or 1/atm, or proportionality constant in eq. (1)
$\bar{b}$	defined by eq. (9b)
C	surface concentration
D	diffusivity, m^2/s
EMA-1D	effective medium approximation in one dimension
EMA-2D	effective medium approximation in two dimensions
f	energy distribution function
J	mass flux
n or q	amount adsorbed, mol/kg
P	pressure, kPa or atm
PPM	parallel-path model
R	gas constant
s	heterogeneity parameter defined by eq. (14), dimensionless
T	temperature, K
x	fraction of surface
z	coordination number

Greek letters

α	defined by eqs (17c) and (17d)
β	defined by eq. (17b)
ε	energy or heat of adsorption, kJ/mol
$\bar{\varepsilon}$	average value of ε, kJ/mol
θ	fractional surface coverage
σ	square root of variance for energy distribution, kJ/mol

Subscripts

i	corresponds to patch i
m	corresponds to monolayer, or mean
min	minimum value
max	maximum value
o	refers to a constant
s	surface

Superscripts

Het	on heterogeneous surface
Hom	on homogeneous surface

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