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Diffusion in Zeolites as Flow of Lattice Gas

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The diffusivity D of pure substances in idealized zeolite crystals is analyzed on the basis of the hopping model and its various extensions. Forces between neigboring molecules are taken into account as well as multiple adsorption in cages and the possibility of extended jumps. Finally, the case of correlated jumps is considered. For each model, D is approximated for small concentrations and in the saturation limit. Only the model with cages permitting at least three molecules is capable of reproducing the prevalent observed behavior.

KEY WORDS: Interacting lattice gas; models of diffusion in zeolites; multiple adsorption in cages.

1. FAILURE OF TRADITIONAL MODEL

Migration of foreign molecules in a zeolite crystal or in any ordered microporous medium is usually modeled as flow of a lattice gas. In view of the great contributions made in this field by Matthieu Ernst,(1-3) there is reason to join the celebration and good wishes in this issue with a discussion of zeolitic diffusion. Only transport diffusivity of pure substances will be considered; mixtures as well as self-diffusivity (=tracer diffusivity) require a more elaborate analysis.

The diffusivity of any substance in a zeolite is a function of temperature and concentration. At not too high T the temperature dependence generally follows the Arrhenius law, $D \propto \exp(-E/kT)$, which is taken as an indication that thermally activated transitions over barriers of height E are involved.(4) On the other hand, the concentration dependence is rather unexpected: D always strongly increases with increasing concentration, often

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by more than a factor of 10 over the available range. (Typical example: heptane in zeolite 5A.(4)) It appears that, in a crude way, the initial value of the derivative can be approximated by

$$\frac{1}{D(0)} \frac{d[D(\theta)]}{d\theta}\bigg|_{\theta=0} \approx \frac{1}{\theta_{\text{sat}}} \tag{1}$$

if θ is the average occupancy of an adsorption site or cage and θ_{sat} the saturation value. For simple adsorption sites $\theta_{\text{sat}} = 1$, whereas voluminous cages containing several adsorption sites allow larger values. Since θ_{sat} is often not known with certainty, Eq. (1) is somewhat tentative.

A mechanism which would simultaneously reproduce condition (1) and high limiting values $D_{\text{sat}} \equiv D(\theta_{\text{sat}})$ is hard to find, as will become clear in the subsequent survey of the traditional hopping model and of several of its possible extensions. In each case the behavior of $D(\theta)$ near $\theta = 0$ and the saturation limit are easy to assess, so that checks against the mentioned two properties can be made.

The traditional model treats the diffusing substance as a noninteracting lattice gas, just as is done in Langmuir's theory of adsorption.(5) A particularly simple model is that of a simple cubic lattice, with simple adsorption sites at the nodes ($\theta_{\text{sat}} = 1$) and with a barrier on each bond. It is assumed that the jumps are uncorrelated and that they occur only between neighboring sites. With a lattice constant l and a jump rate r to any empty neighboring site (so that for an isolated molecule the total jump rate is $6r$), we obtain $D = l^2 r$. In the absence of interaction between the adsorbed molecules r cannot depend upon θ, so that D should be constant, which disagrees with observations.

Some zeolites, like zeolite A, have a structure similar to the above picture, except that they usually permit multiple adsorption in cages at the nodes.(4) Some other types have a noncubic lattice, so that diffusivity tensors must be introduced. Such generalizations, as well as structures with parallel bundles of quasi-one-dimensional channels,(6) will not be considered in the present discussion.

2. REPULSION BETWEEN NEIGHBORS

A concentration-dependent jump rate with the desired sign of the derivative is obtained by allowing for repulsive interaction between adsorbed molecules. We are going to review and extend the respective theory of Reed and Ehrlich,(7) who considered only nearest neighbor interaction using the quasichemical approximation.(8) Actually, one only needs a rudimentary version of this approximation, which ignores the possibility of an ordering phase transition. For ordinary temperatures the simplification appears well justified.

As before, we imagine simple adsorption sites located at the nodes of a simple cubic lattice, where each site has six nearest neighbors. Because of interaction, the energy of an isolated pair of molecules occupying neighboring sites is raised by an amount W. The probability of occurrence of such pairs is depressed by a factor

$$\eta = \exp\left(-\frac{W}{kT}\right) \tag{2}$$

It will suffice to consider steady-state diffusion due to a gradient of θ in the x direction. To evaluate the net flux j through the plane between two adjacent sites i and $i+1$ (along the x axis), we must know the forward and backward average jump rates $r_{i \to i+1}$ and $r_{i+1 \to i}$. But first we need the probabilities of occupation of a pair of sites i and $i+1$ along x. Approximations for small θ will suffice. In the absence of interaction, when there are no correlations,(9) the probability for both sites being occupied is $\theta_i \theta_{i+1}$, which becomes modified to $\theta_i \theta_{i+1} \eta$ by the interaction. Hence the conditional probabilities for $i+1$ to be occupied or empty, if i is known to be occupied, are $\theta_{i+1}\eta$ and $1-\theta_{i+1}\eta$, respectively. For larger θ's the situation is less simple and the quasichemical approximation as used by Reed and Ehrlich would have to be invoked.

Once we prescribe that the site $i+1$ to the right of the occupied one (i) is empty, there can still be up to five occupied sites next to the latter, namely at four places in the plane i and one at $i-1$. Following the same reasoning as before we conclude that for small θ's the average number of neighbors around location i is $\eta(4\theta_i + \theta_{i-1})$. Better to say, this is the probability for having one neighbor; the probability to find more than one is negligible. If the energy level of the barriers in the "windows" between sites remains unchanged, the lifting of the bottom level by W enhances the jump rate by a factor $\eta^{-1} = \exp(W/kT)$. The average jump rate from i to $i+1$ is thus

$$\begin{aligned} r_{i \to i+1} &= r[1 - \eta(4\theta_i + \theta_{i-1}) + \eta^{-1}\eta(4\theta_i + \theta_{i-1})] \\ &= r[1 + (1-\eta)(4\theta_i + \theta_{i-1})] \end{aligned} \tag{3}$$

and similarly for $r_{i+1 \to i}$. The undisturbed jump rate of an isolated molecule into any one direction has been denoted as r without subscript.

Both rates must be substituted into an expression for the flux

$$j = \nu l[\theta_i(1-\eta\theta_{i+1})\, r_{i \to i+1} - \theta_{i+1}(1-\eta\theta_i)\, r_{i+1 \to i}] \tag{4}$$

where $\nu = l^{-3}$ is the number density of adsorption sites. After expressing the differences in terms of derivatives, we obtain Fick's law, $j = -\nu D(\theta)\, d\theta/dx$, and a first-order approximation for the diffusivity,

$$D(\theta) = D_0[1 + 12(1-\eta)\,\theta + O(\theta^2)] \tag{5}$$

where $D_0 = l^2 r$. The approximation agrees with what follows up to this order from expression (41) of Reed and Ehrlich, though the present argument slightly deviates from theirs. The initial slope according to Eq. (1) is reproduced by choosing $\eta = 11/12$. Since $1-\eta = 1/12$ approximates W/kT, the ratio on the left of (1) is expected to be roughly proportional to T^{-1}. This is a much weaker dependence than the exponential one involved in D_0. However, if the theory is justified, accurate measurements over a broad temperature range should reveal deviations from the value on the right of (1).

A generalization of approximation (5) which includes interactions beyond nearest neighbors becomes somewhat tedious. In addition to the parameter η from before, we also must consider $\eta_n = \exp(-W_n/kT)$, where W_n are the interaction potentials with molecules at the distances R_n, $n = 2, 3, \ldots$. Let us look at the first cubic shell around the site under consideration, i.e., at the closest neighbors specified by the indices (100), (110), and (111). The respective distances are $R_1 = l$, $R_2 = \sqrt{2}\, l$, and $R_3 = \sqrt{3}\, l$. By way of example we are going to choose an inverse power-law potential, $W_n = W(l/R_n)^\alpha$, so that $W_2 = W/2^{\alpha/2}$ and $W_3 = W/3^{\alpha/2}$.

The extension will only be consistent if also the effect of the interaction upon the window potential is taken into account. The joint potential energy of a molecule in the window and one adsorbed at distance R'_m is increased by an amount $\Delta E_m = W(l/R'_m)^\alpha$. For the window at halfway between i and $i+1$, the distances to the sites upon the same shell as before are

$$R'_1 = \sqrt{5/4}\, l, \qquad R'_2 = (3/2)\, l, \qquad R'_3 = \sqrt{13/4}\, l, \qquad R'_4 = \sqrt{17/4}\, l$$

so that, for instance, $\Delta E_3 = W/(13/4)^{\alpha/2}$. For the sake of subsequent use we define $\eta'_m = \exp(-\Delta E_m/kT)$.

If a site at distances R_n from the site i and R'_m from the window between i and $i+1$ is ocupied, the joint potential with a molecule waiting at i to jump to $i+1$ is increased by W_n. Then, when the molecule is passing through the window, the increase equals ΔE_m. Hence the barrier that must be overcome is lowered by the amount $W_n - \Delta E_m$. Thereby the jump rate increases by a factor $\eta'_m \eta_n^{-1}$. This factor enters the corresponding term in an expression for the average jump rate and plays a similar role as the η^{-1} in the first line of (3).

Proceeding further as before with Eqs. (3) and (4) and taking account of the number of neighbors, we obtain the approximation

$$D(\theta) = D_0\{1 + 2[4(\eta'_1 - \eta) + 2(\eta'_2 - \eta) + 4(\eta'_2 - \eta_2) + 8(\eta'_3 - \eta_2) + 8(\eta'_4 - \eta_3) + \cdots]\,\theta + O(\theta^2)\} \tag{6}$$

For small W/kT this result reduces to

$$D(\theta) = D_0[1 + 2z_{\text{eff}}(1 - \eta)\,\theta + O(\theta^2)] \tag{7}$$

where the effective coordination number is given by

$$z_{\text{eff}} = \left(6 - \frac{4}{(5/4)^{\alpha/2}} - \frac{2}{(3/2)^{\alpha}}\right) + \left(\frac{12}{2^{\alpha/2}} - \frac{4}{(3/2)^{\alpha}} - \frac{8}{(13/4)^{\alpha/2}}\right) + \left(\frac{8}{3^{\alpha/2}} - \frac{8}{(17/4)^{\alpha/2}}\right) + \cdots \tag{8}$$

For large α, convergence of this series is fast and the resulting z_{eff} is not much different from 6. An abnormally small exponent $\alpha = 3$ is valid if the interaction is mediated by elastic deformation of the lattice. An adsorbed molecule is likely to cause a small compression of the surrounding, thereby acting like a point defect. This produces a displacement $\mathbf{u}(\mathbf{R})$, which in any given direction falls off like R^{-2}.(10) The interaction energy is presumably proportional to $\nabla \cdot \mathbf{u}$. While for an isotropic medium this quantity vanishes, in general it falls off like R^{-3} in any given direction. However, the coefficient then depends upon the direction. According to the sign of the third elastic modulus of the cubic medium,(10) $\nabla \cdot \mathbf{u}$ has one sign along the the crystallographic axes and the opposite sign in diagonal directions,[3] so that the series analogous to (8) contains positive and negative terms. At large distances the angular average of $\nabla \cdot \mathbf{u}$ vanishes, as can be seen by integrating this quantity over a spherical shell and applying the Gauss theorem. Thereby fast convergence of the above expansion is restored.

Let us now turn to the behavior of diffusivity at high concentration. The saturation limit D_{sat} can be derived without relying upon uncertain approximations, simply by considering the random walk of an isolated vacancy. An adsorbed molecule next to the vacancy is totally surrounded

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[3] It is remarkable that similarly anisotropic interaction between adsorbents on surfaces has been inferred by Watanabe and Ehrlich from observed correlations.(11)

by other molecules, except for the vacancy. The jump rate is modified by the corresponding powers of the η's, and the resulting diffusivity is

$$D_{\text{sat}} = D_0 \frac{\eta_1'^8 \eta_2'^9 \eta_3'^4 \eta_4'^4 \cdots}{\eta^5 \eta_2^{12} \eta_3^8 \cdots} \tag{9}$$

With $\eta = 11/12$, and with interaction only between nearest neighbors (so that all higher η's are equal 1), the saturation value of the diffusivity is $D_{\text{sat}} = D_0 \eta^{-5} = 1.55 D_0$. Also, this limit agrees with what can be deduced from Reed and Ehrlich's formula (41). For sensible values of the η's and as long as we stick to the initial slope according to Eq. (1), the more general formula (9) gives similar ratios. Thus we arrive at a rather pessimistic conclusion: Since as a rule much larger limiting ratios D_{sat}/D_0 are observed (as mentioned in the introduction), hopping models with simple adsorption sites cannot fully explain the measured concentration dependence of diffusivity in zeolites, regardless of the presumed kind of interaction between the adsorbed molecules.

3. MULTIPLE ADSORPTION

Somewhat better results are obtained using a model with multiple adsorption in "cages" at the nodes of a simple cubic lattice.(9) Repulsive interaction is allowed only for molecules within a cage, and the maximal number of molecules per cage is taken as $\theta_{\text{sat}} = 2$. (A more general model of this kind has previously been used for explaining deviations from Langmuir's adsorption isotherm.(12)) We shall again only be interested in the behavior of $D(\theta)$ for small and for large θ, which can be derived from a simplified argument.

Let us assume that for a pair of molecules within a cage, compared to two separate molecules, the energy is raised by an amount $2\Delta V$. The probabilities for any cage to contain 0, 1, or 2 molecules are approximated by

$$w_0 = 1 - \theta + \tfrac{1}{2}\varepsilon^2\theta^2 + O(\theta^3), \qquad w_1 = \theta - \varepsilon^2\theta^2 + O(\theta^3),$$
$$w_2 = \tfrac{1}{2}\varepsilon^2\theta^2 + O(\theta^3) \tag{10}$$

as follows from

$$w_0 + w_1 + w_2 = 1, \qquad w_1 + 2w_2 = \theta, \qquad w_0 w_2 = \tfrac{1}{2}\varepsilon^2 w_1^2 \tag{11}$$

The last relation contains $\varepsilon = \exp(-\Delta V/kT)$, and is derived from the grand canonical partition function, under the assumption that the adsorption sites within a cage are indistinguishable.

With the barriers between the cages supposed to remain at the same height, the jump rate from a doubly occupied cage to an empty or singly occupied one equals $(2/\varepsilon^2)\, r$. (This is the rate per cage, not per molecule.) In the sense of Eq. (4), the flux can now be written as

$$\begin{aligned} j = vlr \Big\{ & [w_1(\theta_i)\, w_0(\theta_{i+1}) - w_0(\theta_i)\, w_1(\theta_{i+1})] \\ & + \frac{2}{\varepsilon^2} [w_2(\theta_i)\, w_0(\theta_{i+1}) - w_0(\theta_i)\, w_2(\theta_{i+1})] \\ & + \frac{2}{\varepsilon^2} [w_2(\theta_i)\, w_1(\theta_{i+1}) - w_1(\theta_i)\, w_2(\theta_{i+1})] \Big\} \end{aligned} \tag{12}$$

Advantage has been taken of the finding that correlations between occupancies of adjacent cages are negligible.(9) Substitution of (10) yields the approximation

$$D(\theta) = D_0[1 + 2(1 - \varepsilon^2)\, \theta + O(\theta^2)] \tag{13}$$

where again $D_0 = l^2 r$. Condition (1) is satisfied for $\varepsilon^2 = 3/4$. We then have roughly $2(1 - \varepsilon^2) \approx 2\Delta V/kT$, so that again an approximate $1/T$ behavior of this coefficient in (13) is expected.

To obtain the limit $D_{\text{sat}} = D(2)$, we assume one cage singly and the rest doubly occupied, and look at the random walk of the "semivacancy." With the modified jump rate $(2/\varepsilon^2)\, r$ the result is immediate:

$$\frac{D_{\text{sat}}}{D_0} = \frac{2}{\varepsilon^2} \tag{14}$$

which equals $8/3 = 2.67$ for the chosen ε^2. This is still below the typical measured ratio quoted in the introduction.

In view of the proposed value of ε^2, which implies a rather small ratio $\Delta V/kT$, it seems natural to consider the possibility that a third molecule becomes squeezed into the cage. Thus extending our earlier model,(9) and assuming that further additions are impossible, we set $\theta_{\text{sat}} = 3$. The adsorbed triplet has an energy higher by $3\Delta V'$ compared to three separate molecules, with $\Delta V' > \Delta V$, so that the jump rate from the cage is enhanced by a factor $3/\varepsilon'^3$, with $\varepsilon' = \exp(-\Delta V'/kT) < \varepsilon$. By extending the set of identities (11), we verify that the second-order approximations (10) remain valid, and that the probability for triplets is approximated by $w_3 = \frac{1}{6}(\varepsilon'\theta)^3 + O(\theta^4)$.

Three more terms must now be added to Eq. (12), each of them containing w_3. Clearly they carry the factor θ^2 or higher powers. Thus nothing changes in the first-order approximation (13) for the diffusivity. On the other hand, when the limit $\theta_{\text{sat}} = 3$ is approached, most cages are full, while a few isolated ones contain one molecule less. The probability of finding a singly occupied or empty cage is negligible by comparison. Since the jump rate from any full cage is $(3/\varepsilon'^3)\, r$, the random-walk argument gives

$$\frac{D_{\text{sat}}}{D_0} = \frac{3}{\varepsilon'^3} \tag{15}$$

By a suitable choice of ε' it is always possible to fit any high limiting value without affecting the initial slope.

Another conceivable option is a combination of the idea of multiple adsorption with interaction between molecules in neighboring cages. For the sake of simplicity we now consider only nearest neighbors, and allow a maximum of two molecules per cage. If two neighboring cages are singly occupied, the energy is assumed to be higher by W, which leads to an η^{-1}-fold enhancement of the jump rate, as before. If one cage is singly and the other doubly occupied, the energy change is twice as large, resulting in an η^{-2}-fold enhancement. Finally, if both cages are doubly occupied, the energy shift is $4W$ and the enhancement factor η^{-4}. Plausible results follow:

$$\frac{D(\theta)}{D_0} = 1 + 2[(1-\varepsilon^2) + 6(1-\eta)]\,\theta + O(\theta^2), \qquad \frac{D_{\text{sat}}}{D_0} = \frac{2}{\varepsilon^2 \eta^{22}} \tag{16}$$

In deriving the second equation we observe that the molecule ready to jump from a doubly occupied site is surrounded by five doubly and one singly occupied site, which yields $5 \cdot 4 + 2 = 22$ as the exponent of η^{-1}. While it is trivial to choose $\varepsilon^2 < 1$ and $\eta < 1$ so as to meet condition (1), after such adjustment the ratio D_{sat}/D_0 is between 8/3 and 5.1. As before, these values can be further increased by permitting larger θ_{sat}.

We conclude that among the various versions of the hopping model, only those allowing for more than two molecules per cage are adaptable to both initially mentioned criteria. Though the idea of multiple adsorption in cages with $\theta_{\text{sat}} \geqslant 3$ seems realistic in many cases, it is unpleasant that at least two parameters must be adjusted to meet just two criteria. It seems of interest to try the two models of Ruthven and Goddard,(12) who admit arbitrary $\theta_{\text{sat}} \equiv m$ with a sequence of coefficients ε_s, $s = 2, 3,..., m$ ($\varepsilon_2 \equiv \varepsilon$, $\varepsilon_3 \equiv \varepsilon'$). These depend only upon one parameter, the relative effective volume $\gamma < 1$ of an adsorbed molecule. The model is based upon the idea of excluded volume, with no other interaction ($\eta = 1$), which leads to $\varepsilon_s = 1 - s\gamma$, or to $\varepsilon_s = (1 - s\gamma)/(1 - \gamma)$ in the refined version. In both cases the saturation occupancy $m \equiv \theta_{\rm sat}$ equals the integer part of $1/\gamma$. Unfortunately, with the coefficient as in (13), neither model permits a consistent fit to condition (1).

The difficulty does not arise if instead of the excluded volume we imagine point particles with interaction energy $2\Delta V$ per pair. Accordingly, we postulate $\varepsilon_s = \varepsilon^{s-1}$ for $s = 2, 3,..., m$. Knowing that the first-order term in (13) is insensitive to contributions from multiply occupied cages, we take $\varepsilon^2 = 1 - 1/(2m)$, so as to satisfy condition (1). To assess the limiting behavior, we again consider jumps in an otherwise full lattice to an isolated site with occupation $m - 1$. The result $D_{\rm sat}/D_0 = m\varepsilon_m^{-m} = m\varepsilon^{-m(m-1)}$ equals 5.2 for $m = 3$ and 8.9 for $m = 4$. Thus it seems that we are finally on the right track, though a reliable physical justification of the model (possibly of an intermediate kind) is still lacking.

A possible additional mechanism affecting the diffusivity in zeolites is elastic deformation of the lattice by the adsorbent. For a loose structure permitting multiple adsorption in cages the sign of the potential suggests that forces between single adsorbed molecules and the cage walls are attractive. This must result in a shrinking of the structure. In multiple adsorption, when less space is available to the adsorbent, the described effect is expected to be less than additive, and it is conceivable that for full cages it turns into repulsion. Then the deformation might widen the exits from the cage, thereby lowering the barriers. However, the resulting influence upon the diffusivity would at any rate remain superimposed upon and difficult to distinguish from the more direct effect due to repulsion between molecules within the cage.

4. EXTENDED JUMPS

Experiments with diffusion of palladium atoms on a W(211) surface have shown that occasionally direct jumps to places beyond the nearest neighbors occur.(13) We are going to consider such a possibility as another extension of the lattice-gas model.

The discussion will again be restricted to a simple cubic lattice of simple adsorption sites, with jumps only occurring in the directions of the axes, and with a gradient established along one of them. The jump rate from an occupied site to one of the nearest neighbors (if it is empty) shall be $r_0 \equiv r$; to one of the next-nearest neighbors r_1 (again if it is empty), and so on. We suppose that $r_0 > r_1 > r_2 > \cdots$, and that the sum of the r's converges sufficiently fast to justify the subsequent manipulations. The flux from site i to $i+1$ will be expressed in terms of an average $\langle \cdots \rangle$ involving random occupations Θ_i whose averages are the θ_i:

$$\begin{aligned} j &= \nu l \sum_{j=0}^{\infty} \sum_{k=0}^{\infty} r_{j+k} \langle [\Theta_{i-j}(1-\Theta_{i+k+1}) - \Theta_{i+k+1}(1-\Theta_{i-j})] \rangle \\ &= \nu l \sum_{j=0}^{\infty} \sum_{k=0}^{\infty} r_{j+k} [\theta_{i-j} - \theta_{i+k+1}] \end{aligned} \tag{17}$$

The average has been taken after cancellation of the product terms. In case of a linear gradient we may write $\theta_i = \theta$ and $\theta_{i+k} = \theta + k\,\Delta\theta$. When this is substituted, and $\Delta\theta$ expressed by the derivative, the following result for the diffusivity ensues:

$$D = l^2 \sum_{s=0}^{\infty} (s+1)^2 r_s \tag{18}$$

We have substituted $j+k=s$ and summed over j or k. Clearly D does not depend upon θ, whatever our choice of the r's would be. For the sake of having a specific example, let us take $r_s = r\kappa^s$, with $\kappa < 1$. By manipulating the series for $1/(1-\kappa)$ and for its derivatives, we find

$$D = l^2 r \frac{1+\kappa}{(1-\kappa)^3} \tag{19}$$

Concentration dependence does arise if the jump rate is influenced by the presence of a neighbor. Following an idea of S. Yu. Krylov (private communication), we assume that the rates in one direction are given by r_s whenever the opposite neighboring site is empty but are equal to $(1+\zeta)\,r_s$ when that site is occupied. Then

$$\begin{aligned} j = \nu l \sum_{j=0}^{\infty} \sum_{k=0}^{\infty} r_{j+k} \langle \{ & [\Theta_{i-j}(1-\Theta_{i+k+1}) - \Theta_{i+k+1}(1-\Theta_{i-j})] \\ & + \zeta [\Theta_{i-j-1}\Theta_{i-j}(1-\Theta_{i+k+1}) - \Theta_{i+k+2}\Theta_{i+k+1}(1-\Theta_{i-j})] \} \rangle \end{aligned} \tag{20}$$

If correlations are negligible, then the averaging can be carried out also in the second part of the quoted expression. We again write $\theta_{i+k} = \theta + k\,\Delta\theta$ and neglect the terms of higher order in $\Delta\theta$. The following expression for the diffusivity is obtained:

$$D = l^2 \sum_{0}^{\infty} r_s \{ (s+1)^2 + \zeta(s+1)[2(s+2)\,\theta - (s+3)\,\theta^2)] \} \tag{21}$$

In the example with $r_s = r\kappa^s$, which can be handled in the same way as before, the result reduces to

$$D(\theta) = D(0)\left\{1 + \frac{\zeta}{1+\kappa}\left[4\theta - (3-\kappa)\,\theta^2\right]\right\} \tag{22}$$

with $D(0)$ given by expression (19). The graph of $D(\theta)$ is a down-bent parabola, with the saturation point at

$$D_{\text{sat}} = D(1) = (1+\zeta)\,D(0) \tag{23}$$

In order to satisfy condition (1), we require that $4\zeta/(1+\kappa) = 1$, whereby (22) reduces to

$$D(\theta) = D(0)[1 + \theta - \tfrac{1}{4}(3-\kappa)\,\theta^2] \tag{24}$$

Comments are easiest if $\kappa = 0$, which means that only jumps between nearest neighboring sites are allowed. In such a case $D(\theta) = D(0)[1 + \theta - \frac{3}{4}\theta^2]$, hence $D_{\text{sat}} = \frac{5}{4}D(0)$, which is certainly disappointing.

5. CORRELATED JUMPS

If further extensions of the theory are to be constructed, one should think of correlated jumps. One of the possible causes might be dynamic interaction mediated by the lattice, e.g., by elastic waves. For the sake of simplicity we again assume that only single adsorption in each cage and jumps between neighboring cages are possible. If the adsorbed molecule causes the cage to shrink, then in a jump from i to $i+1$ the first cage relaxes to a larger volume. This triggers a rarefaction shock wave, which temporarily enlarges the adjacent windows, thus lowering the barriers. If the change is sufficiently large, then there is a finite probability ξ for an immediate filling of the vacancy from any occupied adjacent cage. "Immediate" is to be understood as "happening during passage of the shock wave"; this time is certainly short compared to r^{-1}. A second-generation jump followed by further after-jumps may then occur, giving rise to a series of contributions to the flux. Clearly the sum and thereby the diffusivity increase with increasing concentration, and for ξ close to 1 one may perhaps hope for something ressembling a $1/(1-\theta)$ behavior.

Before working out the kinetics, one would wish to know whether a sufficiently strong interaction of the described kind is physically possible. Some preliminary rough arguments do not rule out such a possibility, though the material data seem to be marginal in this respect. Since serious estimates are difficult, and would presumably require a major effort involving molecular dynamics calculations, it seems preferable to proceed in the reverse manner. We are going to assume that an interaction of the desired kind exists, and investigate the consequences for the function $D(\theta)$. Only in case of a satisfactory outcome would an analysis of the interaction be worthwhile.

Let us see what happens after a molecule jumps from site i to $i+1$ in the $+x$ direction. The occupancy is assured for the latter site, whereas for the four neigboring sites in plane i and for the site $i-1$ behind the respective probabilities are θ_i and θ_{i-1}. Hence the probabilities of immediate after-jumps from the various directions are ξ, $\xi\theta_i$, and $\xi\theta_{i-1}$; their contributions to the flux in direction x are negative, zero, and positive, respectively. Analogous events happen after an opposite initial jump. Summation of all terms up to second order in θ yields an approximation for the diffusivity,

$$D(\theta)=D(0)\left[1+\frac{2\xi(2+\xi)}{1-\xi^2}\theta+O(\theta^2)\right] \tag{25}$$

where $D(0)=l^2r/(1+\xi)$. The denominators account for the jumping hence and forth along $\pm x$. We ought to have $\xi=0.215$ in order to satisfy condition (1).

The saturation limit is found by studying the random walk of an isolated vacancy on an otherwise full lattice. Each jump triggers a fast sequence of moves, with their average number equal to $1+\xi+\xi^2+\cdots=1/(1-\xi)$. Since the orientations of the jumps are uncorrelated, the average square of the total fast displacement L is obtained by summing the squares of the individual jump lengths,

$$L^2=\frac{1}{1-\xi}l^2 \tag{26}$$

The rate of such displacements is $6r$, so that the resulting diffusivity is

$$D_{\text{sat}}=L^2r=\frac{1+\xi}{1-\xi}D(0) \tag{27}$$

For the mentioned value of ξ this equals $1.55D(0)$, which is again unrealistically low. At least the present version of a model with correlated jumps must therefore be dismissed.

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REFERENCES

1. M. H. Ernst, In *Recent Developments in Nonequilibrium Thermodynamics: Fluids and Related Topics*, J. Casas-Vásquez, D. Jou, and J. M. Ruby, eds. (Springer, Berlin, 1986).
2. M. H. Ernst, In *Liquids, Freezing, and the Glass Transition*, J.-P. Hansen, D. Levesque, and J. Zinn-Justin, eds. (North-Holland, Amsterdam, 1991).
3. M. H. Ernst and J. R. Dorfman, In *25 Years of Non-Equilibrium Statistical Mechanics*, J. J. Brey, J. Marro, and J. M. Ruby, eds. (Springer, Berlin, 1995).
4. J. Kärger and D. M. Ruthven, *Diffusion in Zeolites and Other Microporous Solids* (Wiley, New York, 1992).
5. D. M. Ruthven, *Principles of Adsorption and Adsorption Processes* (Wiley, New York, 1984).
6. H. van Bekkum, E. M. Flanigen, and J. C. Jansen (eds.), *Introduction to Zeolite Science* (Elsevier, Amsterdam, 1991).
7. D. A. Reed and G. Ehrlich, *Surface Sci.* **102**:588 (1981).
8. R. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, Cambridge, 1949).
9. J. J. M. Beenakker and I. Kuščer, *Zeolites* **17**:346 (1996).
10. J. P. Hirth and J. Lothe, *Theory of Dislocations* (McGraw-Hill, New York, 1968).
11. F. Watanabe and G. Ehrlich, *Phys. Rev. Lett.* **62**:1146 (1989); *J. Chem. Phys.* **95**:6075 (1991); **96**:3191 (1992).
12. D. M. Ruthven and M. Goddard, In *Fundamentals of Adsorption*, K. Kawazoe and G. Belfort, eds. (Engineering Foundation, New York, 1984).
13. D. C. Senft and G. Ehrlich, *Phys. Rev. Lett.* **74**:294 (1995).