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Diffusion in Inhomogeneous Polymer Membranes

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The dual mode sorption solubility isotherms assume, and in instances Zimm–Lundberg analysis of the solubilities show, that glassy polymers are heterogeneous and that the distribution of the solute in the polymer is also inhomogeneous. Under some conditions, the heterogeneities cannot be represented as holes. A mathematical model describing diffusion in inhomogeneous polymer membranes is presented using Cahn and Hilliard's gradient theory. The fractional mass uptake is found to be proportional to the fourth root of time rather than the square root, predicted by Fickian diffusion. This type of diffusion is classified as pseudo-Fickian. The model is compared with one experimental result available. A negative value of the persistence factor is obtained and the results are interpreted. © *1995 American Institute of Physics.*

I. INTRODUCTION

Glassy polymers are heterogeneous at molecular scale. (In semicrystalline polymers heterogeneities are induced due to the crystallites, but the length scales involved are large and such heterogeneities will be excluded here.) One indication that heterogeneities exist comes from the dual mode sorption solubility isotherms.[1] These isotherms are interpreted as in parts due to solubility in the solid polymer and in parts due to adsorption on the walls of holes that are assumed to exist in these systems, and are called microvoids. Even though these microvoids have not been seen (and thus they must most certainly exist only at molecular level), the dual sorption is the norm in glassy polymers and they generally exhibit properties expected of them.

Further information on this model comes from molecular simulation and diffusion in model glassy polymers. It is a very large subject and only salient features are mentioned. The glassy polymer is seen as a system where some segments are frozen, that is, thermal fluctuations which help to overcome energy barriers for the segments to realize all possible configurations cannot do so in this case. Methods of generating such non-Boltzmann distributed structures have been given. They are not without faults, but they predict structure, elastic and surface properties,[2] and free volumes.[3] When small solute molecules are introduced into the system, they spend most of the time in rattling about in cages formed by the frozen segments, till one key polymer segment moves under thermal vibration to let the molecule out. Much work has been done to investigate the solubilities in the Henry's law region. Further restrictive assumption making all segments frozen allows one to compute a full solubility isotherm which is effectively a sum of Langmuir modes, one for each frozen segment.[4] It is easy now to draw conclusions regarding dual sorption isotherm as sum of two Langmuir modes, one for a frozen and one for a less frozen type of segment, with the latter practically linear. It is also possible to suggest that the cages are related to "microvoids," which could be treated as isolated holes or treated as inhomogeneity as proposed here.

The other evidence on heterogeneities also come from solubility isotherms. Zimm–Lundberg[5] analysis of the solu-bilities show on occasions that clusters form, in that the solute–polymer contacts are nonuniform. One instance is that of water in polyacrylonitrile (PAN).[6] It is well known that PAN has a medium range order, in contrast to the short range order expected in amorphous polymer.[7] Such a structure could prevent uniform contact. Another example is that of methylene chloride in semicrystalline and partially stretched polyethylene terephthalate (PET).[8] As this is not seen in the fully amorphous PET, one concludes that it is due to the presence of crystallites. PET has a rigid backbone, and the polymer chain segments in the amorphous domain pass through the crystallites as well. The rigid chains thus anchored lose most of their mobility, and differential scanning calorimetry indicates that changes observed on traversing T_g are minimal. This difficulty in mobility/packing could also result in nonuniform contacts.

Similar to Zimm–Lundberg analysis for determining clusters, there is an analysis due to Kirkwood on the effects of clustering on thermodynamic properties, in that a cluster size can be backed out from the solubility data. Rogers[9] has shown that cracking solutes in glassy polymers reveal clustering under this analysis. Cussler[10] has investigated the nature of diffusion in Kirkwood's nonideal solutions under the assumption that diffusion is Fickian.

Another attempt at incorporating heterogeneities is due to de Gennes.[11] In dilute polymer solutions in the "semidilute" regime, polymer overlap leads to inhomogeneities. De Gennes brought this feature into the chemical potential using the gradient theory of Cahn and Hilliard.[12] Light scattering results were explained satisfactorily.

Returning to the details of a dual sorption model, if the heterogeneities are simple in the form of holes shown in Fig. 1(a), then the transport phenomena in such a medium can be described by classical approaches.[13] Whereas such a description, which is valid only when the holes are large, may suffice in many systems, it may not hold when the holes are small. We know that the density profile of the polymer across a hole, shown in Fig. 1(a), is only a construction and the actual profile is smooth, as shown in Fig. 1(b). If the holes are very small (we know that they cannot be seen), Fig. 1(c), then the density profiles from the two sides overlap and a "hole" cannot be constructed. Such a system is not at ther-
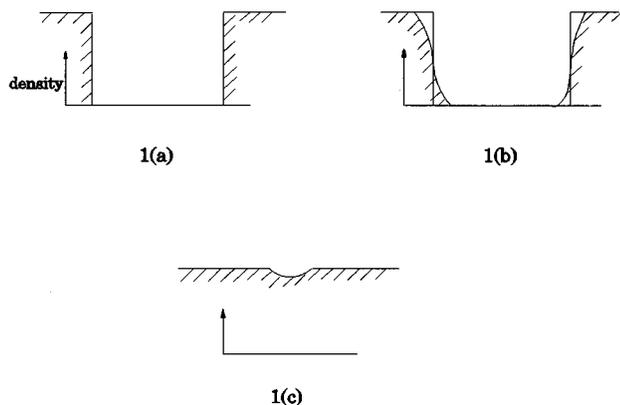
FIG. 1. (a) The density profile of the polymer across a hole when the holes are large. (b) The actual profile which is smooth. (c) The overlap of the density profiles from the two sides if the holes are small, because of which a hole cannot be constructed.

modynamic equilibrium,[14] but neither is the glassy polymer.[15] Consequently, these "bumps," the sum of which forms the heterogeneities, will exist in a real system and their analysis will cover the effects not incorporated in the classical approach.[13] If on the polymer profile in Fig. 1(c), we add the profile of the solute, then two kinds of "interfaces" emerge: polymer-adsorbed solute and adsorbed solute–vapor phase solute (in the microvoid) interfaces. Not only do these two interfaces overlap, they also overlap with those from the other side of the microvoids, making these microvoids more like concentration fluctuations. It is important to point out that whereas in fluctuating systems the length scale and time scale characterizing the fluctuations adjust to the overall conditions, here the glass is frozen at the low solute concentrations in the region where the dual mode sorption applies. The polymer does not contribute directly to the driving forces, but only indirectly by forcing heterogeneity in the solute distribution.

If the inhomogeneities are shrunk to points, then site models of Barrer[16] and Fredrickson and Helfand[17] apply. Fickian diffusion and the dynamic extension of the conventional dual sorption result.

Finally, some disagree completely that sites can exist and assume that the elastic work of swelling plays a key role. The results look very encouraging,[18,19] but the functional form of dual sorption is not predicted. Instead an exponential term is observed which is used to "generalize" dual sorption model, and this term arises out of elastic effects. There is a lot more to be learnt of such a model (at least compared to the enormous work gone in constructing the dual sorption theory) before it can be evaluated.

In our efforts to show that some glassy polymers are inhomogeneous, we have amassed altogether too much a discussion on dual sorption and its implications, particularly when we are interested in heterogeneities of a certain scale and systems showing dual mode sorption may lie outside this region in most cases. Whereas such systems may contribute sufficiently to heterogeneities at a scale discussed in the model which follows, it was pointed out at the start that very often polymer matrices can be inhomogeneous due to a

wider variety of more specific reasons. Our model aims at analyzing non-Ficking response, and is not concerned with the common dual mode sorption system which show Fickian diffusion.

II. FORMULATION

At the interface the chemical potential in the reservoir is taken to be equal to the chemical potential in the membrane. The expression for the chemical potential of the solute in the membrane as given by Cahn and Hilliard for a heterogeneous system is

$$\mu = \mu_\infty(c) + \kappa \nabla^2 c. \tag{1}$$

Here, κ is the persistence factor.[20] The chemical potential in the absence of gradients is

$$\mu_\infty = \mu_0 + RT \ln \gamma c, \tag{2}$$

where μ_0 is the standard state chemical potential and γ is the activity coefficient. Combining Eqs. (1) and (2) one has

$$\mu = \mu_0 + RT \ln \gamma c + \kappa \nabla^2 c. \tag{3}$$

The form of the flux in one dimension is

$$j_x = -\left(\frac{Dc}{RT}\right) \frac{\partial \mu}{\partial x} \tag{4}$$

and substituting μ from Eq. (3), one has

$$j_x = -\frac{Dc}{RT} \left[\frac{RT}{c} \left(\frac{\partial \ln \gamma}{\partial \ln c} + 1 \right) \frac{\partial c}{\partial x} + \frac{\partial}{\partial x} \kappa \frac{\partial^2 c}{\partial x^2} \right]. \tag{5}$$

The conservation of species equation in one dimension which is appropriate in membranes is given by

$$\frac{\partial c}{\partial t} = -\frac{\partial j_x}{\partial x}. \tag{6}$$

Hence,

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left\{ D \left[\left(\frac{\partial \ln \gamma}{\partial \ln c} + 1 \right) \frac{\partial c}{\partial x} + \frac{c}{RT} \frac{\partial}{\partial x} \left(\kappa \frac{\partial^2 c}{\partial x^2} \right) \right] \right\}. \tag{7}$$

The experiments are generally performed by equilibrating the membrane at a base concentration $\bar{c}$ then a small step up in the reservoir is given resulting in a change in the membrane concentration by c_0 at equilibrium, the magnitude of which is kept small. This method is the differential sorption. In the dynamic situation one denotes this concentration difference as a small perturbation c', and the base concentration by $\bar{c}$, then one can express the concentration as a sum of the base concentration and the perturbation

$$c = \bar{c} + c'. \tag{8}$$

We substitute the above expression for concentration in Eq. (7) and expand the concentration dependent diffusivity and persistence factor using the Taylor series about the base concentration $\bar{c}$. Considering only the first two terms in the expansion, one obtains

$$\frac{\partial c'}{\partial t} = \bar{D} \left\{ \frac{\partial^2 c'}{\partial x^2} + \frac{\bar{\kappa} \bar{c}}{RT} \frac{\partial^4 c'}{\partial x^4} \right\}, \tag{9}$$

where $\bar{D}=D[(\partial \ln \gamma)/(\partial \ln c)+1]$ and $\bar{\kappa}=\kappa/[(\partial \ln \gamma)/(\partial \ln c) +1]$ are evaluated at the base concentration and treated as constants. The initial condition is

$$c'=0 \quad \text{at} \quad t=0. \tag{10}$$

The boundary conditions in a membrane of thickness L are

$$\frac{\partial c'}{\partial x}=0 \quad \text{at} \quad x=0 \quad \text{(symmetry)} \tag{11}$$

$$\frac{\partial^3 c'}{\partial x^3}=0 \quad \text{at} \quad x=0 \quad \text{(symmetry)}, \tag{12}$$

$$c'=c_0 \quad \text{at} \quad x=\pm\frac{L}{2} \quad \text{(reservoir)}, \tag{13}$$

$$\frac{\partial^2 c'}{\partial x^2}=0 \quad \text{at} \quad x=\pm\frac{L}{2}. \tag{14}$$

Equation (14) ensures that there are no macroscopic gradients at equilibrium. Equation (9) and the initial and boundary conditions are nondimensionalized to get

$$\theta=\frac{c'}{c_0}, \tag{15}$$

$$\tau=\frac{4\bar{D}t}{L^2}, \tag{16}$$

$$\xi=\frac{2x}{L}, \tag{17}$$

$$\omega=\frac{4\bar{\kappa}\bar{c}}{L^2 RT}. \tag{18}$$

The resultant equation and conditions are

$$\frac{\partial \theta}{\partial \tau}=\frac{\partial^2 \theta}{\partial \xi^2}+\omega\frac{\partial^4 \theta}{\partial \xi^4}, \tag{19}$$

$$\theta=0 \quad \text{at} \quad \tau=0, \tag{20}$$

$$\frac{\partial \theta}{\partial \xi}=0 \quad \text{at} \quad \xi=0, \tag{21}$$

$$\theta=1 \quad \text{at} \quad \xi=\pm 1, \tag{22}$$

$$\frac{\partial^2 \theta}{\partial \xi^2}=0 \quad \text{at} \quad \xi=\pm 1, \tag{23}$$

$$\frac{\partial^3 \theta}{\partial \xi^3}=0 \quad \text{at} \quad \xi=0. \tag{24}$$

III. SOLUTION

Taking the Laplace transform of Eq. (19), one has

$$s\bar{\theta}=\bar{\theta}''+\omega\bar{\theta}''''', \tag{25}$$

where s is the variable of the Laplace transform and the overbar indicates the transformed variable in the s domain. The solution to this equation is

$$\bar{\theta}=A \sinh(\xi s_1)+B \cosh(\xi s_1)+C \sin(\xi s_2)$$
$$+D \cos(\xi s_2), \tag{26}$$

where A, B, C, and D are constants of integration, and

$$s_1=\left\{-\frac{1}{2\omega}+\frac{1}{2}\sqrt{\frac{1}{\omega^2}+\frac{4s}{\omega}}\right\}^{1/2}, \tag{27}$$

$$s_2=\left\{\frac{1}{2\omega}+\frac{1}{2}\sqrt{\frac{1}{\omega^2}+\frac{4s}{\omega}}\right\}^{1/2}. \tag{28}$$

Using symmetry, one has $A=C=0$ from the first and second boundary conditions. B and D can be evaluated using the boundary conditions Eqs. (23) and (24), but the second term in that equation gives rise to an unphysical result in the fractional mass uptake. As s tends to infinity (and time tends to zero), it oscillates very rapidly with time reaching an infinite frequency. Hence, D is set equal to zero. Omitting the fourth boundary condition and using only the third, one has

$$\bar{\theta}=\frac{\cosh(\xi s_1)}{s \cosh s_1}. \tag{29}$$

Hence, the fractional mass uptake is

$$\frac{\overline{M_t}}{M_\infty}=\int_0^1 \frac{\cosh(\xi s_1)}{s \cosh s_1} d\xi. \tag{30}$$

One has

$$\frac{\overline{M_t}}{M_\infty}=\frac{1}{s s_1} \tanh s_1. \tag{31}$$

Using the expansion[21]

$$\tanh(x)=2x\sum_{n=0}^{\infty}\frac{1}{(n+1/2)^2\pi^2+x^2}, \tag{32}$$

one has

$$\frac{\overline{M_t}}{M_\infty}=\frac{2\omega^{1/2}}{s}\sum_{n=0}^{\infty}\frac{1}{\omega^{1/2}\left\{(n+1/2)^2\pi^2-\frac{1}{2\omega}\right\}+\sqrt{s+\frac{1}{4\omega}}}. \tag{33}$$

Inversion using[21]

$$\mathscr{L}^{-1}\frac{1}{s(\sqrt{s+a}+b)}=\frac{\sqrt{a}}{b^2-a} \text{ erfc } \sqrt{a\tau}+\frac{1}{b+\sqrt{a}}$$
$$-\frac{b}{b^2-a}e^{(b^2-a)\tau} \text{ erfc}(b\sqrt{\tau}) \tag{34}$$

with $a=1/4\omega$ and $b=\omega^{1/2}\{(n+1/2)^2\pi^2-1/2\omega\}$, leads to

$$\frac{M_t}{M_\infty}=1+\sum_{n=0}^{\infty}\frac{\text{erfc }\sqrt{\dfrac{\tau}{4\omega}}}{\omega(n+1/2)^4\pi^4-(n+1/2)^2\pi^2},$$

$$-\sum_{n=0}^{\infty}\frac{2\omega(n+1/2)^2\pi^2-1}{\omega(n+1/2)^4\pi^4-(n+1/2)^2\pi^2}$$

$$\times\exp[\{\omega(n+1/2)^4\pi^4-(n$$

$$+1/2)^2\pi^2\}\tau]\text{erfc}[\omega^{1/2}\tau^{1/2}\{(n+1/2)^2\pi^2-1/2\omega\}]. \tag{35}$$

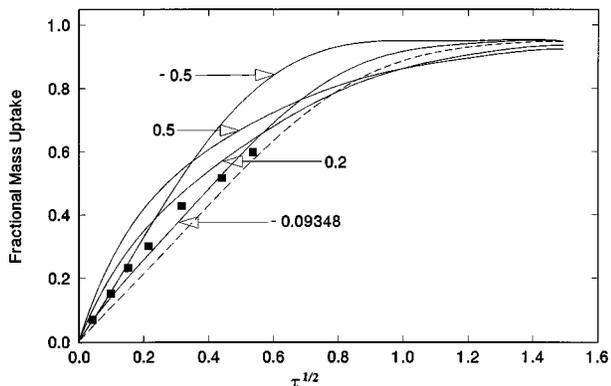Equation (31) can be used to calculate the moments

FIG. 2. Theoretical plots of the fractional mass uptake as a function of the square root of time are shown for four different values of ω. In addition, the dashed line is used to indicate the curve for Fickian diffusion ($\omega=0$). Experimental points (Ref. 8) upto half times are shown.

$$\int_0^\infty \left(1 - \frac{M_t}{M_\infty}\right) dt = \frac{L^2}{12D} \tag{36}$$

and

$$\int_0^\infty \left(1 - \frac{M_t}{M_\infty}\right) t \, dt = \frac{L^4}{16D^2} \left(\frac{2}{15} - \omega\right). \tag{37}$$

They provide a quick means for comparing theory to experiments.

IV. RESULTS

In Fig. 2 are shown the theoretical plots of the fractional mass uptake as a function of square root of time and in Fig. 3 as a function of time to one-fourth power. Only a power of 1/4 is predicted at small times and not a spectrum ranging from 1/2 to 1/4. This is apparent only for positive values of ω, and when it is negative the effective power increases rapidly to 1/2 within $\tau=0.1$. The model predicts for the first time a class of non-Fickian diffusion called pseudo-Fickian on physical grounds. This behavior, where the initial mass uptake is proportional to t^n, where $n<1/2$, was first defined
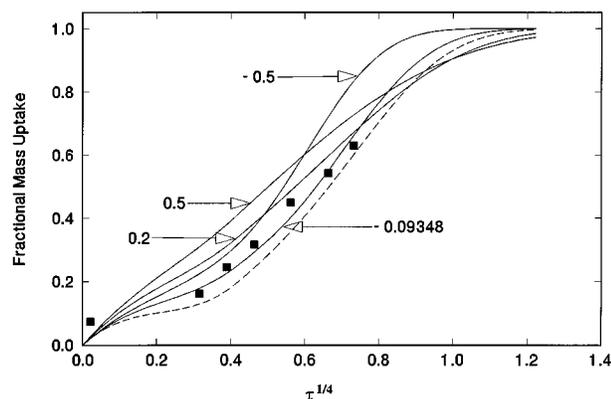

FIG. 3. Theoretical plots of the fractional mass uptake as a function of the fourth root of time are shown for five different values of ω, including the Fickian case which is shown with dashed lines as before. Experimental points (Ref. 8) upto half times are shown.

by Crank[22] based only on a mathematical model. No experimental data appear to have been found except those of Liu and Neogi[8] and no models were available based on physical grounds except that given here, which is capable of showing an exponent n below 1/2. However, the experiments show that n is closer to 1/2 than to 1/4, and strictly speaking the model is restricted to 1/4 only, but as noted earlier it is difficult to differentiate among cases. The theory contains a few assumptions including one in the gradient theory itself which actually has an infinite series[20] and not just one term as in Eq. (1), although only the first term is usually retained.

This feature of non-Fickian diffusion needs more discussion because considerable amount of work has been done on it in the last few years. One model for generating a spectrum of values of the power n has been the memory dependent diffusion. It is too large an area to review here, though the work by Neogi[23] is typical. The memory allows values of n from 1/2 to 1, but not beyond. In comparing non-Fickian diffusion to non-Newtonian rheology, one other model which could give different values of the power n would be a nonlinear constitutive equation. A few standard forms are discussed in the Appendix, where it is seen that these too do not lead to values of n outside 1/2 to 1. This makes the present model even more interesting.

The theory was compared with one set of data from Liu and Neogi[8]. Briefly they have reported the sorption results for methylene chloride vapor in semicrystalline PET using gravimetric method. A Cahn electrobalance was used. The system was thermostatted using an air bath. The stepped up pressure did not change within the accuracy of the device. A differential scheme was used. The equilibrium sorption isotherm showed generalized dual sorption (that is, needed the exponential term) and was shown to form clusters at higher concentrations under Zimm–Lundberg analysis, a feature which was traced squarely to the exponential term, in the dual mode model, which was shown to arise from the work of cluster formation. The results showed Fickian diffusion at low concentrations and at higher concentrations (but still within the range of dual sorption) the power dropped below 1/2, and distinctly so in one case which is treated here. The PET sample was a well characterized semicrystalline (degree of crystallinity of 35%) and partially stretched. No solvent induced crystallization was detected using differential scanning calorimetry and neither was any whitening of the sample seen. When the present theory was compared to these experimental results, a negative value was found for ω. The difficulty with this is that for negative values of ω, Eq. (35) gives us a complex solution, where the real part does not go to one at infinite times.

Another solution is sought in the form of

$$\theta = 1 + \sum_{n=0}^\infty \alpha_n(\tau)\cos\left[(2n+1)\frac{\pi}{2}\xi\right]. \tag{38}$$

Substituting into Eq. (19) and using the orthogonality property of cosine functions and the boundary conditions, Eqs. (20)–(34), one has

$$\alpha_n = -\frac{4(-1)^n}{\pi(2n+1)}$$

$$\times \exp\left[-\left\{\frac{(2n+1)^2\pi^2}{4} - \omega\frac{(2n+1)^4\pi^4}{16}\right\}\tau\right] \quad (39)$$

and

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}$$

$$\times \exp\left[-\left\{\frac{(2n+1)^2\pi^2}{4} - \omega\frac{(2n+1)^4\pi^4}{16}\right\}\tau\right]. \quad (40)$$

It is noteworthy that Eq. (40) is not valid for positive values of ω. Parameter estimation using the method of moments leads to $D = 7.51 \times 10^{-13}$ cm^2/s and $\omega = -0.0935$. The latter value is now consistently negative and leads to $\kappa = -2.59 \times 10^6$ erg cm^5/(g mmol).[2] Plots for negative values of ω have been shown in Figs. 2 and 3 as well and show some differences over those with positive values of this parameter as discussed earlier. The comparison between theory and experiment is reasonable but fails in satisfying details at short times as indicated earlier. As a result the fitted values of the parameters are only estimates, but it should be emphasized here that negative values of persistence factor does a great deal in improving the comparison between theory and experiment, in that the rate of uptake is made adequately faster over corresponding Fickian response to match with the experimental values.

It is interesting to try to interpret a persistence factor which is negative. When the persistence factor is positive, phase separation takes place in the spinodal region.[24] At the interfaces, the interfacial free energy can be related to the persistence factor κ.[20] Consequently, all literature appears to focus on positive values of κ since it explains both the thermodynamics of interfaces and the mechanism by which they are formed. The vapor–liquid surface tension for n alkanes have been used to calculate the values of κ, and there in one typical case κ is 0.108 83 erg cm^5/(g mmol)^2 [25] which is orders of magnitude lower.

There has been considerable work addressing polymer solutions.[26,27] Debye[28] has considered the thermodynamics of concentration fluctuation in a polymer solution close to a critical point. The physical situation here is quite close, with two important differences. First, as noted earlier the size of fluctuations here is frozen because the polymer is glassy. Second, if one had means for relaxing the polymer then the fluctuations would vanish because unlike that in Debye's case the imposed conditions here are not those which are expected to promote fluctuation. Still, there does not seem to be any apparent reason as to why Debye's treatment cannot be extended to this case under the constraint of prescribed length scale and time scale. Since the overall quantities such as temperature and pressure are such that fluctuations cannot arise, in forcing them it is quite possible that persistence factor may turn out to have an extreme value, possibly negative. Cahn's treatment of spinodal decomposition[24] makes it clear that with a negative persistence factor forced fluctua-

tions will not evolve into phase separation; whether it is also enough to show that fluctuations have to be forced is not known.

Finally, it should be pointed out that the dual mode sorption isotherm cannot be resurrected without going through the pains of drawing up dividing surfaces for every hole so that the adsorbed amounts can be calculated, a feature which we have abandoned under the assumption that the dividing surfaces cannot be drawn in the present system for reasons described earlier. Our model leads to pseudo-Fickian diffusion, and in addition compliments the other special cases of heterogeneities treated in the literature.

APPENDIX

Like Ellis' model in rheology one may write in one dimension

$$D = D_\infty + \frac{(D_0 - D_\infty)}{1 + |j_x/j_0|^{(1/\nu)-1}}, \quad (A1)$$

where D_0, D_∞, ν, and j_0 are constants. The model says that at infinite flux the diffusivity is D_∞, and at zero flux it is D_0. If D_∞ is less than D_0 then the fluxes give rise to a jamming effect and decrease the effective diffusivity. These require that $1 < \nu < 0$. When $|j_x/j_0| \gg 1$ and $D_\infty \ll D_0$,

$$j_x = -j_0\left(\frac{D_0}{j_0}\right)^\nu\left|\frac{\partial c}{\partial x}\right|^{\nu-1}\frac{\partial c}{\partial x}. \quad (A2)$$

This is a power law type relation and leads to $n = 1/(1+\nu)$. Thus n lies between 1/2 and 1.

Equation (A1) essentially is of the type that the driving force, proportional to $\partial c/\partial x$, is some complicated function of the flux. One can look at the reverse problem, namely that flux is some complicated function of the driving force. This form has been suggested by Stearn, Irish, and Eyring.[29] It is possible to show that it does not lead to a power law form for the fractional mass uptake. In addition, the system will return to Fickian diffusion in differential sorption.

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