the water-saturated speeds with no adjustable parameters. (4) The Biot theory is seen to effectively cut in half the problem of understanding acoustic propagation in porous media. It now becomes possible to focus on theories of the individual parameters, as has already been done, here, for the tortuosity, α.

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Method for the Exact Solution of a Nonlinear Diffusion-Convection Equation

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For a prescribed adsorption-desorption equilibrium maintained locally through a permeable solid, the concentration of a chemical substance is governed by the diffusion-convection equation $\partial c/\partial t = (D\nabla^2 - \vec{v}\cdot\nabla)[c/(1+K^{-1}c)]$ in which $c/(1+K^{-1}c)$ is the free concentration of the substance. Solutions of this nonlinear equation are shown to be related analytically to solutions of the elementary linear diffusion equation. This remarkable correspondence is utilized to obtain exact solutions to the nonlinear diffusion-convection equation.

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Consider a homogeneous permeable solid filled with a fluid which contains a chemical substance of concentration $c = c(\vec{x},t)$. Suppose that the solid microsurfaces adsorb a fraction of the chemical substance and leave a local free concentration $c/(1+K^{-1}c)$ in the fluid at adsorption-desorption equilibrium,[1] where K is a prescribed constant. With the adsorption-desorption processes relatively rapid and their equilibrium maintained locally, the total concentration c may change as a result of diffusion and convection of the free concentration, and one obtains the governing equation

$$\partial c/\partial t = (D\nabla^2 - \vec{v}\cdot\nabla)[c/(1+K^{-1}c)], \tag{1}$$

where D ($\equiv$ const) is the diffusivity of the chemical substance and $\vec{v}$ is the local convective flow velocity of the fluid. Equation (1) is the diffusion-convection analog of the Langmuir-Hinshelwood (Michaelis-Menten) rate expression featured in catalytic[2] and enzymatic[3] kinetics.

By introduction of the dimensionless dependent variable $\theta \equiv (1+K^{-1}c)^{-1}$, (1) takes the form

$$\partial\theta/\partial t = \theta^2(D\nabla^2\theta - \vec{v}\cdot\nabla\theta). \tag{2}$$

For the special case $\vec{v} \equiv 0$, (2) becomes the equation for nonlinear heat conduction in solid hydrogen,[4] where θ (also positive and less than or equal to unity) is a dimensionless thermal variable. The author has shown that one-dimensional solutions to the latter nonlinear heat-conduction equation are related analytically to solutions of the elementary linear diffusion equation,[4] and this exact correspondence has been employed in recent theoretical work by others.[5,6] It is shown in the following that the general solution to the one-dimensional specialization of (2) with

$$\theta=\theta(x,t),\quad \vec{v}\cdot\nabla\theta=v\,\partial\theta/\partial x,\quad v\,(\equiv\text{const})\neq 0 \tag{3}$$

is also obtained by invoking a transformation which expresses θ in terms of solutions to the linear diffusion equation. Although this analytical procedure is related to the more immediate solutional method[4] for $v\equiv 0$, the transformation formulas below show that $v=0$ is a singular special case precluded by the present treatment.

If one assumes that the one-dimensional uniform-flow conditions (3) hold, it is possible to recast (2) as the integrability condition

$$\frac{\partial}{\partial t}(\theta^{-1})=\frac{\partial}{\partial x}\left(v\theta-D\frac{\partial\theta}{\partial x}\right), \tag{4}$$

which guarantees existence of an extensible distance coordinate $\hat{x}=\hat{x}(x,t)$ such that

$$\theta^{-1}=\partial\hat{x}/\partial x,\quad v\theta-D\,\partial\theta/\partial x=\partial\hat{x}/\partial t. \tag{5}$$

From (5) it follows that the total differential of $\hat{x}$ is[7]

$$d\hat{x}=\theta^{-1}dx+(v\theta-D\,\partial\theta/\partial x)dt. \tag{6}$$

Either (6) or the first equation in (5) and $\theta>0$ implies that $\hat{x}$ is a monotone-increasing function of x for fixed t; thus, the correspondence $x\rightarrow\hat{x}$ is one to one for fixed t, and there exists a single-valued positive function $\psi=\psi(\hat{x},t)$ such that

$$x=-v^{-1}D\,\ln\psi. \tag{7}$$

The function ψ is monotone decreasing with increasing $\hat{x}$ for $v>0$ and monotone increasing with increasing $\hat{x}$ for $v<0$. By virtue of the first equation in (5), the derivative of (7) with respect to $\hat{x}$ at fixed t yields

$$\theta=-v^{-1}D\psi^{-1}(\partial\psi/\partial\hat{x}) \tag{8}$$

and hence

$$v\theta-D\frac{\partial\theta}{\partial x}=-D\left(\frac{\partial\psi}{\partial\hat{x}}\right)^{-1}\frac{\partial^2\psi}{\partial\hat{x}^2}. \tag{9}$$

The substitution of (7), (8), and (9) into (6) produces

$$d\hat{x}=\left(\frac{\partial\psi}{\partial\hat{x}}\right)^{-1}d\psi-D\left(\frac{\partial\psi}{\partial\hat{x}}\right)^{-1}\frac{\partial^2\psi}{\partial\hat{x}^2}dt. \tag{10}$$

But since

$$d\psi=(\partial\psi/\partial\hat{x})d\hat{x}+(\partial\psi/\partial t)dt, \tag{11}$$

(10) implies that ψ satisfies the linear diffusion equation

$$\partial\psi/\partial t=D(\partial^2\psi/\partial\hat{x}^2). \tag{12}$$

Thus, (4) is exactly solvable by use of familiar or easily obtained solutions to the classical equation (12).

For unbounded $\hat{x}$ the general solution to (12) is expressible in terms of the initial condition $\psi(\hat{x},0)$ as

$$\psi(\hat{x},t)=(4\pi Dt)^{-1/2}\int_{-\infty}^{\infty}\exp[-(\hat{x}-s)^2/4Dt]\,\psi(s,0)ds. \tag{13}$$

One obtains the general solution to (4) in parametric form by putting (13) into (7) and (8); a prescribed initial condition $\theta(x,0)$ fixes $\psi(s,0)$ in (13). The following basic solutions serve to illustrate the c-ψ relationship and some of the salient nonlinear aspects of diffusion convection governed by (1).

(a) Uniform steady state, $c\equiv c_1=\text{const}$ for all x and t. The associated solution to (12) depends on both $\hat{x}$ and t,

$$\psi=\exp(-a_1\hat{x}+a_1^2Dt), \tag{14}$$

with the constant $a_1\equiv vD^{-1}(1+K^{-1}c_1)^{-1}$.

(b) Generic x-dependent steady state,

$$c=(c_1+b_1Ke^{vx/D})/(1-b_1e^{vx/D}), \tag{15}$$

defined for $vx<D\ln(b_1^{-1})$ with the constant $b_1>0$. The associated solution to (12) is a slight modification of (14),

$$\psi=\exp(-a_1\hat{x}+a_1^2Dt)+b_1 \tag{16}$$

with a_1 as in (14). Notice that the value of b_1 relates simply to the x coordinate origin in (15).

(c) Steadily propagating fixed-profile wave, $c=K(\theta^{-1}-1)$ with θ in the range $(0<)\ \theta_1\leq\theta\leq\theta_2$ (≤ 1) and given implicitly in terms of the quantity $x-\theta_1\theta_2vt$ by

$$(\theta-\theta_1)^{-\theta_1}(\theta_2-\theta)^{\theta_2}=\exp[(\theta_2-\theta_1)vD^{-1}(x-\theta_1\theta_2vt)]. \tag{17}$$

The fixed-profile wave propagates with constant velocity $\theta_1\theta_2v$ in the same direction as the flow (i.e., toward $x=+\infty$ for $v>0$), and the terminal values of θ are set by the sign of v [i.e., $\theta(+\infty,t)=\theta_1$, $\theta(-\infty,t)=\theta_2$ for $v>0$]. One arrives at (17) by employing a linear superposition of two solutions of the form (14) to satisfy (12),

$$\psi=\exp(-a_1\hat{x}+a_1^2Dt)+\exp(-a_2\hat{x}+a_2^2Dt), \tag{18}$$

with $a_j\equiv vD^{-1}\theta_j$ for $j=1,2$. The substitution of

(18) into (7) and (8) produces two equations from which $\hat{x}$ can be eliminated algebraically, and thus (17) is obtained (modulo a trivial multiplicative constant related to the x or t origin).

(d) Localized variation on a uniform background, with $c(\pm\infty,t)=c_1$. The simplest solution to (12) of this type is the linear superposition

$$\psi=\exp(-a_1\hat{x}+a_1{}^2Dt)+(t_1/t)^{1/2}\exp(-\hat{x}^2/4Dt) \tag{19}$$

with a_1 as above, t_1 a positive constant parameter, and $t \geqslant (t_1/2eD)^{1/2}|a_1|^{-1}$ to insure the monotonicity of (19) with increasing $\hat{x}$ and fixed t. By substituting (19) into (7) and (8), one obtains

$$x=v^{-1}D\{a_1{}^2Dt+2a_1(Dt)^{1/2}\gamma-\ln[1+(t_1/t)^{1/2}\exp-\gamma^2]\}, \tag{20}$$

$$\theta=v^{-1}D\{a_1+(Dt)^{-1/2}\gamma[1+(t/t_1)^{1/2}\exp\gamma^2]^{-1}\}, \tag{21}$$

where

$$\gamma\equiv(\hat{x}-2a_1Dt)/2(Dt)^{1/2}. \tag{22}$$

Observe that the value $c=c_1$ is maintained at the center of the propagating and diffusing region of variation; setting $\gamma=0$ in (21) and (20) yields

$$\theta=v^{-1}Da_1 \rightarrow c=c_1 \tag{23}$$

along the region's trajectory

$$x=v(1+K^{-1}c_1)^{-2}t-v^{-1}D\ln[1+(t_1/t)^{1/2}]. \tag{24}$$

(e) Step-function initial condition,

$$c(x,0)=\begin{cases} c_+ \ (\equiv \text{const}) \text{ for } x>0, \\ c_- \ (\equiv \text{const}) \text{ for } x<0. \end{cases} \tag{25}$$

From (25) and (8) it follows that

$$\psi(\hat{x},0)\equiv\begin{cases} \exp(-a_+\hat{x}) \text{ for } \hat{x}\geqslant 0, \\ \exp(-a_-\hat{x}) \text{ for } \hat{x}\leqslant 0, \end{cases} \tag{26}$$

where $a_\pm \equiv vD^{-1}(1+K^{-1}c_\pm)^{-1}$. The substitution of (26) into (13) produces

$$\psi(\hat{x},t)=\tfrac{1}{2}\{1+\mathrm{erf}[\tfrac{1}{2}(Dt)^{-1/2}\hat{x}-(Dt)^{1/2}a_+]\}\exp(-a_+\hat{x}+a_+{}^2Dt)$$
$$+\tfrac{1}{2}\{1-\mathrm{erf}[\tfrac{1}{2}(Dt)^{-1/2}\hat{x}-(Dt)^{1/2}a_-]\}\exp(-a_-\hat{x}+a_-{}^2Dt). \tag{27}$$

Since the error function has the asymptotic values +1 for a large positive argument and −1 for a large negative argument, (27) manifests a two-step form for ψ; the steps propagate along the $\hat{x}$-space trajectories $\hat{x}=2Dta_+$, $\hat{x}=2Dta_-$, and have a $\Delta\hat{x}$ breadth about equal to $2(Dt)^{1/2}$. The associated solution for c, obtained in parametric form by substituting (27) into (7) and (8), has a relatively complicated structure compared to its one-step linear-theoretic correspondent

$$c=\tfrac{1}{2}(c_++c_-)+\tfrac{1}{2}(c_+-c_-)\mathrm{erf}[\tfrac{1}{2}(Dt)^{-1/2}(x-vt)], \tag{28}$$

which follows from the initial condition (25) and (1) with $K=\infty$.

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[1] The equilibrium of interest here is realized directly if the adsorption process is bimolecular and the desorption process is monomolecular, for then one obtains the equilibrium condition $c'c/c''=K$ where c', c'' denote the concentrations of free and adsorbed molecules, respectively; then from $c'+c''=c$, if follows that $c'=c/(1+K^{-1}c)$.

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Classical Stochastic Diffusion Theory for Desorption of Atoms and Molecules from Solid Surfaces

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A theory of desorption of atoms and molecules from solid surfaces based on a classical stochastic diffusion formulation is presented. A simple rate expression is obtained which has the form $R = (\Omega_0/2\pi) f(T) \exp(-D_e/kT)$, where Ω_0 is the surface-adsorbate vibrational frequency, $f(T) = 1$ for atoms, and for molecules $f(T)$ depends on the parameters for the frustrated rotations at the surface. This theory has been applied to the desorption of both atoms and molecules and excellent agreement with experiment is obtained.

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It is well established experimentally that the rate of first-order desorption of atoms and molecules from surfaces can be described by an Arrhenius expression $R = A \exp(-E/kT)$, where E is assumed to be closely related to the bond enthalpy. Such an expression is obtained from simple thermodynamic arguments applied to the transition state; however, it is difficult to quantify this theory since the transition complex for desorption is not easily identifiable. Although there is considerable disagreement between the experimentally derived preexponential factors for desorption of molecules,[1] most experimental results lead to preexponential factors much larger than expected from transition-state theory.

One would like to obtain the rate expression in terms of the microscopic properties (e.g., vibrational frequencies, bond energy, etc.) and dynamics of the adsorbate-surface system. Unfortunately, despite recent theoretical progress,[2] there is not as yet a theory capable of reproducing the experimental rates of desorption for atoms and molecules.

In the present paper we report such a theory based on a classical stochastic diffusion equation using a general form for the adsorbate-surface interaction. The result is the simple expression

$$R = (\Omega_0/2\pi) f(T) \exp(-D_e/kT), \tag{1a}$$

where Ω_0 is the characteristic frequency of the adsorbate-surface interaction potential. D_e is the well depth of this interaction and $f(T)$ is given by

$$f_{\text{atom}}(T) = 1, \quad f_{\text{mol}}(T) = \frac{2\mu l^2 \Omega_T^2 \vartheta_0^2}{\pi k T}. \tag{1b}$$

for atoms and molecules desorbing from the surface, respectively, where the quantities μ, l, Ω_T, and ϑ_0 are related to the frustrated rotational motion at the surface (*vide infra*). The evaluation of this expression is straightforward, requiring only the basic parameters of the interaction potential between the adsorbed species and the surface. Equation (1) is valid for low coverages, where there is no interaction between the adparticles.

To obtain Eq. (1) consider first the motion of an adatom in the direction perpendicular to the surface and (following Adelman *et al.*[3] and Tully[4]) define on the surface a set of primary zone atoms that are strongly interacting with the adatom. Without loss of generality, this primary zone can be considered to contain one surface atom, leading to a generalized Langevin equation of motion,

$$m_s \ddot{x}_s = -\frac{\partial V(x_{\text{ad}} - x_s)}{\partial x_s} - m_s \omega_0^2 x_s + m_s \int_0^t \Theta(t-\tau) x_s(\tau)\, d\tau + F(t). \tag{2}$$