Diffusive Transport across an Interface

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The kinetics of material diffusion across an interface is analyzed with special emphasis on the effect of the interface permeability on the transport characteristics, such as the mean-square displacement and the residence probability in each of the two phases separated by the interface. Two practically important cases are considered, namely, one-dimensional diffusion in a stepwise potential and three-dimensional diffusion under a spherically symmetric square-well potential. The transport characteristics are shown to be independent of the permeability at asymptotically long times, unless the interface is absolutely impermeable. However, the way the asymptotic behavior is approached can be controlled by the interface permeability. At low permeability values, the kinetics exhibit a characteristic intermediate stage that can last for such a long time that the true asymptotic behavior may not be observed experimentally at all. Along with exact analytical solutions of the diffusion problems at hand, useful approximate expressions are presented for different stages of the kinetics.

Introduction

Material transport across an interface is of fundamental importance in physical kinetics, chemistry, and biology. Ignoring molecular details, the process can often be modeled by an ordinary diffusion equation with a stepwise potential. Strictly speaking, the diffusion equation does not hold in the close vicinity of the interface where the potential changes abruptly and molecular velocities are not thermally equilibrated. A way to avoid this difficulty is to solve the diffusion equation separately for each phase, where the potential is smooth, and then match the two solutions at the interface by applying appropriate boundary conditions. One of the boundary conditions should apparently be the flux continuity. The choice of the second condition is not so straightforward. One of the common assumptions made in the literature is that a local equilibrium is maintained around the interface at all times.[1] This implies that material exchange is infinitely fast between the phases. Generally this is not the case, of course, and there is certain transport resistance. An example of vital importance is material exchange in red blood cells where the transport is, in fact, limited by the interface permeability. The appropriate boundary condition should describe the total flux across the interface as the difference between the fluxes outgoing from each phase, which are proportional to the local concentrations.

In this paper, we analyze the kinetics of material diffusion across the interface with special emphasis on the effect of the interface permeability on the transport characteristics, such as the mean-square displacement and the residence probability in each phase. We were originally drawn to this problem by the work of Morita.[1,2] Here we consider the same two particular cases that he recently addressed, namely, one-dimensional diffusion in a stepwise potential and three-dimensional diffusion under a spherically symmetric square-well potential. A new point in our analysis is that we include transport resistance at the interface and emphasize how important it can be in influencing the overall kinetics. We also resolve a few mistakes in Morita's treament which led him to incorrect conclusions.

Nonequilibrium Partition Constants

In a recent paper,[1] Morita has considered a diffusion process of a solute in a mixture of two immiscible liquids. The key point in his analysis is the derivation of the Green's function $\rho(x|x_0;t)$ for the one-dimensional diffusion equation with a stepwise potential $\mu(x) = \mu_1^{\ominus}\theta(x) + \mu_2^{\ominus}\theta(-x)$ and diffusion coefficient $D(x) = D_1\theta(x) + D_2\theta(-x)$, where $\theta(x)$ is the Heaviside step function (all other notations hereafter are the same as in Morita's work). As mentioned in the Introduction, a proper way to treat this problem is to separately find the Green's function components for each phase, where the potential is smooth, and then match the two solutions at the interface by applying appropriate boundary conditions. One of the boundary conditions is the flux continuity. For the second condition, Morita used the following relation: $\rho_1(0|x_0;t) = e^{-A}\rho_2(0|x_0;t)$, where $A = (\mu_1^{\ominus} - \mu_2^{\ominus})/k_BT$. This implies that material exchange at the interface is infinitely fast. To account for the interface permeability, the appropriate boundary condition at $x = 0$ should be

$$-D_1\frac{\partial\rho_1}{\partial x} = -D_2\frac{\partial\rho_2}{\partial x} = k_2\rho_2 - k_1\rho_1 \qquad (1)$$

where k_1 are the rate constants for crossing the interface starting from phase i. According to the principle of microscopic reversibility

$$k_2/k_1 = e^{-A} \equiv K \qquad (2)$$

Thus, the relation applied in ref 1 works only when both k_1 and k_2 are infinitely large. A boundary condition similar to eq 1 has also proved appropriate in the formulation of the absorption and desorption of a nonreactive gas across an infinite planar gas−liquid phase boundary.[3]

Now, how does the boundary condition affect the Green's function? Taking into account that $\lim_{x\to\pm\infty}\rho(x|x_0;t) = 0$, we obtain, following standard procedures:[4]

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$$\rho_1(x|x_0;t) = \frac{1}{2x_0\sqrt{\pi\tau}}[e^{-(1-\tilde{x})^2/4\tau} + e^{-(1+\tilde{x})^2/4\tau}] - \frac{\kappa_1}{x_0} e^{-(1+\tilde{x})^2/4\tau}\Phi\left(\frac{1+\tilde{x}}{2\sqrt{\tau}} + \kappa\sqrt{\tau}\right) \quad (3)$$

$$\rho_2(x|x_0;t) = \frac{\alpha\kappa_1}{x_0} e^{-(1-\alpha\tilde{x})^2/4\tau}\Phi\left(\frac{1-\alpha\tilde{x}}{2\sqrt{\tau}} + \kappa\sqrt{\tau}\right) \quad (4)$$

where $\tilde{x} = x/x_0$, $\kappa_i = k_i x_0/D_i$, $\kappa = \kappa_1(1 + \alpha K)$, $\alpha = \sqrt{D_1/D_2}$, $\tau = D_1 t/x_0^2$, $\Phi(z) = \exp(z^2)\,\mathrm{erfc}(z)$, and $\mathrm{erfc}(z)$ denotes the complementary error function. Equations 3 and 4 reduce to those derived by Morita in the limit of $k_i \to \infty$. The probability $N_2(x_0,t)$ of finding a given particle in phase 2 at time t after it has started from x_0 in phase 1 is given by

$$N_2(x_0,t) \equiv \int_{-\infty}^{0} \rho_2(x|x_0;t)\,dx = (1 + \alpha K)^{-1}[\mathrm{erfc}(1/2\sqrt{\tau}) - \exp(-1/4\tau) \times \Phi(1/2\sqrt{\tau} + \kappa\sqrt{\tau})] \quad (5)$$

while $N_1(x_0,t) = 1 - N_2(x_0,t)$ due to the conservation constraint. After the initial induction period during which the phase boundary is reached (i.e., $\tau = D_1 t/x_0^2 \gg 1$), eq 5 can be simplified to

$$N_2(x_0,t) \cong (1 + \alpha K)^{-1}[1 - (1 + \kappa)\Phi(\kappa\sqrt{\tau})] \quad (6)$$

If the permeability of the interface is low, the condition $\kappa\sqrt{\tau} \ll 1$ can be met at moderately long times. During this stage, the growth of $N_2(x_0,t)$ is independent of the properties of phase 2 and determined exclusively by the one-way passage through the interface, i.e.

$$N_2(x_0,t) \propto 2\kappa_1\sqrt{\tau/\pi} = 2k_1\sqrt{t/\pi D_1} \quad (7)$$

Clearly, the starting position x_0 plays no important role as long as the interface permeability is low. Whether this intermediate $t^{1/2}$ stage of the kinetics is observable depends on how low the permeability is. Comparing simple criteria we find the corresponding condition to be $\kappa \ll 1$.

At very long times, $\kappa\sqrt{\tau} \gg 1$, the final stage of the kinetics is reached:

$$N_2(x_0,t) \propto (1 + \alpha K)^{-1}[1 - (1 + 1/\kappa)/\sqrt{\pi\tau}] \quad (8)$$

and we see that the correction for the transport resistance at the interface appears only in the second term in the asymptotic expansion ($1/\kappa$, vanishing as $k_i \to \infty$), while the long-time limit, $N_2(\infty) = (1 + \alpha K)^{-1}$, is exclusively determined by the equilibrium partition constant K and the ratio of the diffusion coefficients in the two phases. Thus, the definition of the so-called nonequilibrium partition constant

$$K_D \equiv N_1(\infty)/N_2(\infty) = \alpha K = K\sqrt{D_1/D_2} \quad (9)$$

introduced by Morita[1] is justified. Nonequilibrium partitioning is a natural consequence of the system at hand being infinite. At sufficiently long times, however, after the diffusion front reaches the interface ($\tau \gg 1$), there is a region of a quasi-equilibrium state where the normal partition law holds. This region expands as the diffusion front propagates away from the interface:

$$(1 - 2\sqrt{\tau})/\alpha \ll \tilde{x} \ll 2\sqrt{\tau} - 1 \quad (10)$$

An auxiliary condition, defined by the interface permeability, should also be fulfilled for the quasi-equilibrium state to be realized, i.e., $\kappa\sqrt{\tau} \gg 1$. Clearly, the equilibrium will be eventually attained in the whole system, but only if the system is finite.

The time evolution of $n_2(x_0,t) = N_2(x_0,t)/N_2(\infty)$, as given by eq 5, is shown in Figure 1. The intermediate stage of kinetics (eq 7) is pronounced for low permeability values. Permeability also determines the moment of time where the kinetics enter their final stage (eq 8). Clearly, the overall transport process in the system is governed by the interplay between one-phase diffusion and barrier crossing at the interface and may thus occur in two distinct regimes, namely, a short-time kinetic regime and a long-time diffusive regime. These two regimes can be observed, e.g., in the uptake kinetics of gases by liquid aerosols in atmospheric systems.[3]

Let us now consider the mean-square displacement defined by

$$\langle \Delta x^2(t) \rangle \equiv \int_{-\infty}^{\infty} (x - x_0)^2 \rho(x|x_0;t)\,dx \quad (11)$$

(N.B. The definition given in ref 1 is incorrect and refers, in fact, to the second moment of the probability distribution, i.e., $\langle x^2(t) \rangle \equiv \int_{-\infty}^{\infty} x^2 \rho(x|x_0;t)\,dx$. Only asymptotically do these two definitions predict the same time behavior.) The mean-square displacement is most conveniently expressed in the Laplace space. We obtain

$$\mathcal{L}[\langle \Delta x^2(t) \rangle] = \frac{2D_1}{\epsilon^2}\left\{1 - \left[\frac{\kappa_1}{\kappa + \lambda}\left(1 + \frac{1}{\alpha}\right)\left(1 - \frac{1}{\alpha} - \lambda\right) + \lambda\right]\exp(-\lambda)\right\} \quad (12)$$

where $\lambda = x_0\sqrt{\epsilon/D_1}$, ϵ is the Laplace variable, and $\mathcal{L}$ the Laplace operator, i.e., $\mathcal{L}|f(t)] = \hat{f}(\epsilon) \equiv \int_0^\infty f(t)\exp(-\epsilon t)\,dt$. At short times, before the diffusion front reaches the phase boundary ($\tau \ll 1$ or, equivalently, $\lambda \gg 1$), we have $\langle \Delta x^2(t) \rangle \propto 2D_1 t$, as expected. The long-time behavior of the mean-square displacement also follows the Einstein relation but with an apparent diffusion coefficient:

$$\langle \Delta x^2(t) \rangle \propto 2D_{app} t \quad (13)$$

where $D_{app} = D_1(K_D + D_2/D_1)/(K_D + 1)$. D_{app} is independent of both the initial position x_0 and the interface resistance. This is consistent with that the boundary condition given in eq 1 eventually reduces to $\rho_1(0|x_0;t) = K\rho_2(0|x_0;t)$ in the limit of $t \to \infty$.

The time evolution of the mean-square displacement is illustrated in Figure 2. The permeability controls the way the asymptote is reached. In addition to the condition $\tau \gg 1$, the condition $\kappa\sqrt{\tau} \gg 1$ is also required for eq 13 to be valid. For low permeabilities, the initial single-phase Einstein relation, $\langle \Delta x^2(t) \rangle \propto 2D_1 t$, holds for quite a long time, except a minor perturbation at $\tau \approx 1$. If $\kappa_1 = 0$, $\mathcal{L}[\langle \Delta x^2(t) \rangle] = 2D_1\epsilon^{-2}[1 - \lambda \exp(-\lambda)]$, and $\langle \Delta x^2(t) \rangle \approx 2D_1 t$ for all times, which is trivial.

Diffusion in a Square-Well Potential

Morita[2] also addressed the problem of diffusion under a spherically symmetric square-well potential, $V(r) = -V_0\theta(R - r)$, where R stands for the radius of the well, by introducing into the radial Smoluchowski equation a drift term described

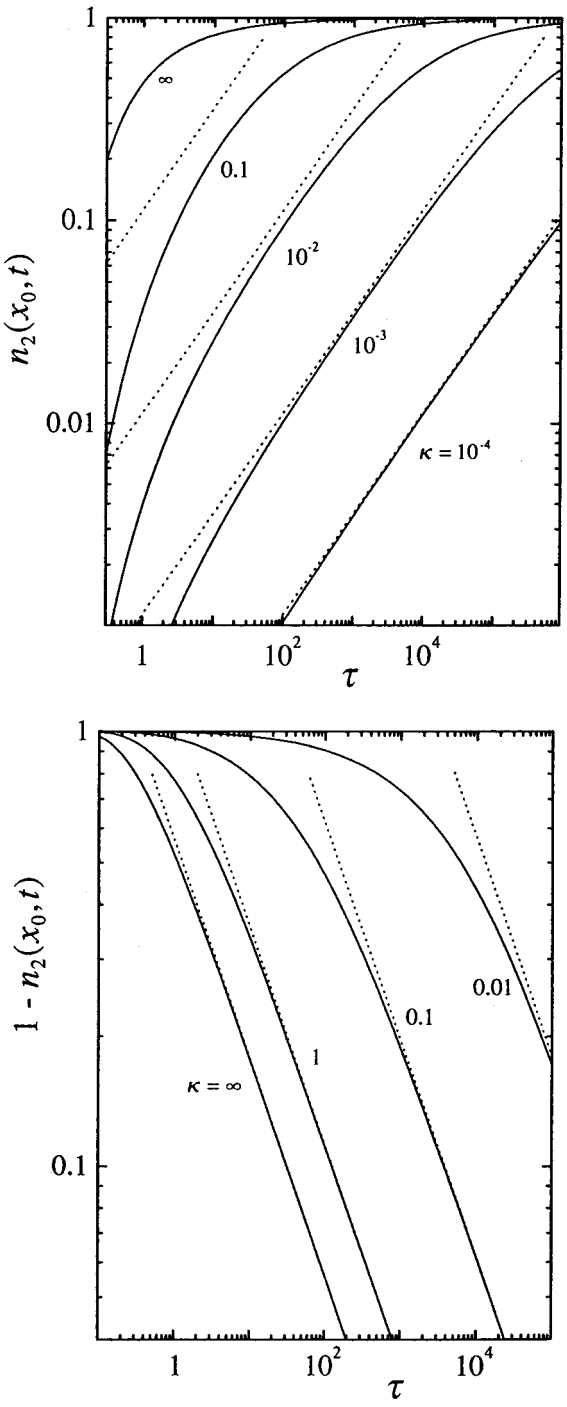

Figure 1. (A, top) Time evolution of the renormalized probability, $n_2(x_0,t) = N_2(x_0,t)/N_2(\infty)$, for a particle having started from x_0 in phase 1 to be found in phase 2 at time t for different values of the effective interface permeability $\kappa = \kappa_1(1 + \alpha K)$ (the numbers attached to the curves). The dotted lines illustrate an approximate expression for the intermediate stage, $n_2(x_0,t) \propto 2\kappa\sqrt{\tau/\pi}$, which becomes more pronounced at lower permeability values. (B, bottom) Time evolution of $1 - n_2(x_0,t)$ at long times for different permeabilities. The dotted lines illustrate the asymptotic behavior, $1 - n_2(x_0,t) \propto (1 + 1/\kappa)/\sqrt{\pi\tau}$.

by a δ function. As mentioned above, this is not appropriate because the diffusion equation is not valid at a point of abrupt change of the potential where the velocities are not equilibrated. Instead, a boundary condition similar to eq 1 has to be used (with x replaced by r). This actually implies a certain barrier at the interface. Taking into account that the particle density should tend to zero at infinity and be finite at the origin (i.e., at

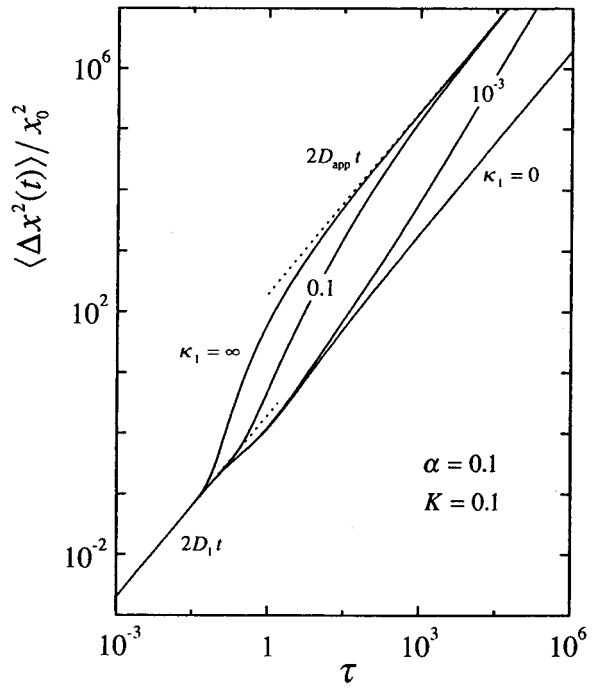

Figure 2. Time evolution of the normalized mean-square displacement, $\langle \Delta x^2(t) \rangle / x_0^2$, for different values of the interface permeability κ_1 (the numbers attached to the curves), with $a = 0.1$ and $K = 0.1$. The dotted lines illustrate the short-time behavior, $\langle \Delta x^2(t) \rangle \propto 2D_1t$, and the asymptotic long-time behavior, $\langle \Delta x^2(t) \rangle \propto 2D_{app}t$, with $D_{app} = D_1(K_D + \alpha^{-2})/(K_D + 1)$ for $\kappa_1 > 0$. If $\kappa_1 = 0$, $\langle \Delta x^2(t) \rangle \propto 2D_1t$ for all times.

$r = 0$), we obtain for the Laplace transform of the components of the Green's function

$$\hat{\rho}_1(r|r_0;\epsilon) = \frac{\sinh(q_1 r_<)}{4\pi r r_0 D_1 q_1} \frac{a_1 q_1 R \cosh[q_1(R - r_>)] - a_2 \sinh[q_1(R - r_>)]}{a_1 q_1 R \cosh(q_1 R) - a_2 \sinh(q_1 R)} \tag{14}$$

$$\hat{\rho}_2(r|r_0;\epsilon) = \frac{\sinh(q_1 r_0)}{4\pi r r_0 D_2} \frac{\kappa_1 R \exp[-q_2(r - R)]}{a_1 q_1 R \cosh(q_1 R) - a_2 \sinh(q_1 R)} \tag{15}$$

where $q_i = \sqrt{\epsilon/D_i}$, $\kappa_i = k_i R/D_i$, $a_1 = \kappa_2 + 1 + q_2 R$, $a_2 = a_1 - \kappa_1(1 + q_2 R)$, $r_< = \min(r,r_0)$, $r_> = \max(r,r_0)$, and the indexes $i = 1, 2$ correspond to the parameter values inside ($r < R$) and outside ($r > R$) the potential well, respectively. The initial position is supposed to be inside the well, i.e., $r_0 < R$. From the Green's function we can calculate any observable required. In what follows we focus on the well occupation probability and the mean-square displacement.

The Laplace transform of the probability $N_1(t)$ to find a particle inside the potential well averaged over the uniform initial distribution is given by

$$\hat{N}_1(\epsilon) = \frac{1}{\epsilon} - \frac{1}{\epsilon^2} \frac{3D_1}{R^2 \xi} \tag{16}$$

where $\xi = [\lambda \coth(\lambda) - 1]^{-1} + \alpha^2 K/(1 + \alpha\lambda) + 1/\kappa_1$ and $\lambda = q_1 R$. $\hat{N}_2(\epsilon) = 1/\epsilon - \hat{N}_1(\epsilon)$ due to the conservation constraint.

The initial stage of the decay is governed exclusively by the transport through the interface, i.e.,

$$N_1(t) \cong \exp[-(3/R)k_1 t] = \exp(-3\kappa_1\tau) \tag{17}$$

Here $3/R$ is the surface-to-volume ratio for a sphere and $\tau =$

D_1t/R^2. This stage can last for a very long period, provided k_1 is sufficiently small.

After relaxation within the well has taken place ($\tau \gg 1$), the expression for ξ can be simplified by expansion in λ, and eq 16 can be brought to the following form:

$$\hat{N}_1(\epsilon) = R^2/D_1(w_1 + \lambda\sqrt{w_2} + \lambda^2)^{-1} \tag{18}$$

where $w_1 = 3/\gamma$, $\sqrt{w_2} = 3\alpha^3K/\gamma^2$, and $\gamma = {}^1/_5 + \alpha^2K + 1/\kappa_1$. The inverse Laplace transform can now be performed analytically:[5]

$$N_1(t) = [z_1\Phi(z_1) - z_2\Phi(z_2)]/(z_1 - z_2) \tag{19}$$

where $z_{1,2} = (1 \pm \sqrt{1-4w_1/w_2})\sqrt{w_2\tau/4}$ and $\Phi(z)$ is defined in eq 3. Equation 19 proves to be very general and describes the asymptotic behavior of the well occupation probability for deep enough potential wells of virtually any form.[5]

The kinetics essentially depend on the value of dimensionless parameter $b = \sqrt{w_2/w_1} = \sqrt{3}(\alpha^2/\gamma)^{3/2}K$. Since $\gamma > \alpha^2K$, $b < \sqrt{3/K} \propto \exp(-V_0/2k_BT) \ll 1$ (we assume the well to be deep). Hence, eq 19 can be simplified by expansion in b as follows:[5]

$$N_1(t) \cong \exp(-\zeta) + (b/\sqrt{\pi})[F(\sqrt{\zeta})(2\zeta - 1) - \sqrt{\zeta}] \tag{20}$$

where $F(z) = -i(\sqrt{\pi}/2)\exp(-z^2)\mathrm{erf}(iz)$ and $\zeta = w_1\tau$. According to eq 20, at $\zeta < \ln(1/b)$ the kinetics are exponential, i.e.,

$$N_1(t) \propto \exp(-w_1\tau) \tag{21}$$

while at $\zeta \gg \ln(1/b)$ the decay law becomes of the inverse power type:

$$N_1(t) \propto b[2\sqrt{\pi}\zeta^{3/2}]^{-1} = b_0\tau^{-3/2} \tag{22}$$

where $b_0 = \alpha^3K/6\sqrt{\pi}$. The exponential stage is typical of a finite-volume system. At very long times, however, the well occupation probability is governed by the time evolution of the probability density outside the well, which results in the inverse power type tail characteristic of free diffusion. Quasi-equilibrium is reached during the final stage of the decay which is reflected in that the decay depends only on the equilibrium (K) but not on the dynamic (k_1) properties of the interface.

The time behavior of the well occupation probability is illustrated in Figure 3 for different permeability values. Two limiting situations are possible. If the permeability of the interface is very low so that $\alpha^2K \ll 1/\kappa_1$ (as in the case of, e.g., transport through bilayer membranes), we have $\gamma = 1/\kappa_1$ and hence $w_1 = 3\kappa_1$ and $b = \alpha^3K\sqrt{3\kappa_1^3}$. Thus, the barrier crossing at the interface governs not only the initial but also the intermediate exponential stage of the decay until $\zeta \approx \ln(1/b)$, where a crossover to the $t^{-3/2}$ kinetics occurs. The crossover time is determined by κ_1: at lower permeability values it takes a longer time for the asymptotic quasi-equilibrium stage to develop. In the opposite limit of high interface permeability such that $\alpha^2K \gg 1/\kappa_1$ (as in the case of, e.g., geminate radical recombination in liquids where the cage effect is modeled by a square-well potential), $\gamma = \alpha^2K$ and so $w_1 = 3/\alpha^2K$ and $b = \sqrt{3/K}$. Since equilibration at the interface is very fast in this case, the decay is totally determined by K (not κ_1), except for a very short ($\tau \ll 1$) initial stage.

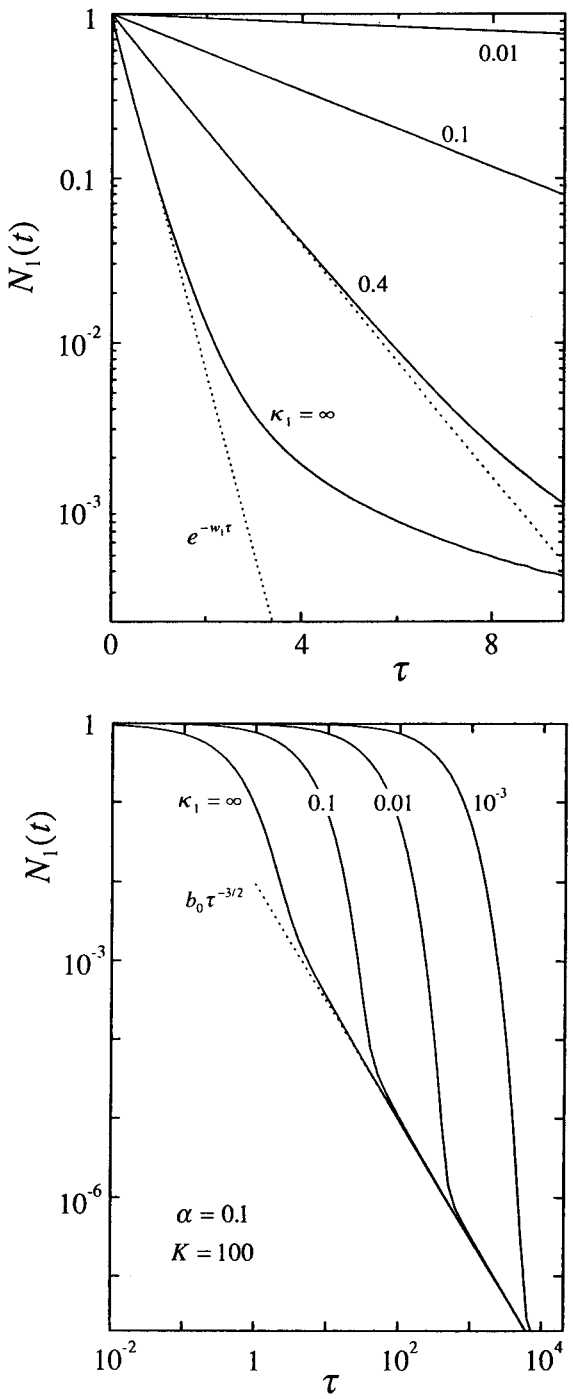

Figure 3. Time evolution of the well occupation probability, $N_1(t)$, for different values of the interface permeability κ_1 (the numbers attached to the curves), with $\alpha = 0.1$ and $K = 100$. The short-time behavior is shown on a semi-log scale (A, top) with the dotted lines illustrating the intermediate exponential stage, $N_1(t) \propto \exp(-w_1\tau)$. The long-time behavior is presented on a log−log scale (B, bottom), and the dotted line shows the asymptotic stage, $N_1(t) \propto b_0\tau^{-3/2}$.

The mean-square displacement averaged over the uniform distribution of the starting position inside the well is defined by

$$\langle\Delta\mathbf{r}^2(t)\rangle \equiv \int(\mathbf{r} - \mathbf{r}_0)^2\rho(\mathbf{r}_0)\rho(\mathbf{r}|\mathbf{r}_0;t)\,\mathrm{d}\mathbf{r}_0\,\mathrm{d}\mathbf{r} \tag{23}$$

where $\rho(\mathbf{r}_0) = ({}^4/_3\pi R^3)^{-1}$. (N.B. The definition given in ref 2, i.e., $\langle r^2(t)\rangle$, is incorrect.) It is clear from eq 23 that the radial Green's function is not sufficient to calculate $\langle\Delta\mathbf{r}^2(t)\rangle$, and one

has to include the angular dependence into the diffusion propagator. We obtain using standard procedures[4]

$$\hat{\rho}_1(r,\vartheta|r_0;\epsilon) = \frac{q_1}{2\pi^2 D_1}\sum_{n=0}^{\infty}(2n+1)P_n(\cos\vartheta)i_n(q_1 r_<)\times \left[k_n(q_1 r_>) + \frac{\Lambda_n^k}{\Lambda_n^i} i_n(q_1 r_>)\right] \quad (24)$$

$$\hat{\rho}_2(r,\vartheta|r_0;\epsilon) = \frac{\kappa_1}{4\pi D_2 R}\sum_{n=0}^{\infty}(2n+1)P_n(\cos\vartheta)\frac{i_n(q_1 r_0)k_n(q_2 r)}{\Lambda_n^i} \quad (25)$$

where ϑ is the angle between $\mathbf{r}$ and $\mathbf{r}_0$, $P_n(x)$ are the Legendre polynomials, $i_n(x)$ and $k_n(x)$ are the modified spherical Bessel functions, and

$$\Lambda_n^\sigma = \phi_n^\sigma(\lambda)\phi_n^k(\alpha\lambda) \pm \kappa_1\sigma_n(\lambda)\phi_n^k(\alpha\lambda) + \kappa_2\phi_n^\sigma(\lambda)k_n(\alpha\lambda) \quad (26)$$

$$\phi_n^\sigma(x) = x\sigma_{n+1}(x) \pm n\sigma_n(x) \quad (27)$$

with "+"and "−" corresponding to $\sigma = i$ and $\sigma = k$, respectively.

Performing the integration in eq 23, we obtain for the Laplace transform of the components of the mean-square displacement

$$L[\langle\Delta\mathbf{r}^2(t)\rangle_1] = \frac{12R^2}{\pi\epsilon}\left\{\frac{1}{\Lambda_0^i}[\Lambda_0^k(\lambda) - \Lambda_0^i(\lambda)][\lambda i_1(\lambda) - 2i_2(\lambda)] + \frac{\lambda i_2(\lambda)}{\Lambda_1^i}[\Lambda_1^i k_2(\lambda) - \Lambda_1^k i_2(\lambda)]\right\} \quad (28)$$

$$L[\langle\Delta\mathbf{r}^2(t)\rangle_2] = \frac{6\alpha\kappa_1 R^2}{\epsilon}\left\{\frac{i_1(\lambda)k_1(\alpha\lambda)}{\Lambda_0^i} - \frac{i_2(\lambda)k_2(\alpha\lambda)}{\Lambda_1^i} + \frac{1}{\alpha\lambda\Lambda_0^i}[i_1(\lambda)k_2(\alpha\lambda) - \alpha i_2(\lambda)k_1(\alpha\lambda)]\right\} \quad (29)$$

The total mean-square displacement is given by the sum of these two components:

$$\langle\Delta\mathbf{r}^2(t)\rangle = \langle\Delta\mathbf{r}^2(t)\rangle_1 + \langle\Delta\mathbf{r}^2(t)\rangle_2 \quad (30)$$

The time evolution of $\langle\Delta\mathbf{r}^2(t)\rangle$ is shown in Figure 4. At short times ($\tau \ll 1$), the effect of the interface is negligible and the mean-square displacement follows the ordinary single-phase Einstein relation with the diffusion coefficient equal to that of the inner phase, i.e., $\langle\Delta\mathbf{r}^2(t)\rangle \propto 6D_1 t$. After relaxation within the well has taken place ($\tau \gg 1$), the cumbersome general expression for the mean-square displacement can be simplified by expansion in λ. We obtain approximately in the time domain

$$\langle\Delta\mathbf{r}^2(t)\rangle \cong \frac{6}{5}R^2\exp(-3\tau/\gamma) + \frac{6R^2}{\alpha^2}\left\{\tau - \frac{\gamma}{3}[1 - \exp(-3\tau/\gamma)]\right\} \quad (31)$$

where $\gamma \cong \alpha^2 K + 1/\kappa_1$. γ also contains a negligibly small numerical constant. If the interface is impermeable ($\kappa_1 = 0$), the mean-square displacement reaches the value of $^6/_3R^2$ at long times, which is precisely the mean-square distance between two point particles uniformly distributed within a sphere of radius R. If $\kappa_1 > 0$, all the particles eventually leave the potential well and the long-time behavior of $\langle\Delta\mathbf{r}^2(t)\rangle$ is determined by diffusion in the outer phase, i.e., $\langle\Delta\mathbf{r}^2(t)\rangle \propto 6D_2 t$. In the case of very low interface permeability or a very deep potential well, there also exists a pronounced intermediate stage for $\tau/\gamma \ll 1$:

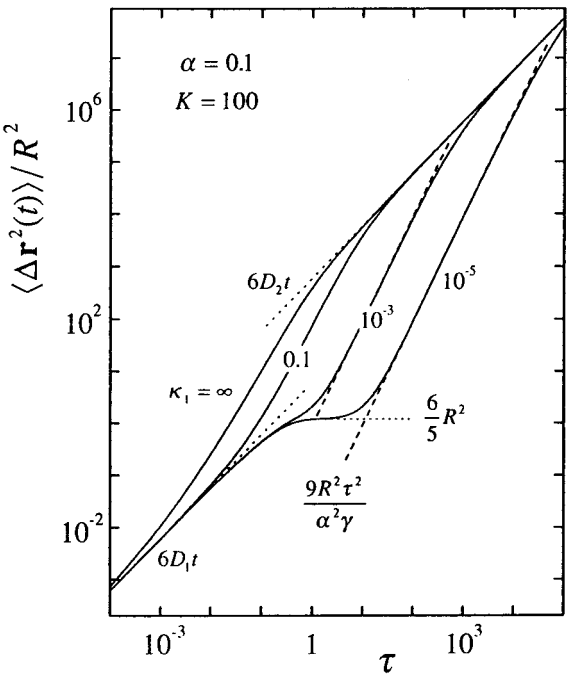

Figure 4. Time evolution of the normalized mean-square displacement, $\langle\Delta\mathbf{r}^2(t)\rangle/R^2$, for different values of the interface permeability κ_1 (the numbers attached to the curves), with $\alpha = 0.1$ and $K = 100$. The dotted lines illustrate the short-time behavior, $\langle\Delta\mathbf{r}^2(t)\rangle \propto 6D_1 t$, and the asymptotic long-time behavior, $\langle\Delta\mathbf{r}^2(t)\rangle \propto 6D_2 t$, for $\kappa_1 > 0$. If $\kappa_1 = 0$, $\langle\Delta\mathbf{r}^2(t)\rangle$ tends to the value of $^6/_5R^2$ at long times, which is the mean-square distance between two uniformly distributed particles in a sphere of radius R. The dashed lines illustrate an approximate expression for the intermediate stage, $\langle\Delta\mathbf{r}^2(t)\rangle \propto 9R^2\tau^2/\alpha^2\gamma$, which becomes more pronounced at lower permeability values.

$$\langle\Delta\mathbf{r}^2(t)\rangle \propto 9R^2\tau^2/\alpha^2\gamma \quad (32)$$

It should be noted that this stage is independent of D_1 since $\tau^2/\alpha^2\gamma = k_1 D_2 t^2/R(1 + k_2 R/D_2)$.

One of the main conclusions in ref 2 is that the asymptotic behavior of the mean-square displacement of a particle diffusing in a square-well potential depends on the potential depth and thus deviates from the Einstein relation. This conclusion is essentially incorrect. As follows directly from the above analysis, the Einstein relation is valid unless the potential is infinitely deep. Having escaped from the well, the particle diffuses in a three-dimensional space and gradually loses memory of the *finite* volume it started from.

Morita has also considered diffusion in a one-dimensional square-well potential and arrived at the same incorrect conclusion that the Einstein relation does not hold. This problem can be treated in the same way as described above for three dimensions, and the same conclusions as those for three dimensions can be obtained. The well occupation probability has already been calculated in the literature for infinite interface permeability.[5]

Conclusions

We have discussed the effect of permeability on the kinetics of diffusive transport across an interface. Two practically important cases have been considered, namely, one-dimensional diffusion in a stepwise potential and three-dimensional diffusion under a spherically symmetric square-well potential. The

transport characteristics, i.e., the mean-square displacement and the residence probability in each phase, have been found to be independent of the permeability at asymptotically long times, unless the interface is absolutely impermeable. However, the way the asymptotic behavior is approached can be controlled by the interface permeability. At low permeability values, the kinetics exhibit a characteristic intermediate stage that can last for such a long time that the true asymptotic behavior may *not* be observed experimentally *at all*. This is where our results are particularly useful. Having included the permeability into the model for diffusive transport across the interface, we are able to correctly describe not only the initial stage of the kinetics but also the later intermediate stage which may be practically the last stage experimentally accessible.

We would like to emphasize two simple approximate expressions we have obtained in eqs 7 and 32. They show well-defined intermediate time dependencies, completely different from either short-time or long-time kinetics. This should be readily observable experimentally, and if so, provide a simple way to determine the permeability.

References and Notes

(1) Morita, A. *J. Phys. Chem.* **1996**, *100*, 12131.
(2) Morita, A. *Phys. Rev. E* **1994**, *49*, 3697.
(3) Huthwelker, T.; Peter, T. *J. Chem. Phys.* **1996**, *105*, 1661.
(4) Carslaw, H. S.; Jaeger, J. C. *Conduction of Heat in Solids*; Clarendon: Oxford, 1959.
(5) Shushin, A. I. *J. Chem. Phys.* **1991**, *95*, 3657.