A simple method for determining the mean passage time for diffusion controlled processes[a)]

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In an interesting recent article, Szabo, Schulten, and Schulten (SSS) present a method for calculating the mean passage time τ for models of diffusion controlled reactions.[1] Such models and the quantity τ are of interest in a number of polymer and biophysics applications.[2]

The purpose of this note is to present a more direct method for obtaining τ than the operator method presented by SSS. In fact, the method follows from recognition that direct integration of the diffusion (Smoluchoski) equation for the probability $P(r, t)$ is a rapid route to τ.

We restrict attention to spherically symmetric systems. In d-dimensions the diffusion equation is

$$\frac{\partial P(r,t)}{dt} = -r^{1-d}\frac{\partial}{\partial r} r^{d-1} j(r,t) = r^{1-d}\frac{\partial}{\partial r} r^{d-1} D(r) \times \left[\frac{\partial P(r,t)}{\partial r} + \beta U'(r) P(r,t)\right] \tag{1}$$

where $D(r)$ is the possibly position dependent diffusion coefficient, $U(r)$ an effective potential and $\beta = (k_B T)^{-1}$. The quantity τ is introduced by an exponential approximation to the probability $N(t)$ that the system is unreacted at time t. More precisely

$$\tau = \int_0^\infty dt \int_a^R dr\, r^{d-1} P(r,t) \equiv \int_0^\infty dt\, N(t) . \tag{2}$$

The boundary condtiions assumed by SSS were a reflective boundary at $r = R$; $j(R, t) = 0$, and a radiation boundary condition at $r = a$; $j(a, t) = -\kappa_a P(a, t)$.

Direct integration of Eq. (1) yields

$$r^{d-1} j(r,t) = \int_r^R dx\, x^{d-1} \frac{\partial P(x,t)}{\partial t} . \tag{3}$$

Substitution of the definition of the flux $j(r, t)$ from Eq. (1), followed by integration from $r = a$ and use of Eq. (3) to eliminate $P(a, t)$ leads to

$$r^{d-1} P(r,t) = -[p_0(r)/\kappa_a p_0(a)] \int_a^R dx\, x^{d-1} \frac{\partial P}{\partial t}(x,t) - p_0(r) \int_a^r dx [D(x) p_0(x)]^{-1} \int_x^R dy\, y^{d-1} \frac{\partial P(y,t)}{\partial t} \tag{4}$$

where $p_0(r)$ is the equilibrium distribution in the absence of any reaction, i.e.,

$$p_0(r) = \left\{ r^{d-1} \exp[-\beta U(r)] \Big/ \int_a^R dr\, r^{d-1} \exp[-\beta U(r)] \right\} . \tag{5}$$

Use of Eq. (2) leads to the desired result[3]

$$\tau = [\kappa_a p_0(a)]^{-1} \int_a^R dr\, r^{d-1} P(r,0) + \int_a^R dr\, p_0(r) \times \int_a^r dx [D(x) p_0(x)]^{-1} \int_x^R dy\, y^{d-1} P(y,0) . \tag{6}$$

For the case where the initial distribution $P(r, 0)$ equals the equilibrium distribution, $r^{d-1}P(r, 0) = p_0(r)$, we obtain[1]

$$\tau = [\kappa_a p_0(a)]^{-1} + I_2;$$
$$I_n = \int_a^R dr [D(r) p_0(r)]^{-1} \left[\int_r^R dx\, p_0(x)\right]^n . \tag{7}$$

For the case of a δ-function initial condition, $P(r,0) = [\delta(r - r_0)/r^{d-1}]$ we obtain

$$\tau_\delta = [\kappa_a p_0(a)]^{-1} + F_1;$$
$$F_n = \int_a^{r_0} dr\, [D(r) p_0(r)]^{-1} \int_r^R dx\, p_0(x) \tag{8}$$

the quantity τ_δ is denoted $\tau(r_0)$ by SSS.

Thus we have demonstrated that the mean passage time τ can be efficiently obtained by direct integration of the diffusion equation. Clearly the method applies for other boundary conditions. For example, if one assumes a radiation boundary condition at $r = R$, $j(R, t) = \kappa_R P(R, t)$ as well as at $r = a$, one obtains the result

$$\tau = \frac{\{1 + I_2 \kappa_a p_0(a) + G_2 \kappa_R p_0(R) + [I_2 G_1 + G_2 I_1 - I_1 G_1] \kappa_a \kappa_R p_0(a) p_0(R)\}}{\{\kappa_a p_0(a) + \kappa_R p_0(R) + \kappa_a \kappa_R p_0(a) p_0(R) [I_1 + G_1]\}} \tag{9}$$

where

$$G_n = \int_a^R dr [D(r) p_0(r)]^{-1} \left[\int_a^r dr\, p_0(x)\right]^n . \tag{10}$$

The method is also applicable to cases where an equilibrium is established in the system in the presence of reacting boundary conditions, i.e., $P(x, \infty) = P_{eq}(x) \neq 0$. In such cases

$$\tau = [1 - N_{eq}]^{-1} \int_0^\infty dt [N(t) - N_{eq}] \tag{11}$$

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where $N_{eq} = \int_a^R dr r^{d-1} P_{eq}(r)$. For example, Weaver[4] has recently considered the one-dimensional problem $j(R, t) = 0$, $P(a, t) = [\kappa(R-a)]^{-1} \int_0^t dt' D(\partial P/\partial x)_{x=a}$ with D constant and $U = 0$. One can find $P_{eq} = [(1+\kappa)(R-a)]^{-1}$ and $\tau = [\kappa/(1+\kappa)](R-a)^2/3D$ by direct integration and avoid the need to solve[4] a second order differential equation with mixed boundary conditions.

Finally we note that this method can also be employed to advantage for other stochastic models where approximate relaxation times are sought for nonequilibrium decay. An example is provided by the discrete Master equation $\dot{\mathbf{P}}(t) = \mathbf{W} \cdot \mathbf{P}(t)$ where $P_n(t)$ is the probability of being in state n at time t and $N(t) = \Sigma P_n(t)$. With $\delta \mathbf{P} = \mathbf{P}(0) - \mathbf{P}_{eq}$ where $\mathbf{W} \cdot \mathbf{P}_{eq} = 0$, the result[5] for the mean passage time, Eq. (11) is

$$\tau = [\mathbf{1}^T \cdot \mathbf{W}^{-1} \cdot \delta \mathbf{P}] [\mathbf{1}^T \cdot \delta \mathbf{P}]^{-1} . \tag{12}$$

Here $\mathbf{1}^T$ is the unit column vector.

This result can be used to advantage to describe approximate exponential relaxation for discrete or continuous[6] master equation systems.

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[1] A. Szabo, K. Schulten, and Z. Schulten, J. Chem. Phys. **72**, 4350 (1980).

[2] See (a) G. Adams and M. Delbruck in *Structural Chemistry and Molecular Biology*, edited by A. Rich and N. Davidson (Freeman, San Francisco, 1968); (b) M. Karplus and D. L. Weaver, Biopolym. **18**, 1421 (1979), and other references cited in Ref. (1).

[3] Here we are concerned with open systems where the boundary conditions lead to total depletion. Thus $P(x,\infty) = P_{eq}(x) = 0$.

[4] D. L. Weaver, J. Chem. Phys. **72**, 3483 (1980).

[5] G. H. Weiss, Adv. Chem. Phys. **13**, 1 (1967).

[6] See for example (a) B. Widom, J. Chem. Phys. **31**, 1387 (1959); (b) Adv. Chem. Phys. **5**, 353 (1963); (c) R. I. Cukier and J. T. Hynes, J. Chem. Phys. **64**, 2674 (1976) and references cited therein; (d) J. L. Skinner and P. G. Wolynes, J. Chem. Phys. **69**, 2143 (1978); **72**, 4913 (1980).

Rates of some reactions of N(^2D and ^2P) near 300 K[a]

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Laboratory studies of quenching and reaction processes of the lowest N metastables have been reported since 1969 when Black *et al.*[1] used the vacuum ultraviolet photolysis of N_2O to infer N(^2D) quenching rates. Resonance line absorption detection of both N(^2D) and N(^2P) as well as O(^3P) in flow tube experiments allowed us[2] to establish that reaction rather than quenching was the principal channel for the interaction of N(^2D) with O_2, CO_2, and N_2O. Other rate measurements have since been reported.[3-8]

These processes are of great importance in the upper atmosphere, because the reaction with O_2, e.g., $N(^2D) + O_2 \rightarrow NO + O(^3P) + 3.8$ eV, is a major source of NO both in the normal and perturbed thermosphere, and also because it leads to substantial vibrational excitation of NO and consequent infrared emission.[9]

The present, brief study was undertaken primarily to reduce the uncertainties in the measurements of the N(^2D, ^2P) reactions with O_2 by use of resonance fluorescence detection of the metastables. An attempt was also made to resolve the discrepancy between the single laboratory value of 1.8×10^{-12} cm^3 s^{-1} [8] and the lower range of $(1-6) \times 10^{-13}$ deduced from airglow intensity data[10-12] for the rate constant of N(^2D) quenching by O(^3P).

The simple flow tube apparatus is similar to that used in our earlier study,[2] the principal differences being (a) a faster pumping line consisting of a Roots blower (Heraeus Model RG-350) backed by a mechanical pump (Stokes, Model 148-H) that allows the use of a larger diameter flow tube (2.5 cm i.d.) and (b) a stainless steel cell at the entrance slit of the vacuum monochromator (Jarrell Ash, 0.5 m, Model 84-110) that allows resonance fluorescence as well as absorption measurements to be made using combinations of microwave discharge lamp and filters as described below. For the $N^* + O_2$ experiments, the excited species were generated 26 cm upstream of the detector in a microwave discharge (Raytheon Microtherm, 2450 MHz) using a stabilized power supply[13] and Evenson cavity. Ar or He carrier gas at about 3 Torr containing about two percent N_2 was used. O_2 was added through a fixed loop injector 14 cm upstream of the detector at concentrations of 10^{13} to 10^{14} cm^{-3}, diluted with approximately 15% of the total carrier gas flow (~60 cm^3 atm s^{-1}) in order to aid rapid mixing. Reaction times ranged from 2.5 to 5 ms.

In the $N(^2D) + O(^3P)$ experiments, variable amounts of NO were added 68 cm upstream of the fluorescence cell to discharged two percent N_2–Ar mixtures at 3 to 3.5 Torr. 48 cm farther downstream, a similarly discharged Ar–N_2 stream entered the flow tube carrying the N(^2D) reactant. Roughly equal flows passed through both branches so that the flow velocity in the upstream length was half that in the reaction zone. N-metastables from the upstream discharge had decayed by wall or gas reac-

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