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The Diffusion Constant for Two-State Brownons

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We calculate the diffusion constant for two-state brownons when the change of state is not, as usually assumed, Markovian. The correction to the noninterchanging species result is found to be exactly expressible in terms of the Laplace transforms of the sojourn time densities.

KEY WORDS: Brownian motion; diffusion process; sojourn time distribution.

A brownon is defined to be a particle moving by Brownian motion; more specifically, it is a particle or molecule whose motion is described by a Langevin equation. A multistate brownon is a particle capable of existing in more than one state, each state being characterized by different parameters in the Langevin equation. The theory of multistate brownons has been discussed in several contexts: in connection with motion in a chromatographic column,(1–8) in connection with chemical exchange as related to NMR measurements,(9) and with regard to the calculation of transport coefficients in electrolyte solutions.(10) In all of these analyses it is assumed that the conversion between states follows first-order kinetics, i.e., the theories include an implicit assumption that the probability density for a sojourn in any state can be written ke^{-kt}. Since exact mechanisms are not always known for the exchange of states, it is probable that the simple isomerization scheme does not describe all the physical situations of interest. In this note we

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present the modifications that are necessary when the sojourn in state i is described by a general density $\varphi_i(t)$ with a finite mean residence time μ_i. We calculate an expression for the diffusion constant of a two-state brownon as a simple example; more complicated models can be handled by the same techniques. The mathematical results generalize those of Takacs$^{(11)}$ for the sojourn time distribution in a two-state semi Markov process.

The starting point of the calculation is the Kubo relation

$$D = \tfrac{1}{3}\int_0^\infty \langle \mathbf{v}(0)\cdot\mathbf{v}(t)\rangle\, dt \tag{1}$$

where $\mathbf{v}(t)$ denotes particle velocity at time t. In the absence of an external applied force the velocity is assumed to be governed by two Langevin equations

$$\dot{\mathbf{v}} + \omega\mathbf{v} = \mathbf{A}(t) \tag{2}$$

where $\mathbf{A}(t)$ is the fluctuating component of the force divided by particle mass, and $\omega_i = \zeta_i/m_i$ is the friction constant divided by mass. This model implies that the velocity correlation function can be written

$$\langle \mathbf{v}(0)\cdot\mathbf{v}(t)\rangle = [\theta_1\langle v_1^2(0)\rangle + \theta_2\langle v_2^2(0)\rangle]\, e^{-\omega_1\tau-\omega_2(t-\tau)} \tag{3}$$

in which τ is the cumulative time spent in state 1 during the time t and θ_i is the probability that the chosen particle is initially in state i. These probabilities are quite generally given by $\theta_i = \mu_i/(\mu_1+\mu_2)$ in terms of the mean residence times. Now let $r_i(\tau; t)$ be the probability density for sojourn time τ conditional on the initial state being i. In terms of these functions, the diffusion constant can be expressed without approximation as

$$D = \tfrac{1}{3}\sum_{i=1}^{2} \theta_i\langle v_i^2(0)\rangle \int_0^\infty dt \int_0^t d\tau\, r_i(\tau; t)\, e^{-\omega_1\tau-\omega_2(t-\tau)} \tag{4}$$

so that we now only need calculate the $r_i(\tau; t)$. In what follows, we use the notation

$$\Phi_i(t) = \int_t^\infty \varphi_i(u)\, du, \qquad \Gamma_i(t) = \Phi_i(t)/\mu_i, \qquad \psi_i(t) = \int_t^\infty \Gamma_i(u)\, du \tag{5}$$

The function $\Phi_i(t)$ is the probability that a single sojourn in state i will be greater than t and $\Gamma_i(t)$ is the equilibrium probability density for the forward recurrence time in state i.

Expressions for the $r_i(\tau; t)$ can be derived by direct enumeration as in the analysis by Friedman and Ben-Naim.[10] For $r_1(\tau; t)$ we find

$$\begin{aligned} r_1(\tau; t) = {} & \psi_1(t)\,\delta(t-\tau) + \Gamma_1(\tau)\,\Phi_2(t-\tau) \\ & + \varphi_2(t-\tau)\int_0^\tau \Gamma_1(\tau')\,\Phi_1(\tau-\tau')\,d\tau' \\ & + \left[\int_0^\tau \Gamma_1(\tau')\,\varphi_1(\tau-\tau')\,d\tau'\right]\left[\int_0^{t-\tau} \varphi_2(u)\,\Phi_2(t-\tau-u)\,du\right] \\ & + \left[\int_0^t d\tau' \int_0^{t'} d\tau''\,\Gamma_1(\tau'')\,\varphi_1(\tau'-\tau'')\,\Phi_1(\tau-\tau')\right] \\ & \times \left[\int_0^{t-\tau} \varphi_2(u)\,\varphi_2(t-\tau-u)\,du\right] + \cdots \end{aligned} \tag{6}$$

The first term describes a situation in which the particle remains in state 1 for the whole period t, the second is the contribution from the sequence 12, the third is from 121, and so on. A similar expression can be written for $r_2(\tau; t)$. The important point is that $r_1(\tau; t)$ can be expressed as a series

$$r_1(\tau; t) = \sum_{n=0}^{\infty} A_n(\tau)\,B_n(t-\tau) \tag{7}$$

where the A's and B's are convolution integrals. An individual term appearing in Eq. (4) therefore has the form

$$J = \int_0^\infty dt \int_0^t d\tau\, A(\tau)\, e^{-\omega_1\tau} B(t-\tau)\, e^{-\omega_2(t-\tau)} \tag{8}$$

If we denote the Laplace transform of $A(t)$ by $A^*(s)$ and that for $B(t)$ by $B^*(s)$, then J can be expressed as

$$J = A^*(\omega_1)\,B^*(\omega_2) \tag{9}$$

Furthermore, since the A's and B's can be written in terms of convolution integrals, the Laplace transforms can be written in terms of products and powers of the Laplace transforms of the $\varphi_i(t)$. Specifically, when Eq. (6) is substituted into Eq. (4), we find after some manipulation that

$$\int_0^\infty dt \int_0^t d\tau\, r_1(\tau; t)\, e^{-\omega_1\tau-\omega_2(t-\tau)} = \frac{1}{\omega_1} + \frac{F(\omega_1, \omega_2)}{\mu_1\omega_1} \tag{10}$$

where

$$F(\omega_1, \omega_2) = \frac{[1-\varphi_1^*(\omega_1)][1-\varphi_2^*(\omega_2)]}{1-\varphi_1^*(\omega_1)\,\varphi_2^*(\omega_2)}\left(\frac{1}{\omega_2}-\frac{1}{\omega_1}\right) \tag{11}$$

In similar fashion, the second contribution can be shown to be equal to $(1/\omega_2) - [F(\omega_1, \omega_2)/(\mu_2\omega_2)]$, so that

$$D = \frac{1}{3}\left[\theta_1 \frac{\langle v_1^2(0)\rangle}{\omega_1} + \theta_2 \frac{\langle v_2^2(0)\rangle}{\omega_2}\right] + \frac{F(\omega_1, \omega_2)}{3}\left[\frac{\theta_1}{\mu_1\omega_1}\langle v_1^2(0)\rangle - \frac{\theta_2}{\mu_2\omega_2}\langle v_2^2(0)\rangle\right] \tag{12}$$

The first set of terms in this last equation is the result for a noninterchanging set of particles for which the diffusion constant is a weighted average of individual diffusion constants. The second term gives the effects of nonzero interchange times. As Friedman and Ben-Naim have pointed out, the dimensionless terms $\mu_i\omega_i$ $(=\zeta_i/m_i k_i)$ for first-order kinetics) are small in electrolyte solutions, for which the two-state brownon model might be a legitimate description. The exact magnitudes range from approximately 10^2 to 10^7 or greater; for typical parameters this implies that the second set of terms in Eq. (12) is at least two orders of magnitude less than the first set. It is possible that there are chromatographic systems for which the interchange corrections are important, but no estimates of ω are available to test this possibility. The present theory can be extended without great difficulty to brownons with $n > 2$ states, but the results require many more parameters for their specification.

REFERENCES

1. J. C. Giddings and H. Eyring, *J. Am. Chem. Soc.* **59**:416 (1956).
2. J. C. Giddings, *J. Chem. Phys.* **26**:169 (1957).
3. J. C. Giddings, *J. Chem. Phys.* **31**:1462 (1959).
4. J. C. Giddings, *J. Chromatogr.* **3**:443 (1960).
5. K. J. Mysels, *J. Chem. Phys.* **24**:371 (1961).
6. T. A. Bak, *Contributions to the Theory of Chemical Kinetics*. Munksgaard, Copenhagen, 1959.
7. D. A. McQuarrie, *J. Chem. Phys.* **38**:437 (1963).
8. G. H. Weiss, *Sep. Sci.* **5**:51 (1970).
9. S. Meiboom, *J. Chem. Phys.* **34**:1 (1961).
10. H. L. Friedman and A. Ben-Naim, *J. Chem. Phys.* **48**:120 (1968).
11. L. Takacs, *Acta Math. Hung.* **8**:169 (1957).