diffusion-fundamentals.org

The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application

A First Passage Time Approach to Diffusion in Liquids

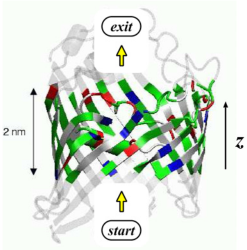
A.J. Dammers [a], *V.J. van Hijkoop* [a] *and M.-O. Coppens* [a,b]

[a]Delft University of Technology, DelftChemTech, Julianalaan 136, 2628 BL Delft, The Netherlands, E-mail: A.J.Dammers@tudelft.nl
[b]Rensselaer Polytechnic Institute, Howard P. Isermann Department of Chemical and Biological Engineering, 110 8th Street, Troy, NY 12189, U.S.A

1. Introduction

Molecular diffusion through a channel is typically characterized by the mean square displacement (MSD) projected onto the channel (z) axis. A diffusion coefficient D might then be obtained through Einstein's relation $\left\langle \left(z(0)-z(t)\right)^2 \right\rangle \sim 2Dt$ after sufficiently long times. The average $\langle ... \rangle$ implies that the diffusing molecules sample chemical and/or geometrical channel heterogeneities in a representative way. However, a finite channel length may hamper such an analysis. Molecular trajectories could extend into the embedding reservoir before proper sampling is achieved, resulting in an intractable mixture of properties of the channel and its environment. To alleviate this limitation, a *first-passage time* (FPT) approach was used [1,2]. The region of interest is bounded by virtual planes at $z=0$ and $z=L$, respectively. A molecule, initially located at $z=z_0$, is monitored until it crosses one of the boundaries. Effectively, this is a *virtual absorption* process. The generic question is: how long does it take a molecule to reach a boundary for the first time? We present two instances of such an analysis, applied to molecular dynamics (MD) simulations of molecular systems. The first one is permeation of water molecules through OmpF, a highly heterogeneous protein channel, [3] and the second one is escape from a virtual slab in a homogeneous liquid [4].

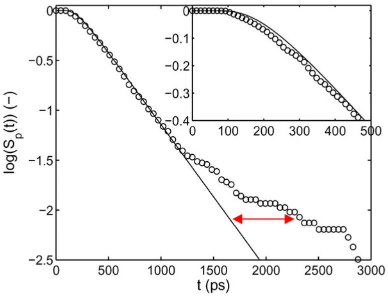
2. Permeation and trapping of water in OmpF



OmpF is a water-filled protein channel in the outer membrane of *Escherichia coli*. The FPT is the time it takes a water molecule, entering at $z=0$, to reach the opposite channel end, at $z=L$, without returning to $z=0$ at intermediate times. Rather than the associated permeation time distribution $F_p(t)$, we examine the survival probability $S_p(t)$. For a homogeneous 1D diffusion process it reads:

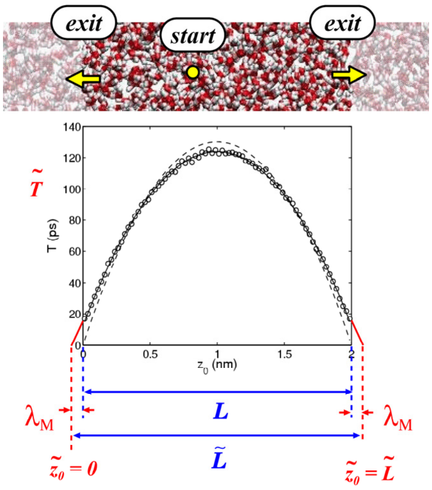
$$S_p(t)=\int_t^{\infty} F_p(t')dt' = 2\sum_{n=1}^{\infty}(-1)^{n-1}e^{-t/\tau_n}$$

with $\tau_n = L^2/n^2\pi^2 D$. The asymptotic behaviour of $S_p(t)$ is governed by the largest time constant $\tau_1 = L^2/\pi^2 D$. Our simulations show that also permeation through the *heterogeneous* OmpF channel can be characterized along these lines by a single diffusion coefficient D. In addition, the



graph of $S_p(t)$ suggests that a small fraction ($10^{-1.5} \sim 3\%$) of water molecules resides in the channel for a longer time. Closer analysis of the data revealed that these molecules are trapped by the protein wall, with a distribution of trapping times exhibiting a power law tail: $\psi(\tau) \sim \tau^{-2.4}$ [3].

3. Velocity persistence in liquids: Milne extrapolation length



Diffusion in bulk liquids is analyzed by defining a virtual slab in the simulation box, bounded by planes at $z = 0$ and $z = L$, respectively. The *mean exit time*, i.e., the time it takes a molecule, initially at (projected) position $z = z_0$, to reach either boundary for the first time, is $T(z_0) = z_0(L - z_0)/2D$ [1]. Surprisingly, rather than $T(0) = T(L) = 0$, our simulations yield nonzero values. However, by *virtually* extending the interval by λ_M at both ends, a parabolic fit $\tilde{T}(\tilde{z}_0) = \tilde{z}_0(\tilde{L} - \tilde{z}_0)/2D$ is recovered. Diffusion coefficients extracted in this way appeared to be consistent with the ones obtained by a standard MSD analysis. We identified λ_M as the *Milne extrapolation length* [5], which is a consequence of persistence of molecular velocities. For simple Brownian motion of a particle with mass m, i.e., subject to a delta-correlated random force, $\lambda_M^{(th)} = |\zeta(1/2)|\, l_v$, where $l_v = D\sqrt{m/k_B T}$ is a velocity correlation length and ζ the Riemann zeta function; $\zeta(1/2) = -1.4603...$. Our simulations show deviations from this theoretical prediction. For simple liquids (Ar, O_2, CO_2) values are roughly 1.5 times larger. For several models of water a factor ~3 is found. We interpret this as a fingerprint of intermolecular dynamic correlations [4].

4. Conclusions

We demonstrated that the FPT approach provides a versatile addition to the "MD toolbox" for analysis of diffusion processes. A permeation time analysis of water diffusing through OmpF, a highly heterogeneous protein channel, disclosed a normal diffusion process, with superimposed (rare) trapping events. Through examination of the mean exit time of molecules from a virtual slab in various bulk liquids, we identified the Milne extrapolation length, a consequence of the persistence of molecular velocities.

References

[1] S. Redner, A Guide to First-Passage Processes, Cambridge University Press, 2001.
[2] M.-O. Coppens, G.F. Froment, Fractals 3 (1995) 807-820.
[3] V.J. van Hijkoop, A.J. Dammers, K. Malek, M.-O. Coppens, J. Chem. Phys. 127 (2007) 085101.
[4] A.J. Dammers, V.J. van Hijkoop, *to be published.*
[5] P.S. Hagan, C.R. Doering, C.D. Levermore, J. Stat. Phys. 54 (1989) 1321.