Position-dependent diffusion profiles in inhomogeneous media

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Diffusion through layered media needs a position-dependent diffusion constant, as the inhomogeneousity makes the standard use of Einstein's equation impractical. Examples are diffusion of guest molecules through porous crystals like zeolites or through molecular sieving membranes, or heat diffusion through layered composite materials.

A position-dependent diffusion profile $D(x)$ gives the mobility, while a free energy profile $F(x)$ gives the concentration distribution of molecules at equilibrium. The time-evolution of the concentration $c(x,t)$ on a free energy surface $F(x)$ with a position-dependent diffusion constant $D(x)$ is described by the Smoluchowsky equation [1]. This equation has been solved previously by spatial discretization and applying adsorbing, reflecting, or periodic boundary conditions for the concentration profile [2]. The Green's function for periodic boundary conditions is the response to a *series of initial delta peaks*, i.e. one peak in each period. At longer lag times, concentration flows to/from neighboring periods and peaks start to overlap. The diffusion information is lost when particles diffuse over a distance of several periods.

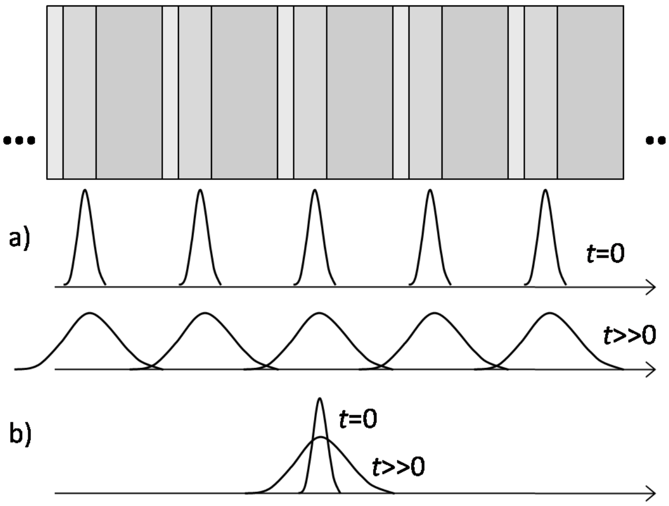

Figure 1 Green's functions in periodic layered medium: concentration response to a) series of delta peaks, b) single delta peak.

In this contribution, this loss of information is avoided by constructing the response to a *single initial delta peak*, in the same periodic medium. This Green's function follows from a Z-transform in the spatial domain, after discretizing the Smoluchowsky equation in space, and a Laplace transform in the time domain. Next, the effective diffusion constant, which is observed at long lag times, is expressed as a closed formula of the diffusion and free energy profiles of a single period of the layered medium.

The closed formula clarifies how medium characteristics influence the effective diffusion constant. This link between medium and effective diffusion not only gives insight, but may also be used to predict overall diffusion properties.

A first application could be the design of layered media towards the requested diffusive behavior. A second application could be the modeling of diffusion in several homogeneous media, which are then combined into a layered medium, whose effective diffusion constant is readily available from the closed formula. These applications will be tested for the diffusion of chemical compounds through porous nanomaterials. Moreover, a combination with a Bayesian parameter estimation is currently implemented, which allows to extract reliable diffusion profiles from molecular dynamics simulations.

References:

[1] D.J. Bicout, A. Szabo, J. Chem. Phys. 109 (1998) 2325.
[2] G. Hummer, New J. Phys. 7 (2005) 34.