Straightforward derivation of the long-time limit of the mean-square displacement in one-dimensional diffusion

Jörg Kärger
Fachbereich Physik der Universität Leipzig, Linnéstrasse 5, 0-7010 Leipzig, Federal Republic of Germany
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Considering one-dimensional diffusion as a sequence of exchange processes between occupied and vacant sites, the long-time limit of the mean-square displacement of the diffusants is shown to be easily calculable as the net effect of the random walk of the vacancies.

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One-dimensional (1D) diffusion is the process of one-dimensional propagation by activated jumps, where the mutual exchange of the diffusants is prohibited. Transport processes of this type may be observed, e.g., for molecules within molecular sieve crystals with parallel channels (1D zeolites), which most recently have attained practical relevance for both molecular sieving and catalysis [1]. The simplicity of the physical situation in such systems is in intriguing contrast to the fact that their theoretical treatment is generally found to be far from straightforward [2–5]. One reason for this difficulty is the correlation between subsequent displacements in one-dimensional systems [6]. It will be shown that the theoretical treatment can be simplified by considering the random walk of the vacancies rather than that of the diffusants. In this way, a straightforward determination of the mean-square displacements becomes possible.

Interpreting the elementary steps of migration as exchange processes between occupied and vacant sites, the displacement $s(t)$ of an arbitrarily selected diffusant (molecule) during a time interval t may be represented as

$$s(t)=l\sum_i [f(m_i(t))-f(m_i(0))] , \qquad (1)$$

where l stands for the distance between adjacent sites (coinciding with the step length), and where $lm_i(t)$ denotes the separation between the ith vacancy and the molecule under consideration. The function $f(m)$ is defined by the relation

$$f(m)=\begin{cases}+\frac{1}{2} & \text{for } m>0\\ -\frac{1}{2} & \text{for } m<0 .\end{cases} \qquad (2)$$

Since the positions of the individual vacancies are independent from each other, with Eq. (1) the mean-square displacement becomes

$$\langle s^2(t)\rangle = l^2\sum_i \langle [f(m_i(t))-f(m_i(0))]^2\rangle . \qquad (3)$$

The sum on the right-hand side of Eq. (3) represents the number of vacancies that have passed the considered molecule either from the left to the right or from the right to the left. The same quantity may be expressed in an alternative way by introducing the "conditional" probability $P(m,m',t)$ that a vacancy, initially at position m, will have migrated to m' at time t. Considering sufficiently large time intervals so that the sum may be replaced by an integral, one thus obtains

$$\langle s^2(t)\rangle = l^2(1-\Theta)\int_{m=0}^{\infty}\int_{m'=-\infty}^{0}[P(m,m',t)+P(m',m,t)]dm\,dm' \qquad (4)$$

with Θ denoting the site occupancy. The factor $(1-\Theta)$ is nothing other than the *a priori* probability of finding a vacancy at a given site.

In Eq. (1) the vacancy positions $m_i(t)$ are referred to the position of an arbitrarily selected molecule. Since with increasing values of the observation time the molecular displacements become negligibly small in comparison to the displacements of the vacancies, in the long-time limit the vacancy coordinates m and m' may be likewise considered as being defined with respect to the single-file system. In Ref. [7] a relation analogous to our Eq. (4) has been used for considering the propagation of polymer segments. The further treatment becomes straightforward after differentiating this relation with respect to time: Replacing the time derivatives of the conditional probabilities on the right-hand side by Fick's second law and taking into account that $\partial P/\partial m=-\partial P/\partial m'$, differentiation and integration compensate each other, and one obtains

$$\frac{d\langle s^2(t)\rangle}{dt}=2(1-\Theta)D_v P(0,0,t) , \qquad (5)$$

with D_v denoting the vacancy diffusivity.

The diffusivity of an isolated vacancy is given by the standard random-walk relation

$$D_{v,\mathrm{iso}}=l^2/(2\tau) \qquad (6)$$

with τ denoting the mean time between succeeding jumps. As soon as a given vacancy is in contact with other vacancies, it cannot be distinguished from them any longer. This is equivalent to an infinite transfer rate over the vacant sites. Thus the mean-square displacement $\langle r_v^2(t)\rangle$ of a given vacancy under the influence of other vacancies is given by the equation

$$\langle r_v^2(t)\rangle\Theta^2=\langle r_{v,\mathrm{iso}}^2(t)\rangle . \qquad (7)$$

Using the general relation

$$\langle r^2(t)\rangle = 2Dt \tag{8}$$

between mean-square displacements and diffusivities, from Eqs. (6) and (7) one obtains

$$D_v = D_{v,\mathrm{iso}}/\Theta^2 = l^2/(2\tau\Theta^2) \ . \tag{9}$$

Inserting this relation into Eq. (5) and using the standard diffusion expression

$$P(m,m',t) = \left[\frac{l^2}{4\pi D_v t}\right]^{1/2} \times \exp[-(lm - lm')^2/(4D_v t)] \ , \tag{10}$$

integration finally yields

$$\langle s^2(t)\rangle = \left[\frac{2}{\pi}\right]^{1/2} l^2 \frac{1-\Theta}{\Theta}\left[\frac{t}{\tau}\right]^{1/2} , \tag{11}$$

which is exactly the previously derived relation [2–5].

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