

Long-time limit of the self-correlation-function of one-dimensional diffusion

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Considering the random walk of the vacancies in a one-dimensional (single-file) system, the moments of the probability distribution curves of molecular displacements are calculated yielding a Gaussian distribution curve.

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The treatment of molecular propagation in linear systems where the molecules are unable to pass each other (single-file systems) is substantially facilitated by considering the displacements of the individual vacancies [1]. Interpreting the elementary step of molecular migration as an exchange process between an occupied and a vacant site, the displacement $s(t)$ of an arbitrarily selected diffusant (molecule) during a time interval t may be represented as [2]

$$s(t) = l \sum_k [f(m_k(t)) - f(m_k(0))], \quad (1)$$

where l stands for the step length, and where $l m_k(t)$ denotes the separation between the k th vacancy and the molecule under consideration. The function $f(m)$ is defined by the relation

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

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

$$\begin{aligned} \langle s^2(t) \rangle &= l^2 \left\langle \left[\sum_k f(m_k(t)) - f(m_k(0)) \right]^2 \right\rangle \\ &= l^2 \sum_k \langle [f(m_k(t)) - f(m_k(0))]^2 \rangle, \end{aligned} \quad (3)$$

where the sum is to be extended over all vacancies. Obviously, only those vacancies contribute to the sum, which at time zero and at time t are on opposite sides of the considered molecule. In Ref. [2], this sum was calculated by integrating the self-correlation function of vacancy diffusion over the two half-spaces on the left and on the right of the considered molecule, yielding in a few lines Fedder's classical result [3]

$$\langle s^2(t) \rangle = (2/\pi)^{1/2} l^2 \frac{1-\Theta}{\Theta} (t-\tau)^{1/2}, \quad (4)$$

where Θ denotes the relative site occupancy.

In this calculation the self-correlation function of vacancy diffusion has been postulated to be governed by a diffusivity D_v , which is related to the diffusivity

$$D_{v,\text{iso}} = l^2 / (2\tau) \quad (5)$$

of an isolated vacancy by

$$D_v = D_{v,\text{iso}} / \Theta^2 = l^2 / (2\tau\Theta^2). \quad (6)$$

This assumption may be rationalized in the following way: In an array of occupied sites with only one vacancy at position m , the probability of finding this vacancy at site m' after time t is obviously given by the standard diffusion expression

$$P_{v,\text{iso}}(m, m', t) = [l^2 / (4\pi D_{v,\text{iso}} t)]^{1/2} \times \exp[-(lm - lm')^2 / (4D_{v,\text{iso}} t)]. \quad (7)$$

On the other hand, Eq. (7) may be also interpreted as the probability that after time t a vacancy initially at position m has disappeared from this position (and with it from the whole interval m, \dots, m'), and has appeared at position m' . This interpretation may even be preserved if there are several vacancies, i.e., in the case of nonisolated vacancies. Now one has to drop, however, the implication that the vacancy appearing at position m' is identical with the vacancy initially at position m , since as soon as two vacancies are in contact with each other they are indistinguishable. However, it is just with respect to this broader interpretation that the self-correction function of vacancy diffusion is used: a particular molecule within a single-file system is shifted by one step if a vacancy disappears on one side of the molecule and appears on the other side, irrespective if it is "the same" or "another" vacancy. With this understanding, vacancy propagation within a single-file system with a finite number of vacancies may be easily derived from the propagation of a single vacancy within a completely occupied single-file system by simply inserting the relevant number of vacancies between the occupied sites. With respect to vacancy propagation such a procedure does not effect anything else than a broadening of the probability distribution corresponding to the dilatation of the space scale by $1/\Theta$ as brought about by the insertion of the vacancies. The self-correlation function of vacancy diffusion in the case of a finite number of vacancies $P_v(m, m', t)$ may be simply derived, therefore, from $P_{v,\text{iso}}(m, m', t)$ as given by Eq. (7) by replacing $D_{v,\text{iso}}$ by $D_{v,\text{iso}}/\Theta^2$, in complete agreement with Eq. (6).

Studying transport phenomena experimentally, e.g., by means of quasielastic neutron scattering [4] or pulsed-field gradient NMR [5], one is generally concerned with the complete probability distribution curve of molecular

displacement $P(s, t)$ (synonymous expressions are "propagator" or "self-correlation function of molecular diffusion" [6]) rather than only with the mean-square displacement. While in the case of ordinary diffusion it is well known that the distribution curve is given by a Gaussian function, besides Monte-Carlo simulations there are no adequate analytical considerations for the case of single-file diffusion in the literature [7]. In the following it shall be demonstrated that the method used in Ref. [2] for the determination of the mean-square displacement may be also applied to calculate the complete

distribution curve $P(s, t)$ in a straightforward way.

$P(s, t)$ is determined if all moments $\langle s^n(t) \rangle$ are known. Using Eq. (1), the n th moment may be represented as

$$\langle s^n(t) \rangle = l^n \left\langle \left[\sum_k \varphi_k \right]^n \right\rangle, \quad (8)$$

where we have used the notation $\varphi_k \equiv f(m_k(t)) - f(m_k(0))$. Due to symmetry reasons, on calculating the right-hand side of Eq. (8) all terms containing φ_k^i with $i = \text{odd}$ vanish, yielding

$$\begin{aligned} \left\langle \left[\sum_k \varphi_k \right]^n \right\rangle &= \sum_{k_1} \cdots \sum_{k_n} \langle \varphi_{k_1} \cdots \varphi_{k_n} \rangle = \sum_{k_1} \langle \varphi_{k_1}^n \rangle + \sum_{k_1} \sum_{k_2} \langle \varphi_{k_1}^{n-4} \rangle \langle \varphi_{k_2}^2 \rangle + \sum_{k_1} \sum_{k_2} \langle \varphi_{k_1}^{n-4} \rangle \langle \varphi_{k_2}^4 \rangle \\ &+ \sum_{k_1} \sum_{k_2} \sum_{k_3} \langle \varphi_{k_1}^{n-4} \rangle \langle \varphi_{k_2}^2 \rangle \langle \varphi_{k_3}^2 \rangle + \cdots + \sum_{k_1} \cdots \sum_{k_{n/2}} \langle \varphi_{k_1}^2 \rangle \cdots \langle \varphi_{k_{n/2}}^2 \rangle \end{aligned} \quad (9)$$

and n even, while for n odd, $\langle (\sum_k \varphi_k)^n \rangle$ is zero. The individual terms of the sums on the right-hand sides of Eq. (9) are equal to 1 for any vacancy k that is on opposite sides of the considered molecule at times 0 and t , and equal to zero otherwise. In particular, with Eq. (3) one has for $n=2$

$$\left\langle \left[\sum_k \varphi_k \right]^2 \right\rangle = \left\langle \sum_k \varphi_k^2 \right\rangle = \langle s^2(t) \rangle / l^2. \quad (10)$$

Correspondingly, the higher sums in Eq. (9) are found to be proportional to $(\langle s^2(t) \rangle / l^2)^m$, where m is the number of sums within one term. Hence, in the long-time limit, i.e., for $\langle s^2(t) \rangle / l^2 \gg 1$, all terms on the right-hand side of Eq. (9) are negligibly small in comparison with the last term, and for n even one obtains

$$\begin{aligned} \left\langle \left[\sum_k \varphi_k \right]^2 \right\rangle &= \sum_{k_1} \cdots \sum_{k_{n/2}} \langle \varphi_{k_1}^2 \rangle \cdots \langle \varphi_{k_{n/2}}^2 \rangle \\ &= (n-1)!! (\langle s^2(t) \rangle / l^2)^{n/2}, \end{aligned} \quad (11)$$

where the second equation follows from combinatorial considerations by use of Eq. (10). All moments with n odd are equal to zero. Inserting Eq. (11) into Eq. (8) finally yields for the n th moment

$$\langle s^n \rangle = (n-1)!! \langle s^2 \rangle^{n/2}, \quad (12)$$

which is exactly the condition for a Gaussian distribution. Hence, as in the case of ordinary diffusion, also under single-file conditions molecular displacements are found to follow a Gaussian distribution curve

$$P(s, t) = (2\pi \langle s^2(t) \rangle)^{-1/2} \exp\{-s^2 / (2 \langle s^2(t) \rangle)\}. \quad (13)$$

In contrast to ordinary diffusion, however, the mean-square displacement is proportional to the square root of the observation time as given by Eq. (4), rather than to the observation time itself.

For an estimate of the space and time scale for which an application of the long-time limit as represented by Eq. (4) might be justified it is useful to consider the opposite limiting case. For sufficiently short times, the molecular mean-square displacement behaves as [7].

$$\langle s^2(t) \rangle = 2 \frac{l^2}{2\tau} (1 - \Theta) t, \quad (14)$$

where $l^2/(2\tau)$ is the diffusivity of an isolated molecule [coinciding with that of an isolated vacancy [Eq. (5)], which is multiplied by the additional factor $(1-\Theta)$ representing the probability that a jump attempt is directed to a vacant site. In the short-time limit, any correlation between subsequent jumps may be neglected. Equating Eqs. (4) and (14), the crossover between both dependences is found to occur for

$$t = \frac{2}{\pi\Theta^2} \tau \quad (15)$$

and

$$\langle s^2 \rangle^{1/2} = [2(1-\Theta)/(\pi\Theta^2)]^{1/2} l. \quad (16)$$

The long-time limit of single-file diffusion should therefore be applicable for observation times much larger than $2\tau/(\pi\Theta^2)$ and root-mean-square displacements much larger than $[2(1-\Theta)/(\pi\Theta^2)]^{1/2} l$.

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