

## LETTER TO THE EDITOR

# An Equation for the Mean Square Displacement in Single File Diffusion

Recently Kärger and co-workers (1) have investigated, through Monte Carlo simulations, the problem of diffusion and reaction in zeolites characterized by one-dimensional channels in which the individual molecules cannot pass each other. The molecular migration is considered to be a sequence of “random walker” steps in which molecules move only if the adjacent site is not occupied. This mechanism is often referred to as single file diffusion. The effect of the interactions between molecules leads to a mean square displacement which varies smoothly from a linear to a square root dependence with time (2). Therefore the self-diffusivity defined according to Einstein’s equation (3) becomes time dependent. In order to compare results from different experimental techniques it is therefore necessary to have appropriate theoretical equations for the dependency of the mean square displacement of tagged molecules with time.

The aim of this letter is to propose a simple equation for the mean square displacement of tagged molecules which reduces to the established theoretical limits for short and long times as well as for high and low sorbate loadings.

The simplest limit is that for a single molecule in a one-dimensional channel. In this case the molecule has equal probability of moving in either direction and the traditional expression holds (3)

$$\langle z^2(t) \rangle = l^2 \frac{t}{\tau}; \quad \theta = 0, \quad [1]$$

where  $l$  is the length of the activated jumps,  $\tau$  is the mean time between jumps, and  $\theta$  is the fractional occupancy. The second simple limit is the case for  $\theta = 1$  for which the molecules cannot move. For intermediate loadings it has been proven formally by Fedders (4) that the following equation applies at long times

$$\langle z^2(t) \rangle = l^2 \frac{1-\theta}{\theta} \sqrt{\frac{2}{\pi}} \sqrt{\frac{t}{\tau}}; \quad \theta > 0; \quad t \rightarrow \infty, \quad [2]$$

while for short times (2, 5)

$$\langle z^2(t) \rangle = l^2 (1-\theta) \frac{t}{\tau}. \quad [3]$$

Monte Carlo simulations (1) show that the transition from Eq. [2] to Eq. [3] is quite smooth. Combining all these limiting forms (Eqs. [1]–[3]) it is possible to suggest a simple

approximate analytical expression given by

$$\langle z^2(t) \rangle = l^2 \frac{(1-\theta)t/\tau}{1 + \theta \sqrt{\pi/2} \sqrt{t/\tau}}. \quad [4]$$

Equation [4] reduces correctly to all three limiting cases and has a transition at time  $t = t_t$  given by

$$\frac{t_t}{\tau} = \frac{2}{\pi \theta^2}, \quad [5]$$

which coincides with that suggested by Kärger (5). For  $t \gg t_t$  Eq. [4] reduces to Eq. [2]. For  $t \ll t_t$ , Eq. [4] reduces to Eq. [3]. The dimensionless mean square displacement obtained from Eq. [4] is shown in Fig. 1. Figure 2 shows a direct comparison between the Monte Carlo results of Kärger *et al.* (1) and the proposed equation. The agreement is quite satisfactory.

From Eq. [4] it is possible to define the following quantity:

$$\frac{2t}{\langle z^2(t) \rangle} = \frac{2\tau}{l^2} \frac{1}{1-\theta} \left( 1 + \theta \sqrt{\frac{\pi}{2}} \sqrt{\frac{t}{\tau}} \right). \quad [6]$$

A plot of this quantity versus the root of time should be linear, as can be seen from Fig. 2, and may be used to compare results obtained from different experimental methods characterized by different observation times, provided that

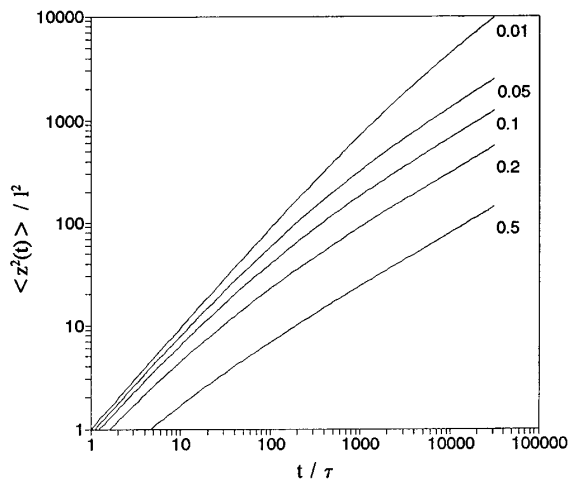


FIG. 1. Mean square displacement as a function of time at different fractional occupancies  $\theta$ .

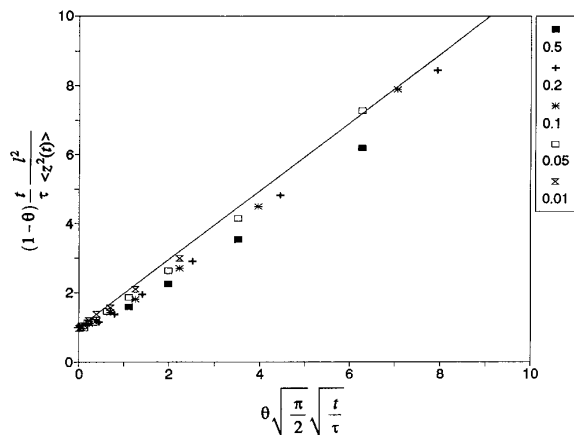


FIG. 2. Comparison of Monte Carlo simulations (1) at different fractional occupancies (symbols) and the proposed equation.

the boundary conditions may be neglected. This should be the case for most microscopic measurements (3) when large zeolite crystals are available.

#### APPENDIX: NOMENCLATURE

##### Arabic

- $l$  step length  
 $t$  time  
 $z$  displacement

##### Greek

- $\theta$  fractional occupancy  
 $\tau$  mean time between jumps

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