JOURNAL OF CATALYSIS **160,** 328–329 (1996)
ARTICLE NO. 0154

# LETTER TO THE EDITOR

# Response to “An Equation for the Mean Square Displacement in Single File Diffusion” by S. Brandani

In his letter, Brandani gives a simple analytical approximation for the mean square displacement in a single-file system comprising the limiting cases of short-time and long-time behavior (Eq. [4] of Ref. (1)). Equations of this type are of particular relevance for the establishment of analytical expressions for measuring techniques, such as quasielastic neutron scattering (2), which cover both time regimes of molecular propagation. On deriving this equation, the particles in the single-file system are assumed to undergo a random walk. Hence, for times $t$ sufficiently small in comparison with the time interval between mutual collisions of the particles, the mean square displacement $\langle z^2 \rangle$ may be expected to be proportional to the time $t$. For sufficiently large time intervals, the effect of the mutual encounters of the particles becomes dominant leading to the proportionality $\langle z^2 \rangle \propto \sqrt{t}$. Brandani's expression fulfills both limiting cases and provides an excellent approximation of the transition range as resulting from Monte Carlo simulations (3). It must be emphasized, however, that the applicability of the Monte Carlo simulations and hence of the proposed analytical expressions to real systems, for example to zeolites of one-dimensional channel structure, is restricted. This is due to the fact that the random walker model itself is an approximation, introduced to describe the long-time behavior of a particle subjected to random forces. In reality, however, at short times such a particle will behave ballistically, i.e., the mean square displacement is proportional to the square of the time, $\langle z^2 \rangle \propto t^2$.

The applicability of Brandani's formula to real systems depends, therefore, on the relation between the characteristic times describing the transition between the ballistic and unrestricted random walk regimes ($t_r$) and between unrestricted random walk and the single-file regimes ($t_t$), respectively. Only for $t_r \ll t_t$ may a well-established regime of unrestricted random walk ($\langle z^2 \rangle \propto t$, for $t_r < t < t_t$) be expected, so that in this case the application of Brandani's equation becomes possible. The range of shorter times ($t \leq t_r$) then simply remains beyond the scope of the equation. For $t_r \approx t_t$, however, the existence of an extended time regime with $\langle z^2 \rangle \propto t$ is excluded and the Brandani equation is no longer applicable.

The requirement of $t_r \ll t_t$ for the applicability of the Brandani equation is particularly stringent, since—as illustrated by Fig. 1 of Ref. (1)—there is no sharp transition between the time regimes $\langle z^2 \rangle \propto \sqrt{t}$ and $\langle z^2 \rangle \propto t$ at $t_t$, but a rather broad transition region, ranging over several orders of magnitude. Therefore, in most cases the transition regions from ballistic to random walk behavior and from unrestricted random walk to single-file behavior will overlap thus excluding the formation of a distinct time regime $\langle z^2 \rangle \propto t$. Hence, only for sufficiently small occupancies $\theta$ when $t_t$ becomes very large (cf. Eq. [5] of Ref. (1)), a resolution between the time regimes of unrestricted random walk and single-file diffusion may be expected.

These considerations may be illustrated by molecular dynamics simulations, which are able to describe the behavior over the whole time scale. The simulations are carried out with particles in a narrow channel, where the random force acting on the particles is simulated by a random change of velocity at time intervals $\Delta t = 5 \times 10^{-14}$ s. This random change is controlled by a parameter $a$ ranging from 0 to 1, where 0 means no velocity change (i.e., deterministic behavior) and 1 means that the new velocity is completely independent of the old one. The resulting velocity autocorrelation function may be shown to be $K_n = (1-a^2)^{-n/2}$, with $n$ denoting the number of time intervals $\Delta t$. Details of the MD simulations may be found in Ref. (4). Figure 1 shows the mean square displacement $\langle z^2 \rangle$ as a function of the time $t$ at a relatively low occupancy of $\theta = 0.1$ for different parameters $a$. As to be expected, the enhancement of the stochastic character of molecular propagation by an increase of the parameter $a$ is found to lead to a faster transition from the ballistic regime to the unrestricted random walk. For the smallest values of the stochastic force ($a = 0.15$), there is essentially an instantaneous transition from the ballistic time regime to single-file behavior. With the medium values of $a$ (0.3 and 0.5) the transition range covers two orders of magnitude in time without exhibiting an extended region with $\langle z^2 \rangle \propto t$. Hence, also in this case, the application of the Brandani relation would be of no use. Only with the strongest random force ($a = 0.9$) the transition range between $t_r$ and $t_t$ becomes sufficiently large so that in this



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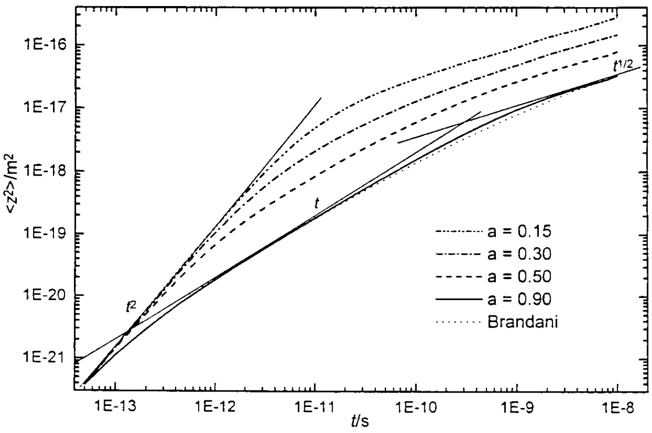


**FIG. 1.** Mean square displacement as a function of the observation time at an occupancy of $\theta = 0.1$ for different values for the intensity of the random forces as resulting from molecular dynamics simulations. Larger values of the parameter $a$ correspond to smaller values for the mean square displacement $\langle z^2 \rangle$. The thin lines reflect the time dependence of $\langle z^2 \rangle$ in the ballistic regime ($\propto t^2$) for unrestricted random walk ($\propto t$) and for single-file diffusion ($\propto \sqrt{t}$), respectively. The dotted line at the bottom of the representation shows the approximation of the MD data for $a = 0.9$ by the Brandani formula.

case a region with $\langle z^2 \rangle \propto t$ is exhibited. It is demonstrated in Fig. 1 that now the transition between the two time regimes of unrestricted random walk and single-file diffusion is well reflected by the Brandani formula.

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Received February 26, 1996; accepted March 19, 1996