

Transition from Knudsen to molecular diffusion in activity of absorbing irregular interfacesJ. S. Andrade, Jr.,^{1,4} H. F. da Silva,^{1,2} M. Baquil,¹ and B. Sapoval^{3,4}¹*Departamento de Física, Universidade Federal do Ceará, 60451-970 Fortaleza, Ceará, Brazil*²*Departamento de Física, Universidade Federal do Maranhão, 65080-040 São Luis, Maranhão, Brazil*³*Laboratoire de Physique de la Matière Condensée, CNRS, Ecole Polytechnique, 91128 Palaiseau, France*⁴*Centre de Mathématiques et de leurs Applications, CNRS, Ecole Normale Supérieure de Cachan, 94235 Cachan, France*

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We investigate through molecular dynamics the transition from Knudsen to molecular diffusion transport towards two-dimensional absorbing interfaces with irregular geometry. Our results indicate that the length of the active zone decreases continuously with density from the Knudsen to the molecular diffusion regime. In the limit where molecular diffusion dominates, we find that this length approaches a constant value of the order of the system size, in agreement with theoretical predictions for Laplacian transport in irregular geometries. Finally, we show that all these features can be qualitatively described in terms of a simple random-walk model of the diffusion process.

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I. INTRODUCTION

The problem of Laplacian transport towards irregular surfaces represents an important subject of research in many fields of technological relevance including heterogeneous catalysis, heat transfer, and electrochemistry. In the particular case of catalysis, the role of the local surface morphology at the pore level on the global diffusion-reaction efficiency of the catalyst had been a subject of great interest in the past years [1–5]. Fractal concepts have been used to model complex surface roughness in the study of Knudsen diffusion in irregular reactive pores [6,7] including catalyst supports and adsorbents [8].

Another interesting point on the subject refers to the problem of the nonuniform accessibility of active sites located along an irregular reactive surface. If the system is diffusion controlled, these so-called *screening* effects may cause a dramatic reduction on the reactivity of the catalyst surface, as compared to the reactivity solely due to the intrinsic chemical reaction mechanism (i.e., the activity of the nominal surface). The extensive research developed in this field has been mainly devoted to the introduction, calculation, and application of the concept of *active zone* in the Laplacian transport to and across irregular interfaces [9,10]. For example, through the coarse-graining method proposed in Ref. [9], it is possible to determine the flux through an arbitrarily irregular surface from its geometry alone, avoiding the solution of the Laplace problem within a complex boundary domain. More recently, it has been shown that this technique provides consistent predictions for the activity of catalyst surfaces [11].

All these studies dealing with an active zone in Laplacian fields rely on the implicit assumption that molecular diffusion is the governing mechanism of mass transport. Such an approximation, however, can only be locally valid inside of the void space between the fins or the extended protrusions of an irregular surface if the mean free path of the diffusing molecules is sufficiently smaller than the width of these irregularities. For example, Knudsen diffusion may become the dominant mechanism of mass transport determining the reactivity of the system if the reagent is a diluted gas for

which the collisions among molecules are less frequent than the collisions between the molecules and the catalytic surface [6,7]. The molecular mean free path therefore constitutes a lower cutoff for the validity of the molecular diffusion description. In a recent study [12], it has been shown analytically and through numerical simulations that the surface roughness can have a significant effect on self-diffusion of gases in nanoporous media in the Knudsen regime.

The aim of this paper is to study the transition in activity of an irregular absorbing interface when the mechanism of mass transport changes from Knudsen to molecular diffusion. Our approach is to use a nonequilibrium molecular dynamics (NMD) technique in order to simulate a nonuniform and steady-state profile of reagent concentration between two active interfaces with an arbitrarily given roughness. This resembles more closely with the experimental conditions frequently used in diffusion-reaction measurements.

II. NMD MODEL

Here we adopt the NMD method that has been originally proposed for the study of self-diffusion in pure fluids [13]. The technique is entirely based on the standard molecular dynamics (MD) at equilibrium, but includes a special scheme to identify and exchange *labeled* and *unlabeled* particles during the simulation.

The MD part of the simulation consists of a two-dimensional cell of size $L_x l \times L_y l$ containing N identical particles that interact through the Lennard-Jones potential $\Phi(\Delta r_{ij}) = 4\epsilon[(\sigma/\Delta r_{ij})^{12} - (\sigma/\Delta r_{ij})^6]$, where Δr_{ij} is the distance between the particles i and j , ϵ is the minimum energy, σ is the zero of the potential, and we use $l/\sigma = 5.86$. Periodic boundary conditions are applied in both the x and y directions. Distance, energy, and time are measured in units of σ , ϵ , and $(m\sigma^2/\epsilon)^{1/2}$, respectively, and the equations of motion are numerically integrated using the Verlet algorithm [14]. In all the simulations we performed, the relative fluctuation around the average of the total energy of the system has always been smaller than 10^{-4} .

After thermalization, two identical irregular interfaces of

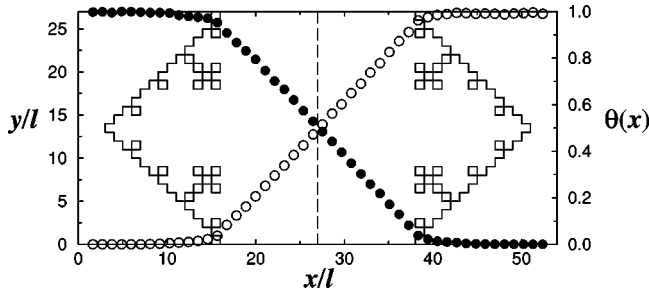


FIG. 1. Schematic representation of the NMD diffusion cell. The absorbing interfaces are square Koch trees. Also shown in this figure is the dependence of the local number fraction θ of labeled (full circles) and unlabeled (empty circles) particles on the position along the x direction in the cell. In the case of the random-walk model, particles are released from random y positions at the dashed line in the center.

size $L_y l$ and perimeter $L_p l$ are symmetrically placed into the system to simulate the roughness geometry of an absorbing material (see Fig. 1). At this point, the nonequilibrium dynamics is put forward through the following scheme: (1) half of the particles in the MD cell are randomly selected to carry a *label*, while the other half is left *unlabeled*; (2) every time a labeled (unlabeled) particle crosses the interface at right (left) moving in the \vec{e}_x ($-\vec{e}_x$) direction, it becomes unlabeled (labeled), and (3) when reinjected from the right (left) through the periodic boundaries in the x axis, the unlabeled (labeled) particle becomes a labeled (unlabeled) one. Although the particles are indistinguishable in terms of their masses and interaction potentials, this labeling technique naturally builds concentration gradients for both “species” that gradually develop to reach a desired nonuniform steady state. In Fig. 1 we show the resulting stationary profiles along the x coordinate of the number fractions $\theta_l \equiv n_l / (n_l + n_u)$ and $\theta_u = 1 - \theta_l$, where n_l and n_u are the number of labeled and unlabeled particles, respectively, inside a vertical slice of fixed length in the system. From this point on, during the simulation, at each time step we keep updating the number n_i of particles being “absorbed” by the element i of the interface in order to compute its local mass flux $q_i = n_i / \Delta t$, where Δt is the elapsed time after the steady state has been established. Here we measure the efficiency of the interface in terms of the active length L_a defined as [15]

$$L_a \equiv 1 / \sum_{i=1}^{L_p} \phi_i^2 \quad (1 \leq L_a \leq L_p), \quad (1)$$

where the sum is over the total number of interface elements L_p , and $\phi_i \equiv q_i / \sum q_j$ is the normalized mass flux of element i . From the definition (1), $L_a = L_p$ indicates a limiting state of equal partition of fluxes ($\phi_i = 1/L_p$, $\forall i$) whereas L_a of order L_y should correspond to the case of a strongly “localized” flux distribution.

Based on this NMD method, we performed simulations for five distinct initial configurations of the dynamical system, different values of the reduced temperature T , and reduced densities in the range $0.025 \leq \rho \leq 0.5$, corresponding to systems with $N = 1250$ – 25000 particles. The evolution with

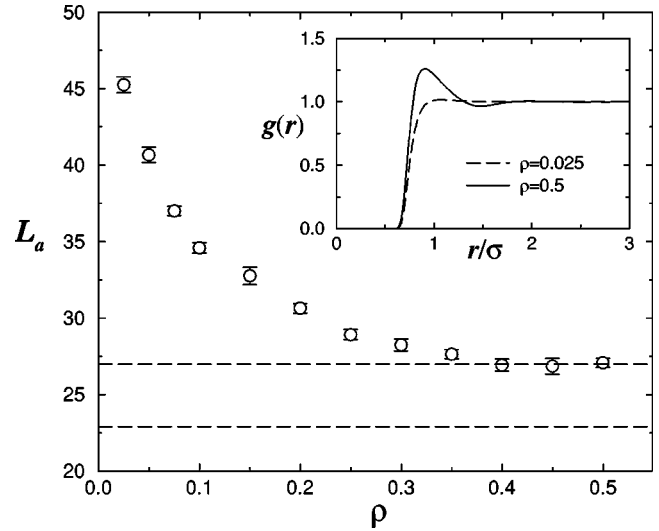


FIG. 2. Dependence of the active length L_a on the reduced density of the NMD cell ($\rho = \rho^* \sigma^2$, where ρ^* is the density) for a fixed temperature $T = 1.25$. The average values with error bars refer to simulations with five different realizations of the NMD process. The horizontal dashed line at the top corresponds to the system size $L_y = 27$ while the one at the bottom indicates the value of the active length obtained from the simulation with the Laplacian cell $L_a = 22.9$. The inset shows the pair-correlation function calculated at the same temperature for a dilute ($\rho = 0.025$) and a more dense ($\rho = 0.5$) fluid.

time of the active length for any NMD realization reveals that, after a transient period, the system reaches a stationary state characterized by an average value of L_a that is representative of the flux distribution. As shown in Fig. 2, the active length decreases sharply with ρ for low density systems at $T = 1.25$, up to a point where it remains constant at $L_a \approx 27$. The results of the simulations performed at a higher temperature, $T = 3.33$, show that the behavior of the active length remains nearly the same, at least within the range of densities considered here.

The decrease with density of the active length L_a reflects the transition from Knudsen to molecular diffusion in the distribution of activity at the interface. Because the mean free path of the particles for small ρ values is larger than the smaller length scale l of the irregular interface, the activity is highly sensitive to geometrical constraints in the Knudsen regime. As shown in the inset of Fig. 2, the difference in the behavior of the pair-correlation function for dilute and more dense fluids indicates that the simulated system undergoes noticeable structural modifications as ρ increases.

At higher densities, the invariant behavior of L_a is a consequence of molecular diffusion and can be explained in terms of an interesting theorem given by Makarov [16] to describe the properties of Laplacian fields on two-dimensional interfaces of arbitrary shape subjected to Dirichlet boundary conditions. The theorem states that *the information dimension of the harmonic measure on a singly connected interface in $d = 2$ is exactly equal to 1*, where d represents dimension. In terms of activity, this means that, regardless the shape of the interface, the total length L_a of the region where most of the activity takes place should be of

the order of the size L of the cell under a dilation transformation (see Ref. [15] for a detailed discussion of the active zone concept). Translating to our diffusion cell, where square Koch trees of third generation are the absorbing interfaces, the theorem of Makarov predicts that the value of L_a should be close to the size $L_y=27$ in good agreement with the NMD limit obtained for high densities.

III. CONTINUUM AND RANDOM-WALK DESCRIPTIONS

One can compute directly the length of the active zone for the two-dimensional continuum Laplacian problem which represents steady-state molecular diffusion [17]. Numerical solutions of the Laplace equation $\nabla^2 C=0$ for the concentration field C inside the diffusion cell are obtained here through numerical discretization by means of finite differences. For this, a constant unitary concentration is imposed at the source line ($C_0=1$) and Dirichlet boundary conditions ($C=0$) are assigned to each elementary unit of the interface. Due to the symmetry with respect to the source line only the concentration field in half of the domain needs to be calculated. The calculated value for the active length of the purely Laplacian cell is found to be $L_a=22.9$, which is compatible with the prediction of the Makarov theorem $L_a \approx L_y$.

Now we show that a simple random-walk model of the diffusion-absorption process can provide a consistent qualitative description of the behavior observed in the NMD simulations. Adopting the same geometry, a particle is released from a random position in the center line. The walker travels through the medium taking steps of random directions, but at a constant length λ , till it crosses one of the wall elements of the irregular interface and gets absorbed. The flux at this element is then updated and the active length L_a of the interface is recalculated. For a fixed value of the step length λ , the simulation goes on with particles being sequentially released and absorbed, till the active length reaches an average value that is approximately constant. This value is usually obtained with less than 10^5 particles launched in the system. In Fig. 3 we show the dependence on the parameter $\xi \equiv (\sigma/\lambda)$ of the average L_a computed for the third generation of the square Koch tree. For a two-dimensional gas, λ can be interpreted as the mean free path, which is inversely proportional to the surface density of the system $\lambda \propto 1/\rho$. Similarly to the NMD simulations, two distinct regimes of activity can be clearly identified and directly related to the different governing mechanisms of mass transport, namely, Knudsen and molecular diffusion. At low values of ξ , the decrease of L_a reflects the strong influence on the mass transport process of the irregular geometry of the interface. The semilog plot shown in the inset of Fig. 3 indicates that this decay in activity characterizing the Knudsen regime is approximately logarithmic in shape.

At sufficiently large values of ξ , the length L_a reaches a plateau of minimum activity that is practically coincident with the value of the active length found for the Laplacian cell $L_a=22.9$ (see dashed line at the bottom in Fig. 3). It is important to show that these two approaches to the problem provide consistent results for denser systems, even at the local scale of the interface geometry. Indeed, as displayed in

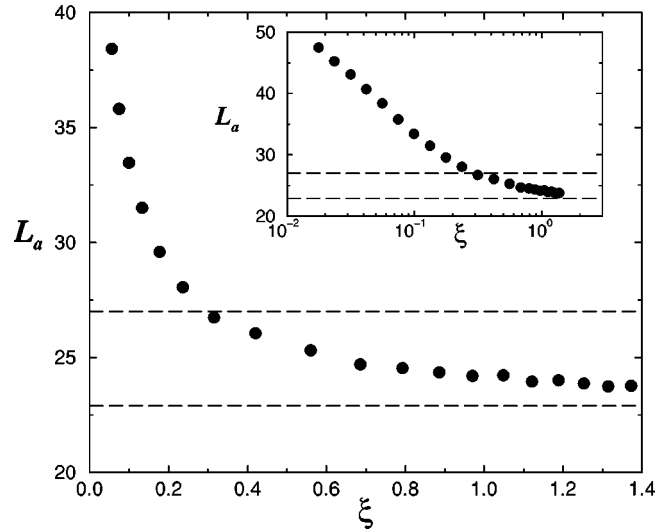


FIG. 3. Dependence on the random-walk parameter ξ of the active length L_a of the irregular interface for the random-walk model. The horizontal dashed line at the top corresponds to the system size $L_y=27$, while the one at the bottom gives the active length of the Laplacian cell $L_a=22.9$. The semi-log plot in the inset shows that L_a decays approximately logarithmically with ξ in the regime of Knudsen diffusion.

Fig. 4, the normalized fluxes at each wall element generated from the continuum and random-walk methods are almost indistinguishable. Compared to the lower limit of the random-walk model $L_a \approx 24$ the higher value found for the active length with the NMD technique is $L_a \approx 27$, which can be explained in terms of the structural features and collective behavior of the simulated fluid. As shown in the inset of Fig. 2, the role of the attractive part of the interaction potential is to induce a smooth peak of short-range correlation. The presence of clusters is also a structural aspect of the many-

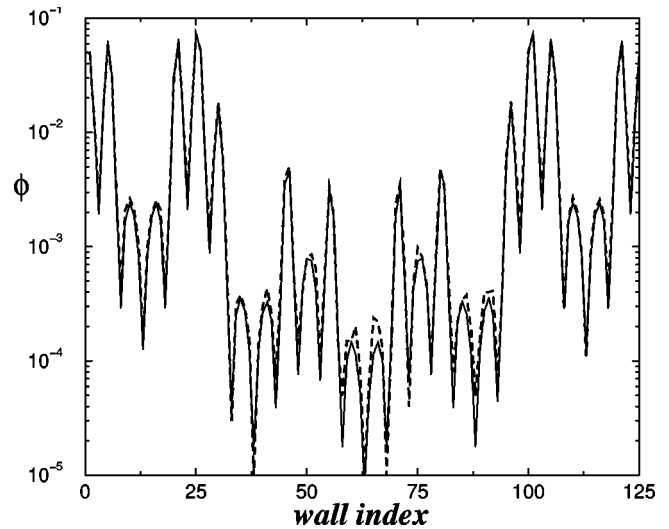


FIG. 4. Distribution of the logarithm of the normalized fluxes crossing the wall elements along the absorbing irregular interface. The dashed line corresponds to a random-walk simulation performed with $\xi=0.63$, and the solid line is the distribution resulting from the numerical simulation with a Laplacian cell.

particle systems that can be simulated with the NMD technique and might influence the measure of active length. As a future work, we will perform computational simulations over a wide range of temperatures and for different forms of the interacting potential. This will provide a more complete picture of the interplay between the physicochemical attributes of the diffusing fluid and the activity of the absorbing interface.

IV. SUMMARY

In conclusion, we have shown through molecular dynamics simulations that the active fraction of an irregular absorbing interface should be sensitive to: (i) its geometrical details, (ii) the governing mechanism of transport, and (iii) the structural aspects of the diffusing fluid. In particular, the active length for absorption of molecular diffusing fluids is found to be very close to that of a purely Laplacian system. These observations may lead to new guidelines to the problem of diffusion and absorption on arbitrarily irregular interfaces. Furthermore, we have proposed a very simple random-walk model that incorporates the basic features of the diffusion-absorption process and is capable to describe, at

least semi-quantitatively, the behavior of the active length for different diffusion regimes. This model provides substantial insight on the effect of the diffusion mechanism on the interface activity and has the virtue of being computationally cheap. Finally, the approach introduced here is flexible enough to represent specific characteristics of irregular interfaces as well as other types of “absorption” mechanisms (e.g., finite-rate chemical reactions) limited by diffusion transport. As a consequence, the implications of this study are certainly relevant for the analysis and interpretation of diffusion and reaction processes occurring in a large variety of catalyst materials. The modeling techniques we adopted should also be useful as design tools to choose a suitable catalytic interface for a given reaction-diffusion system.

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