

# Correlation Effects and Reduction of Dimensionality in Interfacial Reactions

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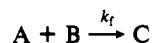
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**Abstract:** A theoretical prediction of Astumian and Schelly on the geometric effects of reduction of dimensionality on the specific rate of diffusion-controlled reactions is re-examined. Using a lattice-statistical approach, we generalize the problem posed [Astumian, R. D.; Schelly, Z. A. *J. Am. Chem. Soc.* 1984, 106, 304] to consider explicitly the influence of down-range (attractive/repulsive) potential correlations between a diffusing coreactant A and a target molecule B<sub>s</sub> anchored on the surface of a colloidal particle and, following adsorption of the species A, the role of surface diffusion in facilitating the interfacial reaction, A + B<sub>s</sub> → C<sub>s</sub>. The results obtained in our analysis generally support the conclusion of Astumian and Schelly that reduction of dimensionality leads to a decrease in the specific rate of diffusion-controlled interfacial reactions. An important exception occurs in the case where excursions off the surface of the colloidal particle of the diffusing coreactant A, once adsorbed, are strictly disallowed; in this case, particularly for reactant pairs interacting via purely repulsive Coulombic forces, reduction of dimensionality leads to an enhancement in the reaction rate, relative to the homogeneous system case. It is suggested that this may provide a rationale for understanding a key reaction in the colloidal platinum-mediated production of hydrogen from water using the electron-acceptor species, methyl viologen.

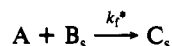
## I. Introduction

In 1984, Astumian and Schelly presented an analysis of some geometric effects of reduction of dimensionality on interfacial reactions.<sup>1</sup> Their theoretical study was motivated by "the apparent discrepancies found between the observed and expected diffusion-controlled rate constants of reactions such as proton transfer and ion-pair formation occurring at the surface of colloiddally dispersed spherical metal oxide particles," experimental work reported in refs 2-6. These authors used collision, transition-state, and diffusion-control theories to explore the consequences of localization on the surface of large particles of one of the reactants in a bimolecular reaction and, within the framework of a certain set of well-defined approximations, showed that the specific reaction rates could be significantly influenced by reduction of dimensionality.<sup>7,8</sup> In particular, relative to the same reaction taking place in a homogeneous phase, this geometric effect led to a decrease in the specific rates.

Of particular interest to us in this contribution is the prediction by Astumian and Schelly of the decrease in rate caused by reduction of dimensionality in diffusion-controlled reactions. We state here the principal result found by these authors for this class of reactions and refer the reader to ref 1 for the detailed formulation of the problem. In brief, these authors considered the elementary reaction



taking place in a homogeneous liquid or gas phase, and contrasted this with reaction



assumed to take place at a solid-liquid or solid-gas interface, this via prior adsorption of the species B; here, B<sub>s</sub> represents the reactive surface site and C<sub>s</sub> the surface-bound product. In the case where B's of radius r<sub>B</sub> are localized on (large) hard spheres of radius r<sub>HS</sub>, the ratio of specific rates k' for the heterogeneous versus homogeneous phase reaction is given by

$$\frac{k_f^*}{k_f} = \frac{r_B^3}{\pi r_{HS}(r_A + r_B)^2}$$

where r<sub>A</sub> is the radius of species A (with r<sub>HS</sub> ≫ r<sub>A</sub>, r<sub>HS</sub> ≫ r<sub>B</sub>). Using atomic radii for r<sub>A</sub> and r<sub>B</sub>, taking r<sub>HS</sub> ~ 1 μm for a typical colloidal particle, and assuming equal global concentrations when considering the specific rates k', it follows at once that localization

of B on the surface of the hard sphere leads to a significant reduction in the specific rates for a diffusion-controlled process. Moreover, the above result was derived assuming complete coverage of the hard spheres by B; for partial coverage, the ratio k<sub>f</sub>'\*/k<sub>f</sub>' is even smaller. In a separate analysis, Astumian and Schelly also showed that the geometric effects of localization on diffusion-controlled reactions are more pronounced than those for slow (chemically-controlled) reactions, the latter case analyzed using transition-state and collision theories.

Despite the important insights gained from the Astumian-Schelly analysis, their approach was based on certain assumptions, the consequences of which are worth exploring. For example, the diffusing coreactant (A) on colliding with the host particle was assumed to "stick" to the surface, and this collision was assumed to involve contact between A and B (only); the possibility of surface diffusion was suppressed so that Eley-Rideal rather than Langmuir-Hinshelwood kinetics (the latter involving surface diffusion) was always assumed. Secondly, the importance of down-range potential correlations between coreactants was not considered in the Astumian-Schelly analysis. The consequences of relaxing these assumptions can be explored using a lattice-statistical approach based on the theory of finite Markov processes, and it is this effort that will be the focus of the present contribution.

## II. Specification of the Model

In our earlier work,<sup>9-11</sup> an approach to the study of encounter-controlled reactive processes taking place on the surface of a molecular organizate (cell, micelle, vesicle) or colloidal catalyst

- (1) Astumian, R. D.; Schelly, Z. A. *J. Am. Chem. Soc.* 1984, 106, 304.
- (2) Astumian, R. D.; Sasaki, M.; Yasunaga, T.; Schelly, Z. A. *J. Phys. Chem.* 1981, 85, 3832.
- (3) Ashida, M.; Sasaki, M.; Yasunaga, T.; Hachiya, K.; Inoue, T. *J. Colloid Interface Sci.* 1978, 67, 219.
- (4) Ashida, M.; Sasaki, M.; Hachiya, K.; Yasunaga, T. *J. Colloid Interface Sci.* 1980, 74, 572.
- (5) Sasaki, M.; Moriya, M.; Yasunaga, T.; Astumian, R. D. *J. Phys. Chem.* 1983, 87, 1449.
- (6) Astumian, R. D. Geometric Effects and Reduction of Dimensionality at Interfaces and in Electric Fields. Ph.D. Dissertation, University of Texas at Arlington, 1983 [*Diss. Abstr. Int. B* 1985, 45(9), 2929].
- (7) Adam, G.; Delbrück, M. Reduction of Dimensionality in Biological Diffusion Processes. In *Structural Chemistry and Molecular Biology*; Rich, A., Davidson, N., Eds.; W. H. Freeman and Co.: New York, 1968; pp 198-215.
- (8) See also: McCloskey, M. A.; Poo, M. *J. Cell. Biol.* 1986, 102, 88. Lee, P. H.; Kozak, J. J. *J. Chem. Phys.* 1984, 80, 705.
- (9) Politowicz, P. A.; Kozak, J. J. *Proc. Natl. Acad. Sci. U.S.A.* 1987, 84, 8175.
- (10) Politowicz, P. A.; Garza-López, R. A.; Hurtubise, D. E.; Kozak, J. J. *J. Phys. Chem.* 1989, 93, 3728.
- (11) Mandeville, J. B.; Hurtubise, D. E.; Flint, R.; Kozak, J. J. *J. Phys. Chem.* 1989, 93, 7876.

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particle (e.g. Adams catalyst) was introduced. The theoretical approach taken was motivated by the experimental observation that the surface of an organozate or catalyst particle is not smooth and continuous, but rather differentiated by the geometry of the constituents and, if the surface composition is not homogeneous, often organized into domains or clusters. It was proposed in refs 9–11 that these structural features could most naturally be taken into account by designing a lattice model and then studying theoretically the influence of different geometries, potential interactions, and initial conditions on the kinetic response of the system by formulating and solving (numerically) the stochastic master equation for the problem considered.

The extent to which the underlying diffusion-controlled reactive event is mediated by the domain and/or channel structure of the surface was the primary focus of the studies presented in refs 9 and 10. Then, in ref 11 we began to consider explicitly the role of intermolecular potentials in influencing the efficiency of reaction; the (otherwise random) motion of the diffusing atom/molecule was assumed to be guided by the presence of attractive/repulsive forces operative between a stationary target molecule and the diffusing coreactant. Moreover, rather than assuming that the coreactant was strictly confined in its motion to the surface of the host particle, (virtual) displacements of the coreactant normal to the surface were also considered. That is, the diffusing atom or molecule was permitted to undergo excursions away from a site on the surface but constrained to return to the surface (at that point) before undertaking further lateral displacements.

Formally, the surface of a host particle of arbitrary shape is topologically equivalent to a Cartesian shell, a closed lattice structure of topological dimension  $d = 2$  and Euler characteristic  $\chi = 2$  situated in three-dimensional space (see the following discussion and/or Figure 1 of ref 11). The Cartesian shell has eight defect sites of local coordination or valency  $\nu = 3$  with all remaining sites of valency  $\nu = 4$ . In ref 11, excursions normal to the surface were accounted for by assigning to a molecule positioned at a given lattice site (two or three) additional degrees of freedom; defect sites were then characterized by an effective valency  $\nu = 3 + 3$  and all regular sites of the Cartesian shell by a valency  $\nu = 4 + 2$ . By introducing these additional degrees of freedom in the motion of the diffusing coreactant, some progress could be made in relaxing the assumption (usual in Fickian approaches to the study of diffusion-reaction processes) that the atom/molecule in its motion is strictly confined to the (topological)  $d = 2$  dimensional surface of the host particle.

The principal generalization carried out in this study is to permit the diffusing coreactant, following an excursion away from the surface, to undergo lateral displacements *above* the surface before returning (eventually) to a (possibly) *different* point on the surface. Thus, the model elaborated in this study allows a quantification of the (physically intuitive) idea that at finite temperatures the diffusing particle can, in its random or biased motion across the surface, "skip over" the surface during parts of its trajectory while still being sufficiently entrained by surface forces to remain in the vicinity of the host colloidal catalyst particle or molecular organozate.

Although there are obviously a continuum of sites above the surface accessible to a diffusing coreactant, we shall sample the reaction space exterior to the surface of the host particle by designing an extended lattice structure. We consider the case of a coreactant migrating on a  $N = 26$  Cartesian shell, with the target molecule anchored either at a defect site ( $\nu = 3 + 3$ ) or at a site ( $\nu = 4 + 2$ ) farthest removed from the (eight) defect sites; these sites will be referred to as sites 3 and 1, respectively (to preserve consistency with the notation of our earlier study<sup>11</sup>). The calculations reported in section IV for  $N = 124, 342,$  and  $728$  then refer to the total number of (representative) sites accessible to a coreactant diffusing on or above the Cartesian shell,  $N = 26$ . In particular, the case  $N = 124$  here comprises the  $N = 26$  basal sites and the  $N' = 98$  sites defining the first overlayer. The case  $N = 342$  includes the  $N = 26$  sites and the first two overlayers,  $N' = 98$  and  $218$ ; the case  $N = 728$  encompasses the basal sites  $N = 26$  and the first three overlayers,  $N' = 98, 218,$  and  $386$ .

Thus, the motion of the diffusing coreactant, strictly confined in ref 11 to the  $d = 2$  dimensional surface of a series of Cartesian shells of ever-increasing spatial extent (surface area), here takes on more and more three-dimensional character ( $2 < d \leq 3$ ) as one considers sequentially the augmented reaction spaces,  $N = 124, 342$  and  $728$ .

### III. Theoretical Background

The theoretical approach taken in this paper is based on the theory of finite Markov processes and, specifically, the relationship between the moments of the underlying distribution function for the process being described and solutions of the stochastic master equation for the problem. This approach has been elaborated and discussed extensively in the literature;<sup>12</sup> the lattice-statistical formulation for problems similar to the one treated in this study is described in ref 11 and will not be reproduced. However, central to the interpretation of the results reported here is a specification of the variables calibrating the strength and range of the potential function  $v(r)$  correlating the motion of the diffusing coreactant with respect to the target molecule. The probability of moving through a field of sites in the vicinity of a multipolar target molecule is defined by

$$p(i/j) = \exp[-\beta(v_j - v_i)]/q_i \quad (1)$$

Here,  $p(i/j)$  is the probability of moving from site  $i$  to site  $j$  in the next step and

$$q_i = \sum_{j=1}^{\nu} \exp[-\beta(v_j - v_i)] \quad (2a)$$

$$\sum_{j=1}^{\nu} p(i/j) = 1 \quad (2b)$$

is the finite temperature, local partition function.

The potential  $v_k$  sensed by the diffusing atom or molecule at the site  $k$  characterized by a connectivity  $\nu$  is specified for each class of interactions considered. Thus, the otherwise random motion of the diffusing particle is modulated by the down-range (multipolar) correlations between the (diffusing) coreactant and the (stationary) target molecule. Short-range quantum-chemical effects operative in the immediate vicinity of the target molecule are taken into account in the lattice-statistical theory by imposing the constraint that upon arriving at a site which is a nearest-neighbor to the one at which the target molecule is located (i.e., one separated by a single lattice spacing  $R$  from the target molecule) the coreactant reacts with the target molecule in the next step.

For the case of interacting ionic species, the Boltzmann factor appearing in eq 1 may be expressed as

$$\begin{aligned} \exp[-\beta v] &= \exp[-Z_A Z_B [s(c,c)/R] l^{-1}] \\ &= \exp[-\mathcal{W}(c,c) l^{-1}] \end{aligned} \quad (3a)$$

where

$$s(c,c) = [1/(4\pi\epsilon_0)\epsilon_r] e^2/kT \quad (3b)$$

$$\mathcal{W}(c,c) = Z_A Z_B [s(c,c)/R] \quad (3c)$$

$$l = r/R \quad (4)$$

Here,  $k$  is Boltzmann's constant,  $e$  is the magnitude of the electronic charge,  $Z_i$  is the signed magnitude of the charge of species  $i$ ,  $\epsilon_0$  is the permittivity of free space, and  $\epsilon_r$  is the dielectric constant of the medium at temperature  $T$ . Thus, the influence of the governing potential on the underlying diffusion-reaction process is seen to be a function of the interplay of two critical lengths: the (reduced) length  $l$  which calibrates the spatial separation  $r$  of the coreactants in terms of the lattice metric  $R$ , and the Onsager length  $s$  which gives the distance at which the mutual electrical

(12) For a general discussion, see: (a) Montroll, E. W.; Shuler, K. E. *Adv. Chem. Phys.* **1958**, *1*, 361. (b) Nicolis, G.; Prigogine, I. *Self-Organization in Nonequilibrium Systems*; Wiley: New York, 1977. (c) Haken, H. *Synergetics*; Springer-Verlag: Heidelberg, West Germany, 1977. (d) Boulu, L. G.; Kozak, J. J. *Mol. Phys.* **1987**, *62*, 1449; **1988**, *65*, 193.

potential energy of a pair of singly-charged, point charges has the magnitude of the thermal energy.

Also considered in this study are the angle-averaged ion-dipole and angle-averaged dipole-dipole potentials. The Boltzmann factor for angle-averaged ion-dipole correlations is

$$\begin{aligned} \exp(-\beta v) &= \exp\{Z_A^2 \mu_B^2 [s(c, \mu) / R]^4 t^{-4}\} \\ &= \exp[W(c, \mu) t^{-4}] \end{aligned} \quad (5a)$$

with

$$s(c, \mu) = (1/3)^{1/4} [1 / (4\pi\epsilon_0\epsilon_r)] (ed/kT)^{1/2} \quad (5b)$$

and

$$W(c, \mu) = Z_A^2 \mu_B^2 [s(c, \mu) / R]^4 \quad (5c)$$

The corresponding expressions for angle-averaged dipole-dipole interactions are

$$\begin{aligned} \exp(-\beta v) &= \exp\{\mu_A^2 \mu_B^2 [s(\mu, \mu) / R]^6 t^{-6}\} \\ &= \exp[W(\mu, \mu) t^{-6}] \end{aligned} \quad (6a)$$

with

$$s(\mu, \mu) = (2/3)^{1/6} [1 / (4\pi\epsilon_0\epsilon_r)] (d^2/kT)^{1/3} \quad (6b)$$

and

$$W(\mu, \mu) = \mu_A^2 \mu_B^2 [s(\mu, \mu) / R]^6 \quad (6c)$$

Here,  $\mu_i$  is the magnitude of the dipole moment of species  $i$  and  $d$  is the unit dipole (in Debyes).

In this paper we quantify the extent to which the rate constant is changed when one "turns on" the intermolecular potential  $v(r)$  between a stationary target molecule and the diffusing coreactant. In general, the kinetic response of the system can be determined by solving numerically the stochastic master equation for the problem (see ref 12). Formally, a ratio of (diffusion-controlled) rate constants can be constructed and placed in correspondence with

$$\frac{k_D[v=v(r)]}{k_D[v=0]} \sim \frac{\langle n \rangle [v=0]}{\langle n \rangle [v=v(r)]} \quad (7)$$

The quantity  $\langle n \rangle$  on the right-hand side of eq 7 is the mean walklength of the diffusing coreactant A before reacting (here, irreversibly) with the stationary target molecule B<sub>s</sub> in a process subject to certain potential  $[v=v(r)]$  and spatial constraints (to be specified below). The theoretical basis for the correspondence in (7), as elaborated in refs 11 and 12, is that in the limit of large system size an exact relationship exists between the smallest eigenvalue  $\lambda_1$  of the stochastic master equation for the problem and the average walklength  $\langle n \rangle$

$$\langle n \rangle = \nu \lambda_1^{-1} \quad (8)$$

where  $\nu$  is the coordination (or valency) of the underlying lattice. The eigenvalue  $\lambda_1$  is related to the zero-mode relaxation time and to the effective rate constant for the process; relation 7 specified above is an intermediate consequence of (8).

For *neutral* reaction pairs, we denote by  $\langle n \rangle$  the mean number of steps before reaction (trapping) for a diffusing coreactant migrating in the reaction space *exterior to*, as well as *on*, the surface of the host particle with the target molecule anchored to the surface of the host. In calculating  $\langle n \rangle$ , excursions off the surface of the host particle, once the diffusing coreactant has encountered the surface, are still permitted. The quantity  $\langle n \rangle_T$  then refers to the average walklength before trapping for a diffusing coreactant but subject to the constraint that once the reactant hits the surface its subsequent (random) motion is restricted to the surface of the host particle, i.e. on encountering the surface, surface diffusion (only) of the diffusing coreactant is permitted. Recall that in the theory of finite Markov processes, the average  $\langle n \rangle$  corresponds to a stochastic process in which one averages over all possible trajectories of the diffusing particle from a *given* initial site, and then to construct the overall average  $\langle n \rangle$ , one considers all possible initial sites accessible to the diffusing

particle; in the present calculation, the only site assumed inaccessible initially to the diffusing coreactant is the site on which the target molecule is localized.

We next consider *multipolar* reaction pairs, i.e. we assume that the motion of the diffusing coreactant is guided by an intermolecular potential function (see eqs 3, 5, and 6) operative between the reactant pairs. The short-range chemical affinity between reaction pairs is taken into account by assuming that if the diffusing coreactant reaches a location which is a nearest-neighbor to the target molecule, reaction occurs on the next displacement of the coreactant. Then, quantities similar to the  $\langle n \rangle$  and  $\langle n \rangle_T$  above can be calculated but taking explicitly into account such short-range potential and quantum-chemical correlation effects, and these are designated here as  $\langle n \rangle_C$  and  $\langle n \rangle_{C,T}$ , respectively.

Returning now to the general eq 7, the following ratios of (diffusion-controlled) kinetic rate constants can be constructed on the basis of the calculation of  $\langle n \rangle$ ,  $\langle n \rangle_T$ ,  $\langle n \rangle_C$ , and  $\langle n \rangle_{C,T}$  using the theory of finite Markov processes. These ratios and the attendant limits are now specified:

$$R_1 = \frac{\langle n \rangle (W=0)}{\langle n \rangle_C (W)} \sim \frac{k_C(W)}{k(W=0)} \quad \text{with} \quad \lim_{\substack{W \rightarrow 0 \\ N \rightarrow \infty}} R_1 = \frac{\langle n \rangle (W=0)}{\langle n \rangle_C (W=0)} \quad (9)$$

$$R_2 = \frac{\langle n \rangle_C (W=0)}{\langle n \rangle_C (W)} \sim \frac{k_C(W)}{k_C(W=0)} \quad \text{with} \quad \lim_{\substack{W \rightarrow 0 \\ N \rightarrow \infty}} R_2 = 1 \quad (10)$$

$$R_3 = \frac{\langle n \rangle_C (W)}{\langle n \rangle_{C,T} (W)} \sim \frac{k_{C,T}(W)}{k_C(W)} \quad \text{with} \quad \lim_{\substack{W \rightarrow 0 \\ N \rightarrow \infty}} R_3 = \frac{\langle n \rangle_C (W=0)}{\langle n \rangle_{C,T} (W=0)} \quad (11)$$

where  $N$  is the total number of sites in the reaction space accessible to the diffusing coreactant (surface sites plus locations in the space exterior to the host particle) and  $W$  is the strength parameter of the governing potential function (see eqs 3, 5, and 6). The limiting values of the ratios noted above are a reflection of the fact that when the intermolecular strength parameter  $W$  goes to zero (i.e., the potential is "turned off") or, alternatively, when the reaction space exterior to the particle becomes sufficiently large (such that the diffusing coreactant tends to spend much of its time well away from the surface on which the target molecule is anchored) then an essentially simpler behavior results. Realization of these limits when  $W \rightarrow 0$  or  $N \rightarrow \infty$  provides an internal check on the numerical results generated, a point illustrated by results reported in the following section.

#### IV. Results

Recorded in Tables I-III are the results of calculations carried out to assess the relative importance of surface diffusion, down-range potential correlations between the diffusing coreactant A and the stationary target molecule B<sub>s</sub>, and short-range chemical interactions between the reactant pairs operative within a critical reaction radius  $r_c$ . As noted in section III, the latter effect can be taken into account by imposing the constraint that when, in its migration through the reaction space, the diffusing coreactant A finds itself at a distance  $r_c$  from the target molecule B<sub>s</sub>, reaction occurs in the next displacement; we set  $r_c = R$  (where  $R$  is the lattice spacing), in order to correlate results reported here with insights drawn from earlier work on surface (only) diffusion-reaction processes.<sup>11</sup>

To access the importance of surface diffusion, two series of calculations were carried out. In the first, we assumed explicitly that in its migration through reaction space, the diffusing coreactant can move on or off the surface of the host catalyst particle until, ultimately, an irreversible reaction occurs with the target molecule, the latter anchored on a surface site; discussion of the results obtained in this case (Tables I) will be presented first. Then, in a second series of calculations (Tables III), we impose the condition that the diffusing coreactant in its migration through the available reaction space, upon encountering the surface of the host catalyst particle for the first time, is constrained to move *on* the surface of the host (only) until reaction with the surface-bound

Table I. The Ratio  $k_C(W)/k(W=0)$  for a Target Molecule Anchored at Sites 1 and 3

potential	N	$\langle n \rangle(W=0)/\langle n \rangle_C(W) \sim k_C(W)/k(W=0)$				
		(a) Site 1				
		W = -9	W = -4	W = -2	W = -1	W = 0
ion-ion (attractive)	26	16.68	10.30	6.58	4.80	3.28
	124	36.08	19.35	10.48	6.71	3.88
	342	54.23	25.92	12.88	7.59	3.87
	728	65.42	29.21	14.00	7.89	3.74
ion-dipole (angle-averaged)	26	16.59	12.35	8.36	5.68	3.28
	124	23.29	15.50	10.35	6.99	3.88
	342	22.17	14.87	10.26	7.04	3.87
	728	19.30	13.36	9.52	6.69	3.74
dipole-dipole (angle-averaged)	26	13.86	10.96	7.94	5.56	3.28
	124	16.23	12.44	9.23	6.60	3.88
	342	14.84	11.71	8.96	6.55	3.87
	728	13.02	10.54	8.29	6.20	3.74
		W = +9	W = +4	W = +2	W = +1	W = 0
ion-ion (repulsive)	26	0.007	0.347	1.22	2.08	3.28
	124	0.001	0.168	0.949	2.01	3.88
	342	0.000	0.086	0.678	1.71	3.87
	728	0.000	0.055	0.535	1.51	3.74
		(b) Site 3				
		W = -9	W = -4	W = -2	W = -1	W = 0
ion-ion (attractive)	26	16.77	10.81	6.98	4.98	3.21
	124	26.49	14.38	8.23	5.42	3.16
	342	39.69	19.32	10.32	6.42	3.45
	728	49.49	22.65	11.60	6.90	3.45
ion-dipole (angle-averaged)	26	12.92	9.67	7.28	5.36	3.21
	124	13.59	9.64	7.06	5.17	3.16
	342	14.32	10.24	7.64	5.68	3.45
	728	14.01	10.18	7.68	5.72	3.45
dipole-dipole (angle-averaged)	26	10.08	8.37	6.76	5.16	3.21
	124	9.66	7.94	6.33	4.87	3.16
	342	10.00	8.33	6.79	5.32	3.45
	728	9.84	8.27	6.79	5.34	3.45
		W = +9	W = +4	W = +2	W = +1	W = 0
ion-ion (repulsive)	26	0.004	0.220	0.974	1.85	3.21
	124	0.001	0.113	0.729	1.62	3.16
	342	0.000	0.077	0.634	1.58	3.45
	728	0.000	0.053	0.519	1.44	3.45

Table II. First Moments  $\langle n \rangle$  of the Distribution Function for  $W = 0$ 

N	site 1			site 3		
	$\langle n \rangle(W=0)$	$\langle n \rangle_C(W=0)$	$\langle n \rangle_T(W=0)$	$\langle n \rangle(W=0)$	$\langle n \rangle_C(W=0)$	$\langle n \rangle_T(W=0)$
26	52.53944	16.03943	52.53944	71.20000	22.20000	71.20000
124	199.3488	51.42014	61.95222	184.2077	58.26856	78.52385
342	551.1100	142.4075	98.78807	479.9728	139.2057	115.0347
728	1189.831	317.9894	177.9112	1023.100	296.8961	194.0545

target molecule occurs. Both of these calculations, then, explore the role of surface diffusion at a more detailed level than that considered in ref 1.

Considering first the data reported in Tables I, we note that in the absence of down-range correlations ( $W = 0$ ) the enhancement of the ratio  $k_C(W)/k(W=0)$  of rate constants ranges from a factor of 3.3 when the diffusing coreactant is strictly confined to the surface of the host catalyst particle (the case  $N = 26$ ), through a maximum of 3.9 as the coreactant begins to take advantage of an expanded reaction space in the near environment of the host particle, to a value of 3.7 when the coreactant is permitted to drift farther and farther away from the host. This falloff in the ratio of rate constants with expansion in the available reaction space is certainly understandable since, as noted earlier, short-range chemical effects are operative only over distances  $\sim R$  in our formulation.

As one "turns on" the down-range biasing potential between the stationary target molecule and the diffusing coreactant, the enhancement in the ratio  $k_C(W)/k(W=0)$  of rate constants increases dramatically for attractive potentials, indeed by an order of magnitude (or more) as  $W$  increases. That the chemical affinity between reactant pairs can dominate the kinetics even in the presence of ion-ion repulsive interactions between coreactants is

seen clearly from the data reported for  $W > 0$ . In particular, for like-charged ion pairs with correlations scaled by values of the strength parameter  $W \sim 1$ , one still finds an effective enhancement in the rate of reaction, thereby reflecting the overriding importance of short-range chemical interactions within the spatial regime,  $r \leq r_c$ .

The enhancement in the ratio of rate constants for the shorter-range attractive potentials (the angle-averaged ion-dipole and the angle-averaged dipole-dipole potentials) as a function of the extent of the reaction space follows the same trends as that noted above for  $W = 0$ , viz. an increase in the ratio through a maximum followed by a falloff in the ratio as the reaction space accessible to the diffusing coreactant is expanded. This turnover in  $k_C(W)/k(W=0)$  is not yet realized for ion-ion attractive potentials for the reaction spaces considered in this study (a consequence of the persisting spatial influence of long-range correlations), whereas for repulsive ion-ion interactions the ratio simply falls off with systematic expansion of the reaction space.

The above trends describe the consequences as regards reaction efficiency of anchoring the target molecule at a surface site at a location maximally separated from the (eight) defect sites on the  $N = 26$  surface (Table Ia). On repositioning the target molecule at one of the defect sites and carrying through the

Table III. The Ratio  $k_{C,T}(W)/k_C(W)$  for a Target Molecule Anchored at Sites 1 and 3

potential	N	$\langle n \rangle_C(W)/\langle n \rangle_{C,T}(W) \sim k_{C,T}(W)/k_C(W)$					$\langle n \rangle(W=0)/\langle n \rangle_T(W=0)$
		(a) Site 1					
		W = -9	W = -4	W = -2	W = -1	W = 0	
ion-ion (attractive)	26	1.00	1.00	1.00	1.00	1.00	1.00
	124	0.996	1.14	1.41	1.66	1.92	3.22
	342	1.00	1.13	1.41	1.75	2.03	5.58
	728	1.00	1.10	1.35	1.67	1.94	6.69
ion-dipole (angle-averaged)	26	1.00	1.00	1.00	1.00	1.00	1.00
	124	1.13	1.31	1.50	1.70	1.92	3.22
	342	1.10	1.25	1.45	1.73	2.03	5.58
	728	1.07	1.19	1.36	1.64	1.94	6.69
dipole-dipole (angle-averaged)	26	1.00	1.00	1.00	1.00	1.00	1.00
	124	1.30	1.43	1.57	1.75	1.92	3.22
	342	1.23	1.34	1.51	1.77	2.03	5.58
	728	1.17	1.27	1.42	1.68	1.94	6.69
		W = +9	W = +4	W = +2	W = +1	W = 0	
ion-ion (repulsive)	26	1.00	1.00	1.00	1.00	1.00	1.00
	124	18.24	6.06	3.41	2.60	1.92	3.22
	342	175.8	17.86	5.76	3.52	2.03	5.58
	728	702.2	26.11	6.57	3.69	1.94	6.69
		(b) Site 3					
		W = -9	W = -4	W = -2	W = -1	W = 0	
ion-ion (attractive)	26	1.00	1.00	1.00	1.00	1.00	1.00
	124	1.04	1.23	1.47	1.68	1.97	2.35
	342	1.04	1.20	1.48	1.77	2.12	4.17
	728	1.02	1.15	1.39	1.69	2.01	5.27
ion-dipole (angle-averaged)	26	1.00	1.00	1.00	1.00	1.00	1.00
	124	1.32	1.47	1.63	1.79	1.97	2.35
	342	1.27	1.20	1.62	1.86	2.12	4.17
	728	1.20	1.33	1.50	1.74	2.01	5.27
dipole-dipole (angle-averaged)	26	1.00	1.00	1.00	1.00	1.00	1.00
	124	1.48	1.57	1.70	1.84	1.97	2.35
	342	1.43	1.54	1.70	1.91	2.12	4.17
	728	1.33	1.42	1.57	1.79	2.01	5.27
		W = +9	W = +4	W = +2	W = +1	W = 0	
ion-ion (repulsive)	26	1.00	1.00	1.00	1.00	1.00	1.00
	124	15.10	4.57	2.93	2.38	1.97	2.35
	342	82.62	13.13	5.12	3.30	2.12	4.17
	728	354.5	25.43	6.53	3.61	2.01	5.27

calculation of  $k_C(W)/k(W=0)$  as a function of the strength/range of governing potential function and the spatial extent of the available reaction space, one generates the data set listed in Table Ib. Upon comparing values of  $k_C(W)/k(W=0)$  for corresponding values of  $(W,N)$  one finds that the enhancement in the ratio of rate constants is systematically *smaller* (in 64 of the 68 cases considered) when the target molecule is positioned at a defect site.

In order to sort out the role of down-range potentials per se in influencing the efficiency of the underlying diffusion-reaction process, one can examine the ratio  $k_C(W)/k_C(W=0)$ . Specifically, the calculation of  $k_C(W)$  can be "normalized" with respect to a strictly random process ( $W=0$ ) which is delimited only by the constraint that when the diffusing coreactant is within the critical distance  $r_c$  of the stationary target molecule, an irreversible reaction occurs in the next displacement of the coreactant. Again, the process is defined assuming always that the coreactant in its migration through the reaction space can move on or off the surface of the host particle until the irreversible reaction between reaction pairs actually occurs. For each setting of  $N$ , the (constant) factor by which results reported in Table Ia,b are to be rescaled can be determined from the data reported in Table II. One finds that if the short-range chemical affinity between reaction pairs is assumed to be invariant, the ratio  $k_C(W)/k_C(W=0)$  of rate constants is a factor  $\sim 3.8$  smaller than the ratio calculated earlier [ $k_C(W)/k(W=0)$ ], with all qualitative trends noted in our discussion of Table Ia,b (necessarily) preserved.

The results reported in Table Ia,b can now be contrasted with those reported in Tables IIIa,b where we consider explicitly the effect on the kinetics of restricting the motion of the diffusing coreactant to the surface of the host catalyst particle upon first encounter. This "entrainment" or "tracking" constraint on the motion of the diffusing coreactant is a realization of the effect

referred to as "reduction dimensionality", a concept first developed in a seminal article by Adam and Delbrück.<sup>7,8</sup> Here, we calculate the ratio  $k_{C,T}(W)/k_C(W)$ , again as a function of the character, range, and strength of the down-range potential operative between reactant pairs, while keeping constant the short-range chemical affinity between coreactants, all as a function of the spatial extent of the available reaction space.

On examining the results displayed in Tables III, one finds that, corresponding to a fixed setting of the control parameters  $(N,W)$ , entrainment of the diffusing coreactant on the surface upon first encounter plays a relatively more important role in influencing the kinetics the shorter the range of the biasing, attractive potential. From Tables I and III, whereas the long-range ion-ion attractive potential influences dramatically the efficiency of the underlying diffusion-reaction process in the *absence* of "surface entrainment", reduction of dimensionality is of less consequence for coulombically-interacting reactant pairs than for reactants correlated by the shorter-range (angle-averaged) ion-dipole and (angle-averaged) dipole-dipole interactions. In fact, the effect of "tracking" is most pronounced for *repulsive* ion-ion interactions, where entrainment of the diffusing coreactant on the surface of the host catalyst particle can increase significantly the possibility of reaction between like-charged ion pairs simply by "concentrating" the reactants on the surface.

For attractive potentials, the "concentration effect" induced by imposing the constraint of "reduction of dimensionality" on the motion of the diffusing coreactant plays a relatively more important role in influencing the kinetics if the target molecule is anchored at a defect site on the surface of the host particle (compare Tables IIIa and IIIb). For repulsive ion-ion interactions, the opposite situation pertains, i.e., somewhat greater enhancements in the ratio  $k_{C,T}(W)/k_C(W)$  are found when the target

Table IV. The Ratio  $k_C(W)$ (interfacial)/ $k_C(W)$ (homogeneous)

potential	N	$\frac{\langle n \rangle_C(W)$ (homogeneous)/ $\langle n \rangle_C(W)$ (interfacial) ~ $k_C(W)$ (interfacial)/ $k_C(W)$ (homogeneous)				
		W = 0	W = -1	W = -2	W = -4	W = -9
ion-ion (attractive)	26	0.341	0.400	0.458	0.562	0.720
	124	0.668	0.674	0.689	0.737	0.836
	342	0.803	0.806	0.815	0.841	0.888
	728	0.850	0.864	0.878	0.902	0.922
ion-dipole (angle-averaged)	26	0.341	0.391	0.452	0.552	0.684
	124	0.668	0.645	0.646	0.670	0.716
	342	0.803	0.800	0.805	0.815	0.824
	728	0.850	0.868	0.884	0.899	0.906
dipole-dipole (angle-averaged)	26	0.341	0.374	0.421	0.493	0.585
	124	0.668	0.640	0.635	0.645	0.668
	342	0.803	0.800	0.804	0.810	0.819
	728	0.850	0.867	0.881	0.895	0.906
ion-ion (repulsive)	26	0.341	0.282	0.227	0.135	0.027
	124	0.668	0.663	0.652	0.594	0.385
	342	0.803	0.802	0.795	0.769	0.668
	728	0.850	0.839	0.828	0.808	0.741

molecule is localized on a site maximally removed from the surface defect sites.

### V. Correspondence with the Astumian-Schelly Analysis

Having sorted out the relative importance of surface diffusion and down-range potential correlations between the diffusing co-reactant and the stationary target molecule for interfacial reactions per se, we now take up the specific problem dealt with by Astumian and Schelly. We examine whether for diffusion-controlled reactions "reduction of dimensionality" induced by localization of the reactant B on the surface of a host particle leads to a decrease in the specific rate when compared with the same reaction taking place in homogeneous solution. The lattice-statistical formulation of the latter problem is straightforward and, in fact, some of the data needed for the present analysis have already been published.<sup>11</sup> To proceed, we consider the target molecule B to be positioned at the centrosymmetric location in a reaction space, the latter defined to be a cubic lattice characterized by the same metric as that defining the problem posed earlier, and then recalculate the various moments  $\langle n \rangle$ . In order to preserve the normalization condition of Astumian and Schelly (the essence of which is that the bulk concentration of the reactants is kept constant in the transition from the homogeneous to heterogeneous case), we choose system sizes (nearly) coincident with those considered in the preceding section; here, we set  $N = 27, 125, 343,$  and  $729$ . The difference in each case between the  $N$ 's here and those of the previous section is one lattice site, a difference which results in a change in the  $\langle n \rangle$ 's calculated for the homogeneous case of a few "displacements", with convergence as  $N \rightarrow \infty$ .

Let us denote by  $\langle n \rangle_C(W)$ (interfacial) the mean number of displacements of a diffusing coreactant A before an irreversible reaction occurs with a stationary target molecule  $B_s$  localized at a surface site (1) of a host particle; as before, surface diffusion will be permitted as well as excursions of the coreactant A on and off the surface before the irreversible reaction  $A + B_s \rightarrow C_s$  occurs. If, on the other hand, the coreactant A "sticks" to the surface of the host particle upon first encounter, subsequently diffusing on the surface until reacting (eventually) with  $B_s$ , we will denote this moment  $\langle n \rangle_C(W)$ (interfacial,tracking). The corresponding moment in the homogeneous case, i.e., the mean number of lattice steps before irreversible reaction occurs with a centrally-disposed target molecule B, is designated  $\langle n \rangle_C(W)$ (homogeneous). The ratios of interest are then

$$\frac{\langle n \rangle_C(W)$$
(homogeneous)}{\langle n \rangle\_C(W)(interfacial)} \sim \frac{k\_C(W)(interfacial)}{k\_C(W)(homogeneous)} \quad (12)

and

$$\frac{\langle n \rangle_C(W)$$
(homogeneous)}{\langle n \rangle\_C(W)(interfacial,tracking)} \sim \frac{k\_C(W)(interfacial,tracking)}{k\_C(W)(homogeneous)} \quad (13)

Table V. The Ratio  $k_C(W)$ (interfacial,tracking)/ $k_C(W)$ (homogeneous)

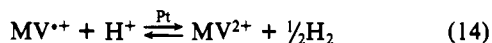
potential	N	$\frac{\langle n \rangle_C(W)$ (homogeneous)/ $\langle n \rangle_C(W)$ (interfacial,tracking) ~ $k_C(W)$ (interfacial,tracking)/ $k_C(W)$ (homogeneous)			
		W = -1	W = -2	W = -4	W = -9
ion-ion (attractive)	26	0.400	0.458	0.562	0.720
	124	1.155	0.970	0.842	0.832
	342	1.409	1.153	0.950	0.889
	728	1.445	1.183	0.989	0.924
ion-dipole (angle-averaged)	26	0.391	0.452	0.552	0.684
	124	1.098	0.967	0.876	0.812
	342	1.385	1.165	1.016	0.908
	728	1.421	1.204	1.066	0.971
dipole-dipole (angle-averaged)	26	0.374	0.421	0.493	0.584
	124	1.118	0.999	0.920	0.867
	342	1.421	1.217	1.088	1.004
	728	1.457	1.254	1.133	1.057
ion-ion (repulsive)	26	0.282	0.227	0.135	0.027
	124	1.724	2.227	3.597	7.022
	342	2.824	4.582	13.73	117.5
	728	3.095	5.443	21.09	520.2

The results of calculating the ratios in (12) and (13) are recorded in Tables IV and V, respectively. It is plain from the results reported in Table IV that the ratio of rate constants,  $k_C(W)$ (interfacial)/ $k_C(W)$ (homogeneous), is less than unity for all cases considered, i.e., all reaction spaces and all potential correlations. Qualitatively, then, these results (and the attendant conclusions) are in complete accord with the theoretical predictions of Astumian and Schelly,<sup>1</sup> i.e., the geometric effects of reduction of dimensionality lead to a decrease in the specific rates. In fact, since our analysis was carried out explicitly taking into account two factors neglected in the Astumian-Schelly analysis (namely, the influence of down-range potential correlations and the role of surface diffusion), it can be argued that our results strengthen the overall conclusion reached by these authors.

The results reported in Table V, i.e., those for the ratio  $k_C(W)$ (interfacial,tracking)/ $k_C(W)$ (homogeneous), are chiefly of interest in quantifying the enhancement in rate (relative to the homogeneous case) when the coreactant A is restricted to the surface of the host particle upon first encounter. Although, relative to the data reported in Table IV for corresponding cases, the ratio increases systematically for all potentials considered, the really dramatic enhancements occur when repulsive potentials are studied, viz. ion pairs charged both positive or both negative. Whereas there is clear evidence that for attractive potentials reduction of dimensionality can lead to an enhancement in rate relative to the homogeneous case when the tracking "boundary

condition" is imposed, for repulsive potentials the calculated ratios are so large that it seems safe to conclude that reduction in dimensionality can play a dominant role in enhancing the progress of a reaction between like-charged ion pairs.

As a possible illustration of this latter case, consider the reaction



the colloidal platinum-mediated production of hydrogen from water using the electron-acceptor species, methyl viologen (MV). This reaction has been studied in considerable detail by using various experimental techniques,<sup>13-21</sup> and a traditional diffusion-reaction analysis of the experimental effects found has been reported.<sup>22,23</sup> Left unanswered in refs 22 and 23 was the question of how/why a reaction between positively-charged species could occur at all on the surface of a host colloidal catalyst particle (Pt). That is, the (detailed) mechanism proposed in refs 22 and 23 simply *assumed* that like-charged species could coexist in the adsorbed state on Pt.

In qualitative terms, the colloidal Pt catalyst is viewed as a "microelectrode", acting as a "storage pool" for electrons. If, then, one argues that the negatively-charged Pt particle modulates the (significant) Coulombic repulsions between reactant species, so that reactants are entrained in the near environment of the surface, then the lattice-statistical results reported in Table V suggest that a reaction, represented (overall) by eq 14, can be enhanced significantly relative to the homogeneous system case by "reduction of dimensionality".

In analyzing reaction 14, or any other surface-mediated process, it is important to keep in mind the strengths and weaknesses of the theoretical approach taken in this paper. Like any calculation based on a "model", the present study has a number of shortcomings. Here, the reaction space has been designed to consist of a series of concentric shells, with a finite number of lattice sites

overall, and with the coreactant (random walker) constrained to move on these lattice sites (only). As a direct consequence of this spatial structure, the interaction between the moving coreactant and the colloidal carrier particle has been modeled, in effect, as an on/off potential (i.e., the molecule is constrained to move either on the particle surface or on a concentric lattice shell). Secondly, it is questionable whether the short-range interaction between the reactants A and B can be represented using a "cage" or "pit" model (reaction occurring on the next displacement when a nearest-neighbor site is reached) and whether the down-range interaction between A and B can be modeled using a centrosymmetric  $1/r^2$ ,  $1/r^4$ , or  $1/r^6$  potential that is unaffected by the presence of the carrier particle at some of the sites near the B molecule. Finally, in considering the relevance of the model's predictions to actual experimental situations, it is clear that some of the most interesting problems (molecule-molecule nonreactive interactions, electron transfer, energy transfer) cannot be represented very realistically using a  $1/r^n$  potential scaling the interaction between coreactants A and B.

Of course, assumptions also have to be made in implementing a theoretical approach based on a continuum model, for example, a diffusion-reaction equation of the Fickian type; solution of this partial differential equation for all but the simplest geometries, initial conditions, and potentials is a major computational problem, so that the range of physical situations that can be studied can be rather limited. However, what is important in developing a model is that the assumptions of the model can be systematically relaxed so that subsequent calculations can isolate the importance of constraints on its generality. This is, of course, the great virtue of the lattice-statistical approach presented here inasmuch as each assumption (see, for example, the preceding paragraph) can be dealt with separately. The price one pays is that a further parametrization of the model is necessary at each stage to bring the model in closer contact with reality. For example, in our study, the orientation of adsorbed molecules with respect to each other has been neglected; we utilized (only) the angle average of the  $1/r^n$  potential. However, the generalization can easily be carried out and, in fact, we have already performed a series of calculations (to be reported later) in which this restriction has been lifted, i.e., the effect of angular orientation of A and B on the dynamics has been considered explicitly and the consequences examined.

Given the difference in approach taken by Astumian and Schelly (i.e., a continuum approach based on a Fickian diffusion-reaction equation) and the present authors (a lattice approach implemented using the theory of stochastic processes), what is important here is that in those regimes where the predictions of the two models can be compared there is correspondence. The further significance of the present study is that when one relaxes some of the assumptions made by Astumian and Schelly, new features emerge and more general conclusions can be drawn on the importance of correlation effects and reduction of dimensionality on interfacial reactions.

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