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Report on the Second International Workshop on Random Sequential Adsorption. Theory and Experiment

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After a most successful workshop on this topic last year in Orsay,(1) random sequential adsorption or addition (RSA) has again formed the basis of an international meeting. Following the recent appearance of a couple of reviews on the subject,(2,3) it is perhaps unnecessary to introduce it, other than to emphasize the strong nonergodicity and highly non-Markovian nature of the process, its intrinsically interesting properties such as jamming and infinite memory, the nontriviality of many results in one dimension which are useful in systems of higher dimensionality, and its demonstrated applicability to many natural processes, which are motivating a growing number of extensions and generalizations to basic RSA, such as addition in the presence of electrostatic or gravitational fields, and the adsorption of soft or deformable particles.

In this year's workshop, three themes in particular emerged: the relationship of RSA to other processes in statistical and quantum mechanics, a relationship which cannot but lead to fresh mutual insights; the growing number of experiments carried out on well-characterized systems with a good signal/noise ratio, which are enabling theories to be tested much more rigorously then hitherto, as well as revealing unexpected new phenomena; and many novel extensions and generalizations of basic RSA.

Tarjus (Paris) showed that suitably generalized techniques, especially the distribution function approach, from the statistical mechanics of liquids are useful in studying RSA, especially in relating macroscopic (e.g., the

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rate of adsorption) to microscopic (e.g., the pair correlation function of adsorbed particles) features. This strategy was illustrated by Boyer (Paris), who presented some exact results for the random sequential adsorption of hard rods onto a one-dimensisonal line. In higher dimensions an approximate integral equation was derived from a Kirkwood–Salsburg-like hierarchy and solved via an iterative procedure. Viot (Paris) investigated the configurations of particles added by a generalized procedure encompassing ballistic deposition as well as RSA. Close to saturation, geometrical analysis of the configurations provides analytical formulas for the asymptotic kinetics.

Stinchcombe (Oxford) set adsorption–evaporation models of k-mers in the wider context of stochastic exclusion processes, and showed how these are related to quantum spin systems. Approaches in the theory of quantum spin models can then be used to show the existence of slow dynamic behavior in adsorption–evaporation systems(4) and to obtain some exact solutions.(5) Time-dependent operator algebra techniques constructed recently for the stochastic systems(6) then have implications for related spin systems such as the Heisenberg model.

Analogies with quantum mechanics were also promoted by Yellin (MIT and University of California-Santa Cruz), who drew parallels between exact transfer matrices for "one -way" filling (RSA) or removal (desorption) processes—including cooperative and "hot" (particles allowed to move on the surface) RSA and adsorption of arbitrary mixtures of k-mers—and "two-way" exact Schrödinger propagators for particles on a spatial lattice. For example, the quantum lattice propagator for a uniform field corresponds in this sense to the transfer matrix for $D=1$ dimer RSA. There are interesting implications for many-body problems. The lattice Green's function for a single particle propagating (in imaginary time) in an $(N-1)$-dimensional cube with (discrete) reflecting boundary conditions has for its stochastic analog symmetric hopping of N hard-core lattice particles in one dimension with periodic boundary conditions. This suggests a simple physical interpretation of the operator-algebraic results of Stinchcombe and Schütz(6) for the N-excitation contribution to the time-dependent Green's function, $\exp(-Ht)$, of the $s=1/2$ Heisenberg spin chain.

Several contributions dealt with new numerical simulation results. Talbot (Purdue) reviewed recent progress in understanding reversible (not thermodynamic reversibility, in the sense of returning to an initial state) kinetics. A density expansion derived using the distribution function approach could accurately describe simulation results for the adsorption of monosized disks only in the low-to-intermediate-coverage regime. It is apparently not possible to solve exactly the general adsorption–desorption problem, even in one dimension; some progress has been made for an infinitely small desorption rate of rods on a line, in which case the system evolves initially exactly according to the RSA kinetics until a jammed configuration results.(7) In two dimensions, infinitely slow desorption leads ultimately to an ordered close-packed configuration. Multicomponent adsorption and desorption have also been examined.(8) An important extension is to consider a *time-dependent desorption rate*. This behavior is expected if, for example, an adsorbed protein undergoes significant denaturation on the surface. The kinetics is conveniently described with the aid of a memory function representing the fraction of particles remaining on the surface after a given time interval.

Surface restructuring is another important extension of RSA which includes not only particles moving on the surface, but also their deformation or spreading. It is attracting more and more interest, and is believed to occur commonly in the case of protein adsorption, although few examples have been adequately characterized. Numerical simulations of RSA in which particles are allowed to spread was reported by van Tassel (CECAM). In this model, macromolecules (modeled as disks of diameter s_a) adsorb onto a surface at a rate k_a. Once adsorbed, the particles spread symmetrically and discretely to a larger diameter s_b at a rake k_s. It was observed that the saturation coverage of spread particles decreases, while that of unspread particles increases with spreading magnitude. The dependence was most pronounced for small spreading: the derivative of the surface coverage of both spread and unspread particles with respect to $S = s_b/s_a$ diverges logarithmically when $S \to 1$. The coverage of unspread particles became nonmonotonic in time for certain values of S and k_s/k_a.(9)

Viot (Paris) presented simulations of an irreversible cooperative sequential addition model in which particles are dropped randomly and adsorb on a surface either directly with a probability $1 - p$ if no overlap with already adsorbed particles occurs, or after following the path of steepest descent on previously deposited particles with a probability p; any particle trapped in an elevated position after rolling is rejected.(10) A tuning parameter $a = p/(1 - p)$ controls the relative contribution of the two deposition mechanisms. Results were compared with a third-order density expansion for the pair density function and for the rate of deposition, which was adequate for small and moderate values of a. For $a = 3.0$, a percolation transition is observed, and the critical properties of this system were investigated, various techniques, such as the Monte Carlo renormalization group theory and finite-size scaling, being applied to obtain the static critical exponents. Percolative properties were also investigated using Monte Carlo techniques by Leroyer (Bordeaux), in this case of highly anisotropic particles (line segments) adsorbed on a square lattice. As the segment length grows, the percolation threshold decreases, passes through a minimum, and then increases slowly for large segments. This nonmonotonic behavior is apparently the consequence of a structural change of the percolation clusters induced by an effect of alignment of the segments. An accurate measurement of the exponent ν and of the fractal dimension D of the incipient infinite percolating cluster for several segment lengths showed that these systems belong to the universality class of random site percolation(11)

Family (Emory) presented results of a detailed study of the scaling and percolation behavior of the submonolayer in a simple adsorption–diffusion model of molecular beam epitaxy, in which atoms are randomly deposited on a lattice and then allowed to diffuse; individual atoms become immobile when they attach themselves to an island of a critical size i. Four distinct scaling regimes were found, corresponding to a low-coverage (nucleation) regime, an intermediate-coverage regime, an aggregation regime, and coalescence and percolation regimes. The scaling of the island size distribution, island density, monomer density, structure factor, and pair correlation function was studied as a function of the coverage and the diffusion rate/deposition rate ratio, and the relationship of the morphology and distribution of islands to the magnitude of i discussed.

Given the analytical intractability of some of the novel extensions of RSA now under consideration, enthusiasm for numerical simulations is highly understandable. Nevertheless, progress is still being made in enlarging the realm of exact solutions. Baram (Soreq NRC) presented work extending previous results for RSA on a lattice strip consisting of two infinite rows to a $3 \times \infty$ strip. Exact solutions exist for these quasi-one-dimensional lattices, which exhibit some features typical of two-dimensional systems.(12)

Among the papers dealing with experimental results, Mann (Strasbourg) presented her work to date on a detailed and careful study of the optical properties of reflecting surfaces covered with colloidal (radius 0.05–0.5 μm) latex particles. A relatively simple model based on Mie theory was shown to well-characterize the reflectance of the surface, and to be able to yield particle size and coverage from experimental reflectance data. This work will now be extended to kinetic adsorption studies.

Reflectometry was also the basis of work reported by Kurrat (Zürich) on the adsorption of a protein, albumin, onto planar metal oxide optical waveguides. The adsorption shows the phenomenon of progressive irreversibility. Detailed kinetic analysis showed that a model with two distinct adsorption states, reversible and irreversible, each only accessible from the solution and presumed to correspond to different orientations of the albumin at the surface, gave better agreement with the experimental data than a model in which the reversible form changes to the irreversible form at the surface.(13) Hence the occupancy of the surface progresses toward the irreversible form through the desorption of reversibly adsorbed proteins which can diffuse and rotate in the solution, and readsorb in the irreversible orientation.

The same experimental technique was used by Ramsden (Basel) to investigate the interaction of proteins differing from each other by only a few amino acids with a variety of surfaces. A first example concerns the proteins called 1A2 and 2B4 belonging to the cytochrome P450 superfamily, which interact with bilayer lipid membranes via a short tail of nonpolar amino acids. At a solution concentration of 0.3 nmol/cm^3 and conditions under which adsorption to lipid bilayers (deposited on optical waveguides using the Langmuir–Blodgett technique) is irreversible, 2B4 shows the expected RSA behavior, but 1A2 shows Langmuir behavior., i.e., the occupied fraction of the surface θ varies according to $d\theta/dt \propto 1-\theta$, a result which is interpreted as evidence for the adsorbed 1A2 molecules being present only as compact clusters, such that the excluded area is small compared with the occupied area. Increasing the concentration of 1A2 tenfold converts the behavior into RSA, whereas decreasing the concentration of 2B4 60fold converts it into Langmuir adsorption. This result is consistent with the clusters arising by lateral diffusion of adsorbed molecules. A second example dealt with two mutants of the related protein cytochrome b5 from which the nonpolar tails had been removed enzymatically, adsorbing at waveguides with modified surfaces, e.g., with layers of polyallylamine or stearic acid, with surface charge densities of $+350$ and $-170\,\mu$C/cm^2, respectively. The adsorption is dominated by electrostatic forces. Detailed analysis of the kinetic data requires the change in the net charge of the protein as it enters the region of extremely high or low pH prevailing in the immediate vicinity of these highly charged surfaces to be taken into account.

Ball (Strasbourg) reported on extensive studies of homomolecular protein exchange processes using radioactively labeled immunoglobulin molecules. It is apparently paradoxical that the exchange rate is much faster than the desorption rate. In two sets of independent experiments, the existence of exchange was confirmed, and the exchange was shown to be first order with respect to the bulk molecule concentration, with a rate constant of 1.6 ± 0.3 dm^3 mol^{-1} sec^{-1}.(14) A detailed study was also made of the adsorption of albumin onto a latex bearing a charge of $-0.68\,\mu$C cm^{-2}. The charge arises from the presence of randomly distributed sulfate groups, to which the albumin binds. By comparing the predictions of a random site model with the experimentally determined jamming coverage (11%), it was inferred that each adsorbed albumin molecule is bonded to two sulfate sites.

While investigating the adsorption of large (radius 2.2 μm) latex particles on silica, Senger (Strasbourg) showed how an apparently innocuous discrepancy led to a profound new insight into the connection between the RSA process and pair correlation functions. The number of adsorbed particles was measured by photographing small areas a of the silica surface through an optical microscope. It was observed that the variance σ^2 of the number n of particles in a photograph was not proportional to a and $\langle n \rangle$, as expected for a Poisson process, but showed a dramatic decrease at large values of $\langle n \rangle$. Analysis based on the relation between the radial distribution function and the variance showed that it could be written as the sum of three contributions, proportional to a, $a^{1/2}$, and a^0, providing good agreement with the observations.

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REFERENCES

1. J. Talbot and G. Tarjus, Report of the CECAM workshop "The random sequential adsorption process and its generalizations," Orsay, France, June 1993 (unpublished).
2. M. C. Bartelt and V. Privman, *Int. J. Mod. Phys. B* **5**:2883 (1991).
3. J. W. Evans, *Rev. Mod. Phys.* **65**:1281 (1993).
4. M. Barma, M. D. Grynberg, and R. B. Stinchcombe, *Phys. Rev. Lett.* **70**:1033 (1993).
5. M. D. Grynberg, T. J. Newman, and R. B. Stinchcombe, *Phys. Rev. E* **50**:957 (1994).
6. R. B. Stinchcombe and G. M. Schütz, Oxford preprint OUTP-94-23SS (1994).
7. X. Jin, G. Tarjus, and J. Talbot, *J. Phys. A: Math. Gen.* **27**:L195 (1994).
8. J. Talbot, X. Jin, and N.-H. L. Wang, *Langmuir* **10**:1663 (1994).
9. P. R. van Tassel, P. Viot, G. Tarjus, and J. Talbot, *J. Chem. Phys.* **101**:7064 (1994).
10. G. Tarjus, P. Viot. H. S. Choi, and J. Talbot, *Phys. Rev. E* **49**:3239 (1994).
11. Y. Leroyer and E. Pommiers, *Phys. Rev. B* **50**:2795 (1994).
12. A. Baram and D. Kutasov, *J. Phys. A: Math. Gen.* **27**:3683 (1994).
13. R. Kurrat, J. J. Ramsden, and J. E. Prenosil, *J. Chem. Soc. Faraday Trans.* **90**:587 (1994).
14. V. Ball, P. Huetz, A. Elaissari, J.-P. Cazenave, J.-C. Voegel, and P. Schaaf, *Proc. Natl. Acad. Sci. USA* **91**:7330 (1994).