TITLE of the contribution to the book *Trends in Statistical Physics:*

Dynamics of Nonequilibrium Processes: Surface Adsorption, Reaction-Diffusion Kinetics, Ordering and Phase Separation

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INTRODUCTION

This short review covers a wide selection of topics from a multidisciplinary area of dynamics of nonequilibrium systems in physics, chemistry, biology. Theoretical models of colloid particle and protein deposition and adhesion at surfaces, accompanied by relaxation processes, of reaction kinetics with and without diffusion, of phase coarsening and nucleation, will be surveyed. The unifying feature of these systems is the importance of fluctuations and many-body, multiparticle collective effects, in determining the dynamical behavior which is typically nonclassical.

Recently a range of methods has been employed to study models of these phenomena, including exact solutions, analytical and asymptotic methods, and large-scale numerical simulations. The review is largely devoted to summary of several recent advances and provides a guide to the literature. No detailed derivations are given; our aim is to overview the field emphasizing the unifying aspects of various phenomena surveyed and list some open research directions.

Most actual applications of the methods of statistical physics to practical problems as well as to scientific experiment interpretation involve time-dependent processes. Generally, nonequilibrium statistical physics has developed slower than equilibrium theories. However, recently there has been a resurgence of interest and activity, as well as reports of new advances, in the field of nonequilibrium statistical mechanical systems.

The reason for this recent progress has been several-fold. Firstly, guided by experience with the equilibrium case, attention was focussed on lattice models with stochastic dynamics, rather than on direct examination of phenomenological, continuum evolution equations popular in "traditional" studies of reaction-diffusion and nucleation phenomena. Secondly, emphasis has been put on identifying those regimes where the system's behavior is dominated by nonclassical, non-mean-field fluctuations. This has lead to consideration of rather low dimensions, one (chains) and two (surfaces).

Finally, theoretical advances have been stimulated by the fact that these low-dimensional models were actually relevant to experimental studies of surface deposition of colloidal particles and proteins, heterogeneous catalysis, reaction kinetics of excitations in polymer chains, interactions of biological molecules such as DNA with small molecules, etc. This new interdisciplinary horizon of applications has boosted research and brought in ideas, nomenclature, and emphases from a diverse scientific background in biology, chemistry, physics.

SURFACE DEPOSITION

Random Sequential Adsorption Models

Random sequential adsorption (RSA) models have been studied extensively due to their relevance to deposition processes on surfaces (reviews by Bartelt & Privman 1991, Evans 1993). The depositing particles are represented by hard-core extended objects; they are not allowed to overlap. In monolayer deposition of colloidal particles and macromolecules (Feder & Giaever 1980, Onoda & Liniger 1986, Ryde et al. 1991, 1992, Song & Elimelech 1993) one can further assume that the adhesion process is irreversible.

However, recent experiments on protein adhesion at surfaces (Ramsden 1992, 1993) indicate that in biomolecular systems effects of surface relaxation, due to diffusional rearrangement of particles, are observable on time scales of the deposition process. The resulting large-time coverage is denser than in irreversible RSA and in fact it is experimentally comparable to the fully packed (i.e., locally semi-crystalline) particle arrangement.

Irreversible RSA has been studied extensively by many authors (reviews by Bartelt & Privman 1991, Evans 1993). The most interesting aspect of such processes is the power-law large-time convergence to the jamming coverage in continuum off-lattice deposition. This slow time-dependence, as opposed to exponential convergence in lattice deposition, is due to gaps arbitrary close in size (and shape) to that of the depositing particles and therefore reached with low probability. Asymptotic arguments describe this rare-event dominated process (Pomeau 1980, Swendsen 1981). Crossover from lattice to continuum can be also elucidated analytically (Privman et al. 1991b).

Diffusional and Detachment Relaxation

Studies of RSA with diffusional relaxation by analytical means encounter several difficulties associated with collective effects in hard-core particle systems at high densities (such as, for instance, phase separation), and with the possibility, in certain lattice models, of locally "gridlocked" vacant sites. The latter effect may actually prevent full coverage in some models; this matter remains an open problem at this time.

Both difficulties are not present in $1d$: there are no equilibrium phase transitions (in models without deposition), traces of which might manifest themselves as collective effects in $d > 1$ deposition with diffusion (Wang et al. 1993a), and furthermore diffusional relaxation leads to simple hopping-diffusion interpretation of the motion of vacant sites in $1d$ which recombine to form larger open voids accessible to deposition attempts. As a result, both accurate numerical studies and their analytical interpretation have been possible in $1d$ (Nielaba & Privman 1992a, Privman & Barma 1992, Privman & Nielaba

1992).

For $d > 1$ models, a low-density-expansion approximation scheme was applied (Tarjus et al. 1990) to off-lattice deposition of circles on a plane, accompanied by diffusional relaxation. However, no analytical studies of the high-density behavior and the associated collective effects, were reported for circles.

Recently, rather extensive numerical simulations were reported (Wang et al. 1993a), of the RSA process with diffusional relaxation, for the $2d$ lattice hard-square model (review by Runnels 1972), i.e., the square-lattice hard-core model with nearest neighbor exclusion. This model is well studied for its equilibrium phase transition (review by Runnels 1972) which is second-order with disordered phase at low densities and two coexisting ordered phases, corresponding to two different sublattice particle coverage arrangements at high densities. Another simplifying feature of the hard-square model is that the only possible gridlocked (locally frozen) vacancies are parts of domain walls (Wang et al. 1993a). As a result the coverage reaches the full crystalline limit at large times, by a process of diffusional domain wall motion leading to cluster growth reminiscent of quenched binary alloys and fluids at low temperatures (Gunton et al. 1983, Mouritsen 1990, Sadiq & Binder 1984).

For 2×2 lattice squares, extensive numerical results were reported as well (Wang et al. 1993b). However, their interpretation is still incomplete. Indeed, 2×2 lattice squares form for large times and on periodic lattices of even dimensions, a state with frozen single-site gridlocked vacancies. Diffusional interpretation of the relaxation processes is less apparent, and many open questions remain to be answered by future more extensive numerical studies; see Wang et al. (1993b) for details.

Relaxation by detachment is much more difficult to quantify experimentally, at least in colloidal systems, because there are many types of adhesion states of particles, each detaching differently. However, some interesting theoretical aspects present themselves to investigation. Indeed, similar to diffusional relaxation the late stages will be dominated by recombination of smaller empty area regions into larger ones which can accommodate arriving particles. Power-law tails are expected in some regimes. Systematic theoretical studies are very recent (Chen et al. 1993, Dhar & Barma 1993, Krapivsky & Ben-Naim 1993); the field is still widely open.

Multilayer Deposition

Multilayer deposit formation is a rather wide field of research with most theoretical activity recently focussed on growing interface fluctuations. However, in colloid deposition experiments (Ryde et al. 1992, Song & Elimelech 1993; see also Ryde et al. 1991) one is frequently interested in the regime where the amount deposited is limited, and the dynamics of the formation of amorphous deposits is RSA-like, i.e., governed by a combination of exclusion effects (due to particle size) and screening. Theoretical progress has proved difficult and the available results were either mean-field theories (Privman et al. 1991a) which in fact were applied to the experimental data analyses (Ryde et al. 1992, Song & Elimelech 1993), or large-scale numerical simulations (Bartelt & Privman 1990, Lubachevsky et al. 1993, Nielaba & Privman 1992b, Nielaba et al. 1990).

Specifically, numerical simulations of deposition on $2d$ substrates (as well as model

$1d$ substrates) provide data on the deposit density and morphology as it varies from the wall-induced density oscillations (Lubachevsky et al. 1993) to the bulk, interface-fluctuation dominated power-law behavior (Jullien & Meakin 1987, Krug 1989, Krug & Meakin 1990). Much work remains to be done; the main challenge is the numerical effort needed for such simulations.

REACTION KINETICS

Low-Dimensional Models and Fluctuations

Reaction-diffusion systems in low dimensions have been investigated extensively recently with emphasis on fluctuation-dominated effects, specifically, the breakdown of the standard chemical rate equations which correspond to the "mean-field" approximation of the reaction kinetics. Recent interest has been largely focused on the simplest reactions of two-particle coagulation, $A + A \to A$, and annihilation, $A + A \to$ inert, on the $1d$ lattice (Amar & Family 1990, Balding & Green 1989, ben-Avraham et al. 1990, Bramson & Griffeath 1980, Bramson & Lebowitz 1988, Doering & ben-Avraham 1988, Kang et al. 1984, Kuzovkov & Kotomin 1988, Liggett 1985, Lin et al. 1990, Lushnikov 1987, Privman 1992a, 1993a,b, Racz 1985, Spouge 1988, Torney & McConnell 1983). Indeed, in the diffusion-limited, instantaneous reaction case, these processes show non-mean-field power-law decay of the A-particle density. Experimental verification of the theoretical predictions has been initiated recently (Kopelman et al. 1990, Kroon et al. 1993).

Exact solutions provide convenient reference and guide to more complicated and more realistic systems. As usual in other fields, the number of exactly solvable cases is limited both in dimensionality, to $d = 1$, and in the variety of models that can be solved. Thus, future progress in this field will be largely based on approximation techniques such as diffusive description of the interparticle distribution, elaborate mean-field approximations, and extensive numerical Monte Carlo simulations.

Partial-Probability Reactions

Experimentally, reactions (Kopelman et al. 1990, Kroon et al. 1993) are never instantaneous. There is always some probability for the particles, identical $A + A$ or different-species $A + B$, to bounce off (modeled, e.g., by the hard-core repulsion) rather than interact to yield the reaction products. While the first numerical results for the simplest, $(A + A)$-type $1d$ reactions have been reported (Braunstein et al. 1992, Martin & Braunstein 1993, Shi & Kopelman 1992a,b) recently, theoretical progress has been achieved only for the $1d$ coagulation-reaction case (Privman et al. 1993) by an approximate model description of the interparticle distance distribution within a diffusive scheme in which the partial reaction is modeled phenomenologically by the radiation boundary conditions while the hard-core is modeled by a certain drift term in the diffusion current.

Generally, the field is still wide open; numerical studies and analytical efforts are needed, in $d > 1$ as well as for more complicated reactions, specifically, $(A + B)$-type, reversible reactions, and particle-input reactions. In the latter cases, there is a steady state which may be easier to handle in the diffusive-approximation schemes (Nielaba

& Privman 1992a, Privman & Barma 1992, Privman et al. 1993, Privman & Grynberg 1992, Privman & Nielaba 1992) which are typically nonlinear in time but linear in the spatial coordinate dependence. The analytical model building is slow and requires good physical insight into the underlying reaction process. Thus, extensive numerical data generation and interpretation will be essential to ensure progress.

Fast-Diffusion Mean-Field Theories

Consideration of reactions with more than two particles in the input, for instance $kA \rightarrow$ inert, etc., leads to use of mean-field theories in $d = 1, 2$. Indeed, such reactions are asymptotically mean-field even in $1d$, for $k > 3$. The marginal case $k = 3$ should have logarithmic corrections to the rate-equation behavior. These were observed numerically recently (see ben-Avraham 1993), and also derived by field-theoretical methods (Lee 1993). The two-particle reactions are marginal in $d = 2$ or higher.

Study of multiparticle reactions has been emphasized recently due to relevance to certain deposition processes (Nielaba & Privman 1992a, Privman & Barma 1992, Privman & Grynberg 1992, Privman & Nielaba 1992). The usual mean-field approximations involve closures of hierarchies of relations for correlation functions. However, in $d = 1$ a different, "fast-diffusion" mean-field approach is possible based on the use of the interparticle distance distribution (which is in a sense a complicated correlation function) from the fast-diffusion limit. The advantage of this approach is that it allows derivation of criteria of the applicability of the mean-field theory (Privman & Grynberg 1992) for reaction-diffusion systems, reminiscent of the Ginzburg criteria in static critical phenomena. An open challenge is extension to $d > 1$: for large densities of particles, in $d > 1$, fast diffusion can lead to collective effects, as mentioned earlier. Accommodation of these within the mean-field approach has not been clarified thus far.

Immobile Reactants

Another solvable limit, in $1d$ (Kenkre & Van Horn 1981), is the case of no diffusion at all. Generally such models of immobile reactants have received less attention in the literature (Kenkre & Van Horn 1981, Schnörer et al. 1989, 1990, Majumdar & Privman 1993). The reason is that unless longer-range reactions are included (Schnörer et al. 1989, 1990), the time dependence involves exponential relaxation to an absorbing state rather than power-law behavior typical of the fast diffusion reactions. Thus there are no universal fluctuation effects involved.

On the other hand, immobile-reactant systems provide an example of freezing in an absorbing state with a nonuniversal, initial-condition-dependent behavior persistent at all times and, again, not consistent with mean-field rate equations. It is therefore of interest to derive exact results whenever possible. In a recent work (Majumdar & Privman 1993) we reported an exact solution for $A + A \rightarrow$ inert on the Bethe lattice. In $d = 1$ we also derived exact results for the reaction $A + B \rightarrow$ inert, extending the previously know solution of $A + A \rightarrow$ inert (Kenkre & Van Horn 1981). The techniques used are similar to RSA and to certain models surveyed in the section on ordering, below. Thus there are further cases to be studied, specifically, multiparticle-input and systems of more than two species.

ORDERING AND NUCLEATION

Lattice Models of Phase Separation

Recently there has been much interest in modeling phase separation and spinodal decomposition (Gunton et al. 1983, Mouritsen 1990, Sadiq & Binder 1984) by simple irreversible, effectively zero-temperature low dimensional stochastic dynamical systems (Hede & Privman 1991, Privman 1992a, Scheucher & Spohn 1988). Specifically, some variants of nonconserved order parameter dynamical models in $d = 1$, corresponding effectively to $T = 0$ Glauber-type spin systems, have been solved exactly for properties such as the structure factor and average domain size, as functions of time; see Bray (1990), Privman (1992a) for details. The underlying mechanism leading to cluster growth in $d = 1$ is pairwise annihilation of interfaces separating ordered domains. The interfacial motion is diffusional and it corresponds also to diffusion-limited particle annihilation models discussed earlier.

Recently, pairwise particle-exchange models on linear and Bethe lattices were solved exactly by a new rate-equation method (Krapivsky 1993, Lin & Taylor 1993, Majumdar & Sire 1993, Privman 1992b). Lattice sites are occupied by particles A and B which can exchange irreversibly provided the local energy in reduced. Thus, the model corresponds to a zero-temperature Kawasaki-type phase separation process. Due to local order parameter conservation, the dynamics reaches an absorbing, frozen state at large times, the structure of which depends on the initial conditions.

Nonconserved Order Parameter Models

The $T \to 0$ limiting model with Glauber-type dynamics involves interface annihilation which is a process lowering the local energy and therefore has Boltzmann factor $+\infty$ associated with its transition probability at $T = 0$. Interface diffusion does not change the local energy and therefore has Boltzmann factor 1. Finally, interface generation (birth) has Boltzmann factor 0 (due to energy cost) at $T = 0$. The $T = 0$ models referred to earlier, correspond to allowing for both annihilation and diffusion. Exact results for such models in $1d$ yield the structure factor (Bray 1990, Privman 1992a).

In order to model nonsymmetric growth of a stable phase from an unstable-phase (or mixed) initial state, the above ordering mechanism was supplemented by spontaneous creation of the stable phase, $+1$, regions by overturning the unstable phase, -1, spins with probability p (Privman 1992a). For cluster coarsening at phase coexistence, $p = 0$, the conventional structure-factor scaling applies. The ± 1 cluster sizes grow diffusively, $\sim \sqrt{t}$, and the two-point correlation function obeys scaling. However, for $p > 0$, i.e., for the dynamics of formation of stable phase from unstable phase, the structure-factor scaling breaks down; the length scale associated with the size of the growing $+1$ clusters reflects only the short-distance properties of the two-point correlations.

Conserved Order Parameter Models

For conserved order parameter, spin-exchange Kawasaki-type dynamical models, there are several new features as compared to the nonconserved models just surveyed. Notably, interfacial processes even at $T = 0$ are more complicated for the conserved case. Specifically, let us consider the $d = 1$ binary AB-mixture model: each site of the $1d$ lattice is occupied by particle A or particle B. The dynamics generally involves nearby particle exchanges; the locally conserved order parameter is the difference of the A- and B-particle densities.

Energy-conserving interfacial motion in $1d$ is no longer simple free diffusion (Privman 1992b). Freezing rather than full phase separation occurs asymptotically for large times in models with both energy-lowering and energy-conserving moves allowed, or with only energy-lowering moves allowed. Several numerical studies were reported (Alcaraz et al. 1986, Levy et al. 1982, Meakin & Reich 1982, Palmer & Frisch 1985) of such particle-exchange models for d up to 5. As in the nonconserved case, some of the properties of the $d = 1$ models are different from $d > 1$. However, the general expectation of the "freezing" of the domain structure at large times applies, for conserved dynamics, in all space dimensions.

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