Coarsening dynamics of adsorption processes with diffusional relaxation

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We investigate the late coarsening stages of one-dimensional adsorption processes with diffusional relaxation. The nonequilibrium domain size distribution is studied by means of the field theory associated with the stochastic evolution. An exact asymptotic solution satisfying dynamical scaling is given for cluster sizes smaller than the average domain length. Our results are supported and compared with Monte Carlo simulations. [S1063-651X(97)04812-5]

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Random sequential adsorption models have been systematically investigated as basic prototypes of monolayer growth in many physical, chemical, and biological processes [1,2]. The characteristic feature dominating the late stage dynamics of such phenomena is the jamming of the available area of deposition, leading to the formation of partially covered and fully blocked states. Recent experimental advances indicate that even for large colloidal particles, monolayer deposits may further redistribute on the substrate by particle diffusion on time scales comparable with the adsorption process [3]. A range of theoretical efforts, including exact solutions, asymptotic methods, and extensive numerical simulations based on simple microscopic models, has been used to understand the role of fluctuations and collective effects in these processes [1,2]. There is ample simulational evidence for the existence of a scaling regime where the system is effectively made up of pure phase regions separated by narrow interfaces, highly reminiscent of quenched binary alloys and fluids at low temperatures [4]. For large times t a network of domains emerges such as can be characterized by a *single* length scale $\mathcal{L}(t)$, namely, the average domain size, which coarsens continuously. On general grounds, typical statistical quantities are expected to be scaling functions of a single argument involving both space and time [5].

Although there are several exact results in coarsening dynamics available mostly in one dimension [5], they essentially refer to the dynamical scaling of two-point correlations (structure factor), and average properties of the domain size distribution (DSD). More complete descriptions of cluster growth at the submicrometer level clearly require knowledge of the DSD itself, a quantity of fundamental interest in modern nucleation theories and accessible to light microscope studies [4]. As a contribution in this direction, here we present an asymptotic analysis of nonequilibrium DSD in a simpler system lending itself more readily to this calculation and still capturing basic aspects of coarsening phenomena.

Specifically, we consider an extension of the random dimer deposition problem of Flory [1] where *vacant* pairs of nearest-neighbor lattice sites are filled randomly by two hard core particles at a time, say with adsorption rate R. To prevent an otherwise jamming behavior (resulting from both hard core interactions and the lack of nearest-neighbor vacancies), we enable the system to relax diffusively by single particle hopping between nearest neighbors with probability h, though yet avoiding multiple occupancy. This leads to an effective hopping motion of vacant sites that recombine to form larger voids accessible to deposition attempts, ultimately covering the full crystalline limit at large times.

Turning to the evaluation of DSD, in what follows we shall restrict our discussion to one-dimensional systems. Far from being trivial, asymptotic solutions in $d=1$ share many features emphasized in higher dimensions and do provide a demanding test for theories of late stage coarsening, particularly for the dynamical scaling hypothesis. The strategy is to study the field theory that can be associated with the master equation of our adsorption-diffusion process [6]. This can be achieved by means of a (pseudo)fermionic representation in which its occupation numbers 1 or 0 at site j correspond to particle or vacancy at that location. After introducing creation (annihilation) Fermi operators $C_j^\dagger$ (C_j) along with the local density fields $\hat{n}_j \equiv C_j^\dagger C_j$, the stochastic evolution at a given time can be represented by the action e^{-Ht} of the quantum ''Hamiltonian''

$$H = -R\sum_j C_j^\dagger C_{j+1}^\dagger - h\sum_j (C_j^\dagger C_{j+1} + \text{H.c.}) + NR + (R-2h)\sum_j \hat{n}_j\hat{n}_{j+1} + 2(h-R)\sum_j \hat{n}_j, \qquad (1)$$

operating over a periodic chain with N locations. Here, deposition (hopping) of dimers (particles) is described by the effect of the first (second) sum in Eq. (1), whereas conservation of probability requires the action of the remaining (diagonal) field operators. We address the reader to Ref. [6] for a more detailed derivation in this and related systems.

The analysis of DSD requires one to consider the number of domains having at least L consecutive particles (with L arbitrarily large), by averaging over all possible histories up to a certain instant. For a given initial probability distribution $|P(0)\rangle$, this is related to the L-point correlation function [7]

$$F(L,t) = \frac{1}{N}\sum_j \langle\widetilde{\psi}|\hat{n}_{j+1}\cdots\hat{n}_{j+L}e^{-Ht}|P(0)\rangle, \qquad (2)$$

where $\langle\widetilde{\psi}|$ is an equally weighted sum of all accessible configurations, i.e., the *left* steady state of H. Although the diagonalization of the evolution operator becomes fairly standard by choosing $R=2h$, i.e., dimer adsorption and particle

diffusion occurring with the same probability [8], the difficulties associated to the evaluation of these high order correlators, as we shall see, are simplified significantly by *detaching* dimers with rate $\epsilon \equiv 2h - R$, whether or not the selected pair of adjacent particles arrived together. Though this fictitious process introduces additional terms in Eq. (1) [6], the latter constraint ensures that H remains bilinear in C, $C^\dagger$ operators. Therefore, it can be readily verified that after a Bogoliubov-type similarity transformation in momentum space [9], we are finally left with the free fermion Hamiltonian

$$H = \sum_{-\pi<q<\pi} \lambda_q \xi_q^+ \xi_q \quad \lambda_q = b + a\,\cos\,q, \tag{3}$$

where $a = R - \epsilon$, $b = R + \epsilon$, and the elementary ξ excitations are given by

$$\vec{\xi}_q = -\frac{e^{i(\pi/4)}}{\sqrt{N}} \sum_j e^{iqj} \begin{pmatrix} -\alpha\,\cos\,\theta_q & i\alpha^{-1}\,\sin\,\theta_q \\ \alpha \sin\theta_q & i\alpha^{-1}\,\cos\,\theta_q \end{pmatrix} \vec{C}_j,$$

$$\alpha = (R/\epsilon)^{1/4}, \quad \tan\theta_q = \alpha^2 \cot\frac{q}{2}, \tag{4}$$

with $\vec{\xi}_q$, $\vec{C}_j^\dagger$ denoting, respectively, $\binom{\xi_q^+}{\xi_{-q}^+}$, $\binom{C_j^\dagger}{C_j}$. So, in the limit $\epsilon \to 0$ in which the original process is recovered, the dynamical evolution becomes critical as it is dominated asymptotically by low-lying massless modes $q_0 = \mp\pi \pm q$ with spectrum $\lambda_{q_0} \propto q^2$.

We are especially interested in elucidating the long time behavior of the correlators (2) for which it is convenient to expand the initial probability distribution in terms of these fermions. In particular, starting from an empty substrate, it is a simple matter to check that $|P(0)\rangle$ corresponds to the coherent pair state

$$|P(0)\rangle = \prod_{0<q<\pi} (1 + \tan\theta_q\ \xi_q^+ \xi_{-q}^+)|\psi\rangle, \tag{5}$$

where $|\psi\rangle$ is the right vacuum (steady) state of H. Hence, from Eqs. (2) and (3) it follows that for nonvanishing desorption rates, $F(L,t)$ can be expanded perturbatively in powers of $u \equiv e^{-4\epsilon t}$ as $\rho_s^L + (1/N)\Sigma_j \Sigma_{n=1}^L F_{n,j}(L,t)$, where

$$F_{n,j}(L,t) = \frac{u^n}{n!} \sum_{q_1} \cdots \sum_{q_n} \langle \tilde{\psi} | C_{j+1}^\dagger C_{j+1} \cdots C_{j+L}^\dagger C_{j+L} \prod_{i=1}^n e^{-2a(1+\cos\,q_i)t} \tan\theta_{q_i} \xi_{q_i}^+ \xi_{-q_i}^+ |\psi\rangle, \tag{6}$$

$0 < q_i < \pi$ and, $\rho_s = 1/(1+\sqrt{\epsilon/R})$ is the coverage of the steady state. To evaluate the vacuum expectation value of this product, we use Wick's theorem [10] for which we compute all pair contractions (in this case, steady state expectation values) contributing to such a typical term. The seven kinds of contractions that occur are readily obtained if we combine the inverse of Eq. (4) along with its associated anticommutative algebra. In the limit $N \to \infty$ this finally yields

$$\langle C_l C_m \rangle = -\langle C_l^\dagger C_m^\dagger \rangle = \frac{\sqrt{R\epsilon}}{2b}(1+\beta^2)\beta^{n-1}, \tag{7}$$

$$\langle C_l^\dagger C_m \rangle = -\langle C_l C_m^\dagger \rangle = -\langle C_l C_m \rangle, \tag{8}$$

$$\langle C_l \xi_q^+ \rangle = \frac{e^{i\pi/4}}{\sqrt{N}}\,\cos\,\theta_q e^{iql}, \tag{9}$$

$$\langle C_l^\dagger \xi_q^+ \rangle = \frac{e^{-i\pi/4}}{\sqrt{N}}\,\sin\,\theta_q e^{iql}, \tag{10}$$

where $n = m - l > 0$, and $\beta = (\sqrt{\epsilon} - \sqrt{R})/(\sqrt{\epsilon} + \sqrt{R})$. Since $|P(0)\rangle$ has zero total momentum, notice that the sum over all these pairings in Eq.,(6) (with their corresponding permutation signature), results independent of the site location, i.e., $F_{n,j}(L,t) \equiv F_n(L,t)$. Thus, $F(L,t)$ remains translationally invariant for all subsequent times, as it should.

Clearly, for *finite* detaching rates ϵ, there is an exponentially large number of pairing groups contributing to Eq. (6). Even the calculation of the leading order F_1 becomes prohibitively involved. However, in the limit $\epsilon \to 0$ contractions (7), (8), and (9) vanish as $\sqrt{\epsilon}$. Thus, by taking into account the Bogoliubov angles appearing in Eqs. (4) and (6), a moment of reflection shows that there are only two relevant pairing forms contributing to F_1, namely, $\langle C^\dagger \xi^+ \rangle^2\ \langle CC \rangle$, e.g., $\langle C_l^\dagger \xi_q^+ \rangle \langle C_m^\dagger \xi_{-q}^+ \rangle \langle C_l C_m \rangle$, and $\langle C^\dagger \xi^+ \rangle\ \langle C \xi^+ \rangle$, a remarkable simplification. Using the *multiplicity* and signature of these products, and after introducing the integrals

$$f_n^\pm(\tau) = \frac{1}{\pi} \int_0^\pi \frac{e^{-\tau\,\cos\,q}}{\sin\,q} \sin\,nq(1 \pm \cos\,q)dq, \tag{11}$$

it is straightforward to show that

$$F_1(L,t) = -e^{-\tau}\left[L I_0(\tau) + \sum_{n=1}^{L-1} (-1)^n (L-n) f_n^+(\tau) \right], \tag{12}$$

where $I_0(\tau)$ is a modified Bessel function of the first kind [11], and $\tau \equiv 2Rt$. Similarly, the number of pairing groups that yield a net contribution to higher orders of Eq. (6) remains bounded irrespective of the domain size L, though proliferating very rapidly with the order n. For instance,

there are 24 products of the form $\langle C\xi^+\rangle^2\,\langle C^\dagger\xi^+\rangle^2$, 72 $\langle C^\dagger\xi^+\rangle^4\,\langle CC\rangle^2$, and 72 $\langle C^\dagger\xi^+\rangle^3\,\langle C\xi^+\rangle\,\langle CC\rangle$ to be considered in the calculation of $F_2(L,t)$. The analysis is simple albeit in fact rather lengthy. In the long time limit and *fixed* domain size, it can be shown that the former 24 products contribute as L^2/t, whereas the latter 144 are bounded by L^5/t^3. More specifically, employing the integrals (11) along with modified Bessel functions of integer order I_n, we find

$$F_2(L,t)=\frac{e^{-2\tau}}{2}\Bigg\{L(L-1)I_0^2(\tau)-\sum_{n=1}^{L-1}(L-n)\times[I_n^2(\tau)+f_n^+(\tau)\,f_n^-(\tau)]\Bigg\}+O(L^5/t^3). \quad (13)$$

We are not concerned here with the possibility of improving the second order calculation, which is a problem of great technical difficulty, but in showing that the approach, even in lowest order, can be successfully applied to late coarsening stages. It should be borne in mind, however, that for *arbitrarily large* domain sizes the prefactors involved in higher orders of Eq. (6) become increasingly weighted. Nevertheless, it turns out that these contributions become irrelevant within the scaling regime $t\to\infty$, $L\to\infty$, with $L^2/t\ll 1$, where they provide solely subdominant large-time corrections.

In studying this asymptotic region it is helpful to consider the number $N_L(t)$ of filled L intervals between two vacancies, along with the density of domains $N_d(t)$ averaged up to a given instant. Clearly, the probability of observing a cluster having *exactly* L particles at that time is $P(L,t)=N_L(t)/N_d(t)$. It can be easily checked that $N_L=F(L)+F(L+2)-2F(L+1)$, $\forall t$, while on the other hand N_d coincides with the number of particle-vacancy interfaces, and therefore can be calculated as $\langle\,\hat{n}_j\,(1-\hat{n}_{j+1})\rangle$ (the brackets indicate an average over histories). Following a similar analysis discussed as in [6], $N_d(t)$ can be shown to yield $e^{-\tau}I_1(\tau)$. Hence, by virtue of the asymptotic behavior of Eqs. (12) and (13), it finally turns out that for $z\equiv L/\sqrt{2\pi\tau}\ll 1$, $P(L,t)$ satisfies the dynamical scaling hypothesis, namely, $P(L,t)=\mathcal{P}(z)/\sqrt{2\pi\tau}$, where $\mathcal{P}(z)$ is a universal scaling function given by

$$\mathcal{P}(z)=\frac{\pi}{2}ze^{-\pi z^2}[1+\mathrm{erfc}(\sqrt{\pi}z)]+\frac{1}{2}(1-e^{-2\pi z^2})+O(z^5), \quad (14)$$

and $\mathrm{erfc}\,(x)=(2/\pi)\int_x^\infty e^{-u^2}du$ is the complementary error function [11]. Thus, there is an emerging typical length scale $\mathcal{L}(t)=\sqrt{2\pi\tau}$ that characterizes the whole domain structure at large times. In a statistical sense, the domain morphology becomes self-similar if all lengths are measured in units of $\mathcal{L}(t)$. In fact, this characteristic scale can be ultimately identified with the average domain size, since by construction $\langle L\rangle=\rho(t)/N_d(t)$, where $\rho(t)=\Sigma_L LN_L(t)\to 1$, is the particle coverage; so in the long time limit $\langle L\rangle\equiv\mathcal{L}(t)$. Moreover, it is known [6] that *two* point vacancy-vacancy correlation functions $C(L,t)=(1/N)\,\Sigma_j\langle(1-\hat{n}_j)(1-\hat{n}_{j+L})\rangle$ scale asymptotically as

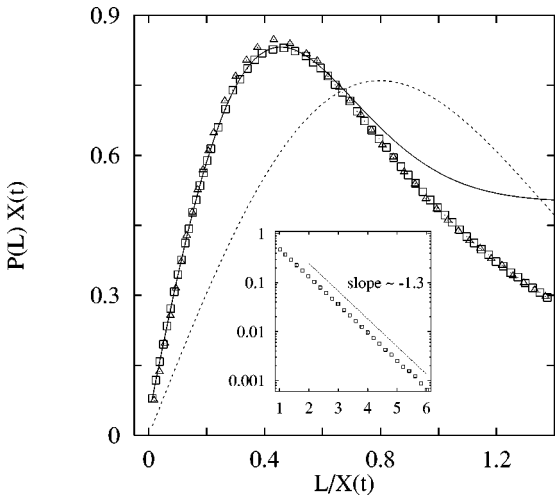

FIG. 1. Asymptotic domain size distribution at $t=10^3$ for $R=1,h=0.5$ (squares), and $R=1,h=0.1$ (triangles, nonsoluble case). The averages were taken over 3×10^4 histories starting from an empty chain of 10^5 sites. For domain sizes L smaller than the average domain size $\propto t^{1/2}$ [here denoted as $X(t)$], the numerical data follow closely the theoretical results given by Eq. (14) in the text (solid line). For comparison, we show the scaling distribution of the birth process discussed in the text (dashed line). The inset provides evidence of exponential distribution for large domain sizes.

$$C(L,t)=\frac{e^{-\pi z^2}}{\mathcal{L}^2(t)}\left[\frac{\pi}{2}z\,\mathrm{erfc}(\sqrt{\pi}z)+2\,\sinh(\pi z^2)\right], \quad (15)$$

where the scaling parameter is taken as in Eq. (14). Thus, we see that both average domain size and pair correlation length coalesce into a *single* physical scale that is typically diffusional. This is in line with the coarse grained (hydrodynamic) level of description, the so-called (noiseless) model *A* or time-dependent Ginzburg-Landau approach [4,12], in which there is a single nonconserved scalar field (in our case, the particle density) leading to a characteristic scale that grows as $\sqrt{t}$. In addition, these results reveal a close asymptotic relationship between DSD and two point correlations, namely,

$$P(L,t)=2\mathcal{L}(t)C(L,t)+O(L^2/t^{3/2}), \quad (16)$$

so, apart from a global change of scale they closely follow each other.

We have conducted Monte Carlo simulations to confirm the validity of our theoretical expectations in a periodic chain of $N=10^5$ sites. The microscopic dynamical rules accounting for the stochastic process described by Eq. (1) are as follows. Starting from an empty lattice, dimer deposition attempts on randomly targeted *bonds* are made with probability R while maintaining single occupancy throughout. Alternatively, a particle hopping attempt with probability h takes place isotropically within the selected bond provided it contains a vacant site; otherwise the move is rejected. The unit Monte Carlo step is defined such that each bond is checked once on average. This corresponds to N trials per unit time. We direct the reader's attention to Fig. 1, where we display the DSD results obtained for a wide range of domain sizes,

after averaging over 3×10^4 histories up to 10^3 steps. This has been adequate to suppress numerical fluctuations arising particularly from large sizes L yet smaller than the typical system length.

As expected, by setting $R=2h$ our results for $L\ll\mathcal{L}(t)$ reproduce completely the asymptotic scaling distribution (14). However, for arbitrarily large domain sizes the relevance of the high order corrections referred to above is evidently reflected in the progressive departure between theory and simulation. Nevertheless, our approach turns out to be still successful to yield an accurate estimate of the most probable cluster size $\sim0.468\ \mathcal{L}(t)$, occurring in fact within a regime of intermediate lengths. For $L\gg\mathcal{L}(t)$ we content ourselves with giving just the numerical results displayed in the inset of Fig. 1, which suggest the DSD follows an exponential distribution scaling as $\mathcal{P}(z)\sim P_0\ e^{-kz}$, with $k=1.3(1)$ and $P_0=1.8(1)$. Similar results were observed starting with other initial conditions, the scaling distribution always appearing in the long time limit, as long as only short-range spatial correlations are initially present. It is worth remarking that this robustness applies as well to the unrestricted general case $R\neq2h$ (also shown in Fig. 1), where the dynamics cannot be solved explicitly.

The existence of dynamic scaling, however, appears to be associated with a clean separation between fast microscopic time scales $\propto1/R$ and slow collective modes, such as the gapless ξ excitations of Eq. (4). For instance, no scaling behavior seems to hold for finite detaching rates ϵ. In fact, the noncritical dynamics includes a subcase ($\epsilon=R=h$) entirely soluble by standard transfer matrix techniques [6], in which there is no dynamic scaling of any kind. Thus, the issue of universality in critical dynamics arises immediately. Whether or not slightly different nonequilibrium systems share a similar set of exponents and scaling functions is still an open problem that is receiving systematic attention [13]. In this context, we conclude by examining a number of common aspects between the dynamics discussed so far and an alternative process of cluster growth on a lattice, in which hard-core particles diffuse and eventually give birth to another particle at an adjacent site [14]. At the level of the average domain size, it is by now well established that both processes coarsen diffusively [13,14]. Furthermore, even the dynamics of two point correlations can be described asymptotically by the *same* scaling function (15) [6,14]. However, at the more demanding microscopic level of DSD universality no longer holds. In fact [14], the birth process follows a scaling distribution $\mathcal{P}(z)=(\pi/2)ze^{-(\pi/4)z^2}$, whose Gaussian tail indicates the occurrence of relatively smaller domains (see Fig. 1), whereas on the other hand it cannot be either rescaled into Eq. (14) beyond third order in $L/\mathcal{L}(t)$.

In summary, we have presented a scaling picture that accounts for the late coarsening stages of simple adsorption processes where, however, fluctuation-induced behavior is essential. As often in nonequilibrium statistical mechanics, even the solution of the simplest models helps to convey a clearer understanding of the many characteristics present in complex systems. While progress has been accomplished in $d=1$, a similar understanding of spatial structures in higher dimensional systems still requires further investigations.

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