Brownian-Vacancy Mediated Disordering Dynamics

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Abstract. – The disordering of an initially phase segregated system of finite size, induced by the presence of highly mobile vacancies, is shown to exhibit dynamic scaling in its late stages. A set of characteristic exponents is introduced and computed analytically, in excellent agreement with Monte Carlo data. In particular, the characteristic time scale, controlling the crossover between increasing disorder and saturation, is found to depend on the exponent scaling the number of vacancies in the sample.

The structure and formation of surfaces and interfaces is of great scientific and technical importance and has attracted considerable interest over the past decade. A second problem of similar relevance concerns the morphology and dynamics of ordering in bulk systems after a rapid temperature quench. The evolution of spatial structures in both of these processes exhibits dynamic scaling in the late-time regime so that typical configurations at different times are self-similar after an appropriate rescaling of space and time. Clearly, the “inverse” scenario, i.e., the destruction of interfaces and the bulk disordering of an initially phase-segregated system, are also of major significance, being related to natural erosion phenomena. Mobile defects, present in many materials, can obviously play a major role in the disordering process, especially if their dynamics is fast on the time scale governing the bulk particles. In this Letter, we consider a simple model for defect-mediated interface destruction and bulk disordering in a finite system, corresponding to a real material in which the characteristic time scale for vacancy diffusion is much faster than the ordinary bulk diffusion time. A fixed number of vacancies are initially located at a smooth, nonelastic interface separating two ordered bulk phases. These vacancies perform a homogeneous Brownian random walk, by exchanging positions with the otherwise completely passive bulk particles. As a result, the interface is gradually destroyed, and the system approaches a completely disordered equilibrium state. Three distinct temporal

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regimes, separated by two crossover times, are observed. Our key result is that the late stages of this process exhibit dynamic scaling. The characteristic exponents are computed analytically. In particular, the late crossover time is found to scale as a power of system size, determined by the spatial distribution of the defects.

This Letter is organized as follows: We first describe our model, followed by a summary of our simulation results. Turning to analytic methods, we characterize the initial configuration and the final state exactly. The intermediate regime is described by a set of mean-field equations of motion which correctly predict both the scaling form for an appropriately defined “disorder parameter” and the characteristic exponents controlling its size and time dependence. We conclude with some comments and questions. More details will be published elsewhere.

Our model is defined on a two-dimensional square lattice of \( L^2 \) sites, with \( L \) ranging from 10 to 100. Each lattice site can be occupied either by a white particle, a black particle or a hole (vacancy), so that multiple occupancy is forbidden. The number of vacancies is denoted by \( M \). For simplicity, we restrict our attention only to the case of \( L^2/2 \) black particles and \( L^2/2 - M \) white particles. Since we wish to describe bulk disordering rather than the “evaporation” of the two bulk phases into an empty region, we will keep the number of holes small, i.e., \( M/L^2 \ll 1 \). Initially, the upper (lower) half of the system is occupied by white (black) particles only, and the vacancies are randomly distributed along the flat interface. At each Monte Carlo step (MCS), a hole is chosen at random and changes place, with equal probability, with one of its four nearest neighbors. All particle-particle exchanges are forbidden. The boundary conditions at the right and left edge are periodic; for the top and bottom edges, we have simulated both brickwall and periodic boundary conditions, without detecting any significant differences in the scaling form and exponents.

We are interested in the dynamics of the interface destruction and bulk disordering caused by these vacancies. Monitoring the evolution of a typical configuration in a 60x60 lattice, shown in Fig.1, we observe that the interface is gradually destroyed, via increasing fragmentation, until it ceases to be identifiable. As a quantitative measure for the growing disorder, we consider the total “surface area” of the black regions, i.e., the total number of black-white and black-hole bonds, after \( t \) MCS. In analogy with the Ising model, we will refer to these pairs as “broken bonds”. Averaging this quantity over many configurations (200 for \( L \leq 40 \) and 20 otherwise) we obtain the “disorder parameter”, \( \mathcal{A}(L, M, t) \), which depends on system size \( L \), vacancy number \( M \), and ‘time’ \( t \). Since \( M/L^2 \ll 1 \), the dominant contribution to this quantity is just the average number of black-white bonds. Fig. 2a shows \( \mathcal{A}(40, 1, t) \), i.e., the average surface area in a 40 \times 40 system containing a single vacancy. One clearly distinguishes three

Fig. 1. – An initially smooth interface (a) gradually becomes rough (b) \((2 \cdot 10^3 \text{ steps})\), and destroyed after (c) \((5 \cdot 10^5 \text{ steps})\). (d) represents the completely mixed, equilibrium state \((\text{more than } 2 \cdot 10^7 \text{ steps})\). Here, \( L = 60 \).
regimes, drawn schematically in the inset: an early regime (I), the intermediate, or scaling, regime (II), and finally a late or saturation regime (III) in which the system has effectively reached the steady state. Physically, the three regimes are easily interpreted: Tracking the position of the vacancy, we observe that, for early times, it is confined to a small (yet growing) region centered on its starting point, far from the boundaries of the system. Thus, the early regime is strongly dependent on the dimensionality of the system (see [5]).

In contrast, for intermediate and late times, the vacancy is found with essentially equal probability anywhere in the system. The difference between intermediate and late stages lies in the degree of disorder among the black and white particles.

Our key observation is that, independent of dimension, Regimes II and III exhibit dynamic scaling. To characterize this behavior, we define a set of exponents: First, the saturation value of $A$ scales with system size according to $\lim_{t \to \infty} A(L,1,t) \equiv A_{sat}(L,1) \sim L^\alpha$. Second, in the intermediate regime, $A(L,1,t)$ grows as $A(L,1,t) \sim L^\alpha t^\beta$. The $L$-dependent factor is required here to absorb a nontrivial shift along the $\ln t$ axis in dimensions other than two in order to collapse curves associated with different system sizes. Finally, the two crossover times (“early” and “late”) scale as $t_e \sim L^{z_e}$, and $t_l \sim L^{z_l}$. In $d = 2$, the data give $\alpha = 2 \pm 0.1$, $\beta = 0.5 \pm 0.06$, $z_e = 2 \pm 0.2$, $z_l = 4 \pm 0.2$, $\sigma = 0 \pm 0.1$. Since $\sigma$ is effectively zero, excellent data collapse is obtained by plotting $A(L,1,t)/L^\alpha$ versus $t/L^{z_l}$, shown in Fig. 2b for a range of system sizes. Thus, the intermediate-to-late time crossover can be summarized by the usual Family-Vicsek [3] scaling form

$$A(L,1,t) \sim L^\alpha f\left(\frac{t}{L^{z_l}}\right)$$  \hspace{1cm} (1)

with a scaling function $f$, satisfying $f(x) \simeq const$ for $x \gg 1$, and $f(x) \sim x^\beta$ for $x \ll 1$ (but large enough to fall within Regime II). The consistency condition $A(L,1,t_l) \simeq A_{sat}(L,1)$ yields the scaling law

$$\sigma + z_l \beta = \alpha,$$  \hspace{1cm} (2)
which is manifestly satisfied by the measured exponents. The same indices are observed for several vacancies, provided their number remains constant as the system size $L$ is varied. We stress that, due to the presence of the novel exponent $\sigma$, our scaling law (2) is distinct from the familiar $z\beta = \alpha$ which controls surface growth in, e.g., the Edwards-Wilkinson [7] or KPZ [8] models.

In a real system it is to be expected that the number of vacancies itself depends on the system size. For generality, we allow $M \sim L^\gamma$, where $\gamma \in [0,d]$ will be called the vacancy number exponent. The data reported above then correspond to $\gamma = 0$ (and $d = 2$). Another natural case is $\gamma = d - 1$, which could arise if we imagine welding two different solids along a common surface with vacancies uniformly distributed thereupon. If the two surfaces were of equal fractal dimensions, a uniform distribution of vacancies on the interface would lead to $M$ being extensive in the initial interfacial length, $\ln t$ significance, depending $\beta$ and $\phi$ for our simulations, [9]. The data reported above then correspond to $\phi$ jump from $\gamma$ in from a neighboring site. The second term accounts for a loss, due to a black particle "diffuses" in from a neighboring site. This equation simply tallies the local change in black particle density at position $x$: the first term reflects a gain, provided a vacancy is initially present and a black particle "diffuses" with $\tau$. For generality, we define $\phi(x, \infty) = M/V$. A well-defined continuum limit is obtained by letting the lattice constant $a$ vanish and identifying the microscopic time scale with $\tau \equiv a^2/2d$. In this limit, physical distances such as the system size $L$ remain fixed while the number of sites approaches infinity. For convenience, we define $V \equiv L^d$.

First, we note that each of the vacancies performs a simple random walk. As a result, the final state is, of course, trivial: $\phi(x, \infty) = M/V$. A similar evolution equation for the black particle density, $\psi(x, t)$, is easily derived from a microscopic master equation. Truncating all correlations, we find

$$a^{-d}\partial_t \psi(x, t) = \phi(x, t)\nabla^2 \psi(x, t) - \psi(x, t)\nabla^2 \phi(x, t).$$

This equation simply tallies the local change in black particle density at position $x$: the first term reflects a gain, provided a vacancy is initially present and a black particle "diffuses" in from a neighboring site. The second term accounts for a loss, due to a black particle jumping from $x$ to a vacant nearest-neighbor site. Similar equations have been discussed in the context of biased diffusion of two species [4]. The prefactor $a^{-d}$, appears for dimensional
In two dimensions our theory predicts density whose diffusion “coefficient” is \( \phi(x,t) = O(1/V) \). Performing a simple random walk, the vacancies reach the edge of the system after a time of order \( L^2 \). Thus, we identify the early crossover time \( t_e \propto L^2 \) and read off \( z_e = 2 \). For later times, the holes are uniformly distributed over the system, and we may replace \( \phi \) by its final value, \( \frac{\sigma}{V} \), so that (1) reduces to a simple diffusion equation, \( \partial_t \psi = D \nabla^2 \psi \), where \( D \equiv a^d M/V \). Its solution, subject to the initial and fully periodic boundary conditions, is easily found:

\[
\psi(x,t) = \frac{1}{2} + 2 \sum_{n=1}^{\infty} \frac{\sin[2\pi(2n-1)y/L]}{2n-1} e^{-\epsilon t(2n-1)^2},
\]

where \( \epsilon = 4\pi^2 D/L^2 \).

To make contact with the “disorder parameter”, \( A \), measured in the simulations, we could define an operator on the lattice configurations for the total number of broken bonds, make a meanfield approximation for pair correlations, and take the continuum limit [4]. Here, let us present a short cut, based on the analogy with the Ising model and its associated coarsegrained version. The local magnetization density, \( \Phi(x) \), of the former clearly maps into \( \psi(x,t) - \frac{1}{2} \) for our case. Meanwhile, the local energy density of the Ising model is given precisely by the broken bonds. In the standard literature [10], the total energy of the Ising model is written as \( K_1 - K_2 \int_V \Phi^2 \), where the constants \( K_1 \) may be fixed by the scale and the “zero” of the energy. Since our interest is also the total number of broken bonds, we may write \( A \propto KV - \int_V \left[ \psi(x,t) - \frac{1}{2} \right]^2 \). Note that this form expresses the extensivity of \( A \). Of course, since the total number of broken bonds at \( t = 0 \) is only \( O(L^{d-1}) \), we set the initial value of \( A \) to be 0. Demanding the final value be \( dV/2 \), we have

\[
A(L,M,t) = \frac{d}{2} V - 2d \int_V \left[ \psi(x,t) - \frac{1}{2} \right]^2.
\]

Using (1), we find the time evolution of this quantity:

\[
A(L,M,t) = \frac{d}{2} V [1 - S(2\epsilon t)],
\]

where \( S(\xi) = \frac{1}{2\pi} \sum_{n=1}^{\infty} e^{-\xi(2n-1)^2}/(2n-1)^2 \). Since \( S(0) = 1 \) and \( S(\infty) = 0 \), we verify that \( A \) does take on the correct initial and final values. To capture the time dependence in the intermediate regime (II), i.e., \( ct \ll 1 \), we reexpress the infinite sum via a Poisson resummation [11]. Introducing \( u_m \equiv \pi m/2\sqrt{2\epsilon t} \), we find

\[
A(L,M,t) \sim \frac{2d}{\pi^{3/2}} V \sqrt{2\epsilon t} \left\{ 1 + \sum_{m=1}^{\infty} (-1)^m \left[ e^{-u_m^2} - u_m \Gamma\left(1/2,u_m^2\right)\right] \right\}
\]

where \( \Gamma(\bullet,\bullet) \) denotes the incomplete Gamma function. In this form, the sum over \( m \) is suppressed for small \( \epsilon t \). Thus, \( A(L,M,t) \propto V \sqrt{2\epsilon t} \propto L^d \sqrt{M/Mt/L^{2+d}} \), yielding the remaining exponents, namely \( \beta = \frac{1}{4} \) independent of dimension, and \( \sigma = \frac{1}{2} (d + \gamma - 2) \). The late crossover time, naturally defined by \( ct_l = 1 \), scales as \( t_l \sim L^{2d-\gamma} \) whence one obtains \( z_\gamma = 2 + d - \gamma \). In two dimensions our theory predicts \( z_\gamma = 4 \) and \( \sigma = 0 \) for \( \gamma = 0 \), while \( z_\gamma = 3 \) and \( \sigma = \frac{1}{2} \) for \( \gamma = 1 \), in complete agreement with the Monte Carlo data.
To summarize, we have analyzed the disordering process of an initially phase segregated system, driven by highly mobile Brownian vacancies distributed according to the exponent $\gamma$. The late stages of the evolution exhibit dynamic scaling. A set of exponents $\{z_e, z_l, \alpha, \sigma; \beta\}$ can be defined, characterizing, respectively, the system size dependence of two crossover times, the final saturation value of the number of broken bonds, $A(L, M, t)$, and its amplitude in the intermediate regime. The temporal growth of $A$ during the latter regime is captured by the exponent $\beta$. All indices can be computed analytically, in excellent agreement with the data. Our key result is that the typical time scale $t_l \sim L^{z_l}$, which controls the crossover between increasing disorder and saturation, is set by $z_l = 2 + d - \gamma$, and thus depends explicitly on both the space and fractal dimensionalities, $d$ and $\gamma$. Measurements of $z_l$ can therefore provide information about the vacancy distribution in a sample. In the most familiar case, standard vacancy diffusion in solids, the number of vacancies is extensive ($\gamma = d$), so that the well-known result $z_l = 2$ is reproduced \[12\]. Even though our model is very simple, it forms the basis for the description of a large variety of related problems. Work is in progress to analyze the effect of external driving forces, interparticle interactions and vacancy-induced catalytic reactions.

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