

Microscopic Kinetics and Time-Dependent Structure Factors

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The time evolution of structure factors (SF) in the disordering process of an initially phase-separated lattice depends crucially on the microscopic disordering mechanism, such as Kawasaki dynamics (KD) or vacancy-mediated disordering (VMD). Monte Carlo simulations show unexpected “dips” in the SFs. A phenomenological model is introduced to explain the dips in the odd SFs, and an analytical solution of KD is derived, in excellent agreement with simulations. The presence (absence) of dips in the even SFs for VMD (KD) marks a significant but not yet understood difference of the two dynamics.

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After a temperature “downquench” into a coexistence region, binary systems such as magnets or alloys develop long-range order in a universal fashion [1]. Determined by symmetries and conservation laws, the dynamic coarsening follows one of a small number of scenarios, characterized by dynamic scaling and universal exponents. Considerable work has been devoted to the theoretical foundations of this behavior [2]. By contrast, far less attention has focused on the opposite phenomenon, i.e., *disordering* following an *upquench* in temperature, even though it is hardly less important in materials science: It determines, e.g., the time evolution of an interface between two materials or the waiting times which must elapse before a heated material has mixed sufficiently.

A key ingredient in the physics of these processes is the kinetic mechanism by which two particles exchange. In many materials, it is dominated by the diffusion of vacancies or defects [3], rather than direct atom-atom exchanges. Vacancy concentrations are typically very small ($\sim 10^{-5}$) [4]. For this type of dynamics, it has recently been shown [5] that a simple mean-field theory suffices to obtain a *quantitative* description of disordering characteristics which are controlled by short-range correlations.

In this Letter, we show that this mean-field theory fails dramatically, even at the qualitative level, to predict the dynamics of observables which include correlations over *larger* distances in the system. A typical example is the time-dependent equal-time structure factor. We present Monte Carlo (MC) simulation data and a microscopic theory, illustrating the crucial role played by the details of the whole vacancy path. Comparing data for vacancy-mediated and direct exchange dynamics, we obtain a key result of our study, namely, that experimental data for the equal-time structure factor can identify the *microscopic kinetic mechanism* by which a material evolves. We conclude with a list of open questions.

We consider a d -dimensional square lattice of size L^d (L even, for simplicity) with periodic boundary conditions. Each site \vec{i} is occupied by one of two types of particles, which we label as spins: $s_i = \pm 1$. A single spin is *tagged*, playing the role of a vacancy or defect. Only this “va-

cancy spin” is allowed to move, all others being passive. Turning to the microscopic dynamics, we define two versions: (i) The vacancy performs a Brownian random walk on the lattice, exchanging with nearest-neighbor spins and thus scrambling the spin configuration, or (ii) the tagged spin performs one single step and then passes the tag to another, randomly selected spin. This sequence is then repeated. Note that both versions strictly conserve particle number (or total magnetization, $\sum_i s_i$). The first is known as vacancy-mediated dynamics (VMD) [3,4]; the second is precisely Kawasaki dynamics (KD) [6]. In the language of Ising models, they correspond to $T = \infty$ dynamics, since energy costs are ignored. Yet, we consider a perfectly phase-segregated initial configuration (up and down spins separated by two planar domain walls perpendicular to, say, the x axis), corresponding to $T = 0$. At time $t = 0$, the system experiences a temperature upquench, from zero to infinity, and we monitor the disordering process as a function of time. For $t \rightarrow \infty$, the system clearly reaches the infinite temperature equilibrium state, characterized by completely random configurations.

We monitor the time-dependent structure factors, $S_{\vec{k}}(t) \equiv L^{-d} \langle |\sum_j s_j(t) \exp(-i\vec{k} \cdot \vec{j})|^2 \rangle$. Here, $\langle \bullet \rangle$ denotes the time-dependent average over a large number (1000 for our data) of independent runs, starting from the same $T = 0$ configuration differing only in the random initial position of the tag. MC time is incremented by 1 for each exchange. The most interesting structure factors are those whose wave vector \vec{k} is perpendicular to the initial phase boundary, $\vec{k} = (2\pi n/L, 0, \dots, 0)$, with n integer. For odd $n \ll L$, they are sensitive to the initial order so that $S_{\vec{k}}(0)$ is of the order L^d , while for even n , $S_{\vec{k}}(0) = 0$ (since L is even). For brevity, these two classes are referred to as odd and even \vec{k} . Clearly, $\lim_{t \rightarrow \infty} S_{\vec{k}}(t) = 1$ for all \vec{k} , due to the random final state.

For reference, we review a few key results from [5]. The disordering process displays three regimes, separated by two characteristic times, $t_E \approx L^2$ and $t_L \approx L^{d+2}$. For $t \lesssim t_E$ only a fraction of sites has been visited by the vacancy, and the equilibrium state is reached for $t \gtrsim t_L$. Between these well-separated bounds lies the “intermediate

regime,” in which the vacancy visits each site many times without destroying much of the initial order. Here, the disorder parameter, being the number of broken nearest-neighbor bonds, displays dynamic scaling with universal exponents before reaching its equilibrium value.

Turning to structure factors, in Fig. 1 we compare MC data for a 160×160 lattice, with (a) VMD and (b) KD. First, note that three regimes emerge again. The final regime is easily identified by all S_k 's reaching unity. In the intermediate regime, the odd S_k 's clearly display the decay of the initial order which remained largely unaffected during the earliest regime. Second, we emphasize a rather peculiar feature, namely, that several structure factors develop a minimum, manifested as a small “dip” before they finally tend to their equilibrium value. For VMD this dip appears in *all* structure factors *except* the two lowest ones, i.e., $n = 1, 2$ (strictly speaking, in $n = 4$ it emerges as a “shoulder”). In contrast, for KD it exists only in the *odd* S_k 's. At first sight, these dips might suggest a temporary rebound towards *order*. We show below, however, that their origin is different.

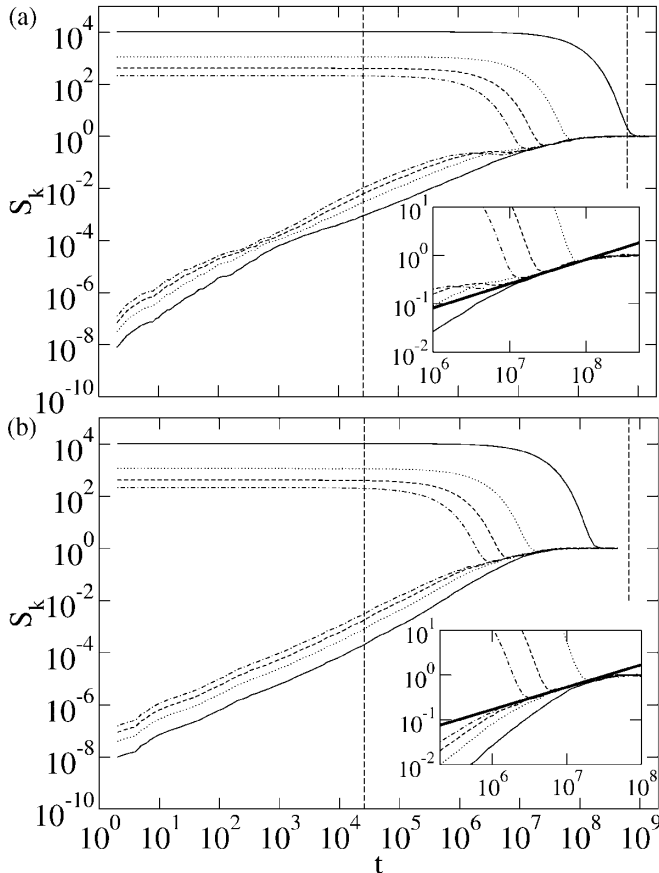


FIG. 1. Time evolution of the first eight structure factors S_k with $k = (2\pi n/L, 0)$, $n = 1, 3, 5, 7, 8, 6, 4, 2$ from top to bottom, on a $d = 2$ lattice of size $L = 160$ with (a) VMD and (b) KD. The thick solid straight lines in the insets, which show the magnified crossover region, have slope $1/2$. The two dashed vertical lines window the intermediate regime.

Third, turning to “short” times, just after the onset of the intermediate regime, we observe a clear difference in the *even* structure factors for the two types of dynamics, displayed more visibly in the data for a much larger ($L = 500$) lattice (Fig. 2): The short-time behavior for a VMD system appears to be $S_k \sim t^{\gamma_V}$ with a short-time exponent $\gamma_V \approx 1$, whereas the KD system follows $S_k \sim t^{\gamma_K}$ with $\gamma_K > 1$. Below, we see that $\gamma_K = 3/2$ exactly, in the $L \rightarrow \infty$ limit. Thus, the presence or absence of dips and the short-time behavior offer a simple signature to distinguish VMD from KD. Finally, Fig. 1 indicates that disordering by KD is faster than VMD by a factor of about 4.5. This factor is roughly independent of the lattice size but decreases with d [7]. We emphasize that, in all figures, the error bars are of the order of the line thickness and therefore not shown.

We now turn to the theoretical descriptions of our model.

A “two-fluid” model.—To motivate this approach, we briefly recall the key ingredients of the mean-field theory [5]. Coarse graining the microscopic dynamics in space and time, we identify two slow variables, namely, the local vacancy and magnetization densities, $\varphi(\vec{r}, t)$ and $\psi(\vec{r}, t)$. In the intermediate regime, the vacancy distribution has already reached its equilibrium value, $\varphi_o = L^{-d}$, so that the only nontrivial dynamics is embodied in $\psi(\vec{r}, t)$, which obeys a simple diffusion equation: $\partial_t \psi = D \nabla^2 \psi$. Here, the diffusion coefficient $D \propto \varphi_o$ reflects the presence of a single vacancy. The solution, with initial condition $\psi(\vec{r}, 0) = \text{sgn}(x)$, $|x| \leq L/2$, and periodic boundary conditions, is $\psi(x, t) = \sum_k \frac{4}{ikL} e^{ikx} e^{-Dk^2 t} \delta_{n\text{odd}}$, where $k = 2\pi n/L$ and $\delta_{n\text{odd}} \equiv 1$ for n odd and 0 otherwise.

We propose to describe the local spin density by the *incoherent sum* of two components (“fluids”), representing the ordered and disordered fractions. The *ordered* component, starting from being 100% phase segregated

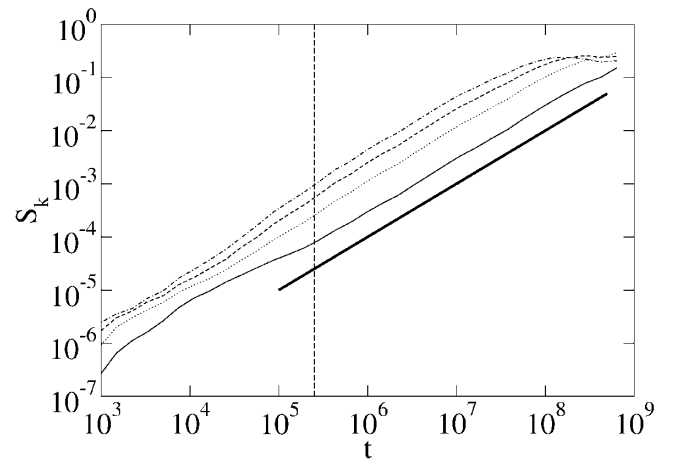


FIG. 2. Short-time behavior of the first four even structure factors on a $d = 2$, $L = 500$ lattice with VMD, averaged over 1000 runs. The thick solid line has slope 1; the vertical line indicates the beginning of the intermediate region.

and ending at zero, can be taken as $\psi(x, t)$. The remaining component, with density $1 - |\psi(x, t)|$, is *fluctuating* so that it will be represented by $(1 - |\psi(x, t)|)\eta(x, t)$, where $\eta(x, t)$ is a delta-correlated noise with zero mean. Summarizing, we write the *spin density* $s(x, t)$ as

$$s(x, t) = \psi(x, t) + (1 - |\psi(x, t)|)\eta(x, t). \quad (1)$$

Taking the Fourier transform of $s(x, t)$ and averaging over η to obtain $S_k(t)$, we find the final result

$$S_k(t) = L^d \left[\frac{2e^{-n^2 t/\tau}}{\pi n} \right]^2 \delta_{n \text{ odd}} + \sum_{n' \text{ odd}} \left[2 \frac{1 - e^{-n'^2 t/\tau}}{\pi n'} \right]^2, \quad (2)$$

where $\tau \equiv L^2/(4\pi^2 D)$ plays the role of t_L . The first term captures the decay of the initial ordered fraction. Note that only the *odd* k 's are present. By contrast, the second term is *k independent* and reflects the buildup of the disordered component.

The origin of the dips is now apparent: The first term starts with a macroscopic amplitude but decays on the time scale $\tau/2n^2$. Meanwhile, due to the sum over all n' , the second term rises to unity with τ , regardless of n . Therefore, $S_k(t)$, for odd k , does not decay to unity monotonically. Further, these dips occur at earlier times for larger k 's, a feature which agrees with the data, at least qualitatively (Fig. 1). We believe that the contrasting terms may be interpreted physically, the first being associated with the relatively *fast* deterioration of the initial phase boundary while the second represents the *slower* buildup of the disordered component.

Equation (2) leads us to another prediction, namely, how the final state is approached. By Poisson resummation [8], it can be shown that the second term increases as $t^{1/2}$ for times $t \lesssim \tau$. This effect is most easily seen in the even S_k 's where the ordered contribution is absent. The simulation data show excellent agreement with this behavior for both VMD and KD (Fig. 1).

Not surprisingly, this simple approximation has its shortcomings: According to Eq. (2), all even structure factors share the same behavior, which is clearly not borne out by the simulations. Moreover, Eq. (2) gives no indication of an early-time crossover from a t^γ to a $t^{1/2}$ behavior. To improve our understanding, we now turn to an *exact* formulation of the dynamics.

Exact lattice calculation.—In the following, we analyze the microscopic motion of the vacancy on the lattice. The resulting equation of motion for the structure factor is exact and can be solved in the case of KD. Here, we summarize the key features of this approach, deferring all details to a later publication [7].

Clearly, the dynamics at each time step (for both VMD and KD) depends on the exchange of *only two* spins, so that the Liouvillian in the master equation $\partial_t P(\{s_i\}; t) = \sum_{\{s_i'\}} \mathcal{L}(\{s_i'\}; \{s_i\}) P(\{s_i'\}; t)$ consists of a sum over terms of the form $\delta(s_i'; s_j)\delta(s_i; s_j')$. As a result, the equation

for $G(\vec{x}; t)$, the two-point function, is *linear* and involves no higher correlations. Specifically, in the KD case, one obtains (for $\vec{x} \neq \vec{0}$)

$$\frac{dL^d}{2} \partial_t G(\vec{x}; t) = \Delta_{\vec{x}} G(\vec{x}; t) + \sum_{\{\vec{b}\}} \delta_{\vec{x}, \vec{b}} [G(\vec{b}; t) - G(\vec{0}; t)], \quad (3)$$

where ∂_t , $\Delta_{\vec{x}}$, and $\{\vec{b}\}$ stand for discrete time differences, the lattice Laplacian, and the set of $2d$ lattice vectors, respectively. Taking the Fourier transform of Eq. (3), we may write an equation for the structure factor in the form

$$\partial_t S_{\vec{k}} = \sum_{\vec{k}'} X_{\vec{k}\vec{k}'} S_{\vec{k}'}. \quad (4)$$

An alternative approach starts with an equation of motion [9]: $\partial_t s_i(t) = [s_{\vec{v}+\vec{b}}(t) - s_{\vec{v}}(t)](\delta_{i\vec{v}} - \delta_{i\vec{v}+\vec{b}})$, where \vec{v} is the position of the tag at time t and \vec{b} is a lattice vector which specifies the direction of the exchange. In Fourier space, $\tilde{s}_{\vec{k}}(t+1) = \sum_{\vec{k}'} M_{\vec{k}\vec{k}'}(\vec{v}, \vec{b}) \tilde{s}_{\vec{k}'}(t)$, where $M_{\vec{k}\vec{k}'} = \delta_{\vec{k}\vec{k}'} - e^{-i(\vec{k}-\vec{k}')\vec{v}}(1 - e^{-i\vec{k}\vec{b}})(1 - e^{i\vec{k}'\vec{b}})/L^d$. Since the structure factor is defined by $S_{\vec{k}}(t) = \langle \tilde{s}_{\vec{k}}(t) \tilde{s}_{-\vec{k}}(t) \rangle$, where the average is over all possible moves over the entire time period $[0, t]$, we obtain, formally,

$$S_{\vec{k}}(t) = \sum_{\{\vec{p}_i\}, \{\vec{q}_i\}} \langle M_{\vec{k}\vec{p}_{t-1}} M_{-\vec{k}\vec{q}_{t-1}} M_{\vec{p}_{t-1}\vec{p}_{t-2}} M_{\vec{q}_{t-1}\vec{q}_{t-2}} \cdots M_{\vec{p}_1\vec{p}_0} M_{\vec{q}_1\vec{q}_0} \rangle \tilde{s}_{\vec{p}_0}(0) \tilde{s}_{\vec{q}_0}(0). \quad (5)$$

For VMD, the allowed moves are correlated leading to a nontrivial average. For KD, however, the position of the vacancy is randomized before each exchange, so that the above average *factorizes* into t factors. Cast in the form of an evolution equation, the result is precisely Eq. (4), with $X_{\vec{k}\vec{k}'} = \langle M_{\vec{k}\vec{k}'} M_{-\vec{k}-\vec{k}'} \rangle_{\vec{v}, \vec{b}} - \delta_{\vec{k}\vec{k}'}$.

With either approach, the eigenvectors and eigenvalues can be found exactly in the $L \rightarrow \infty$ limit. Deferring details to [7], we quote only the result for $d = 2$. With the reminder that $\vec{k} = (2\pi n/L, 0)$ and the initial value $S_{\vec{k}}(0) = (2L/\pi n)^2 \delta_{n \text{ odd}}$, we obtain

$$S_{\vec{k}}(t) = S_{\vec{k}}(0) e^{-(2\pi n/L)^2 t} + \frac{4}{\pi^2} \sum_{l \neq n} \frac{n^2 [1 - e^{-(2\pi l/L)^2 t}]}{l^2 (n^2 - l^2)} \delta_{l \text{ odd}}. \quad (6)$$

As in the two-fluid model, the two terms carry the same interpretations, confirming a key mean-field result: the associated crossover time scaling with L^4 . In addition, comparing the first terms in Eqs. (2) and (6), we may identify the diffusion constant D as $1/(2L^2)$. The main improvement is the \vec{k} dependence in the disordered component. In more detail, Eq. (6) correctly accounts for the presence (absence) of dips in the odd structure factors for

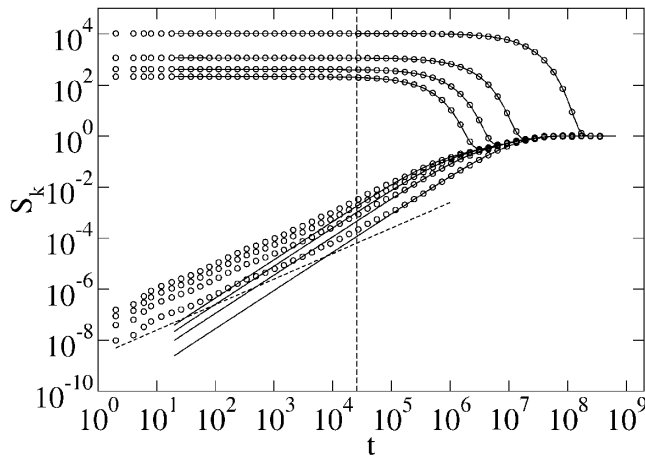


FIG. 3. Comparison of Monte Carlo data (circles) for KD [same data as in Fig. 1(b)] and the exact calculation (solid lines) for the same structure factors as in Fig. 1. The dashed line has slope 1; the solid lines have slope $3/2$ for small times.

$n > 1$ ($n = 1$). Turning to early behavior within the intermediate regime, we notice that for short times ($t \approx L^2$), the behavior of the sum in Eq. (6) is controlled by the large l contributions, whence $l^2 - n^2 \approx l^2$. Using Poisson resummation, we find $S_k(t) \propto n^2 t^{3/2}$. Both the t and the n dependence are borne out by the data. For larger times, $n^2 t/L^4 \approx 1$, a third power law emerges which is particularly noticeable for large n . Here, the sum is dominated by smaller l , so that $n^2 - l^2 \approx n^2$. Resummation now yields $t^{1/2}$, with an n -independent amplitude. For large n , this power law sets in at earlier times, so that structure factors with larger n merge *before* being joined by S_k 's with smaller n . Figure 3 shows a direct comparison of MC data with Eq. (6). Excellent agreement is observed over many orders of magnitude without *any* fit parameters.

Conclusions.—Using MC simulations and analytic arguments, we analyzed two types of microscopic kinetics (vacancy-mediated and Kawasaki dynamics). The structure factors display several remarkable features, which characterize different temporal regimes. Just before the onset of equilibration, the competition of surface- vs bulk-dominated time scales generates unexpected minima in several structure factors. These are particularly prevalent in the “odd” structure factors that are sensitive to the initial order. In contrast, the “even” structure factors grow via a sequence of different power laws before saturating. This sequence includes a $t^{3/2}$ regime for KD and a t regime for VMD. Moreover, VMD generates dips in even structure factors which are absent in KD. All of these features carry over to larger system sizes and $d = 3$; in fact, the range of the power law behaviors increases significantly with system size. Thus, the structure factors carry a clear signature of the underlying microscopic dynamics. We believe that this could lead to a simple experimental identification of

the dominant kinetic mechanism in a material, e.g., via small-angle x-ray or neutron scattering.

Two complementary theoretical approaches—a phenomenological coarse-grained two-fluid model and an exact lattice calculation—provide quantitative insight into the physical origin of these features. Several questions remain open. First, our *exact* lattice analysis can be carried out only for KD, where the dynamics of the spins is Markovian. For VMD, in contrast, though the vacancy path is random, it induces nontrivial correlations in the spins. Work is in progress to extend our analysis to this case [7]. Presumably, these correlations are also at the root of the observation that VMD equilibrates more slowly than KD, by a factor of about 4.5 in $d = 2$. It is not clear at this stage, however, whether this effect can be captured by an appropriate generalization of correlation factors [10]. Finally, the effect of several vacancies or tags should be investigated, as well as upquenches to temperatures other than infinity. These cases have so far been studied only at the mean-field level [5].

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