# Long Crossover Times in a Finite System

Charles R. Doering[(a)] and Martin A. Burschka[(b)]
*Department of Physics, Clarkson University, Potsdam, New York 13676*
(Received 5 September 1989)

We study a stochastic interacting-particle system which displays a nonequilibrium transition in its relaxation dynamics in the infinite-volume limit. The transition is destroyed by restriction to a finite volume, but its remnants remain until a crossover time $T_c(L,\epsilon)$, where $L$ is the system size and $\epsilon$ is the control parameter measuring the distance from the bulk transition. We find that the crossover time $T_c(L,\epsilon)$ *diverges* when $\epsilon \to 0$ in a *fixed volume*. Thus this finite-volume system displays arbitrarily long time scales near the transition.

PACS numbers: 05.40.+j, 02.50.+s, 05.70.Jk, 82.20.Mj

The effect of finite system size near critical points of equilibrium phase transitions has attracted much attention because of its important role in Monte Carlo simulations in condensed-matter and high-energy physics.[1-5] Finite volumes round off the transitions, mollifying the divergence of correlation lengths and times at the critical point. Most studies of time scales in finite volume have concentrated on correlation or relaxation times,[3] and these time scales are bounded at the transition point in a fixed finite volume. Attention on long time scales in nonequilibrium systems has focused on metastable states, whose lifetimes diverge only in the thermodynamic limit. Little or no attention has gone to the crossover time, i.e., the time when the effects of the system size start to influence the dynamics.

In this Letter we study an interacting-particle system, specifically a reversible system of coalescing random walks in one spatial dimension, which displays a sharp transition in its relaxation kinetics in infinite volume.[6] The transition is marked by the appearance of long-lived correlations in the particle positions, resulting in anomalously slow asymptotic relaxation rates when the initial concentration of walkers is below a critical fraction of the equilibrium concentration. The anomalous dynamics disappears in the limit $t \to \infty$ in a finite volume $L$, but they appear to exist until the crossover time $T_c$ [defined precisely in Eq. (15) below] when a uniform asymptotic decay sets in. The exact solution of the model in finite volume yields the crossover-time scaling

$$T_c(L,\epsilon) \sim L^2 \ln[\epsilon^{-1}], \tag{1}$$

for $L \gg 1$ and $\epsilon L \ll 1$, where $\epsilon$ measures the distance from the bulk transition point. Thus, this system possesses a characteristic finite-size time scale which is *arbitrarily large* as the apparent transition point ($\epsilon = 0$) is approached.

In usual (1D) transfer-matrix approaches to finite-size effects, the convergence of *eigenvalues* controls the longest time scale as $L \to \infty$.[4,5] There, the longest scales are identified with the inverse of a vanishing mass gap. We find that it is not just this spectral development, but also the critical behavior of the *coefficients* of the order-parameter expansion (in our case, the macroscopic concentration) near the transition which determines the scaling of the crossover time.

We formulate our model on a one-dimensional lattice and then take the continuum limit to simplify the solution. The model consists of particles which diffuse independently with macroscopic diffusion coefficient $D$ until two of them meet. Upon encounter, two particles fuse into one. Additionally, each particle randomly gives birth to another at an adjacent lattice site at a fixed rate $\gamma$. This system is a one-dimensional model of reversible diffusion-limited coagulation,[6] denoted $A+A \leftrightarrow A$. The physical quantity of interest is the time-dependent concentration of particles, $C(t)$. Spatial correlations can dominate the kinetics of such diffusion-limited processes, and the usual "mean-field" rate equations for the macroscopic concentration often do not apply in low spatial dimensions.[7-9] This is the case for this process in particular and, in fact, $C(t)$ satisfies *no* autonomous ordinary differential equation of finite order.[6,10]

We analyze the system by considering the time-dependent probability, $E(x,t)$, that an interval of length $x$ is empty. The exact (closed) kinetic equation for $E(x,t)$ follows simply from an analysis of the terms which contribute to its time development: An interval of length $x$ can become empty only if it is occupied by a single particle at one of its end points and this particle diffuses out. The probability that a particle is at the end of an otherwise empty interval of length $x$ is $E(x-\Delta x,t)-E(x,t)$, and the diffusive hop rate is $D/\Delta x^2$, where $\Delta x$ is the lattice spacing. Because there are two ends of the interval, the contribution of this process to the rate of change of $E(x,t)$ is

$$[\partial E(x,t)/\partial t]_{\text{diff out}} = 2D[E(x-\Delta x,t)-E(x,t)]/\Delta x^2. \tag{2}$$

If an interval of length $x$ is empty, particles enter into it by two processes. First, a particle just outside the interval can diffuse in. The probability that there is a particle just outside one end point is $E(x,t)-E(x+\Delta x,t)$, and it hops into the interval at rate $D/\Delta x^2$. Because of the two ends of the interval, this contributes

$$[\partial E(x,t)/\partial t]_{\text{diff in}} = -2D[E(x,t)-E(x+\Delta x,t)]/\Delta x^2. \tag{3}$$

Second, a particle just outside the empty interval [probability $E(x,t)-E(x+\Delta x,t)$] can give birth to a particle

at an end point of the interval. It gives birth to another particle in the interval at rate $\gamma/2$, and taking into account both ends of the interval, this process contributes

$$[\partial E(x,t)/\partial t]_{\text{birth in}} = -\gamma[E(x,t)-E(x+\Delta x,t)]\,. \quad (4)$$

Adding these terms together and taking the continuum limit $\Delta x \to 0$, we arrive at the kinetic equation

$$\partial E(x,t)/\partial t = 2D\,\partial^2 E/\partial x^2 + v\,\partial E/\partial x\,, \quad (5)$$

where $v=\gamma\Delta x$. Note that $\gamma\to\infty$ as $\Delta x\to 0$, keeping $v$ finite, to obtain a nontrivial continuum limit. The boundary condition for Eq. (5) at $x=0$ is

$$E(0,t)=1 \quad (6)$$

because the point particles occupy a set of zero measure. (In fact, it is this boundary condition which imposes the coagulation reaction.) As long as the concentration is nonzero, the other boundary condition is

$$E(L,t)=0\,, \quad (7)$$

where $L$ is the interval length, $0<L\le\infty$. When $L$ is finite we take periodic boundary conditions so that we retain translation invariance.

The concentration $C(t)$ is recovered from $E(x,t)$ by noting that the probability that any particular site is occupied is the probability that it is not empty, i.e., $1-E(\Delta x,t)=E(0,t)-E(\Delta x,t)$. The concentration is this probability per unit length, so in the continuum limit we have

$$C(t)=-\partial E(x,t)/\partial x\,|_{x=0}\,. \quad (8)$$

This formulation of the problem allows us to solve for the exact time-dependent concentration of interacting random walkers in (statistically) spatially homogeneous systems. This is *not* to say that spatial fluctuations in the microscopic density are ignored as in a mean-field approximation. Provided only that the initial state is statistically homogeneous, all correlations that develop during the relaxation are fully accounted for without approximation.

We now discuss the system's behavior in the thermodynamic limit, displaying the sharp transition in the relaxation dynamics. We consider initial conditions consisting of the "experimentally" accessible equilibrium states at various values of the system parameters $D$ and $v$. The stationary solution to Eq. (5) with the infinite-volume boundary conditions is

$$E_{\text{eq}}(x)=e^{-vx/2D}\,, \quad (9)$$

yielding the equilibrium concentration

$$C_{\text{eq}}=v/2D\,. \quad (10)$$

If the system starts out with concentration $C(0)=C_0$ and relaxes to a new equilibrium with concentration $C(\infty)=C_{\text{eq}}$, then the exact time dependence of the transient depends on the initial concentration. For $t\to\infty$, the deviation from the equilibrium concentration is[6]

$$\delta C(t)=C(t)-C_{\text{eq}}\sim\begin{cases}2\pi^{-1/2}C_{\text{eq}}[1-(1-2C_0/C_{\text{eq}})^{-2}](v^2t/2D)^{-3/2}\exp\{-v^2t/8D\}\,, & C_0>C_{\text{eq}}/2\,, \quad (11a)\\ -\pi^{-1/2}C_{\text{eq}}(v^2t/2D)^{-1/2}\exp\{-v^2t/8D\}\,, & C_0=C_{\text{eq}}/2\,, \quad (11b)\\ -C_{\text{eq}}(1-2C_0/C_{\text{eq}})\exp\{-v^2[C_0/C_{\text{eq}}-(C_0/C_{\text{eq}})^2]t/2D\}\,, & C_0<C_{\text{eq}}/2\,. \quad (11c)\end{cases}$$

The infinite-volume relaxation dynamics, with the leading exponential time dependence for $C_0>C_{\text{eq}}/2$ [i.e., $\exp\{-v^2t/8D\}$] removed, is shown in Fig. 1 for several initial concentrations. The relaxation dynamics undergoes a sharp transition when the initial concentration is exactly half of the equilibrium concentration. While the exponential relaxation time has the value $\tau=8D/v^2$ *uniformly* in the initial condition for $C_0\ge C_{\text{eq}}/2$, it becomes *initial-condition dependent* when $C_0<C_{\text{eq}}/2$. The fact that the asymptotic dynamics in Eq. (11a) for $C_0>C_{\text{eq}}/2$ does not depend on the precise value of $C_0$ is what one would expect from any system that admits a "hydrodynamic" description. The relaxation process slows down, however, if $C_0<C_{\text{eq}}/2$, reflecting the dominance of microscopic density fluctuations in the system's macroscopic kinetics. At low initial concentrations there are typically relatively large empty regions of length of the order $1/C_0$. These empty spaces must be filled up to reach equilibrium, and the only mechanism for this is the diffusion of newly born particles from the end points of these gaps. Concentration fronts permeate empty re-

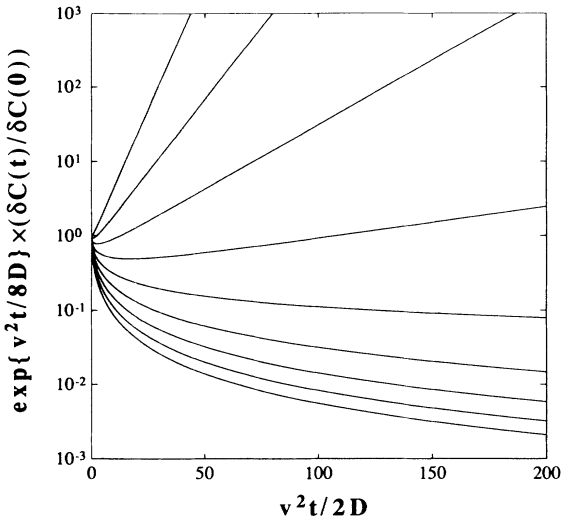


FIG. 1. Concentration perturbation vs time for a selection of initial conditions around $C_0=C_{\text{eq}}/2$. The leading time dependence of $C_0>C_{\text{eq}}/2$ is factored out to highlight the sharp transition in the relaxation kinetics in the infinite system. From top to bottom, the initial concentrations are $C_0=0.1C_{\text{eq}}$, $0.2C_{\text{eq}},\ldots,0.9C_{\text{eq}}$.

gions at speed $v$, so a typical time scale is $\tau \approx (C_0 v)^{-1} = (2D/v^2)C_{eq}/C_0$, in accord with the exponential relaxation time in Eq. (11c) for $C_0 \ll C_{eq}/2$. The remarkable point about this permeation mechanism is that its influence on the asymptotic dynamics becomes negligible precisely when $C_0 = C_{eq}/2$.

We now turn to the finite-volume process. As before, we consider the equilibrium states of the system at fixed values of the system parameters as initial conditions. The stationary solution of Eq. (5) with finite $L$ is

$$E_{eq}(x) = [e^{-vx/2D} - e^{-vL/2D}]/[1 - e^{-vL/2D}], \quad (12)$$

and the equilibrium concentration in finite volume is

$$C_{eq} = (v/2D)/[1 - e^{-vL/2D}]. \quad (13)$$

We denote the value of $v/2D$ at which the system is initially prepared by $\alpha$ $(0 < \alpha < \infty)$, and we treat $\alpha$ as the system control parameter, so that the bulk transition occurs at $\alpha = \alpha_c \equiv v/4D$.

The time-dependent solution of Eq. (5), with the initial condition Eq. (12) (with $v/2D = \alpha$) and the finite-$L$ boundary conditions, is straightforward using a spectral decomposition. The exact time-dependent deviation of the concentration from its equilibrium value is

$$\delta C(t) \equiv C(t) - C_{eq} = (2/L) \sum_{n=0}^{\infty} a_n e^{-\lambda_n t}, \quad (14a)$$

where

$$\lambda_n = (v^2/2D)\{(2\pi n D/vL)^2 + \tfrac{1}{4}\}, \quad (14b)$$

and

$$a_n = \frac{1 - (-1)^n e^{(v/4D - \alpha)L}}{1 - e^{-\alpha L}} \left\{ \frac{1}{1 + (vL/4\pi n D)^2} - \frac{1}{1 + (1 - 4D\alpha/v)^2 (vL/4\pi n D)^2} \right\}. \quad (14c)$$

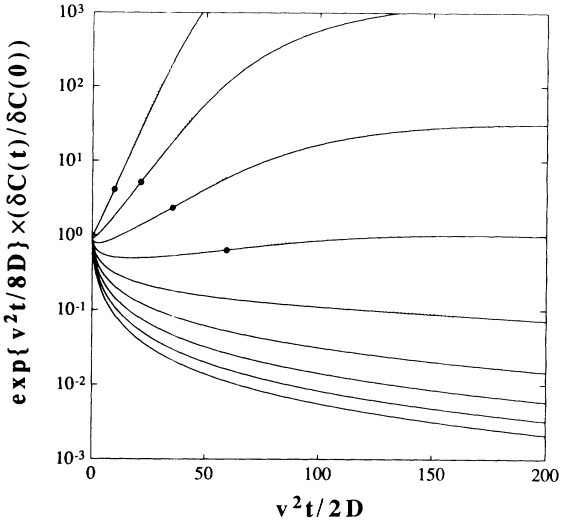


FIG. 2. Concentration perturbation vs time in finite volume. As in Fig. 1, the leading bulk time dependence for $C_0 > C_{eq}/2$ is factored out. The dotted lines are the corresponding infinite-volume curves. Below the transition point the anomalous decay persists until the crossover time $T_c$ defined in Eq. (15), and indicated by the dot on the curves for $\alpha < \alpha_c = 0.5(v/2D)$. From top to bottom, the initial concentrations are given by $C_0 = \alpha/[1 - \exp(-\alpha L)]$ with $\alpha = 0.1(v/2D), \ldots, 0.9(v/2D)$. The system size here is $Lv/D = 100$.

The exact relaxation dynamics in finite volume, with the leading *bulk* exponential time dependence (i.e., $\exp\{-v^2 t/8D\}$) removed, is shown in Fig. 2. For any initial concentration the decay is eventually dominated by the first term in the sum in Eq. (14a), but remnants of the infinite-volume transition are visible, for $\alpha < \alpha_c$, for times short compared to the "crossover time." We identify the crossover time, for $\alpha < \alpha_c$, as the time where the qualitative shape of the curve departs from the bulk shape. More precisely, we define the crossover time $T_c$ as the location of the inflection point of curves in Fig. 2:

$$0 = d^2 \ln[|\delta C(t)|]/dt^2|_{t=T_c}. \quad (15)$$

This specific definition is just one out of many possible *specific* definitions of the crossover time. The time where "the qualitative shape of the curve departs from the bulk shape" is not unambiguously defined by these words alone but, as indicated in Fig. 2, Eq. (15) certainly captures its essence. In any case, the qualitative validity of our observations is not affected by minor quantitative variations in the crossover-time definition.

We define $\epsilon \equiv (\alpha_c - \alpha)/\alpha_c \geq 0$, measuring the distance from the critical initial concentration for $\alpha \leq \alpha_c$. The crossover time is certainly a function of the system size and, referring to Fig. 2, it is also clearly a function of $\epsilon$, increasing as $\epsilon$ decreases. Direct numerical evaluation of $T_c(L, \epsilon)$ near $\epsilon = 0$ yields crossover times large compared to $L^2/D$. Thus we may perform an asymptotic analysis considering only the first two corrections to the leading behavior of the series in Eq. (14). Indeed, for times $t \gg L^2/D$, $|a_n| e^{-\lambda_n t}$ decreases very quickly with increasing $n$, justifying the neglect of all but the earliest terms in the sum. Hence, near the crossover time we write

$$\ln[|\delta C(t)|] \approx \ln[|a_1 e^{-\lambda_1 t} + a_2 e^{-\lambda_2 t} + a_3 e^{-\lambda_3 t}|] + \ln[2/L] \quad (16a)$$

$$\approx -\lambda_1 t + \ln[|a_1|] + (a_2/|a_1|) e^{-(\lambda_2 - \lambda_1)t} + (a_3/|a_1|) e^{-(\lambda_3 - \lambda_1)t} + \ln[2/L]. \quad (16b)$$

The crossover time is then simply evaluated from Eqs. (15) and (16b):

$$T_c \approx (\lambda_3 - \lambda_2)^{-1} \ln[-a_3/a_2] + (\lambda_3 - \lambda_2)^{-1} \ln[(\lambda_2 - \lambda_1)^2/(\lambda_3 - \lambda_1)^2]. \quad (17)$$

The behavior of the coefficients $a_n$ near $\epsilon = 0$ is found from Eq. (14c). For large volumes (strictly speaking, when the equilibrium *number* of particles is large,

$vL/2D \gg 1$) we find

$$a_1 \approx -2, \quad a_2 \approx \epsilon vL/2D, \quad a_3 \approx -2. \tag{18}$$

Thus for a fixed large system size, close to the transition point such that $0 < \epsilon \ll D/Lv$, the crossover time is given by the asymptotic formula

$$T_c(L,\epsilon) \approx (5\pi^2)^{-1}(L^2/2D)\ln[1/\epsilon]. \tag{19}$$

This is the scaling presented in Eq. (1). Note our main result that $T_c(L,\epsilon)$ is *unbounded* for finite system size near the transition at $\epsilon = 0$. Equation (19) agrees quantitatively with a direct numerical evaluation of the crossover time from Eq. (14).

The mathematical mechanism responsible for the existence of the crossover time is the alternation of the signs of the coefficients $a_n$. When $\alpha < \alpha_c$, the even and odd terms in the series for $\delta C(t)$ have opposite signs (+ and −, respectively). This permits the vanishing second logarithmic derivative; in Eq. (17), $a_3/a_2 < 0$ is a necessary condition for the existence of $T_c$. At the transition point the even coefficients all vanish. If $\alpha_c < \alpha < v/2D$, the coefficients are all negative. The $a_n$'s vanish identically if the system is initially in equilibrium ($\alpha = v/2D$), and they are all positive for $\alpha > v/2D$. Thus no crossover time, as defined by Eq. (15), exists unless $\alpha < \alpha_c$.

The mathematical mechanism for the infinite-volume transition[6] appears to be quite different from the manifestation of its remnants for $L < \infty$. The relaxation spectrum is continuous for the infinite system [this is not surprising in light of Eq. (14b)], but it also extends continuously all the way down to $\lambda = 0$ [this *is* surprising in light of Eq. (14b), which suggests a gap of $v^2/8D$]. The eigenfunctions of Eq. (5) with the infinite-volume boundary conditions are, however, qualitatively different for $\lambda < v^2/8D$ or $\lambda > v^2/8D$: The *temporally* slow modes all decay in *space* slower than $e^{-C_{eq}x/2}$, and are recruited into the dynamics only for initial conditions corresponding to equilibrium concentrations less than exactly $C_{eq}/2$. This "spectral" mechanism is not clearly identified within the finite-size analysis described above. The infinite-volume limit of the apparently simple, linear, constant-coefficient partial differential equation in Eq. (5) is a surprisingly singular limit of the finite-volume problem.

One natural question that arises concerns the role that the continuum limit plays in the phenomena described in this paper. In fact, it plays no role qualitatively. The unbounded behavior of the crossover time arises in this model as long as it has at least three eigenvalues,[11] corresponding to a four-site system with periodic boundary conditions. We thus arrive at the conclusion that even very small discrete interacting stochastic dynamic systems can possess time scales of arbitrarily large magnitude.

We are indebted to G. Forgacs, S. Redner, N. Svrakic, Y. Ueno, and especially V. Privman for enlightening discussion. We acknowledge extensive discussions and collaborations with D. ben-Avraham. Numerical computations were performed with the MATLAB software system, provided by The Math Works, Inc. This research was supported by NSF Grants No. PHY-8958506 and No PHY-8907755.

[a]Also at Institute for Nonlinear Studies, Clarkson University, Potsdam, NY 13676.

[b]Also at Laboratory of Biophysics, The Rockefeller University, New York, NY 10021. Current address: Elsterweg 10, D-41 Duisburg 14, West Germany.

[1]M. E. Fisher, in *Critical Phenomena,* International School of Physics "Enrico Fermi," Course 51, edited by M. S. Green (Academic, New York, 1971); M. N. Barber, in *Phase Transitions and Critical Phenomena,* edited by C. Domb and J. L. Lebowitz (Academic, New York, 1983), Vol. 8.

[2]V. Privman, in "Finite Size Scaling and Numerical Simulation of Statistical Systems," edited by V. Privman (World Scientific, Singapore, to be published).

[3]Y. Y. Goldschmidt, Nucl. Phys. **B280 [FS18]**, 340 (1987); **B285 [FS19]**, 519 (1987); H. W. Diehl, Z. Phys. B **66**, 211 (1987).

[4]W. Kinzel, in *Percolation Structures and Processes,* edited by G. Deutscher, R. Zallen, and J. Adler (Adam Hilger, Bristol, 1983); V. Privman and N. M. Svrakic, *Directed Models of Polymers, Interfaces and Clusters: Scaling and Finite Size Properties,* Lecture Notes in Physics Vol. 338 (Springer-Verlag, Berlin, 1989).

[5]W. Kinzel, Z. Phys. B **58**, 229 (1985).

[6]M. A. Burschka, C. R. Doering, and D. ben-Avraham, Phys. Rev. Lett. **63**, 700 (1989).

[7]K. Kang and S. Redner, Phys. Rev. A **32**, 435 (1985).

[8]R. Kopelman, J. Stat. Phys. **48**, 315 (1986); Science **241**, 1620 (1988).

[9]M. A. Burschka, J. Stat. Phys. **45**, 715 (1986).

[10]C. R. Doering and D. ben-Avraham, Phys. Rev. Lett. **62**, 2563 (1989); Phys. Rev. A **38**, 3035 (1988).

[11]M. A. Burschka and C. R. Doering (unpublished).