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Conserved Moments in Nonequilibrium Field Dynamics

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We demonstrate with the example of Cahn–Hilliard dynamics that the macroscopic kinetics of first-order phase transitions exhibits an infinite number of constants of motion. Moreover, this result holds in any space dimension for a broad class of nonequilibrium processes whose macroscopic behavior is governed by equations of the form $\partial\phi/\partial t = \mathscr{L} W(\phi)$, where ϕ is an "order parameter," W is an arbitrary function of ϕ, and $\mathscr{L}$ is a linear Hermitian operator. We speculate on the implications of this result.

KEY WORDS: Phase segregation; pattern formation; field dynamics; nonequilibrium.

1. INTRODUCTION

Many problems in nonequilibrium field dynamics such as spinodal decomposition[(1)] and pattern formation[(2)] have a unifying description. Namely, their macroscopic behavior can be described by equations of the form

$$\partial\phi/\partial t = \mathscr{L}(W(\phi) + \eta) \tag{1}$$

where ϕ is an "order parameter" (possibly a vector or tensor), $\mathscr{L}$ is a linear, Hermitian operator, $W(\phi)$ is a function of ϕ, and η is a stochastic variable.

It was recently shown[(3)] that processes described by (1) on an arbitrary d-dimensional manifold $\mathscr{M}$ possess an infinite number of conserved quantities:

$$C_n = \int_{\mathscr{M}} \psi_n \phi \, d^d\mathbf{x} \tag{2}$$

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where $\mathscr{L}\psi_n = 0$. That is, the projections of ϕ on the null space of $\mathscr{L}$ are time invariant. If $\mathscr{M}$ is infinite (e.g., R^d), then $W(\phi)$ should decay sufficiently fast as $r \to \infty$ if the ψ_n diverge as $r \to \infty$, or at the origin if the ψ_n diverge at the origin. The criterion that C_n is constant is very simple: C_n should be finite. This result is an extension of previous results[4] corresponding to the singular limit when ϕ is a step function on the moving boundary.

A proof of this general result is remarkably simple, and we sketch it here. Since the eigenfunctions ψ_n are independent of time,

$$\frac{dC_n}{dt} = \int_{\mathscr{M}} \psi_n \frac{\partial \phi}{\partial t} d^d\mathbf{x} \tag{3}$$

which from (1) gives

$$\frac{dC_n}{dt} = \int_{\mathscr{M}} \psi_n \mathscr{L}(W(\phi) + \eta)\, d^d\mathbf{x} \tag{4}$$

Since $\mathscr{L}$ is Hermitian and $\mathscr{L}\psi_n = 0$,

$$\frac{dC_n}{dt} = \int_{\mathscr{M}} (\mathscr{L}\psi_n)(W(\phi) + \eta)\, d^d\mathbf{x} = 0 \tag{5}$$

Therefore the "moments" C_n are constant in time.

In view of the complexity that these systems often exhibit (W can be nonlocal and highly nonlinear), it is surprising to observe that there exist an infinite number of constants of motion. It is precisely these conservation laws which are attributed to the exactly integrable interface dynamics in Laplacian pattern formation.[5] In this paper, we discuss the application of this observation to several problems in nonequilibrium statistical mechanics, in particular the kinetics of first-order phase transitions.

2. PHASE SEPARATION

When a uniform binary alloy is quenched from equilibrium at high temperature to a lower temperature at which the uniform state is no longer stable, it undergoes phase segregation. Typically the macroscopic dynamics of a phase transition is described by an equation of the form

$$\frac{\partial \phi}{\partial t} = L\nabla^2 \frac{\delta H}{\delta \phi} \tag{6}$$

where H is the free energy functional for the order parameter ϕ, and L is a kinetic coefficient. A common choice for H is the Ginzburg–Landau potential,

$$H_{\mathrm{GL}}[\phi] = \int \left[\frac{\xi^2}{2} (\nabla\phi)^2 - \frac{1}{2a} \phi^2 + \frac{1}{4a} \phi^4 \right] d^d x \tag{7}$$

This choice is suitable for modeling the order parameter dynamics in phase segregation for solid alloys without elastic interactions. The order parameter ϕ (a scalar in this case) represents, for example, the local difference in concentration between alloy components, ξ is the correlation length, and $1/4a$ is the depth of the double-well potential. This choice of free energy leads to the Cahn–Hilliard (CH) equation[1]

$$\partial\phi/\partial t = \nabla^2(\xi^2 \nabla^2 \phi + (\phi - \phi^3)/a + \eta) \tag{8}$$

Note that this is of the form (1), and that the order parameter ϕ is conserved globally in time.

Due to the complexity and nonlinearity of these and other nonequilibrium processes, the current theoretical understanding is far from complete. Therefore, here we restrict ourselves to a study of the CH equation as a model for phase transition kinetics. The CH equation (8) is particularly useful since it qualitatively describes a variety of pattern formation and phase separation processes, and with additional terms one can model a variety of other physical phenomena (e.g., pure diffusion and growth in a random field). Moreover, this is a limiting case of a phase-field equation[6] describing pattern formation when the appropriate relaxation time tends to zero. In the limit $\xi \to 0$ and $a \to 0$ in the phase field model this problem degenerates to the Stefan problem (generally with nonzero surface tension).[7] It was shown[3] that in this limit, the interface dynamics problem can be exactly integrable, and the conserved quantities C_n of (2) play the role of polynomial conservation laws.

It follows from the observation (5) that although ϕ initially may be composed of only a finite number of modes, because of the nonlinearity, superharmonics will in general be generated in the course of the evolution. For example, in R^2, with $\mathscr{L} = \nabla^2$, the eigenfunctions ψ_n from (2) are chosen to be z^n, where $z = re^{i\theta}$. If only the first n modes are present at $t = 0$, then

$$\phi(r, t=0) = \sum_{k=-n}^{n} \phi_k(r, t=0)\, e^{ik\theta} \tag{9}$$

where r and θ are polar coordinates. However, from (5) and the orthogonality of the $e^{ik\theta}$, each harmonic should adhere to the following constraint:

$$\int_0^\infty r^{k+1}\phi_k(r, t)\, dr = 0 \tag{10}$$

for $k > |n|$. It follows from (9) that although $\phi_k = 0$ initially, these modes evolve to some nonzero value with the constraint (10). This implies an oscillatory, decaying behavior of $\phi_k(r)$.

In higher dimensions the eigenfunctions must be chosen appropriately. If, for example, $\mathcal{M} = R^3$ with $\mathcal{L} = \nabla^2$, then $\psi^l_m = Y^l_m \equiv r^m P^l_m(\theta, \phi)$, the spherical harmonics.

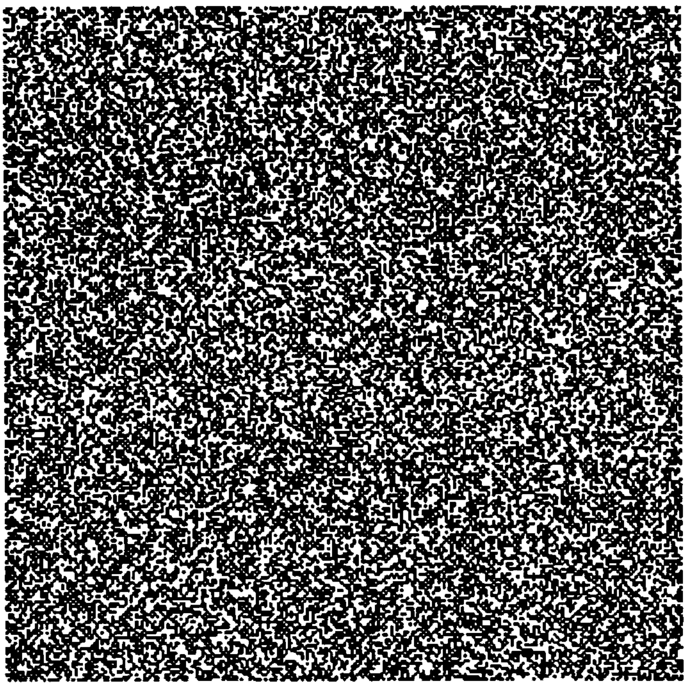
3. NUMERICAL SIMULATIONS

As is evident from (1), the same initial distribution of order parameter ϕ for different forms of the function W will produce the same constants of motion C_n. That this should hold on a lattice is not guaranteed, since the discretized version of the operator $\mathcal{L}$ will in general not be *Hermitian*. To demonstrate that a somewhat weakened version of the continuum result also holds on a lattice, we decided to study three qualitatively different physical processes in the framework of CH dynamics: linear diffusion and spinodal decomposition in the presence and absence of a random magnetic field. The results of our numerical investigations are that while the evolution of ϕ is very different for each of these processes (see Figs. 1b, 1c, and 1d), the moments C_1 to C_7 are constant throughout the length of the evolution, and higher "harmonic" moments are unchanging to within machine accuracy. We speculate on the possible impact on the topology of the final distribution of ϕ and on the physics of this process.

We carried out our simulations on two-dimensional periodic lattices of size 1024×1024. Periodic lattices were chosen for simplicity, but since the times of the runs were short enough, they imitate an infinite system. Longer runs would have allowed sites to interact with their periodic images, and the choice of eigenfunctions would have been different.

The initial configuration of the order parameter ϕ was chosen to be identical for all three dynamics. It was generated according to the distribution $P[\phi(x, t=0)]$, where $P[\phi]$ is Gaussian with $\langle\phi\rangle = 0$ and $\langle\phi^2\rangle = 0.05$. For $r > R = 256$ lattice units, $\phi = -1$. We used a first order Euler scheme to integrate (6). Instead of discretizing the Laplacian as

$$\nabla^2 f(z) = f(z+i) + f(z-i) + f(z+1) + f(z-1) - 4f(z) \tag{11}$$



a

Fig. 1. (a) Initial conditions for the quench described in the text and then after $2000\delta t$ for (b) spinodal decomposition, (c) linear diffusion, and (d) spinodal decomposition in a magnetic field. Black represents regions of $\phi > 0$, while for white, $\phi < 0$. Only a 257×257 lattice site portion of the entire system is shown.

which would exactly conserve the moments C_0, C_1, C_2, and C_3 but not higher ones, we chose a discretization which conserves the next four higher moments as well. In our simulations we used

$$\begin{aligned}\nabla_L^2 f(z) = {} & f(z+i) + f(z-i) + f(z+1) + f(z-1) - 4f(z) \\ & + 1/4[f(z+i+1) + f(z-i+1) + f(z+i-1) \\ & + f(z-i-1) - 4f(z)]\end{aligned} \tag{12}$$

Thus we have the finite-difference scheme

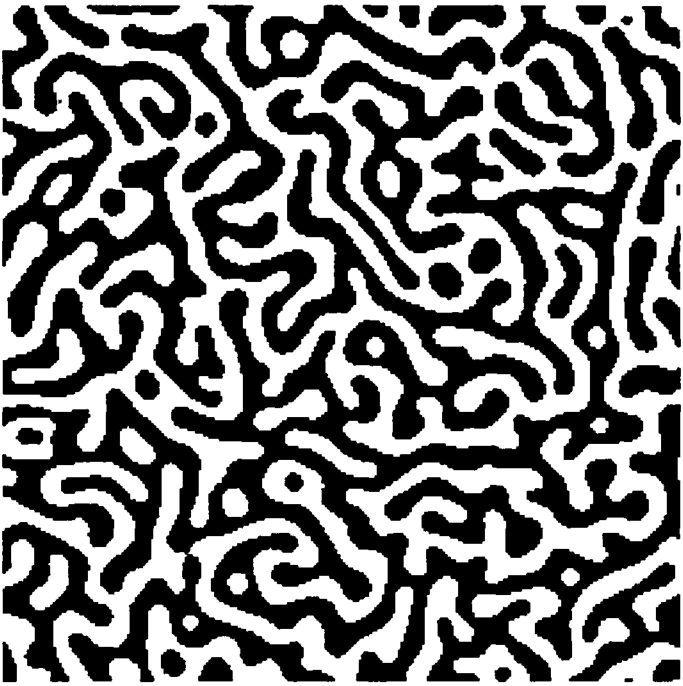
$$\begin{aligned}&\phi(x, t+1) \\ &\quad = \phi(x, t) + \frac{\delta t}{2(\delta x)^2} \nabla_L^2 \left(-\beta\phi + \alpha\phi^3 - \gamma \frac{1}{2(\delta x)^2} \nabla_L^2 \phi + \tilde{h}(x)\,\phi \right)\end{aligned} \tag{13}$$

b

Fig. 1. *Continued*

For the case of linear diffusion we chose $\delta t = 0.3$, $\delta x = 1.7$, $\alpha = 0$, $\beta = -1.0$, $\gamma = 0$, and $\tilde{h}(x) = 0$ for all x. For CH without a magnetic field we chose parameters identical to those in ref. 8: $\delta t = 0.3$, $\delta x = 1.7$, $\alpha = 1.0$, $\beta = 1.0$, $\gamma = 1.0$, and $\tilde{h}(x) = 0$ for all x. In the case of CH with a random magnetic field we used $\delta t = 0.025$, $\delta x = 1.0$, $\alpha = 1.0$, $\beta = 1.0$, $\gamma = 1.0$, and $\langle \tilde{h}(x) \rangle = 0$ and $\langle \tilde{h}^2(x) \rangle = 2$.

Note that in the CH equation single-phase domains grow like $t^{1/3}$,[8] while in in the presence of a random magnetic field they grow logarithmically in time.[9] In diffusion, the initial noise is smeared out, and domains of the same sign of ϕ grow like $t^{1/2}$, i.e., diffusively. Although the order parameter configurations are different at different times and for different dynamics, each of the first 18 harmonic moments are time and dynamics *independent*. Our choice of discrete Laplacian guarantees that $C_1, \ldots, C_7$ will have this property, but to machine accuracy, C_8 to C_{18} also do.

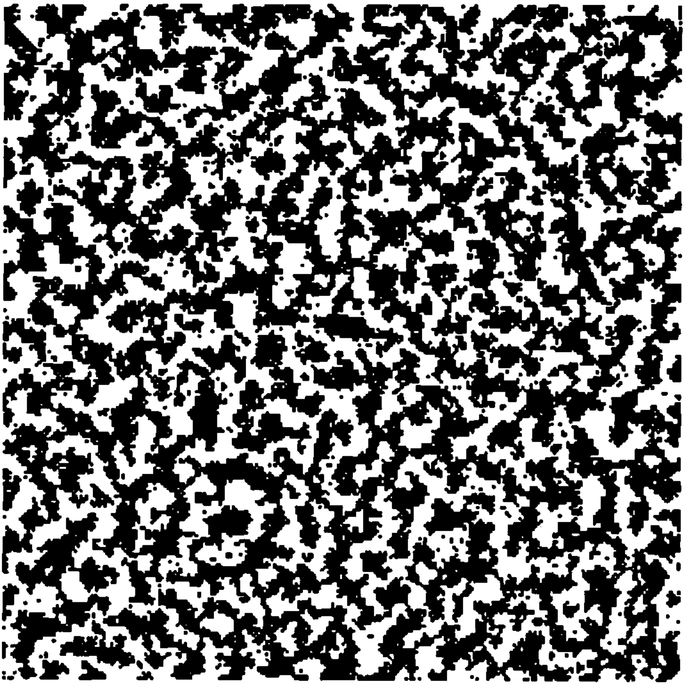


c

Fig. 1. *Continued*

To demonstrate that $C_n = \text{const}$ holds only for ψ_n that are solutions of $\nabla^2\psi_n = 0$ in two dimensions $\psi_n = z^n$, we also studied the evolution of the so-called "anharmonic" moments, i.e., $C_{mn} = \int \phi z^m \bar{z}^n \, dx$, where $n \neq 0$. We found that in general the C_{mn} are not conserved. This indicates that the conservation of the harmonic moments C_m is not due to a slow evolution of the field. A similar analysis was performed earlier[10] to demonstrate that two-dimensional diffusion-limited aggregation has potentially an infinite number of conservation laws.

Recently Tomita[11] showed that the dipole moment $\mathbf{d} = \int \mathbf{x}\phi$ is conserved in two-dimensional CH dynamics, but that the moment of inertia $I = \int \phi(x^2 + y^2) \, d^d\mathbf{x}$ is not. This clearly follows from our results, since z is harmonic, whereas $x^2 + y^2 = z\bar{z}$ is not. Rather $\int \phi(x^2 - y^2) \, dx \, dy$ is the second moment which should be (and is) conserved.



d

Fig. 1. *Continued*

4. PHYSICAL IMPLICATIONS

The integrals C_n have a very clear physical interpretation: they are the coefficients of the multipole expansion of a "potential" $\mathcal{U}$ created by a "charge density" $q=(\phi+1)/2$ in the domain where $q=0$ (i.e., in a far field),[4]

$$\mathcal{L}\mathcal{U}=(\phi+1)/2 \tag{14}$$

The following arguments (for the 2D case where $\mathcal{L}$ is the Laplacian operator) may aid in understanding the last statement: One can imagine matter with density $\psi=(\phi+1)/2$ distributed in the finite part of the space so that it vanishes in the far field. This matter creates a Newtonian potential in space

$$U(x, y)=\int \log |z-z_1|\, \psi(x_1, y_1)\, dx_1\, dy_1 \tag{15}$$

Taking the gradient and considering $|z|$ to be so large that $|r_1/z|<1$ everywhere where the density $|\phi|$ is not zero, one has (making a series expansion of the right-hand side with respect to $|z_1/z|$) $\nabla U(r)=\sum C_k z^{-k}$.

This means that the moments C_k we deal with are nothing else but multipole moments of the potential created by the "density" $(\phi+1)/2$ in the far-field region. Therefore, the problem of recovering the dynamics of $\phi(\mathbf{x}, t)$ is reduced to the inverse potential problem,[12] that is, to obtaining the charge density from the far-field potential.

Because the inverse problem is in general ill-posed (i.e., has a multitude of solutions), it is clear that far from the nonzero q one can measure the same potential corresponding to the same initial configuration of ϕ but with different dynamics during the evolution. Therefore, the knowledge of this potential is not enough to specify the evolution. The evolution takes place only beyond the null space of $\mathscr{L}$, while the projection of ϕ to the null space of the operator $\mathscr{L}$ is not changed in time. Therefore, that the C_n are constants does not provide us with much information about the *dynamics*, but can shed light on the quasiequilibrium properties of these systems.

We believe that knowledge of the quantities C_n can help in the long-time limit where ϕ attains a quasiequilibrium state governed by $\nabla^2(\delta H/\delta\phi)=0$. This equation, typically nonlinear, has many solutions, and we do not know which one to select as the final state for a given initial distribution of ϕ. While the conserved quantities do not select a unique final state, they nevertheless dramatically reduce the number of possible choices. It seems that the initial distribution of the order parameter $\phi(x, t=0)$ creates topological constraints on possible final states, and the evolution occurs subject to these constraints.

As mentioned above, the singular limit of the CH equation when both a and ξ tend to zero corresponds to Laplacian growth which can be integrable at least in two dimensions for a singly connected domain.[5] This corresponds to a bistable case of $\phi=\phi_\pm$ ($\phi=\pm 1$ for H_{GL}). In this case the associated inverse problem becomes a well-posed one. This implies that the conserved quantities C_n appear to be enough to characterize the shape of a cluster of $\phi=+1$ surrounded by a "sea" of $\phi=-1$. In the context of phase transition kinetics this corresponds to the Ising limit, where the order parameter ϕ at each site can only have two values $\phi=\pm 1$. Our results imply that in this limit knowledge of the C_n (from the initial data) can determine the final spin configuration uniquely (if the spin-up cluster is singly connected) or can at least considerably reduce the selection of possible final configurations in the case of a multiply connected topology (which is typical in phase transition kinetics). So it appears that *the Stefan limit corresponds to the Ising limit.*

In conclusion, we have shown that the nonlinear dynamics of a field given by Eq. (1) possesses an infinite number of conserved quantities C_n, Eq. (2), corresponding to the coefficients of a multipole expansion of a potential created by ϕ. Numerical simulations have shown that very different examples of (1) give rise to the same C_n, even on a lattice. We discussed that in the Ising limit of phase transition kinetics this problem can be uniquely solved in a long-time limit, where the order parameter reaches its quasiequilibrium state. Because of nonperturbative effects, it might prove useful to investigate the behavior of the harmonic moments for a spin exchange Ising model where the effects of noise and discrete spin are present. Even more interesting would be an experimental measurement of the C_n in a phase-separating binary fluid or alloy.

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