Theory of Unstable Thermodynamic Systems

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A first-principles global theory of unstable thermodynamic systems is developed which properly describes the growth kinetics of quenched systems from early through late times and includes sharp interfaces in the late stage description.

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The inclusion of sharp interfaces in a first-principles theory of the dynamics of unstable thermodynamic systems has been a difficult proposition. A global theory of "spinodal decomposition" is presented here which is valid over the entire time regime initiated by a deep temperature quench at time t_0 to late times where coarsening takes place via the motion of sharp interfaces. The theory in the long-time limit gives a structure factor satisfying scaling,[1] obeying Porod's law[2] (short-distance scattering from a sharp interface), and gives growth exponents in agreement with classical arguments [$n=\frac{1}{2}$ for a nonconserved order parameter[3] (NCOP) and $n=\frac{1}{3}$ for a conserved order parameter[4] (COP)]. In the case of COP the $\frac{1}{3}$ exponent occurs only for long times after a crossover from an effective exponent of $\frac{1}{4}$.

In earlier work[5] by Mazenko, Valls, and Zannetti (MVZ) an appropriate theoretical framework for treating field-theoretical growth kinetics problems was established. The theory of MVZ indicated how one could separate the ordering and equilibrating contributions to the evolving structure factor and identify the two important length scales in the problem—the average domain size $L(t)$ and the equilibrium correlation length ξ. This theory allows one to calculate various observable quantities over the entire time scale and these quantities approached their appropriate final-equilibrium-state values unlike in earlier theories. While this theory is qualitatively appealing, it does not correspond to an ordering system with sharp interfaces. The theory presented here remedies this problem by reformulating the MVZ treatment of the ordering component.

The system treated here is the time-dependent Ginzburg-Landau (TDGL) model in the presence of Gaussian noise. In terms of dimensionless time and length scales the basic equation of motion satisfied by the order parameter field $\psi(\mathbf{R},t)$ is

$$\frac{\partial\psi(\mathbf{R},t)}{\partial t}=\tfrac{1}{2}\hat{\Gamma}(\mathbf{R})[\psi(\mathbf{R},t)-\psi^3(\mathbf{R},t)+\nabla^2_{\mathbf{R}}\psi(\mathbf{R},t)]+\eta(\mathbf{R},t)\,, \quad (1)$$

where the noise satisfies

$$\langle\eta(\mathbf{R},t)\eta(\mathbf{R}',t')\rangle=\epsilon\hat{\Gamma}(\mathbf{R})\delta(\mathbf{R}-\mathbf{R}')\delta(t-t')\,,$$

ϵ is a dimensionless measure of the final temperature, and $\hat{\Gamma}(\mathbf{R})=(-\nabla^2_{\mathbf{R}})^p$ with $p=0$ for an NCOP, while $p=1$ for a COP. This equation of motion is supplemented by an initial probability distribution governing ψ at time t_0 which is assumed to be Gaussian and the initial structure factor is given by $\langle\psi(\mathbf{R},t_0)\psi(\mathbf{R}',t_0)\rangle=\epsilon_I\delta(\mathbf{R}-\mathbf{R}')$.

The mapping of this formulation of the problem onto a functional-integral representation is described by MVZ. For our purposes here it will suffice to note that the dynamics of the ψ field can be fully described in terms of a probability distribution $P[\psi]$. The key point in the MVZ development is the introduction of an auxiliary field, $m(\mathbf{R},t)$, which governs the ordering component of the field. The mathematical steps are simple. First, let $P[\psi]\rightarrow P[\psi,m]=P[\psi]P[m]$, where $P[m]$ is a properly normalized probability distribution governing the m field. Next translate the original field via

$$\psi(\mathbf{R},t)=\sigma(\mathbf{R},t)+\phi(\mathbf{R},t)\,, \quad (2)$$

where σ is a functional of the field m. In MVZ σ was chosen as an Ising-type variable which is related to the field m in a complicated fashion that will not be discussed here. In the present formulation σ is chosen to be the nonlinear functional of m given by $\sigma(\mathbf{R},t)=\tanh[m(\mathbf{R},t)]$. As emphasized in MVZ the translation given by (2) is useful only if there is a clear separation of time scales for $\sigma(\mathbf{R},t)$ and $\phi(\mathbf{R},t)$. In particular, the "peak" or ordering variable $\sigma(\mathbf{R},t)$ has spatial correlations governed by the "growth law" $L(t)$, while the correlations of the "phonon" field $\phi(\mathbf{R},t)$ are spatially local and equilibrate exponentially to the final equilibrium (Ornstein-Zernike) form governed by ξ.

The theory developed here in its most elementary form is specified primarily by two requirements: (i) $P[m]$ is a Gaussian distribution. (ii) The variance of $P[m]$ is determined by requiring

$$\left\langle\sigma(2)\left[\frac{\partial}{\partial t_1}\sigma(1)+\hat{\Gamma}(1)[\sigma(1)-\sigma^3(1)+\nabla^2_{\mathbf{R}_1}\sigma(1)]\right]\right\rangle=\langle\sigma(2)\delta(t_1-t_0)\sigma(1)\rangle\,, \quad (3)$$

where the average is over $P[m]$, $\sigma(1)=\sigma(\mathbf{R}_1,t_1)$, and $\hat{\Gamma}(1)=\hat{\Gamma}(\mathbf{R}_1)$. The first requirement is motivated by simplicity. The second requirement[6] demands that σ satisfies (1) on average and insures that the long-time coupling between the σ and ϕ variables vanishes as $t\rightarrow\infty$. It is also required that we specify the initial conditions satisfied by the σ and m fields. A full discussion is rather technical, and follows the parallel development

in MVZ. The upshot is, however, rather simple. The early-time behavior of the full structure factor is very insensitive to the choice of initial conditions for σ. It is therefore useful to choose σ to have the same initial conditions as for ψ. For quenches to zero temperature ($\epsilon=0$) this completely specifies the theory. For quenches to $\epsilon>0$ one must be careful in treating the effect of noise on the ordering contribution.

The structure factor $C_\psi(12)=\langle\psi(1)\psi(2)\rangle$, after using (2), has a coupling between the variables σ and ϕ. As discussed fully by MVZ, one can treat the coupling between σ and ϕ using perturbation theory which is valid for low temperatures (small ϵ). The analysis of this perturbation theory for the theory studied here follows that in MVZ rather closely so it will not, for lack of space, be reproduced here. For now we focus on the dynamics of the ordering peak contribution.

To proceed further one must carry out the average over $P[m]$ implied in (3). This leads implicitly to a determining equation of motion for the correlation function $C_0(12)=\langle m(1)m(2)\rangle$. The key technical point in relating $C_0(12)$ to $C(12)=\langle\sigma(1)\sigma(2)\rangle$ is the use of the integral representation

$$\sigma(1)=\tanh[m(1)]=\int_0^{+\infty}\frac{dz\sin[m(1)z]}{\sinh(\pi z/2)}. \tag{4}$$

It is then convenient to carry out Gaussian averages over the fields using the exponential form for the sine function. Let us restrict ourselves, for simplicity, to equal times.[7] It is easy to show, assuming translational invariance, that

$$C(\mathbf{R},t)=\int_0^{+\infty}\frac{dz_1}{\sinh(\pi z_1/2)}\int_0^{+\infty}\frac{dz_2\exp[-\frac{1}{2}S_0(t)(z_1^2+z_2^2)]}{\sinh(\pi z_2/2)}\sinh[z_1z_2C_0(\mathbf{R},t)], \tag{5}$$

where $S_0(t)=C_0(\mathbf{0},t)$. In carrying out the average over the nonlinear part of the equation of motion in (3) one can find an identity similar to (4) for $\sigma-\sigma^3$ by taking the second derivative of (4) with respect to m. It is then easy enough to work out the Gaussian average determining $K(12)=\langle[\sigma(1)-\sigma^3(1)]\sigma(2)\rangle$, which can be put into the convenient form for equal times

$$K(\mathbf{R},t)=-\tfrac{1}{2}\partial C(\mathbf{R},t)/\partial S_0(t)\,|_{C_0(\mathbf{R},t)}, \tag{6}$$

where $C(\mathbf{R},t)$ is given by (5). Using these results in (3) one obtains the equation of motion for $C_0(\mathbf{R},t)$

$$I(\mathbf{R},t)\partial C_0(\mathbf{R},t)/\partial t=2\,\partial S_0(t)/\partial t K(\mathbf{R},t)+2\Gamma(\mathbf{R})[K(\mathbf{R},t)+\nabla_{\mathbf{R}}^2C(\mathbf{R},t)], \tag{7}$$

where

$$I(\mathbf{R},t)=\partial C(\mathbf{R},t)/\partial C_0(\mathbf{R},t)\,|_{S_0(t)}. \tag{8}$$

Together (5)–(8) form a nonlinear integro-differential equation determining $C_0(\mathbf{R},t)$ and, in turn, $C(\mathbf{R},t)$.

Before proceeding to discuss the solution to (7) it is profitable to briefly discuss the basic nature of the expected solution. The main point is that the local quantity $S_0(t)$ grows with time without bound. When S_0 grows very large then

$$S(t)=C(\mathbf{0},t)=1-[2/\pi S_0(t)]^{1/2}+O(S_0^{-3/2}). \tag{9}$$

For the case of sharp interfaces[8] one expects that $S-1\sim O(1/L)$ and one can identify $S_0\sim L^2$.

The next step in the development is to explicitly show that Eqs. (5)–(8) lead to a dynamics where, indeed, S_0 increases without bound with time. This set of equations has been solved by first finding good analytic approximations for C, K, and I in terms of C_0 and S_0 (asymptotically exact for long and short times) and then integrating (7) by direct forward time step integration. In Fig. 1 the results for $S_0(t)$ are presented for both a COP and an NCOP. In the COP case $\epsilon_I=0.01$ while for an NCOP $\epsilon_I=\frac{1}{3}$. In both cases one finds, as promised, that S_0 grows apparently without bound.

In the limit where S_0 is large [and $C_0(\mathbf{R})/S_0$ is held fixed] the theory simplifies considerably, for example (for $\mathbf{R}\neq\mathbf{0}$), (5) can be inverted to obtain[9]

$$C_0(\mathbf{R})/S_0=\sin[\pi C(\mathbf{R})/2]. \tag{10}$$

Using (6) and (8) we find in this limit

$$K(\mathbf{R},t)=(\pi S_0)^{-1}\tan[\pi C(\mathbf{R})/2] \tag{11}$$

and

$$I(\mathbf{R},t)=\frac{2}{\pi S_0}\frac{1}{\cos[\pi C(\mathbf{R})/2]}. \tag{12}$$

It is easy to compute the corrections of one higher order in $1/S_0$ to (10), (11), and (12). Let us define

$$L^2\equiv 2(1-S)^{-2}=\pi S_0, \tag{13}$$

where the second identity holds to leading order in S_0 as follows from (9). Then after inserting (10), (11), and

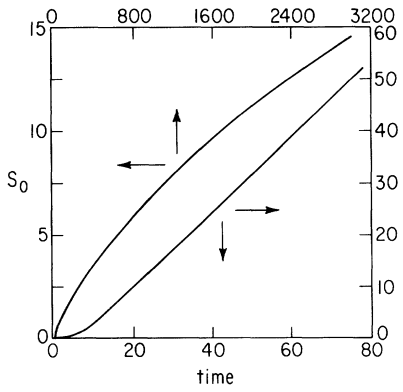

FIG. 1. S_0 vs t for the full theory for an NCOP, with the initial condition $\epsilon_I=\frac{1}{3}$, is given by the approximately straight line. S_0 vs t from the full theory for a COP, with the initial condition $\epsilon_I=0.01$, is given by the curved line. Notice the very different time scales for the two cases.

(12) into (7), we obtain the very appealing equation

$$\frac{\partial}{\partial t}C(\mathbf{R},t)=2\hat{\Gamma}(\mathbf{R})\{L^{-2}\tan[\pi C(\mathbf{R},t)/2] +\nabla_{\mathbf{R}}^2 C(\mathbf{R},t)\} \quad (14)$$

which is valid for $S_0\gg 1$. This equation is similar in structure to the basic equation for the peak correlation function studied by MVZ with two major differences. We obtain the zero-temperature version of Eq. (3.22) in MVZ if we linearize the tangent term and replace $\pi(1-S)^2/4$ by $1-S$. As we shall see the nonlinear terms are necessary in order to recover truly sharp interfaces. The change from $1-S$ to $(1-S)^2$ changes the behavior of S from $1-O(1/L^2)$ in MVZ to the more appropriate form $1-O(1/L)$ behavior discussed above.

If we assume a long-time scaling solution $C(\mathbf{R},t)=F\times[\mathbf{R}/L(t)]$, then (14) reduces to

$$-\mu\mathbf{x}\cdot\nabla_x F(\mathbf{x})=(-\nabla_x^2)^p[\tan(\pi F/2)+\nabla_x^2 F], \quad (15)$$

where $\mathbf{x}=\mathbf{R}/L$, and we assume $\mu=L^{2p+1}\partial L/\partial t$ is a constant.[10] If (15) holds, then for long times $L\sim t^{1/2p+2}$. For an NCOP, $p=0$ and $L\sim t^{1/2}$ as expected from the Lifshitz-Cahn-Allen curvature-driven arguments. While for a COP, $p=1$ and $L\sim t^{1/4}$ which is associated with the process of surface diffusion. For both a COP and an NCOP one can proceed to solve (15) for small $\mathbf{x}$ and obtain in d dimensions

$$F(\mathbf{x})=1-\left(\frac{2}{\pi}\right)^{1/2}\frac{|\mathbf{x}|}{(d-1)^{1/2}}(1-\beta x^2+\cdots), \quad (16)$$

where $\beta=(4d+2)^{-1}[\pi/6+\mu(1-p)]$. As pointed out by Oono and Puri[11] the form (16) for the structure factor leads to Porod's law[2] in Fourier space $C(\mathbf{q},t)\sim q^{-(d+1)}$, for $|\mathbf{q}|\to\infty$. For large x the solutions for the COP and NCOP cases differ qualitatively. For the NCOP case

$$F=F_0 x^{-(d-\pi/2\mu)}e^{-\mu x^2/2}, \quad (17)$$

while for the COP case

$$F=F_0 x^{-2d/3}\exp\left[-\Gamma x^{4/3}\left(1-\frac{\pi}{2\mu}x^{-2/3}\right)\right] \times\cos\left[\sqrt{3}\Gamma x^{4/3}\left(1-\frac{\pi}{2\mu}x^{-2/3}\right)+\phi_0\right], \quad (18)$$

where $\Gamma=\frac{3}{8}\mu^{1/3}$ and F_0 and ϕ_0 are constants which must be determined numerically.

The theory developed here allows a very detailed analysis of the sharp interfaces. Let us look at the solutions of (14) of the form $C(\mathbf{R},t)=1-W(\mathbf{R})/L$, for $W\ll L$. We find that W satisfies the time-independent equation $2/\pi W(\mathbf{R})=\nabla^2 W(\mathbf{R})$ for both a COP and an NCOP. The solution to this equation for small $\mathbf{R}$ is given by

$$W(\mathbf{R})=\left(\frac{2}{\pi}\right)^{1/2}a_0\left[1+\frac{1}{2d}\left(\frac{R}{a_0}\right)^2-\frac{1}{8d(2+d)}\left(\frac{R}{a_0}\right)^4+\cdots\right], \quad (19)$$

where from (9) and (13), $a_0=\sqrt{\pi}$. For large $\mathbf{R}$

$$W(\mathbf{R})=\left(\frac{2}{\pi}\right)^{1/2}R\left[\frac{1}{(d-1)^{1/2}}+\frac{1}{R^{d/2}}f\cos(\gamma\ln R+\phi)+\cdots\right], \quad (20)$$

where $\gamma=\frac{1}{2}(8d-8-d^2)^{1/2}$ and f and ϕ can be determined numerically. The leading term in (20) agrees with the scaling result (16) leading to Porod's law. The other terms represent corrections to scaling.

These analytical results can be shown to follow from the full theory (7) by a direct numerical solution. The calculations were carried out on a square lattice where $S(t)$ and the first zero of $C(\mathbf{R})$ were computed[12] for the full theory (7) and for the "long-time" theory (14) with the same initial condition $\epsilon_I=0.01$. The long-time theory is in remarkably good agreement with the full theory even for intermediate times. They both converge to the same long-time results.

Our analysis for the NCOP case seems acceptable in all respects. In the COP case, however, one expects[13] from the arguments of Lifshitz and Slyozov and Bray[14] to obtain a long-time growth law of $t^{1/3}$ in contrast to the $t^{1/4}$ results found above. Indeed a careful analysis shows that the theory given above for the peak contribution is unstable in the COP case to a set of weak perturbations which leads to a long-time crossover to $t^{1/3}$. In constructing the basic equation of motion (3) satisfied by the peak variable $\sigma(1)$ we assumed that we could ignore any coupling to the phonon field ϕ and that correlations between σ and ϕ vanish in the long-time limit. This decay of correlation is correct, but for sufficiently long times we have, for example, $\partial C(12)/\partial t_1\sim O(L^{-4})$ and the small coupling between σ and ϕ may be of this order. One finds in perturbation theory that there is a coupling between ϕ and σ which adds a term $H(\mathbf{R},t)=-2\times\nabla_{\mathbf{R}}^2 3S_\phi(t)C(\mathbf{R},t)$, where $S_\phi=\langle\phi^2(\mathbf{R},t)\rangle$, to the right-hand side of (7) or (14). To the same order of approximation $C_\phi(\mathbf{R},t)=\langle\phi(\mathbf{R},t)\phi(\mathbf{0},t)\rangle$ satisfies

$$\frac{\partial}{\partial t}C_\phi(\mathbf{R},t)=-2\nabla_{\mathbf{R}}^2(\mathbf{R})\{[1-3S(t)]C_\phi(\mathbf{R},t) +\nabla_{\mathbf{R}}^2 C_\phi(\mathbf{R},t)\}. \quad (21)$$

In the long-time limit $S(t)\to 1$, one can drop the $\nabla_{\mathbf{R}}^4 C_\phi(\mathbf{R},t)$ term in (21) and C_ϕ can be associated with

diffusion in the system. In this case $S_\phi \sim t^{-d/2}$ and, in the scaling regime, $H(\mathbf{R},t) \sim L^{-2} t^{-d/2} \ll L^{-4}$ and it is consistent to not include $H(\mathbf{R},t)$ in (7). Note, however, that the diffusive process described by (21) is decoupled from the sharp interfaces in the system. By redefining how we separate σ and ϕ in (2) we can couple C_ϕ to the interfacial motion and add to the right-hand side of (21) a term which at late times is given by

$$2\Gamma(\mathbf{R})(g_0/L^2)\tan[\pi C(\mathbf{R},t)/2],$$

where g_0 is a constant. This is at the expense of subtracting a similar term from the right-hand side of (7). We see that the term added to (21) goes as L^{-4} in the scaling ($R \sim L$) regime but as L^{-3} for $R \ll L$, due to the sharp interfaces. With such a term the solution of (21), for large times and $1 \ll R \ll L$, is given by

$$C_\phi(\mathbf{R},t) \sim (g_0/L)[\pi W(R)]^{-1} \sim g_0/RL, \qquad (22)$$

which is just the solution for a diffusion field in three dimensions. Note, however, under these circumstances that $S_\phi \sim O(1/L)$. The term $H(\mathbf{R},t)$ added to the right-hand side of (7) or (14) is then of $O(1/L^3)$ in the long-time limit. One immediately has, from power counting in $1/L$, that the perturbation proportional to g_0, no matter how small, will lead to a long-time crossover to a growth law of $t^{1/3}$. The associated mechanism seems qualitatively in agreement with that discussed by Lifshitz and Slyozov. The results here are in agreement with those obtained by Bray.[14] His method is restricted to the COP case and the longest distance and time scales where the diffusion mechanism discussed above should be operative. As one might guess, the full treatment of this coupling between the ϕ and σ variables is complicated and the analysis of the crossover nonuniversal. A main consideration in this development is that the short-distance behavior (Porod's law) is not strongly influenced by this crossover. It is also clear that there is some substantial time regime over which the surface diffusion[15] is dominant since it is relevant for setting up the sharp interfaces. Discussion of the nature of the crossover and many other details will be discussed elsewhere.

The range of applicability of the theory developed here appears broad. Clearly the problem of nucleation and front propagation[16] within the context of a TDGL model can be treated using this technique and are under current investigation. Less well understood is how transferable this approach will be for treating other systems. In particular, the robustness of the functional transformation given by (4) has not been systematically investigated. One could consider more general nonlinear transformations and relax the constraint that $P[m]$ be Gaussian. It is not yet clear, however, that this offers any particular advantage, while clearly it will complicate the structure of the theory.

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[6]A very clean separation of variables would occur if the σ variable satisfied Eq. (1) with zero noise. This constraint is too strong to be compatible with the requirement that m be a Gaussian variable. The compromise that works is to require σ to satisfy a noiseless equation of motion (1) on average.

[7]See M. Zannetti and G. Mazenko [Phys. Rev. B **35**, 5043 (1987)] for a discussion of unequal time quantities.

[8]The argument is simple. If a system consists of sharp interfaces of width l separated by a distance L then the total volume is $(L+l)^d$. The volume over which the order parameter is nonzero is L^d so one can estimate $S = \langle \psi^2 \rangle \sim [L/(L+l)]^d = 1 - dl/L + \cdots$ for $L \gg l$.

[9]One finds similar expressions in the late-stage interfacial theory developed by K. Kawasaki and T. Ohta, Prog. Theor. Phys. **68**, 129 (1982); T. Ohta, D. Jasnow, and K. Kawasaki, Phys. Rev. Lett. **49**, 1223 (1983); K. Kawasaki and T. Ohta, Physica (Amsterdam) **118A**, 175 (1983). The substantial difference between the theories these workers developed and theory developed here is the existence of a determining equation like (7), valid for all times.

[10]In the NCOP case it has been verified numerically that μ is a constant independent of the initial state represented by the parameter ϵ_I. In the isotropic case in three dimensions $\mu = 0.623$.

[11]Y. Oono and S. Puri (to be published).

[12]Explicit numerical results for the NCOP case and additional numerical results for the COP case, including the structure factor, will be presented elsewhere.

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