Scaling and the Small-Wave-Vector Limit of the Form Factor in Phase-Ordering Dynamics

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The consequences of the scaling hypothesis in phase-ordering dynamics are examined. Dynamics governed by the time-dependent Ginzburg-Landau and Cahn-Hilliard-Cook equations are studied. An upper bound is found for the dynamical exponents. It is also found that for a critical quench with Cahn-Hilliard-Cook dynamics, if the length scale of the patterns increases as $t^{1/3}$ and the form factor behaves as k^δ for small k, then δ must be ≥ 4. Experimental and numerical results give $\delta \simeq 4$.

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There has recently been a renewed interest in the ordering dynamics of thermodynamically unstable systems (e.g., spinodal decomposition). The most significant results obtained so far are that, asymptotically, the form factor shows scaling behavior and for dimensions ≥ 2 the length scale of the patterns increases algebraically with time.[1] This has been demonstrated experimentally by quenches of binary alloys,[2] glasses,[3] and polymer blends[4] and numerically by Monte Carlo and Langevin-equation simulations[5,6] and cell-dynamical systems (CDS) methods.[7] Furthermore, for the case with nonconserved order parameter (NCOP), there is a theory for the form factor by Ohta, Jasnow, and Kawasaki using interface-dynamics arguments.[8] This has been found to agree well with simulations.[9] The form factor for a critical quench with conserved order parameter (COP) has not been obtained analytically.

In this Letter, I consider dynamics governed by the time-dependent Ginzburg-Landau (TDGL) and Cahn-Hilliard-Cook (CHC) equations. The scaling hypothesis is assumed to be true and its consequences are examined. It will be shown that the scaling hypothesis gives an upper bound for the dynamical exponents. I then assume that the dynamical exponent is $\frac{1}{3}$ for the COP case. It will be shown that, for a critical quench, if the form factor $S_{\mathbf{k}}(t)$ at large t behaves as $\sim k^\delta$ for small k, then $\delta \geq 4$. This is compared with numerical and experimental results.

The form factor has an asymptotic scaling regime in which it behaves as

$$S_{\mathbf{k}}(t) = l(t)^\nu f(q), \tag{1}$$

where $q = l(t)|\mathbf{k}|$, $\mathbf{k}$ is the wave vector, t is time, ν is the spatial dimension, and $f(q)$ is the scaling function. $l(t)$ is the time-dependent length scale. In the COP case $f(q)$ may not be universal, but in some limits $f(q)$ should have universal characteristics. At large q, Porod's law[10] gives $f \propto 1/q^{\nu+1}$. Strictly speaking, Porod's law only applies in the limit of interface thickness $\ll l(t)$ and so it is only obeyed for $k < k_i$, where $k_i^{-1} \propto$ interface thickness.[9] For critical quenches Furukawa[11] conjectured that there is a q regime where $f(q) \sim q^{-2\nu}$ due to entangled interfaces. For small q, Furukawa guessed that, because of thermal fluctuations and conservation of the order parameter, $f(q)$ may be proportional to q^2.

I start with a stochastic partial-differential-equation model of the phase-separation dynamics,[12]

$$\partial\psi(\mathbf{r},t)/\partial t = -L(i\nabla)^\beta \mu(\mathbf{r},t) + \theta(\mathbf{r},t), \tag{2}$$

where ψ is the order parameter, L is the kinetic coefficient, and μ is effectively the chemical potential. θ is a Gaussian noise obeying the fluctuation-dissipation theorem,

$$\langle\theta(\mathbf{r},t)\rangle = 0,$$
$$\langle\theta(\mathbf{r},t)\theta(\mathbf{r}',t')\rangle = 2L(i\nabla)^\beta \delta(\mathbf{r}-\mathbf{r}')\delta(t-t'). \tag{3}$$

If $\beta = 0$ the order parameter is not conserved and (2) is the TDGL equation. If $\beta = 2$ the order parameter is conserved and (2) is the CHC equation.

I assume that $\mu(\mathbf{r},t)$ can be separated into two parts,

$$\mu(\mathbf{r},t) = \mu^0(\mathbf{r},t) - D\nabla^2\psi(\mathbf{r},t), \tag{4}$$

where D is a positive constant and μ^0 is the local portion of μ (i.e., μ^0 does not contain any gradients). μ^0 is usually taken to be the Landau-Ginzburg form, $-\tau\psi + g\psi^3$, but other forms of μ^0 may also be used. $\mu^0(\psi)$ must be an odd function of ψ and have three zeroes, corresponding to the two stable fixed points at the equilibrium values of $\psi = \pm\psi_{\rm eq}$ and the one unstable fixed point at $\psi = 0$. A quench is called critical if $\int d^3r\, \psi(\mathbf{r},0) = 0$.

The form factor is just the Fourier transform of the two-point correlation function, $S_{\mathbf{k}}(t) = \langle|\psi_{\mathbf{k}}(t)|^2\rangle$. The angular brackets indicate an ensemble average. The time evolution of $S_{\mathbf{k}}(t)$ is then given by

$$\partial S_{\mathbf{k}}(t)/\partial t = -2Lk^\beta[\mathrm{Re}\langle\mu^0_{-\mathbf{k}}(t)\psi_{\mathbf{k}}(t)\rangle - 1] - 2LDk^{2+\beta}S_{\mathbf{k}}(t), \tag{5}$$

where $\mu_{\mathbf{k}}^0$ is the Fourier transform of μ^0. I now make the central hypothesis of this Letter. I assume that the scaling hypothesis holds and the length scale grows as $t^a = t^{1/\phi}$ in the scaling regime (for $\nu \ge 2$). Substituting the scaling form (1) into (5) gives

$$\nu f(q) + q\, df(q)/dq \propto -l^{\phi-\beta-\nu} q^{\beta} \langle \mu^0_{-\mathbf{k}}(t) \psi_k(t) \rangle + l^{\phi-\beta-\nu} q^{\beta} - D l^{\phi-\beta-2} q^{2+\beta} f(q), \tag{6}$$

where $l = l(t)$. In order for scaling to be true the right-hand side of (6) must be independent of t as $t \to \infty$.

Let us inspect Eq. (6). The second term is due to thermal fluctuations. If $\phi < \beta + \nu$ this term must go to zero as $t \to \infty$. If $\phi < \beta + 2$ the third term must also go to zero as $t \to \infty$. In the first term, $\langle \mu^0_{-\mathbf{k}}(t) \psi_{\mathbf{k}}(t) \rangle$ is the Fourier transform of $\int d^3R \langle \mu^0(\mathbf{R}+\mathbf{r},t) \psi(\mathbf{R},t) \rangle$. $|\psi(\mathbf{r},t)|$ must be bounded, say, by $\psi_{\max} > 0$. Then

$$\int d^3R \langle \mu^0(\mathbf{R}+\mathbf{r},t) \psi(\mathbf{R},t) \rangle \le \psi_{\max} \int d^3R \langle |\mu^0(\mathbf{R},t)| \rangle. \tag{7}$$

For large t, μ^0 is only nonzero at the interfaces and the interface profile does not change, so that $\int d^3R \times \langle |\mu^0(\mathbf{R},t)| \rangle / V$ must be proportional to the interface area density which decreases as $1/l(t)$. Therefore, $\int d^3R \langle \mu^0(\mathbf{R}+\mathbf{r},t) \psi(\mathbf{R},t) \rangle$ must decrease at least as fast as $1/l(t)$ as a function of t and the Fourier transform $\langle \mu^0_{-\mathbf{k}}(t) \psi_{\mathbf{k}}(t) \rangle$ must increase at most as $l(t)^{\nu-1}$ as a function of t [a factor of $l(t)^{\nu}$ comes from the Fourier transformation]. Now suppose that $\phi < 1 + \beta$. Then all three terms on the right-hand side of (6) must go to zero as $t \to \infty$. Then (6) can be easily solved to get $f(q) \propto q^{-\nu}$. This is unphysical as it is not bounded, and so ϕ must be $\ge 1 + \beta$ ($a \le 1$ for TDGL and $a \le \frac{1}{3}$ for CHC). This bound is consistent with the generally accepted results of $a = \frac{1}{2}$ for the NCOP case and $a \le \frac{1}{3}$ for the COP case.

In the rest of this Letter, I will only consider the COP case. The experimental and numerical evidence points to $a = \frac{1}{3}$ ($\phi = 3$) for the COP case (although this is still a point of controversy[6a]). So I assume $\phi = 3$ for the CHC equation. Then the last two terms on the right-hand side of (6) must go to zero at large times[13] and scaling requires that $\langle \mu^0_{-\mathbf{k}}(t) \psi_{\mathbf{k}}(t) \rangle$ must increase as $l(t)^{\nu-1}$ as a function of t for large t.

I can now find restrictions on the form of $f(q)$. I assume a critical quench. $S_k(t) = l(t)^{\nu} f(q)$ is just $\langle |\psi_{\mathbf{k}}(t)|^2 \rangle$ averaged over all $|\mathbf{k}| = k$. For the COP case, $f(0) = 0$ for a closed system. I assume that $f(q)$ is continuous and increases algebraically near $q = 0$, so that $f(q) \propto q^{\delta}$ with $\delta \ge 0$. Then the Chebychev inequality gives

$$\mathrm{Prob}(\psi_{\mathbf{k}}: |\psi_{\mathbf{k}}|^2 > l(t)^{\nu} q^{\delta'}) < q^{\delta}/q^{\delta'}. \tag{8}$$

Therefore, for sufficiently small q, almost surely, $|\psi_{\mathbf{k}}| \le l(t)^{\nu/2} q^{\delta'/2}$, $\forall \delta' < \delta$.

Now assume that $\mu_k^0(t)/l(t)^{\nu/2-1}$ is bounded near $k = 0$ for all t. Actually, since $\mu^0(\psi)$ is an odd function of ψ, by symmetry arguments one would expect μ_k^0 to vanish as $k \to 0$. The left-hand side of (6) must be the same order as $f(q)$ for small q. Then for sufficiently small q,

$$\begin{aligned} q^{\delta} &\propto q^2 \langle \mu^0_{-\mathbf{k}}(t) \psi_{\mathbf{k}}(t) \rangle / l(t)^{\nu-1} \\ &\le q^2 \langle |\mu^0_{-\mathbf{k}}(t)| \, |\psi_{\mathbf{k}}(t)| \rangle / l(t)^{\nu-1} \\ &\le \kappa q^{2+\delta/2-\epsilon/2}, \end{aligned} \tag{9}$$

almost surely, for $\forall \epsilon > 0$, where κ is a positive constant independent of q. Therefore for small q there is a consistency condition for δ,

$$\delta > 2 + \delta/2 - \epsilon/2, \quad \forall \epsilon > 0, \tag{10}$$

i.e., $\delta > 4 - \epsilon$ for $\forall \epsilon > 0$. Therefore, if $f(q)$ behaves as $\sim q^{\delta}$ for small q, then δ must not be less than 4.

The term resulting from fluctuations in (5) is $\propto k^2$, so that $S_k(t)$ should also be proportional to k^2 for sufficiently small k. This should be true for early times, but the corresponding term in (6) goes to zero as $1/l(t)^{\nu-1}$ for large t. Therefore the $f(q) \propto q^2$ regime becomes smaller as $l(t)$ increases, and vanishes in the asymptotic limit. This is consistent with numerical simulations which show that the scaling function is independent of the magnitude of the noise,[7a] as well as with experimental results, in which the scaled form factor generally becomes sharper at later times.[2-4]

I now examine numerical results. Figure 1 shows a log-log plot of the small-q scaling function from a CDS simulation corresponding to the Cahn-Hilliard equation (the CHC equation without noise). This method gives scaling properties consistent with the Cahn-Hilliard

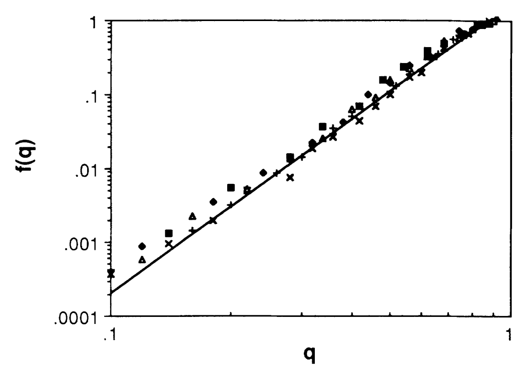

FIG. 1. A log-log plot of the scaled form factor for the CDS simulation on a 128×128 lattice. Units are arbitrary. Data from five different update times are shown (crosses=750 updates, plusses=1080, triangles=1500, diamonds=2000, squares =2700). The line has a slope of 4 and is drawn as a guide to the eye. The plot is linear over 3 decades in f and $\frac{3}{4}$ decade in q. There a a tail at small q with slope less than 4. This tail is more noticeable at later update times.

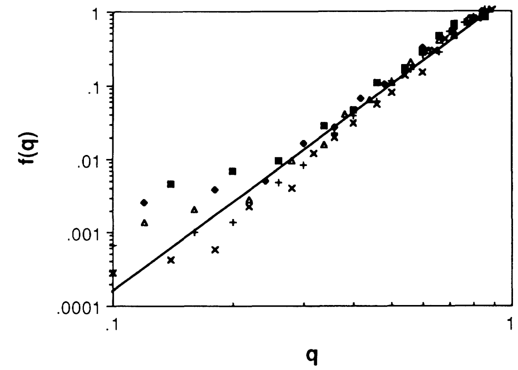

FIG. 2. The same plot as in Fig. 1, except the data are from a simulation on a 64×64 lattice. In this case, the lower-slope tail is much more prominent at much earlier times than in Fig. 1.

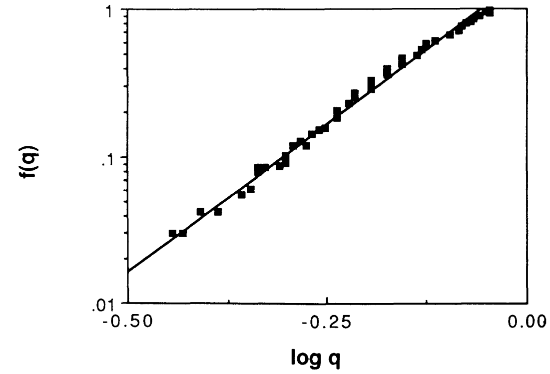

FIG. 3. The same type of plot as in Fig. 1, except the scaled form factors are late-time results from polymer-blend experiments by Wiltzius, Bates, and Heffner. The line in the plot has a slope of 4.

equation (see Ref. 7a for a complete description of CDS). The simulation was performed on a 128×128 lattice and the scaling function was averaged over 48 initial conditions. The scaling functions for five times, from 750 to 2700 updates, are shown.

Figure 1 is linear over about 3 decades in f and $\frac{3}{4}$ decade in q. The line in Fig. 1 has a slope of 4 and is drawn as a guide for the eye. Least-squares fitting of the data sets gives a slope of 4.0 ± 0.1, and so $\delta = 4$. In fact it is surprising that the log-log plot is linear for such high values of $f(q)$ $(f/f_{\max} \sim 0.5)$. For $q < 0.15$ $[f(q) < 0.002]$ there is a tail which grows at a slower rate than the linear portion of the plot. This portion is larger for later times when finite-size effects may be important. That this is probably a finite-size effect is shown in Fig. 2. This is the same plot as Fig. 1 except that the simulations are on a 64×64 lattice with twenty runs. It is clear that the tail is much more noticeable at much earlier times than for the 128×128 simulation. I also examined 2D simulations of the CHC equation by Viñals.[14] The small-q scaling function is again compatible with $\delta = 4$, although in this case there are only three data points for small q. Comparison with 2D Monte-Carlo Kawaski spin-exchange simulations by Amar, Sullivan, and Mountain[5] gives a $\delta \sim 3$. However, it is possible that their scaled form factor is not yet asymptotic since the scaled form factor may still be getting sharper at the latest times.

Most experimental investigations of the form factor have concentrated on the area near the peak, but I can still test the present bound (10) against experiment. Figure 3 shows a log-log plot of scaled form factor versus q for a critical quench of a mixture of perdeuterated and protonated polymers by Wiltzius, Bates, and Heffner.[4b] Only a limited range of small-q data are available so that the plot is only over about $\frac{1}{2}$ decade in q and 2 decades in f, but the linear portion is consistent with $\delta = 4$ (a line with slope of 4 is shown).[15] Comparison with limited small-q data from a quench of a Fe-Cr alloy by Katano and Iizumi[2a] is also consistent with $\delta = 4$. Komura *et al.* have investigated quenches of Al-Zn and Al-Zn-Mg alloys.[2b] They fitted their scaled form factors by a form with $f(q) \sim q^2$ for small q and $f(q) \sim 1/q^{\nu+1}$ for large q. In some cases the fits are quite good, but these are for quenches very far from critical, for which the dynamics is much slower. Furthermore they do not find $\alpha = \frac{1}{3}$, which indicates that their experiment did not reach the asymptotic regime.

In summary, I have viewed the problem of phase-ordering dynamics from the opposite of the usual direction. I have assumed the experimentally observed facts [i.e., the form factor scales and $l(t)$ grows algebraically] and examined the consequences. Starting from the TDGL and CHC equations, it was shown that the scaling gives an upper bound for the dynamical exponent, α, with $\alpha \leq 1$ for TDGL dynamics and $\alpha \leq \frac{1}{3}$ for CHC dynamics. Then I used $\alpha = \frac{1}{3}$ for the COP case. For a critical quench, it was shown that if the scaling function behaves as q^δ for small q, then scaling requires $\delta \geq 4$. The restriction on δ was found to be consistent with simulations of CDS models and the CHC equation as well as for criitical quenches of polymer blends and binary alloys. In all the cases examined, δ is about 4.

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