# Asymptotic Form Factor for Spinodal Decomposition in Three-Space

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Exploiting the computational efficiency of the cell-dynamical-system modeling of spinodal decomposition, a large three-dimensional, critically quenched binary-alloy system was studied. The primary result is the conclusive determination of the time-asymptotic scaled form factor, which satisfies Porod's law, Tomita's sum rule, and the exponent inequality for the small-wave-number limit by Yeung.

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Our understanding of the phenomenon of spinodal decomposition has developed very slowly. There is yet to be a fully coherent, consistent and calculable theory of late-stage spinodal decomposition, even without hydrodynamic or strain effects. Because of this, computational studies are valuable sources of information.

In this Letter, we report on the results from a (deterministic) cell-dynamical-system[1] (CDS) study of spinodal decomposition[2] with critical quench. The largest feasible system ($192^3$) was used to avoid finite-size effects which occur when only a few domains dominate a small system. The well established computational efficiency of the CDS scheme[3] made it possible to study a large system size, allowing us to accurately sample many data points about the peak intensity region of the form factor $S(\mathbf{k},t)=\langle\psi_{\mathbf{k}}(t)\psi_{-\mathbf{k}}(t)\rangle$. Here, $\psi_{\mathbf{k}}$ is the spatial Fourier transform of the order parameter $\psi$ describing the local composition: $\psi=\pm 1$ corresponds to completely segregated phases and $\psi=0$ to a disordered mixture phase.

In the late stages, the domain pattern formed by the segregated phases at one time is conjectured to be statistically similar to the pattern at a later time. This should lead to a master form factor, scaled by a single time-dependent length scale $l(t)$ proportional to the representative size of the growing domains, $F(x)=l(t)^{-3}\hat{S}(k,t)$, where $x=kl(t)$.[4] One form of this length scale may be $\langle k\rangle^{-1}$, defined through

$$\langle k\rangle(t)=\frac{\int_0^\infty dk\, kS(k,t)}{\int_0^\infty dk\, S(k,t)}\,,$$

where $S(k,t)$ is the circularly (in $\mathbf{k}$ space) averaged form factor $S(\mathbf{k},t)$, normalized so that $\int d^3k\, S(\mathbf{k},t)=1$.

The theoretically established facts about the scattering form factor $S(k)$ concern the limits $k\to 0$ and $k\to\infty$. The Tomita sum rule[5] states that there is a positive number $A$ such that

$$\int [S(k)k^4-A]dk=0\,.$$

This contains Porod's law for the tail: $S(k)\sim k^{-4}$. Yeung[6] demonstrated that $S(k)\sim k^{\delta}$, where $\delta\geq 4$ for small $k$ (see also Ref. 7), under a natural assumption about the chemical potential.[8]

Many experiments[9] and numerical simulations[10,11] have pointed to a universal growth law for the length scale, $\langle k\rangle^{-1}\sim t^{\phi}$, where $\phi=\frac{1}{3}$, and the existence of a universal form factor at the very late stages of development. Numerically, the form factor as well as the exponent $\phi$ has been reliably determined in two-space with the aid of a CDS scheme.[10] To date, only two other late-time, three-space numerical studies of a binary alloy are known to the authors.[12,13] Only the study by Chakrabarti, Toral, and Gunton was a critical quench, but the small system size ($66^3$) precluded a reliable determination of the form factor.[13]

We used the following CDS model for spinodal decomposition:[2]

$$\psi_{t+1}(\mathbf{n})=\psi_t(\mathbf{n})+I_t(\mathbf{n})-\langle\langle I_t(\mathbf{n})\rangle\rangle\,,$$

$$I_t(\mathbf{n})=D[\langle\langle\psi_t(\mathbf{n})\rangle\rangle-\psi_t(\mathbf{n})]+\mathcal{F}(\psi_t(\mathbf{n}))-\psi_t(\mathbf{n})\,,$$

where $\psi_t(\mathbf{n})$ is the order parameter at time $t$ in the cell at $\mathbf{n}$. We chose an easily computable approximation $\mathcal{F}(\psi)=A\tanh[(\operatorname{arctanh}A^{-1})\psi]$. $A$ controls the quench depth, and $D$ is the static coupling strength among nearby concentration fluctuations. $\langle\langle\cdot\rangle\rangle$ is an averaging over a neighborhood of cells. We chose the ratio 6:3:1 for weighting nearest, next-nearest, and next-next-nearest neighbors. The parameters used were $A=1.15$ and $D=0.7$. Twenty samples were studied to 10000 time steps, and two samples were studied to 20000 time steps. Initial conditions were a random distribution between $\pm 0.1$. The computation required roughly 260 hours of Cray-2 time, and main memory usage of roughly 14 megawords. The patterns we obtained exhibited a domain-wall thickness (between $\psi=\pm 0.9$) of 3 cells, and a mean domain size of roughly 11.5 cells at time step 10000 and 14.4 cells at time step 20000. Our scheme is about 10 times as fast as that used by Chakrabarti, Toral, and Gunton.[13]

We calculated $\phi_{\rm eff}\equiv -\partial\ln\langle k\rangle/\partial\ln t$ vs $\langle k\rangle$ between time 4000 and 10000. $\phi_{\rm eff}$ increases with decreasing $\langle k\rangle$. Using a linear regression, we extrapolated the data to the

 

$\langle k \rangle = 0$ axis. From this, we estimate the asymptotic exponent to be $0.334 \pm 0.005$. Further, it is estimated that to clearly see an effective exponent $\phi_{\rm eff} \gtrsim 0.32$, the system would have to be at 30000 time steps or greater. Our form factors scaled well after time step 4000 with minor changes evolving over time (Fig. 1). The scaled form factor is in good agreement with the one obtained by Ohta and Nozaki[14] for $x \equiv k/\langle k \rangle \geq 0.5$ but not with the recent result by Mazenko.[15] The form factor in three-space is significantly narrower than the two-space case about the peak. The three-space form factor is symmetric in appearance about $x = 1$ while the two-space form factor is somewhat asymmetric.[16]

Our main result is the estimation of the truly asymptotic functional form of the scaled form factor up to $x \simeq 4$ (the peak position is at $x \simeq 0.95$). We conjecture a stronger version of the scaling hypothesis: The physically relevant length scales that determine the form factor in the preasymptotic regime are the domain size and the domain-wall thickness. More precisely, we conjecture that the transformation $\psi \rightarrow \mathrm{sgn}(\psi)$ removes any effect on the form factor due to the finiteness of the ratio $\rho$ of the wall thickness and the domain size in the preasymptotic regime. We will refer to all data from this transformation as "hardened." This conjecture has been substantiated in the nonconserved-order-parameter case.[17] If this stronger scaling hypothesis is correct, then the hardened scaled form factor should be time independent. If this is the case, the resultant form factor can be interpreted as the truly asymptotic form factor.

Figure 2 is a graph of $F(x)x^4$ vs $x$ (the Porod plot). The form factor for $x \leq 2$ already scales well beyond time 5000, but a significant second peak is still evolving over time. Such a peak has been recognized by large-scale, late-time CDS studies in two dimensions, but it is not as pronounced.[16] Interestingly, the Ohta-Nozaki theory predicts such a second peak. The tail part of the form factor is steadily rising, solely due to the decrease of the ratio $\rho$ as demonstrated by Oono and Puri.[17] They showed that to see a clear sign of Tomita's sum rule, $\rho < \frac{1}{30}$ is required. In our present simulation, the best we achieve is $\rho = 0.21$.

In Fig. 3, the scaled hardened form factors exhibit clear time independence for $0 \leq x \leq 4.0$ for a wide range of times from 5000 to 20000 time steps. Thus our stronger scaling hypothesis is substantiated. We conclude that up to $x \simeq 4.0$, the hardened form factor has the asymptotic functional form. The upward rise in the hardened form factors for $x \gtrsim 4.0$ comes from the jagged domain wall due to the hardening of a discrete system. Hardening with "softer" transformations like $\psi \rightarrow \tanh(C\psi)$ have shown this to be true, where $C$ controls the softness of the wall. At later times, the hardened tail reduces, as the lower-length-scale cutoff due to the cell size scales out of the figure. The discrepancy between the hardened and unhardened form factors around the first peak is mainly due to the normalization; the tail part rises for the hardened form factor, so that the relative weight of the first peak decreases.

Porod's law and Tomita's sum rule are obeyed by the hardened form factor after accounting for the rise in the tail. This is confirmed by the hardened data from time step 20000 which are nearly flat up to $x \simeq 7$ thus obeying $F(x) \propto x^{-4}$ (Porod's tail). We feel that the form

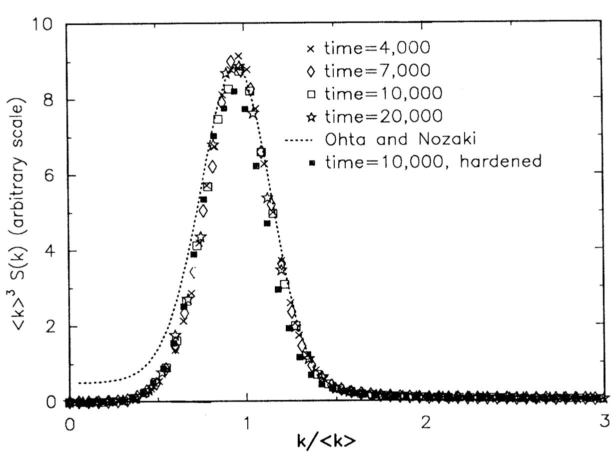


FIG. 1. The scaling of the form factor over time. The Ohta-Nozaki form factor is normalized such that the peak coincides with the peak for time step 20000. The form factor for hardened data at time step 10000 has a peak which is reduced from the unhardened data due to normalization. Also, $\langle k \rangle$ for the hardened form factor is about 4% greater than for the unhardened data.

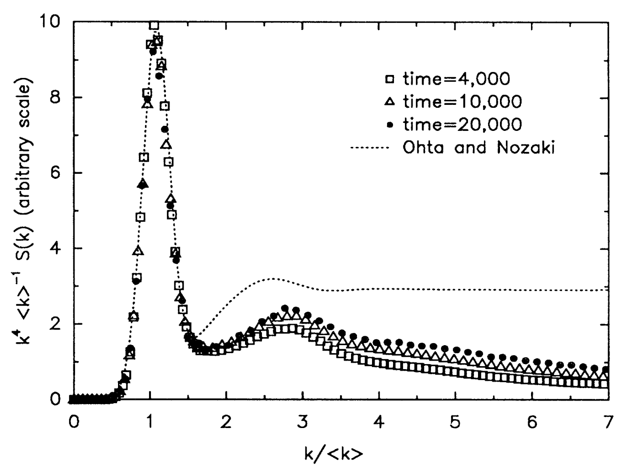


FIG. 2. Comparison over time of $x^4F(x) = (k^4/\langle k \rangle)S(k,t)$, where $x = k/\langle k \rangle$. Unlike the Ohta-Nozaki form factor, the data do not exhibit a flat tail characteristic of Porod's law. This is due to the large ratio $\rho$. However, as $\rho$ decreases, the tail rises toward a constant. For clarity, we removed every other data point for $x > 1.75$.

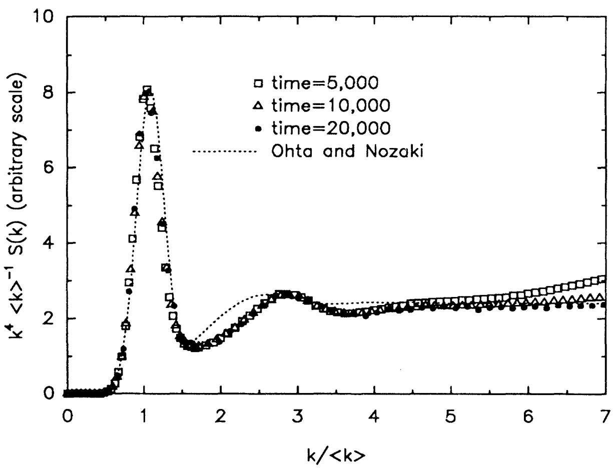


FIG. 3. Comparison over time of $x^4F(x)$, where $x=k/\langle k\rangle$, for hardened data. The rise in the tail for earlier times is due to the discreteness of the system. At time step 20000, the tail is generally flat to the end of the plot since the small-length-scale cutoff has scaled out of the plot. From time 5000 to 20000, the structurally interesting region of $0\leq x\leq 4$ shows universal behavior and can be interpreted as asymptotic. The Ohta-Nozaki form factor is plotted for comparison, with normalization to the peak of the hardened form factors. For clarity, every other data point is removed for $x>1.75$.

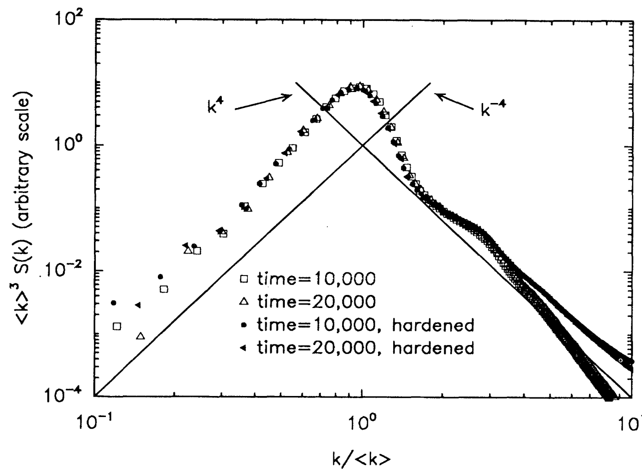


FIG. 4. Log-log plot of unhardened and hardened form factors. The lowest-$k$ data points are quite scattered due to the small number of points involved in the averaging procedure (Ref. 18). However, the small-$k$ region is consistent with Yeung's inequality. This plot shows a clear second-order hump.

factor from the hardened 20000-time-step data correctly portrays the asymptotic form factor up to $x\simeq 7$. Current computational techniques offer almost no hope in getting the unhardened form factor to clearly exhibit the precursor of Tomita's sum rule. To reduce the ratio $\rho$ to 0.1 (which is still much larger than $\frac{1}{30}$) would require an estimated 180000 time steps using the current model, and would also require a larger system ($\geq 256^3$) to avoid finite-size effects and to obtain adequate resolution of the form factor.

In Fig. 4, we plot a log-log graph of the scaled form factors. This graph clearly shows that at small $x$ the form factor is consistent with $F(x)\sim x^{\delta}$ with $\delta\geq 4$. However, there is a large error in $S(k)$ for the smallest and the next smallest $k$.[18] The log-log plot also exhibits a hump at about $x=3$.

In summary, for the first time, the true asymptotic form of the scattering form factor for a critically quenched system is known. All the major characteristic features of the asymptotic form factor, the bound on the small-$k$ exponent, Porod's law, and Tomita's sum rule, are supported by our study. Although the elegant and simple theory by Ohta and Nozaki is somewhat successful, our data clearly indicate that the theoretical understanding of the asymptotic form factor is yet to come.

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[1]Y. Oono and A. Shinozaki, Forma **4**, 75 (1989).

[2]Y. Oono and S. Puri, Phys. Rev. Lett. **58**, 836 (1987); Phys. Rev. A **38**, 434 (1988); S. Puri and Y. Oono, Phys. Rev. A **38**, 1542 (1988). We empirically know that the form factor is quite insensitive to the actual choice of maps so long as the map is a hyperbolic homeomorphism with two sinks located symmetrically around the unique source at the origin. We can derive the CDS from the Cahn-Hilliard equation with the aid of a discretization scheme called the semigroup scheme (Ref. 1), and we can demonstrate that the form factors from the CDS and from the Cahn-Hilliard equation are actually identical [ Y. Oono (to be published)]. Also, this demonstrates that all the physics captured by the partial differential equation is captured by the CDS, and vice versa.

[3]C. Yeung and D. Jasnow, University of Pittsburgh report, 1989 (to be published); A. Onuki and H. Nishimori, Kyoto University report, 1990 (to be published); see also J. D. Gunton, E. T. Gawlinski, A. Chakrabarti, and K. Kaski, J. Appl. Cryst. **21**, 811 (1988).

[4]K. Binder and D. Stauffer, Phys. Rev. Lett. **33**, 1006

(1974); Adv. Phys. **25**, 343 (1976).

[5]H. Tomita, Prog. Theor. Phys. **72**, 656 (1984); **75**, 482 (1986).

[6]C. Yeung, Phys. Rev. Lett. **61**, 1135 (1988); University of Illinois at Urbana-Champaign, Ph.D. thesis, 1988 (unpublished).

[7]H. Tomita, Kyoto University report, 1990 (to be published).

[8]H. Furukawa, J. Phys. Soc. Jpn. **58**, 216 (1989); Phys. Rev. B **40**, 2341 (1989).

[9]M. Hennion, D. Ronzaud, and P. Guyot, Acta Metall. **30**, 599 (1982); A. F. Craievich, J. M. Sanchez, and C. E. Williams, Phys. Rev. B **34**, 2762 (1986); B. D. Gaulin, S. Spooner, and Y. Morii, Phys. Rev. Lett. **59**, 668 (1987).

[10]A. Chakrabarti and J. D. Gunton, Phys. Rev. B **37**, 3789 (1988).

[11]J. Viñals and D. Jasnow, Mod. Phys. Lett. B **2**, 522 (1988); Phys. Rev. B **37**, 9582 (1988); C. Roland and M. Grant, Phys. Rev. B **39**, 11971 (1989); T. M. Rogers, K. R. Elder, and R. C. Desai, Phys. Rev. B **37**, 9638 (1988); E. T. Gawlinski, J. Viñals, and J. D. Gunton, Phys. Rev. B **39**, 7266 (1989).

[12]S. Puri, Phys. Lett. A **134**, 205 (1988).

[13]A. Chakrabarti, R. Toral, and J. D. Gunton, Phys. Rev. B **39**, 4386 (1989). In this work they directly integrated the Cahn-Hilliard equation. By inspection of $g(r,t)=\langle\psi(r,t)\psi(0,t)\rangle$, we note that our CDS time step is identical to their unit of time. Also our length scales are nearly identical. Their scheme required 10 time integrations to generate one unit of time. Statistically, out longest study is comparable to 50 samples of size $66^3$ since each of our samples has roughly 25 times the scattering volume of a $66^3$ sized sample. We note that for $k/\langle k\rangle > 1$ the system self-averages well (see also Ref. 18).

[14]T. Ohta and H. Nozaki, in *Space-Time Organization in Macromolecular Fluids,* edited by F. Tanaka, M. Doi, and T. Ohta, Springer Series in Chemical Physics Vol. 51 (Springer-Verlag, Berlin, Heidelberg, 1989). We choose $A$ in their theory to be 7, while they chose $A$ to be 7.5. The shape of the form factor is quite insensitive to this choice.

[15]G. Mazenko, University of Chicago report, 1990 (to be published).

[16]M. Bahiana (private communication).

[17]Y. Oono and S. Puri, Mod. Phys. Lett. B **2**, 861 (1988).

[18]For the form factor obtained from 20 samples at time step=10000, the standard error from sample to sample is $\pm 18\%$ for the smallest-$k$ data point and $\pm 9\%$ for the next data point. At the peak the error is $\pm 1.2\%$ and beyond $x>2$ the error is $<0.7\%$. The estimated error for time step beyond 10000 is generally 3 times as large. Strictly speaking, the $k\to 0$ limit must be taken under the condition that $kL \gg 1$, where $L$ is the system size. Practically, to have reliable statistics $kL$ must be at least 2 or 3, so that in our case the three or four smallest-$k$ data points should be disregarded from the estimate of the slope. In two-space, the finite-size effect has been studied by Yeung (Ref. 6); the region where the slope is less than 4 near $k=0$ is shifted toward $k=0$ as the system size is increased. We expect the same in three-space.