

**Light-scattering studies of phase separation in isobutyric acid + water mixtures: Hydrodynamic effects**

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The growth of droplets in a binary fluid mixture undergoing phase separation has been studied by light scattering. The measurements have focused on the dependence of growth rate on the overall composition of the mixture. For mixtures of the critical composition, there is a crossover:  $k_m$ , the wave number corresponding to the maximum in the scattering, decreases initially as  $t^{-1/3}$  and at long times as  $t^{-1}$ . In accordance with hydrodynamic arguments of Siggia [Phys. Rev. A **20**, 595 (1979)], the existence of the crossover can be related to the volume fraction of the new phase  $v$ . Only for  $v \geq 0.10$  are crossovers observed. In more dilute mixtures we find  $|k_m| = At^{-1/3}$  with  $A$  proportional to  $v$  for  $0.10 \geq v \geq 0.02$ . Lifshitz-Slyozov growth, for which  $A$  is independent of  $v$ , is found for  $v < 0.02$ .

**I. INTRODUCTION**

Light-scattering studies of phase separation in fluid mixtures<sup>1,2</sup> have provided a wealth of information about the complex, highly nonlinear processes by which a new phase forms in a system that was originally homogeneous. Measurements of the scattered light  $I(\vec{k}, t)$  as a function of the scattering vector  $\vec{k}$  and the time after quench  $t$  have been compared with the behavior of the structure factor  $S(\vec{k}, t)$  predicted by the only quantitative nonlinear theory, that of Langer, Bar-on, and Miller (LBM),<sup>3</sup> and with computer simulations on model systems.<sup>4</sup> So long as the effects of multiple scattering are small, the scattered intensity is proportional to the structure factor.

In qualitative terms, close agreement has been found between experiment, theory, and computer simulation. The structure factor, which is initially broad, grows and narrows with time. The wave number corresponding to the position of the maximum in  $S(\vec{k}, t)$ ,  $k_m(t)$ , moves toward smaller values as a result of "coarsening", the growth of the average droplet size.

The quantitative differences between experiment, theory, and simulation are significant, however. As reported in the first paper in this series, (hereafter called I), in "off-critical" quenches, i.e., those for compositions other than the critical (see Fig. 1), the experimental coarsening rate can be expressed<sup>2</sup> as a power law  $|k_m(t)| = A't^{-a'}$ , with  $a' \approx \frac{1}{3}$ , while the growth of the intensity at  $\vec{k}_m$  can similarly be

written  $I(\vec{k}_m, t) = A''t^{a''}$ , with  $a'' \approx 1.2$ . On the other hand, LBM find  $a' = 0.21$  and  $a'' = 0.8$ , values similar to those obtained from the Monte Carlo<sup>4</sup> calculations.

A more striking difference is apparent in critical quenches. We observed that the coarsening rate depends on quench depth, the exponent  $a'$  changing from 0.3 to 1 with increasing quench depth. The intensity exponent  $a''$  shows a parallel increase from about 1 to 2. This acceleration, which was not predicted by LBM and is not found in the simulations, was verified in the experiments of Chou and Goldberg.<sup>5</sup> If the data are appropriately scaled,<sup>2</sup> the change in the exponents can be seen as a dependence on the reduced time.

The LBM theory and the simulations are more

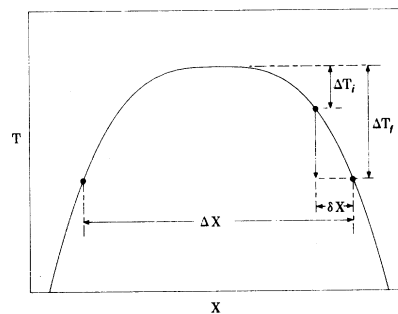


FIG. 1. The overall composition is specified by  $\Delta T_i$ , the temperature at which, under equilibrium conditions, a second phase first appears. For a "critical" quench,  $\Delta T_i = 0$ . When the system is quenched to a temperature specified by  $\Delta T_f$ , the volume fraction of new phase is given by  $v = \delta x / \Delta x$ . Substitutions with Eq. (4) yield Eq. (5).

appropriate to solid mixtures than to fluids.

Kawasaki and Ohta<sup>6</sup> have attempted to introduce the hydrodynamics by grafting mode coupling onto the LBM model. Their results, which do produce an increase in  $a'$  and  $a''$ , apply only at relatively early times and therefore correspond to only very shallow quenches.

Binder and Stauffer<sup>7,8</sup> have discussed the dynamics of phase separation in terms of the diffusion and reactions of clusters. Their arguments, which rely on scaling, lead to a  $t^{-1/3}$  growth law for fluid mixtures. However, long-range hydrodynamic interactions are not included.

More recently, Siggia<sup>9</sup> has focused on what he terms the "late stages" of phase separation. This regime can be defined in terms of the reduced wave number  $q$ , which is the wave number scaled by the equilibrium correlation length  $\xi$ ,

$$q_m = k_m \xi \leq 0.1 .$$

Siggia has enumerated several different coarsening mechanisms that apply in this regime and are experimentally distinguishable. The simple coalescence of spherical droplets of diameter  $a$  leads to a growth law that can be written

$$a^3 = 12Dvt , \quad (1)$$

where  $D$  is the diffusion constant,  $t$  is the time, and  $v$  is the volume fraction of the droplets. To connect Eq. (1) to light-scattering measurements, we take  $a = k_m^{-1}$ . Then, if we define a reduced time

$$\tau = Dt / \xi^2 , \quad (2)$$

we can rewrite (1) in scaled form

$$q_m^{-3} = 12v\tau . \quad (3)$$

As shown in Fig. 1, the volume fraction can be calculated from the lever rule. The computation is simplified by the use of the well-known relations for the coexistence curve

$$2(x' - x_c) \approx x' - x'' = B[(T_c - T)/T_c]^\beta . \quad (4)$$

In these expressions,  $\beta$  is a critical exponent,  $x_c$  is the mole fraction at the critical composition, and  $x'$  and  $x''$  are the mole fractions of the coexisting phases at the temperature  $T$ . If we define  $\Delta T_f = T_c - T_f$  as the temperature difference between the critical temperature and the temperature to which the mixture is quenched and  $\Delta T_i = T_c - T_i$  as the temperature difference that corresponds to the composition of the system before a quench, we can write

$$v = [1 - (\Delta T_i / \Delta T_f)^\beta] / 2 . \quad (5)$$

When hydrodynamic interaction, which results from the squeezing out of fluid between spheres that diffuse toward each other, is added to the simple coalescence model, a growth law somewhat different from Eq. (3) is obtained,

$$q_m^{-3} = \frac{16\pi v \tau}{\ln(0.55/q_m)} . \quad (6)$$

This equation applies when the interfacial thickness of the drop is of the order of the correlation length, a condition that holds for the experiments that we will consider.

At low supersaturations, when the volume fraction of droplets is small, growth will take place by the evaporation-condensation mechanism analyzed by Lifshitz and Slyozov.<sup>10</sup> The growth rate for this process is independent of the volume fraction of the droplets:

$$q_m^{-3} = 0.053\tau . \quad (7)$$

If the volume fraction exceeds the percolation limit, estimated by Siggia as 0.15, the droplets are connected and another growth mechanism can be envisaged. It results from the necking down of undulations in tubular regions of the new phase and is driven by the interfacial tension. Dimensional analysis leads to the relation

$$k_m^{-1} \approx \frac{0.1\sigma t}{\eta} , \quad (8)$$

where  $\sigma$  is the interfacial tension and  $\eta$  is the viscosity; the numerical factor is very uncertain. To a good approximation,<sup>11</sup>  $\sigma = 0.2k_B T / \xi^2$ , so Eq.(8) can be written

$$q_m^{-1} \approx 0.3\tau . \quad (9)$$

For the critical mixture, then, the initial stages of growth are expected to be diffusional (i.e.,  $q_m \propto \tau^{-1/3}$ ) but there will be a crossover to  $\tau^{-1}$  behavior at a point that can be estimated by equating growth rates

$$k_m^{-2} \approx \frac{k_B T}{\sigma} \approx 5\xi^2$$

or, in scaled form,

$$q_m^2 \approx 0.2 . \quad (10)$$

A second crossover to gravity-dominated motion is expected as well. The difference in density between isobutyric acid and water is so small, however, that this regime would occur only at very late stages of

coarsening.

The behavior of off-critical mixtures will depend on the relative quench depth; i.e., on  $\Delta T_i/\Delta T_f$ . If  $\Delta T_i \lesssim 0.35\Delta T_f$ , the volume fraction exceeds the percolation limit and some region of  $\tau^{-1}$  behavior would be expected. Quenches for which  $0.35\Delta T_f \lesssim \Delta T_i \lesssim 0.9\Delta T_f$  should initially exhibit  $\tau^{-1/3}$  growth with a volume-fraction-dependent prefactor. After the supersaturation has been reduced, a crossover to Lifshitz-Slyozov (volume-fraction-independent) growth should be observed. Only Lifshitz-Slyozov growth should be observed when  $\Delta T_i \geq 0.9\Delta T_f$ .

The sharp distinction in behavior between the critical and off-critical quenches that was reported in I can be seen then as merely reflecting the difficulty in achieving large volume fractions in off-critical quenches, basically because the coexistence curve is very flat. For example, in a quench for which  $\Delta T_i = 10$  mK, a volume fraction of 0.40 can be achieved only for  $\Delta T_f = 1250$  mK. Such deep quenches could not be accomplished with our apparatus. Of the 11 off-critical quenches studied, only three were at volume fractions greater than 0.10. Quenches *J* and *M*, for which  $v = 0.14$  and 0.18, respectively, show some evidence of crossover at very late times; no deviation from  $\tau^{-1/3}$  behavior can be seen in Quench *I* ( $v = 0.21$ ), but measurements were made for only 300 sec. Thus, although the experiments described in I are consistent with Siggia's models, they are not satisfactory probes of the dependence on volume fraction. The work that we will discuss here was planned to investigate explicitly the transition between critical and off-critical behavior and therefore provides a more meaningful test of the theory.

## II. EXPERIMENTAL

Details of the pressure-quench method used to drive the isobutyric-acid + water mixture from a one-phase region into a two-phase region, and a description of the apparatus, have been given in I. Since we were interested only in the position of maximum in  $S(\vec{k}, t)$ , the intensity was recorded photographically rather than with a digital technique. In the initial experiments, the position of the maximum was located with a recording densitometer. This method was abandoned when we recognized that equivalent results could be obtained by making measurements on the films with a vernier caliper.

All the measurements in I were performed on

samples of critical composition; off-critical quenches were accomplished by starting with two coexisting phases in the cell and studying phase separation in one phase or the other. The advantage of such a procedure is that it allows the critical temperature of the sample to be determined periodically, making it possible to relate all temperature measurements to  $T_c$ .

In contrast, only the first set of the current series of measurements was performed on a critical mixture. This set consisted of five quenches that began with the cell at a temperature about 0.5 mK above  $T_c$  and were produced by pressure jumps of 2, 4, 8, 16, and 32 cm Hg. Since, for isobutyric acid + water,  $dT_c/dp = -0.055$  K atm<sup>-1</sup>, these pressure jumps correspond to temperature changes of 1.5, 2.9, 5.8, 11.6, and 23.2 mK, respectively.

At the completion of the measurements on the critical sample, the bath was cooled 4.90 K below the critical temperature and the cell was allowed to equilibrate. A small portion of the lower phase was then withdrawn with a syringe attached to a length of 0.8-mm i.d. Teflon tubing that had been threaded through the side arm of the cell. For convenience, the volume of liquid removed was gauged from the length of the column of mixture withdrawn into the tubing. The 30-cm-long column removed was found by calibration to correspond to 0.148 cm<sup>3</sup>.

After heating the sample above  $T_c$  and stirring it thoroughly, we determined its temperature of phase separation. A series of quench measurements was then performed with the same set of pressure jumps employed in the critical-quench set.

The sample withdrawal procedure was repeated eight more times and, on each occasion, the same volume of lower phase was removed and the same set of jumps was utilized. The first photograph was taken five or ten seconds after a quench and data taking continued until the maximum in the scattering was at an angle less than 0.01 rad. Observation times varied from 300 to 2000 sec depending on the coarsening rate. Corrections to the scattering angle were applied for the differences in refractive index between sample, bath, and air. All measurements were made in the upper, isobutyric-acid-rich phase.

Given the volume of the initial critical sample (10.89 cm<sup>3</sup>) and the density<sup>12</sup> and weight fraction<sup>13</sup> of the lower phase along the coexistence curve, it is possible to calculate the compositions after each withdrawal and the corresponding temperatures of phase separation. If there were no change of the

critical temperature with time, the accuracy of the calculation could be checked by comparison with observed phase-separation temperatures. Unfortunately, the critical temperature of isobutyric acid + water mixtures in contact with mercury has been shown to drift downward with time.<sup>2</sup> Thus, although we calculate that the relative separation temperature  $\Delta T_i$  in the tenth set of measurements is 25 mK, the measured separation temperature was only 3 mK lower than that recorded for the critical sample. This 22-mK discrepancy could certainly be accounted for by a drop in  $T_c$  over the three months during which the experiments were performed. We therefore will base our estimate of  $\Delta T_i$  on the volumetric measurements alone.

The principal source of random error in  $v$  is the 4% uncertainty in the volume of fluid removed. An error of this size produces at most an uncertainty of  $\pm 0.02$  in  $v$ . All the volume fractions in a given set would be either systematically high or low, depending on the direction of the volume error.

A summary of the experiments performed is given in Table I, where the volume fractions calculated from Eq. (5) are listed for each initial temperature and pressure jump, 50 quenches in all. The number of photographs taken following a quench was 12–20 for the 1.5-, 2.9-, and 5.8-mK quenches, 6–8 for the 11.6-mK quenches, and 1–8 for the deepest quenches.

### III. RESULTS

The changes in the coarsening rate with composition and quench depth are typified by Figs. 2–6,

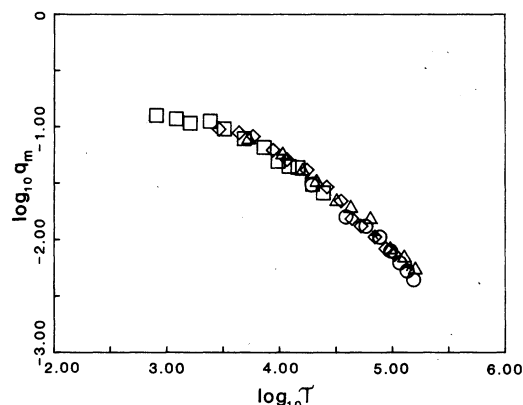


FIG. 2. Dependence of  $\log_{10} q_m$  on  $\log_{10} \tau$  for the critical quench, set 1. Symbols represent different quench depths:  $\square$ , 1.5 mK;  $\diamond$ , 2.9 mK;  $\triangle$ , 5.8 mK;  $\circ$ , 11.6 mK;  $*$ , 23.2 mK. The choice of symbols is the same in the other figures.

which show, in scaled form, the results for sets 1, 4, 7, 8, and 10, respectively. Values of  $D$  and  $\xi$  used in the scaling were calculated by the relations  $D/\text{cm}^2 \text{ sec}^{-1} = 1.5 \times 10^{-6} (\Delta T_f/T_c)^{0.60}$  and  $\xi/\text{cm} = 1.8 \times 10^{-8} (\Delta T_f/T_c)^{-0.61}$ , taken from the work of Chu and co-workers.<sup>14</sup>

There is a clear progression in the figures from “critical” to off-critical behavior. For the early sets, in which the volume fractions are high, all quenches show crossovers from  $\tau^{-1/3}$  to  $\tau^{-1}$  behavior. As the concentration moves further away from the critical, however, the crossover no longer appears in the shallower quenches, which correspond to small volume fractions. On the other hand,  $\tau^{-1}$  behavior persists in deeper quenches,

Table I. Initial relative temperatures  $\Delta T_i$ , temperature jumps  $\delta T$ , and corresponding volume fractions  $v$ .

Set	$\Delta T_i/\text{mK}$	$\delta T/\text{mK}$				
		1.45	2.89	5.79	11.6	23.2
1	0	0.50	0.50	0.50	0.50	0.50
2	0.01	0.39	0.41	0.43	0.44	0.45
3	0.14	0.26	0.31	0.34	0.37	0.40
4	0.55	0.16	0.22	0.27	0.31	0.34
5	1.5	0.10	0.14	0.20	0.25	0.29
6	3.0	0.06	0.09	0.14	0.19	0.24
7	6.0	0.03	0.06	0.09	0.14	0.19
8	10.2	0.02	0.04	0.06	0.10	0.15
9	17.1	0.01	0.02	0.04	0.07	0.12
10	24.7	0.01	0.02	0.03	0.06	0.09

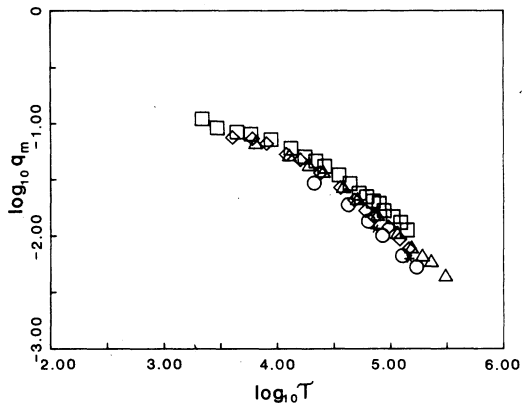


FIG. 3. Quenches in set 4.

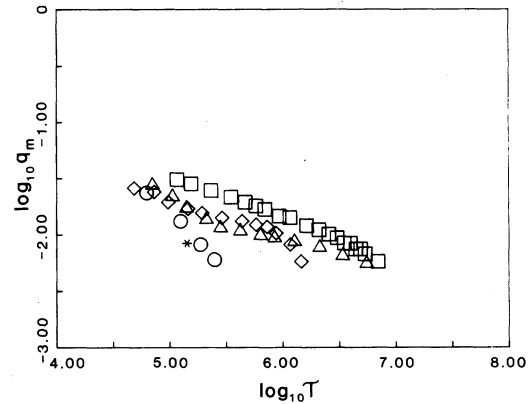


FIG. 5. Quenches in set 8.

for which  $\nu$  remains high.

In order to be able to make more quantitative comparisons between experiment and theory, we have fitted the  $\log_{10} q_m - \log_{10} \tau$  data by unweighted linear least squares. Where there are crossovers, the limiting low- and high-slope regions were fitted separately. There is clearly a degree of arbitrariness in the grouping of points and the small amount of data precludes meaningful tests of the sensitivity of parameters to truncation. Statistical estimates of the uncertainties in the derived quantities are therefore misleading and will not be given. The numbers we cite are useful in demonstrating trends and in checking consistency with theory.

With three exceptions, rapid coarsening rates are found only in quenches for which  $\nu \geq 0.10$ . The power-law exponents that characterize this behavior range from 0.8 to 1.1 and their average lies close to 0.9. Within a given off-critical set, there is a trend toward higher exponents with increasing quench depth. Three relatively shallow

quenches, those for volume fractions of 0.06 and 0.09 in set 6 and that for  $\nu=0.06$  in set 7, also have high exponents (0.89, 0.88, and 0.80, respectively).

The coefficient of  $\tau$  in Eq. (9) can be compared with the value derived from the constant term obtained from the linear fit. We find  $(4 \pm 2) \times 10^{-3}$  for the average of all the quenches showing crossover, which is two orders of magnitude smaller than Siggia's estimate. The rather poorly determined coefficients show no evidence of a dependence on  $\nu$ .

Crossover regions in the shallow quenches of sets 2–5 are sufficiently sharp to allow the early time data to be fitted. For the 10 quenches examined, the average slope is 0.31, with an average deviation of 0.03. The location of the crossover can be fixed by equating the functions obtained from fitting the early and late-time behavior. This procedure gives  $q_m = 0.5$  with an average deviation of 0.01.

In sets 8, 9, and 10, we find the  $\tau^{-1/3}$  behavior

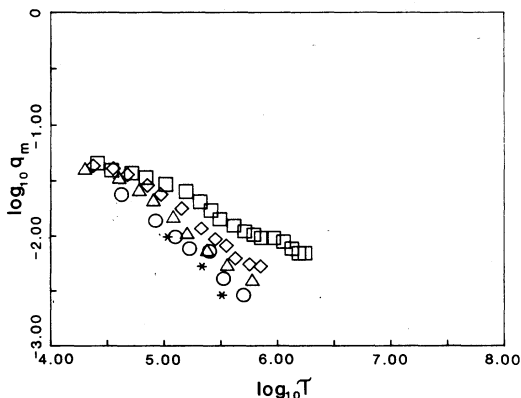


FIG. 4. Quenches in set 7. Note change in abscissa.

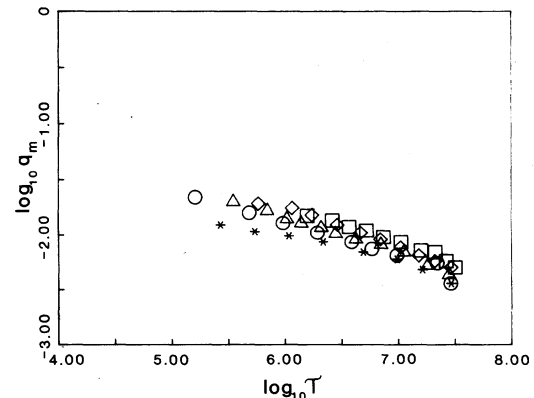


FIG. 6. Quenches in set 10.

without crossover that was observed in the off-critical quenches in I. The coarsening rate in these quenches can be compared with that predicted by Eqs. (3), (6), and (7). Values of  $a'$ , the exponents, and  $A$ , the coefficients of  $\tau$ , obtained by fitting the data, are presented in Table II.

For the shallowest quenches ( $v < 0.02$ ),  $A$  lies close to the Lifshitz-Slyozov value, 0.053. The coefficients for the deeper quenches show a dependence on volume fraction and with one exception lie within a factor of 2 of  $12v$ , the value consistent with Eq. (3). In the range of  $q$  values measured in these quenches, the average value of the coefficient of  $\tau$  in Eq. (6) is  $13v$  and a  $\log_{10} q_m - \log_{10} \tau$  plot of the equation is very nearly linear and has an average slope of  $-0.31$ . Clearly, then, we are not able to distinguish the simple coalescence behavior from that involving hydrodynamic interaction. The coefficients obtained by fitting the early time  $\tau^{-1/3}$  portions of those quenches with crossovers are systematically smaller than  $12v$ . They are better represented as constant ( $0.6 \pm 0.2$ ) than as a function of  $v$ .

#### IV. CONCLUSIONS

Siggia's hydrodynamic analyses provide an appealing physical picture of droplet growth mechanisms and the crossovers between them. For the  $t^{-1/3}$  growth, the agreement between experiment and theory is semiquantitative: The predicted volume-fraction dependence of the prefactors, magnitudes of the prefactors, and location of the crossover to Lifshitz-Slyozov growth are all consistent with the experiments.

The description of the  $t^{-1}$  growth is qualitatively correct but a prefactor two orders of magnitude smaller than Siggia's estimate is needed to account for both the observed growth rate and the crossover from  $t^{-1/3}$  to  $t^{-1}$  growth. Chou and Goldburg,<sup>5</sup> who, with a microscope, studied the late stages of droplet growth in a phase-separating fluid, found that the ratio of the average droplet diameter  $l(t)$  to  $k_m^{-1}(t)$  ranged from 5 to 10. If we

TABLE II. Exponents and coefficients of  $\tau$  for sets 8, 9, and 10.

Set	$\Delta T_f/mK$	$a'$	$A$	$A/v$
8	1.5	-0.40	0.055	3
	2.9	-0.36	0.98	24
	5.8	-0.33	0.76	13
9	1.5	-0.36	0.041	4
	2.9	-0.40	0.016	8
	5.8	-0.30	0.67	17
	11.6	-0.28	0.10	1.4
10	1.5	-0.36	0.052	5
	2.9	-0.36	0.052	3
	5.8	-0.34	0.22	7
	11.6	-0.32	0.85	14

assume that this relation holds throughout the growth process and we substitute  $10 k_m^{-1}$  for  $a$  in the expressions for the concentrated mixtures, we can reduce the discrepancy by an order of magnitude. At the same time, however, the use of  $10 k_m^{-1}$  in the other equations destroys the concordance found for the dilute mixtures. It is also observed<sup>5</sup> that  $l$  decreases more rapidly than  $k_m^{-1}$  and with a time dependence that can be greater than  $t^{-1}$ . Thus,  $k_m^{-1}$  appears to be a generally better measure of the characteristic size than  $l$ .

The  $t^{-1}$  behavior appears to be restricted to  $v \geq 0.10$ . Of the three quenches that are exceptions to this limit, one certainly lies at  $v=0.10$  within the experimental error. The other two, for which  $v=0.06$ , differ significantly from  $v=0.10$ , however, and their behavior is inconsistent with that of other quenches with similar volume fractions. Further study of this crossover region is needed.

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