

## Analysis of Light-Scattering Measurements Near a Cloud Point

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An analysis is reported of earlier light-scattering measurements by Wong and Knobler on a liquid mixture undergoing phase separation. When the system was quenched into the two-phase region to a temperature near the cloud point, the growth of intensity with time displayed two characteristic regions: an initial rapid rise followed by a sharp crossover to slower growth. It is shown that such behavior is consistent with the predictions of the Langer-Schwartz description of the homogeneous nucleation and growth of droplets.

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Experimental studies of nucleation in binary liquid mixtures in the neighborhood of a critical solution temperature<sup>1-3</sup> have revealed apparent anomalies in the nucleation rate and have stimulated several theoretical investigations of the nucleation and growth of droplets in near-critical mixtures. The most successful of these theories is that of Langer and Schwartz,<sup>4</sup> who amplified a suggestion by Binder and Stauffer<sup>5</sup> that the anomalies were the result of the critical slowing down of growth rather than a gross departure of the nucleation rate from that predicted by the classical theory.<sup>6</sup>

The Langer-Schwartz (LS) theory predicts that the character of the nucleated phase depends sensitively on the initial supersaturation. The phase may appear as a cloud of small droplets that grow slowly beyond the critical droplet size, or it may form as isolated droplets that rapidly grow to very large size. The average droplet size grows in a complicated fashion that resembles power-law behavior during limited periods of time and asymptotically approaches the  $t^{1/3}$  growth law predicted by the Lifshitz-Slyozov<sup>7</sup> model of diffusive growth.

The LS theory has been used in the analysis of several experiments on liquid mixtures<sup>2,3</sup> and on solid mixtures as well.<sup>8</sup> These applications have not been decisive tests of the theory, however, and have shown only that the experiments are not inconsistent with it. A recent measurement of the nucleation rate by a technique that makes it possible to decouple nucleation from growth<sup>9</sup> has demonstrated that the nucleation rate is not anomalous near a critical point, but did not test the arguments concerning growth.

Recently, Simon<sup>10</sup> has studied x-ray scattering from a binary alloy undergoing phase separation. He observed that at low supersaturations the intensity at the scattering maximum showed two distinct regimes of growth, both of which could be fitted by power laws. The rise of intensity at early times was steeper than that at late times, and the transition between the two regimes was sharp. The average size of the regions of precipitated phase, as indicated by the position of the scattering maximum, grew relatively slowly with time.

Similar behavior was observed by Wong and Knobler<sup>11</sup> in their study of light scattering from isobutyric acid plus water mixtures that were undergoing phase separation. After this system was quenched into the two-phase region, a characteristic ring of light scattered in the forward direction appeared; it grew in intensity and decreased in diameter with time. For most of the quenches studied, the rise in the intensity exhibited a simple power-law behavior, but in two of the quenches (labeled *P* and *L*) there were two regimes of growth, which were described as having "dog-leg" behavior, Fig. 1. These quenches were also distinguished by the low value of the power-law exponent describing the ring collapse. Wong and Knobler suggested that this distinctive behavior arose because the phase separation was occurring close to the cloud point, the supersaturation that is the practical limit of metastability, but they offered no arguments to support the conjecture. The fact that Simon's observations were also made in the vicinity of the cloud point suggests that the conjecture was correct. In this Letter, we report the results of some approximate calculations based on the LS theory that also support this conclusion.

Calculations with the LS theory are most conveniently carried out in terms of reduced variables.<sup>4</sup> The

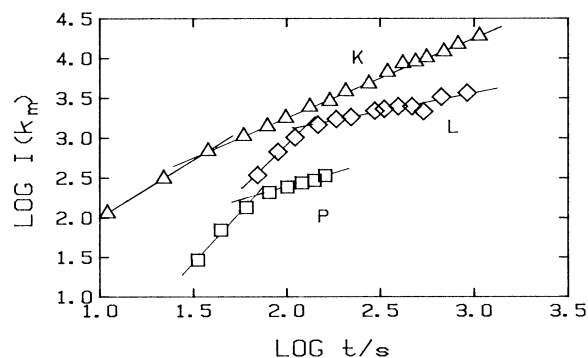


FIG. 1. Intensity (arbitrary units) at the scattering maximum as a function of time for quenches *K*, *L*, and *P*. Intensity scale factor for *K* not identical to that for *L* and *P*.

reduced number density of droplets  $n$ , average droplet radius  $\rho$ , and nucleation rate  $\tilde{J}$  can be calculated as a function of the reduced time  $\tau$  and the initial supersaturation  $y_1$ . Once  $y_1$  has been specified, the evolution of the other variables with time can easily be computed by the numerical solution of the differential equations

$$\begin{aligned} d\rho/d\tau &= (\rho/\rho^* - 1)/\rho^2 + \tilde{J}(a - \rho + \rho^*)/n + bd\rho^*/d\tau, \\ dn/d\tau &= \tilde{J} - nb(d\rho^*/d\tau)/(\rho - \rho^*), \end{aligned}$$

where  $a$  and  $b$  are constants,  $\rho^* (= 1/y)$  is the critical droplet radius, and  $\tilde{J}$  is given by

$$\tilde{J} = 3.08y^{2/3}(1+y)^{3.55} \exp(-1/y^2).$$

To compare the calculations with the light-scattering measurements, we assume that the intensity at the scattering maximum is proportional to  $n\rho^6$  and that the wave number at the maximum  $k_m$  is proportional to  $\rho^{-1}$ . The first of these approximations is exact for scattering by droplets whose diameter is very small compared to the wavelength of the scattered light.<sup>12</sup> This is not the case for the conditions of the quenches studied by Wong and Knobler, but it remains a reasonable first approximation. Comparisons between optical-microscope measurements of droplet sizes and concurrent light-scattering studies<sup>13</sup> have demonstrated the validity of the second assumption.

The behavior of the intensity of the scattered light and the droplet diameter can easily be derived for two special cases.<sup>4</sup> At early times, the supersaturation has not decreased appreciably and  $\tilde{J}$ , which is a function only of  $y$ , therefore remains constant. This is a period of free growth during which  $\rho$  increases as  $\tau^{1/2}$  and  $n$  as  $\tau$ ; hence the intensity should increase as  $\tau^4$ . At late times,  $\rho$  grows as  $\tau^{1/3}$  and  $n$  decreases as  $\tau$ ; the intensity therefore is proportional to  $\tau$ . Thus, power-law plots of the rise of intensity with time might be expected to have at least two distinct regions, one of large

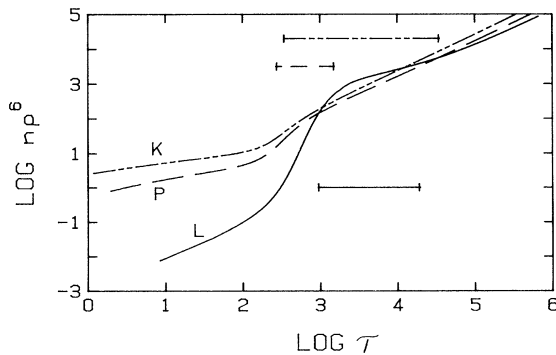


FIG. 2. Calculated variation of  $n\rho^6$  with  $\tau$  for values of  $y_1$  corresponding to quenches  $K$ ,  $L$ , and  $P$ . Horizontal lines indicate time periods during which measurements were made.

slope at relatively early times, and another of smaller slope at late times.

Figure 2 shows the calculated variation of  $n\rho^6$  with  $\tau$  for  $y_1 = 0.24$ , a value of the initial supersaturation that corresponds to quench  $L$ ; the corresponding variation of  $\rho$  with  $\tau$  is plotted in Fig. 3. Over this range of reduced times, which starts at the initial stages of growth and extends to a point at which the supersaturation has fallen to 0.1 of its initial value, the "intensity" displays a sigmoidal dependence on time that can roughly be described by three regions of power-law behavior. The behavior of  $\rho$  is more complex, as already shown by LS.<sup>4</sup>

Similar plots for  $y_1 = 0.34$  and  $y_1 = 0.50$  are also presented in Figs. 2 and 3. These values of  $y_1$  correspond to quench  $P$  and to quench  $K$ , which did not appear to show the dog-leg behavior but is the shallowest of the quenches that was thought to have a single power-law growth of the intensity. It is evident that as  $y_1$  increases the marked high-slope intermediate region of the intensity curve diminishes; it is barely distinguishable at  $y_1 = 0.50$ . At the same time, the position of the second distinct break in the curve shifts slightly to earlier times. The sigmoidal shape of the  $I$ - $\tau$  curves is attributable to the maximum that occurs in the number density (Fig. 6 in LS) and the associated steep rise in the droplet diameter. Only a trace of the intermediate high-slope region can be seen for quench  $K$  because there is no pronounced maximum in  $n$  for this initial supersaturation.

The dog-leg character of the experimental intensity curves would appear to correspond to the second break in the calculated curves. To examine this supposition we must convert the calculated curves to real time. The relation between the time scales is given in terms of the critical amplitudes for the diffusion constant and correlation length,  $D_0$  and  $\xi_0$ , the relative distance from the critical solution temperature,  $\epsilon (= 1 - T/T_c)$ , the critical exponent,  $\nu$ , and  $x_0$ , a substance-dependent constant of order unity:  $\tau = (d_0 x_0^3 / 24 \xi_0^2) \epsilon^{3\nu} t$ . For isobutyric acid plus water,<sup>14</sup>  $D_0 = 1.51 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  and

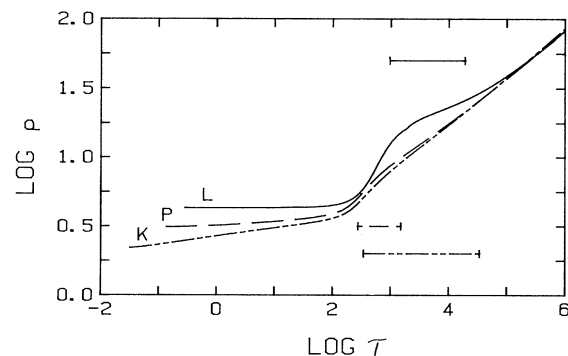


FIG. 3. Calculated variation of  $\rho$  with  $\tau$  for quenches  $K$ ,  $L$ , and  $P$ .

TABLE I. Comparison between experimental and calculated characteristics of  $\log I$ - $\log t$  and  $\log \rho$ - $\log t$  curves.

Quench	$t_2$ (meas.) (s)	$t_2$ (calc.) (s)	$a_1''$ (meas.)	$a_1''$ (calc.)	$a_2''$ (meas.)	$a_2''$ (calc.)	$a'$ (meas.)	$a'$ (calc.)
<i>K</i>	35	27	1.5	1.5	1.08	1.06	0.31	0.34
<i>L</i>	100	70	3	4.5	0.52	0.61	0.18	0.21
<i>P</i>	70	76	2.2	1.9	0.61	1.02	0.27	0.38

$\xi_0 = 1.8 \times 10^{-8}$  cm; we take  $\nu = 0.62$  and  $x_0$  as 1.07, a value that provides the best fit to recent nucleation studies.<sup>9</sup>

The experimental and calculated features of the three quenches are compared in Table I, which gives the positions in time of the kinks in the  $\log I$ - $\log t$  curves, and the slopes of the straight lines that can be drawn through the segments of the curves. Relatively few points were measured at early times, hence the initial slopes are relatively uncertain; the lines have been drawn by eye, since there are too few points for least-squares analysis.

For quench *P*, the measurements were carried out in the period from 30 to 160 s after the quench. By drawing straight lines through the segments of the calculated curves, we find that the break between the initial slow growth of intensity and the rapid rise occurs at  $t_1 = 16$  s, too early to have been seen, so a dog-leg shape rather than the full sigmoid form is predicted. The observed kink occurred at  $t_2 = 70$  s, in good agreement with the 70 s found from the calculation. The experimental and calculated initial slopes,  $a_1''$  (meas.) and  $a_1''$  (calc.) agree well, but the slopes at longer time,  $a_2''$ , are in poorer agreement.

Quench *L* was studied from 50 to 1000 s after the quench. Here the calculations lead to  $t_1 = 12$  s, again before observations were made. The calculated time of the second kink, 70 s, is earlier than the 100 s observed, but this is probably within the overlap of the uncertainties in defining  $t_2$ . The slope  $a_1''$  is much smaller than that calculated, but the slopes at long times agree well.

Although Wong and Knobler considered quench *K* to have a constant slope, the first two points measured lie systematically low. If one connects these points with a straight-line segment, the resulting kink occurs at about 35 s, in good agreement with the calculated 27 s; the observed and calculated values of  $a_1''$  and  $a_2''$  agree extraordinarily well.

The calculated  $\rho$ - $\tau$  trajectories that correspond to the supersaturations in quenches *K*, *L*, and *P* are shown in Fig. 3. Over the range of times during which the experiments were performed, the trajectory for quench *K* closely approaches the asymptotic  $t^{1/3}$  limit. Although

it is clear from the curves that a power-law description is not correct, the experimental variation of  $k_m$  with  $t$  was analyzed in this way and it is interesting to determine the exponent that best fits the calculated curve in the region of interest. To ensure that the weighting of both the experimental and calculated results is the same, we have performed a least-squares fit to a data set that consists of calculated  $k_m$  values of the radius for the same times at which  $k_m$  was measured. This fit gives a power-law exponent  $a' = 0.34$ , in good agreement with the observed value 0.31. When the same procedure is applied to the calculations that correspond to quench *L*, we obtain  $a' = 0.21$  as compared to the measured value  $a' = 0.18$ . The agreement between calculation and experiment is less satisfying for quench *P*; here we find a calculated slope of 0.38 while the experiment yielded 0.27.

Wong and Knobler showed that  $k_m^{-1}$  agreed well with estimates of the droplet size. It is interesting to see if this correspondence holds for the radii calculated from the LS theory. In Fig. 4 we have replotted the values of  $k_m$  for each of the quenches as a function of the time<sup>15</sup> and added curves that represent the inverse of the calculated average radius,  $R^{-1} = x_0/2\xi\rho$ . For quenches *K* and *P*, the agreement is remarkably good;

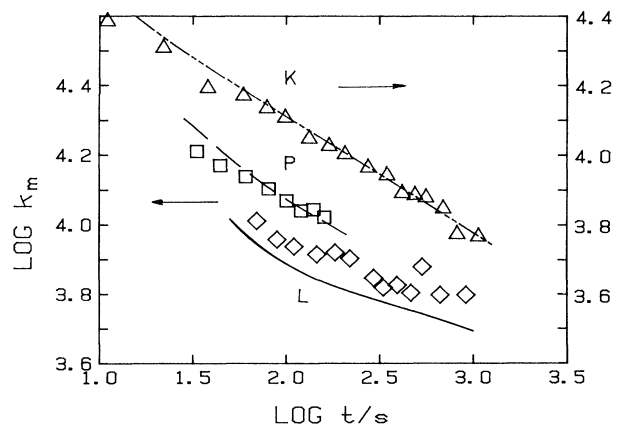


FIG. 4. Measured values of  $k_m$  (points) and calculated values of the reciprocal of the average radius (lines) as functions of the time.

the relation of quench  $P$  to the other data is predicted well, but the radii are too large.

In summary, we find that although the characteristic features of the LS calculations do not agree quantitatively with those observed in the experiments, there is sufficient agreement to lend strong support to the model. It provides an explanation for the shape of the  $I-t$  curves, their variation with quench depth, and the corresponding low values of the exponent describing droplet growth. Additional light-scattering measurements on mixtures that have been quenched to the neighborhood of the cloud point must be performed if the theory is to be confirmed. Such experiments are underway.

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<sup>15</sup>The ordinate in the upper half of Fig. 13 in Ref. 11 is in error and the values of  $k_m$  shown here for quenches  $P$  and  $L$  are therefore different. The error in the figure did not affect any of the numerical values in the paper or any of the conclusions.