# Dynamical Scaling in the Glass System $B_2O_3$-PbO-$Al_2O_3$

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An experimental small-angle x-ray scattering study of a phase-separating quasibinary glass $B_2O_3$-PbO($Al_2O_3$) is compared with the predictions of nonlinear theories for advanced stages of decomposition. The time evolution of the moments and the scaling of the structure function show a reasonable agreement, suggesting the validity of the scaling hypothesis in glassy systems.

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Since Cahn's original work on spinodal decomposition,[1] the time evolution of phase separation in alloys has been a subject of great interest to both theoreticians and experimentalists. Among the most significant additions and contributions to the theory of spinodal decomposition were the introduction of random thermal fluctuations,[2] the study of nonlinearities in the kinetic equation,[3-5] the study of cluster formation and coagulation in real space,[6,7] and simulations by the Monte Carlo method.[8-11]

From the study of the asymptotic time dependence of the kinetic equation[12,13] and from the Monte Carlo simulations, a remarkably simple picture for the final stages of decomposition has emerged: The structure function $S(q,t)$ for an isotropic three-dimensional system obeys the the following scaling relation:

$$S(q,t)=[K(t)]^{-3}F[q/K(t)], \qquad (1)$$

where the characteristic reciprocal length $K(t)$ evolves with time $t$ according to a power law of the type

$$K(t)\propto t^{-a}. \qquad (2)$$

Since the exponent $a$ is in general model dependent, a relatively wide range of values has been predicted. Langer, Bar-on, and Miller[5] obtained $a=0.212$ from a time-dependent Ginzburg-Landau model in three dimensions. On the basis of a cluster reaction model, Binder and Stauffer[6] arrived at $a=1/(d+2)$ for intermediate temperatures and $a=1/(d+3)$ for low temperatures ($T<0.6T_c$), where $d$ is the dimensionality. The value of $a=1/(d+2)$ at low temperatures has also been predicted by Furukawa[12] from his analysis of the asymptotic behavior of the kinetic equation, and under the assumption of the scaling relation (1) for the structure function.

The strongest theoretical evidence for the validity of the scaling hypothesis comes from recent computer simulations by Marro, Lebowitz, and Kalos.[11] In their three-dimensional Monte Carlo simulations, they have specifically observed the scaling behavior of Eq. (1) for the late stages of decomposition. According to the computer simulations, the exponent $a$ in Eq. (2) increases from $a\simeq 0.2$ at concentration 0.59 (center of the miscibility gap) to $a\simeq 0.28$ near the coexistence line.[11]

Most of the features predicted for the time evolution of the structure function have been corroborated reasonably well by experimental studies in binary alloys, particularly in the Al-Zn system.[14-16] Recently Hennion, Ronzaud, and Guyot[17] have carried out a detailed neutron small-angle scattering study of the decomposition process in Al-Zn at different concentrations and temperatures. The experimental evidence strongly suggests the validity of the scaling relation (1). Nothwithstanding the observed agreement between experiment and theory, the analysis and interpretation of the scaling hypothesis in most crystalline systems is severely hampered by the fact that, in the late stages of decomposition, the structure function is highly anisotropic. In the particular case of Al-Zn, there is an additional complication at long annealing times due to the presence of a structural transition of the Zn-rich precipitates to the hcp structure. Thus, for most of the systems which have been investigated so far, the scaling hypothesis cannot be expected to hold strictly.

Vitreous systems, for which all anisotropic effects can be safely ignored, stand out as the best candidates for testing the validity of Eq. (1). The

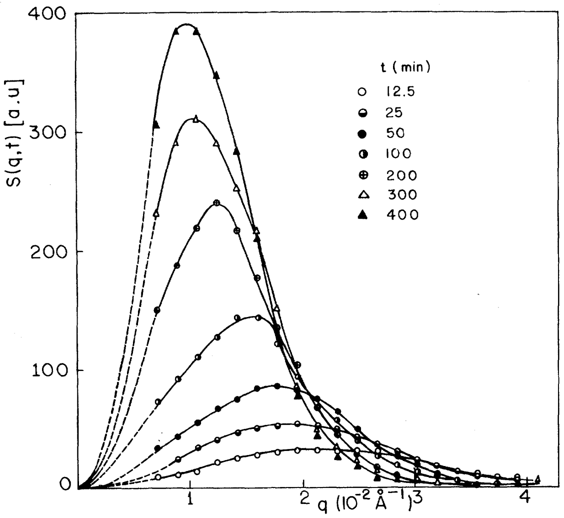

FIG. 1. Time evolution of the corrected structure function (arbitrary units) at 450 °C for a $B_2O_3$-PbO-$Al_2O_3$ sample with composition 80-15-5 (wt.%).

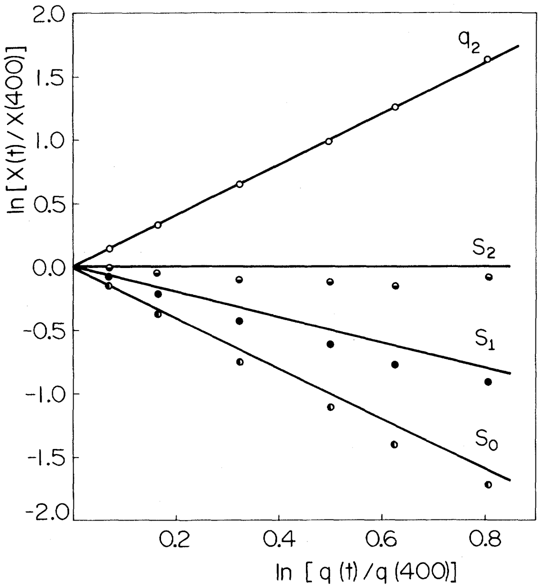

FIG. 2. Double logarithmic plot of $q_2$, $S_2$, $S_1$, and $S_0$ vs the first moment $q_1$ of the structure functions. All quantities are normalized to their values at 400 min. Full lines indicate the behavior predicted by scaling hypothesis.

object of this Letter is to report the results of a preliminary analysis of small-angle x-ray intensity data in the vitreous system $B_2O_3$-PbO-$Al_2O_3$. This particular glass system has been studied by one of the authors in a $B_2O_3$-PbO-$Al_2O_3$ sample at the composition 80-15-5 (in weight percent) and at two different temperatures (380 and 450 °C).[18] For details concerning sample preparation and experimental procedures the reader is referred to Ref. 18. Here it will suffice to point out that the quasibinary system $B_2O_3$-PbO($Al_2O_3$) shows a typical miscibility gap with a critical temperature of approximately 657 °C and with a critical composition of 80-15-5 (wt.%).

Figure 1 shows the time evolution of the structure function $S(q,t)$ (arbitrary units) at 450 °C ($T \simeq 0.65 T_c$) for a sample with the critical composition. The intensity curves in Fig. 1 have been corrected for aberrations resulting from the finite cross section of the primary beam.[19]

A trivial consequence of the scaling hypothesis is that the unnormalized $n$th moment of the structure function behaves as

$$S_n(t) = \int q^n S(q,t)\,dq = C_n K^{n-2}(t), \tag{3}$$

where $K(t)$ is defined in Eq. (1) and where $C_n$ is a constant given by

$$C_n = \int x^n F(x)\,dx,$$

where $x = q/K(t)$. Thus, the moments of the struc-

TABLE I. Time evolution of different moments of the structure function.

| Time (min) | $10^{-2}S_0$ (a.u.) | $S_1$ (a.u.) | $10^2 S_2$ (a.u.) | $10^{-1}S_0/S_1^2$ (a.u.) | $10^2 q_1$ (Å$^{-1}$) | $10^4 q_2$ (Å$^{-2}$) | $q_2/q_1^2$ |
|---|---|---|---|---|---|---|---|
| 12.5 | 0.88 | 2.27 | 8.30 | 1.70 | 2.58 | 9.44 | 1.41 |
| 25.0 | 1.20 | 2.58 | 7.74 | 1.79 | 2.16 | 6.47 | 1.39 |
| 50.0 | 1.62 | 3.06 | 7.96 | 1.72 | 1.89 | 4.92 | 1.37 |
| 100.0 | 2.31 | 3.68 | 8.13 | 1.70 | 1.59 | 3.51 | 1.38 |
| 200.0 | 3.35 | 4.55 | 8.64 | 1.62 | 1.36 | 2.58 | 1.40 |
| 300.0 | 4.22 | 5.12 | 8.99 | 1.55 | 1.24 | 2.13 | 1.39 |
| 400.0 | 4.91 | 5.66 | 9.08 | 1.53 | 1.15 | 1.85 | 1.39 |

ture function are

$$q_n(t) \equiv S_n(t)/S_0(t) \propto K^n(t). \qquad (4)$$

The testing of Eqs. (3) and (4) is somewhat critical since accurate measurements of the structure function can only be obtained over a restricted range of reciprocal vectors $q$, namely that corresponding to real-space distances in the range of 15 to 200 Å. The long-wavelength cutoff in the structure function will introduce errors in the lower moments, particularly at later times, whereas the short-wavelength cutoff will mainly affect the higher-order moments. Nevertheless, for the first few moments ($n \leq 2$) the calculated values are estimated to be reliable to within 10%.

The results of the analysis are shown in Table I and in Figs. 2 to 4. Table I shows the time evolution of the first three unnormalized moments $S_n$ ($n = 0, 1, 2$) together with $q_1(t)$ and $q_2(t)$. The fifth and last columns of Table I give a list of the ratios $S_0/S_1^2$ and $q_2/q_1^2$ which, according to Eqs. (3) and (4), should remain constant for latter times. The two ratios in question are related by the total integrated intensity $S_2$:

$$S_0/S_1^2 = (1/S_2)q_2/q_1^2. \qquad (5)$$

As seen in Table I, the ratio $q_2/q_1^2$ attains an essentially constant value early in the decomposition process. The fact that the measured integrated intensity $S_2$ is not constant (see column 4 in Table I) is therefore responsible for the stronger time dependence of the ratio $S_0/S_1^2$ which, in fact, provides a more critical test of the scaling hypothesis.

The different quantities shown in Table I are plotted in Fig. 2 versus the first moment $q_1(t)$ [proportional to $K(t)$ in Eq. (1)]. All quantities have been normalized to their values for the longest annealing time measured (400 min). For comparison, the behavior predicted by the scaling relation (1) [see Eqs. (3) and (4)] is indicated by full lines.

The time dependence of the first moment $q_1(t)$ is indicated in Fig. 3. The exponent $a$ [see Eq. (2)] is found to be equal to 0.23 in agreement with theoretical predictions and with the Monte Carlo simulations near the center of the miscibility gap.

By substituting the structure and scaled functions by the normalized functions, $\tilde{S}(q,t)/S_2(t)$ and $\tilde{F}(x) = F(x)/\int x^2 F(x)\,dx$, Eq. (1) becomes

$$\tilde{F}(x) = q_1^3(t)\tilde{S}(q,t)$$

with $x = q/q_1$. The plots of $q_1^3\tilde{S}(q,t)$, for different times, are shown in Fig. 4, where a reasonably good agreement with the scaling hypothesis can be seen.

In conclusion, the analysis presented here strongly suggests the validity of the dynamical scaling hypothesis in the vitreous system $B_2O_3$-PbO-$Al_2O_3$. It is also apparent that the asympototic behavior becomes operative for times which are essentially in the limit of accessibility by conventional x-ray techniques. However, with the increased availability of highly collimated and very intense x-ray sources, one can expect that dynamical scaling will be brought into closer scrutiny in the near future. For such a purpose, glasses appear to be particularly suitable not on-

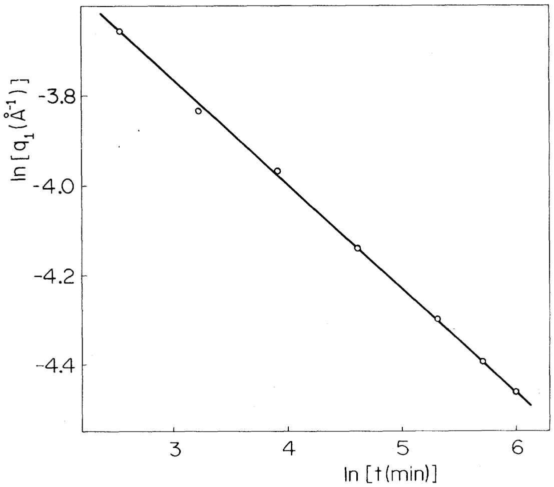

FIG. 3. Time dependence of $q_1(t)$. Full line corresponds to $a = 0.23$ [see Eq. (2)].

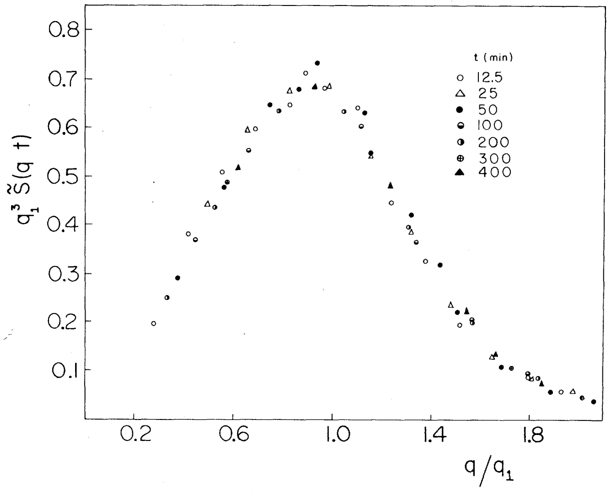

FIG. 4. Scaling of the normalized structure functions.

ly because of their isotropic properties, but because of the time and length scales over which most of the decomposition process takes place.

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# Evidence of Phasons in the Specific Heat of Potassium

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The low-temperature specific heat of potassium has been remeasured and evidence for the existence of phasons is found. The fraction of phonons converted to phasons is $2\times 10^{-5}$ and the Debye temperature of these phasons is 6 K.

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Traditionally the low-temperature specific heat of a pure, normal metal has been analyzed using the equation

$$C_0=\gamma T+\alpha T^3+\beta T^5. \qquad (1)$$

Recently Overhauser and his collaborators studied the effect of a charge-density wave (CDW) on the specific heat of alkali metals.[1,2] The existence of a CDW in simple metals would have important ramifications for many-electron theory, as has been discussed in several publications.[2-5] Therefore it seems important to test the theoretical predictions for the case of a fundamental property such as the specific heat.

A CDW is a broken-symmetry state, accompanied by a lattice distortion. The new collective excitations are low-frequency modes called phasons.[6] Phasons are linear combinations of "old phonons" and produce an extra contribution to the specific heat, $\Delta C_{\mathrm{CDW}}$, to be added to $C_0$. Using this concept Giuliani and Overhauser[2] analyzed the specific heat of rubidium and found a low-temperature anomaly similar to that expected for a CDW structure. However, Taylor *et al.*[7] showed that for Rb Eq. (1) is valid only below 0.4 K. The observed anomaly could be explained by the dispersion of the slow shear acoustic mode. They based their calculation on a lattice-dynamics model that fit the phonon spectrum determined from inelastic neutron scattering. They carried out similar calculations for potassium and found that Eq. (1) should be valid below 3 K. Since a CDW heat-capacity anomaly in potassium is estimated to appear between 0.5 and 2 K, its appearance would be less ambiguous. Prior measurements[8,9] in this temperature range gave signs of experimental difficulty.

We have considered carefully the different sources of error in the specific heat, and these will be discussed elsewhere in more detail.[10] The temperature scale, and also the agreement of the thermometer calibration with the accepted scale, are extremely important. For example, just the change from the $T_{62}$ to the $T_{76}$ scale re-