Dynamical scaling for spinodal decomposition - a small-angle neutron scattering study of porous Vycor glass with fractal properties

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Abstract. A model is developed for analysing small-angle scattering data for systems undergoing spinodal decomposition. This model is expressed as an integration of a series of Fourier components of the density fluctuation $A(\beta) \sin(\beta r + \varphi)$ based on Cahn's linear theory of spinodal decomposition. Hence the time evolution of the characteristic crossover phenomenon and the width of the crossover of the scaling function of the structure factor are predicted to be associated with the maximum spinodal wavenumber β_m and the correlation length ξ_m, respectively. The rough surfaces and fractal network of porous materials are also considered in the model. Results of calculations based on this model are compared with small-angle neutron scattering data for dry and wet porous Vycor glass and give an excellent agreement.

1. Introduction

Small-angle scattering (SAS) of neutrons and x-rays have been widely used to study the kinetics of phase separation (nucleation and spinodal decomposition) of quenched binary alloys [1], glasses [2] and liquid mixtures [3]. The determination of the properties of such materials is of great importance from both theoretical and experimental points of view. The process of spinodal decomposition has been relatively well studied in the past. The existence of dynamical scaling, i.e. a structure factor $S(Q, t)$ for the spinodal decomposition of binary mixtures has been proposed by several authors, based on phenomenological and statistical models [4–6] as well as on detailed computer simulations [7, 8]. However, a satisfactory model of a scaling structure factor that could fit both early and late stages of the time evolution of the structure function is still not available. A fairly successful approximation was developed by Langer et al [9] and this has been extended by Kawasaki and Ohta [10], Binder et al [11], Billotet and Binder [12] and Horner and Jungling [13]; this theory yields a prediction for $S(Q, t)$ in fair agreement with the computer simulations during the early stages, at least for quenches at the critical concentration. A simple relationship for the later stages of decomposition has been proposed more or less independently by a number of authors [3, 14]: the structure function $S(Q, t)$ for an isotopic three-dimensional system obeys the scaling relationship $S(Q, t) \propto K^{-3}(t) F[Q/K(t)]$, where $K(t)$ is some characteristic time-dependent length. However, a quantitative theory for predicting both $K(t)$ and $F[Q/K(t)]$ is still not available. There have been several attempts to predict $F[Q/K(t)]$. The first theoretical prediction that the structure function should scale was made by Binder and Stauffer [4]. Their work primarily dealt with predicting the growth rate of clusters in terms of the cluster-reaction model. There are only two adjustable parameters in this model, and hence it seems likely that this scaling theory is too simplified to be

accurate. Wiltzius *et al* [15] used a very similar model to fit $S(Q)$ for porous Vycor glass. The results are rather unsatisfactory; however, recently Hohr *et al* [16] suggested a liquid-like hard-sphere model for porous Vycor glass as used in scattering from microemulsions [17], except that the spheres are replaced by clusters with a fractal surface. The resulting scattering curve has a sharp peak at 0.025 Å^{-1} together with a series of oscillations on the high-Q side that were not observed in experimental data. There are several other models in the literature [18–20], but they also have their drawbacks. In the present paper, we represent a new approach based on Cahn's linear theory for spinodal decomposition [21], where both the fractal rough surface and fractal pore network of the porous media are also taken into account. The small-angle neutron scattering (SANS) data from porous Vycor glass, which is produced by spinodal decomposition following which one component, B_2O_3, is leached out using acid, have been well fitted using this model. For the first time, this model gives an analytical formula for the scattering function $F[Q/K(t)]$ which can be applied to a variety of other systems undergoing spinodal decomposition.

2. Theory

For an inhomogeneous system consisting of two separated macroscopic domains that can be distinguished by different nuclear species, the scattering intensity per unit volume from the sample is given by

$$I(Q) = V^{-1} \left\langle \sum_{n}^{N} \sum_{m}^{N} b_n b_m \exp[iQ \cdot (r_n - r_m)] \right\rangle \tag{1}$$

where N is the total number of atoms in the system, V is the volume of the sample. Q is defined by $Q = k_0 - k_1$, where k_0 and k_1 are the incident and scattered wave vectors of the radiation, and r_n and r_m are the position vectors of the nth and mth atoms, respectively. When the masses of the molecules in the sample are significantly greater than the mass of a neutron, the energy transfer between the nucleus and neutron is negligibly small, hence $k_0 = k_1 = 2\pi/\lambda$ and $Q = 4\pi \sin\theta/\lambda$; λ is the neutron wavelength, θ is the half scattering angle and V is the volume of the sample. Because small-angle scattering detects large-scale compositional or density fluctuations, it is more convenient to consider each domain (cluster) as a scattering centre. The position vector of the nth nucleus in the ith cluster can be represented by a sum of $R_i + r_{in}$, where R_i is the position vector of the centre of mass of the ith cluster and r_{in} is the relative position vector of the atom n in the cluster. Thus the intensity can be expressed as

$$I(Q) = V^{-1} \left\langle \sum_{i} \sum_{j} \exp[iQ \cdot (R_i - R_j)] \sum_{n} \sum_{m} b_{in} b_{jm} \exp[iQ \cdot (r_{in} - r_{jm})] \right\rangle. \tag{2}$$

We can define the form factor as

$$F_i(Q) = \sum_{n} b_{in} \exp[iQ \cdot r_{in}] \tag{3}$$

or alternatively as

$$F_i(Q) = \int \int \rho_i(r_i) \exp[iQ \cdot r_i] \, dV_i \tag{4}$$

where $\rho_i(r_i) = \sum_n b_{in}\delta(r - r_{in})/V_i$ is defined as the scattering length density of the ith cluster centred on R_i and V_i is the volume of the cluster. If we wish to describe the scattering from clusters in a uniform density ρ_0 background, it is convenient to modify equation (4) by subtracting ρ_0 everywhere as a constant-density component that only contributes to $I_{coh}(Q)$ in the forward direction ($Q = 0$), i.e.

$$F_i(Q) = \int \int [\rho_i(r_i) - \rho_0] \exp[iQ \cdot r_i] \, dV_i \qquad Q \neq 0. \tag{5}$$

If the system has identical spherical particles, the form factors are the same, and hence the coherent scattering intensity can be written in the familiar form

$$I_{coh}(Q) = (N/V)F^2(Q)S(Q) \tag{6}$$

where N is the total number of clusters and $F(Q)$ is obtained from the spherical particles. The structure factor $S(Q)$ is

$$S(Q) = N^{-1} \left\langle \sum_i \sum_j \exp[iQ \cdot (R_i - R_j)] \right\rangle. \tag{7}$$

For a polydisperse system the coherent scattering intensity takes a more complicated form

$$I(Q) = V^{-1} \sum_i^N \sum_j^N F_i(Q)F_j^*(Q) \exp[iQ \cdot (R_i - R_j)]. \tag{8}$$

Because F_i varies from cluster to cluster for such a system, this summation is difficult to evaluate. However, we can average the form factors by introducing a function [22]

$$b(Q, R) = \int_0^\infty \int_0^\infty F_i p_1(F_i, Q)(p_1(F_i, Q) - p_2(F_i, F_j, R, Q))F_j \, dF_i \, dF_j \tag{9}$$

where p_1 is a probability density function of the form factor F_i between the values of F_i and $F_i + dF_i$, while p_2 is a similar function concerning ensembles of factors F_i and F_j, where F_i and F_j are functions of Q. When $r \to \infty$, $b(Q, R) \to 0$ so that equation (7) can be rewritten [22]

$$I(Q) = \frac{N}{V} \left(\langle F^2(Q) \rangle + \langle F(Q) \rangle^2 \int_0^\infty 4\pi r^2 [g(r) - 1] \frac{\sin Qr}{Qr} \, dr - \int_0^\infty g(r)b(Q, r) \frac{\sin Qr}{Qr} \, dr \right) \tag{10}$$

where

$$\langle F(Q) \rangle = \int_0^\infty F_i(Q)p_i[F_i(Q)] \, dF_i(Q)$$

$$\langle F^2(Q) \rangle = \int_0^\infty F_i(Q)F_i^*(Q)p_i[F_i(Q)] \, dF_i(Q). \tag{11}$$

The first term in equation (10) is the contribution from individual clusters, the second term is related to the density fluctuation in the system and is model dependent, and the third term is a correction term associated with the size distribution of the clusters and the correlation between clusters as a function of r. We will discuss these terms individually as follows.

2.1. The first term—scattering from separated particles

The general expression for the first term of equation (10) is

$$I_1(Q) = (N/V)\langle F^2(Q)\rangle = \frac{N}{V} \sum_i^\nu p_i[F_i(Q)]F_i^2(Q) \qquad (12)$$

which means that the total scattering is simply the sum of the scattering intensities for each different type of cluster weighted by its respective probability distribution, $p_i[F_i(Q)]$. For smooth surface clusters, the Porod approximation [22] is valid for all the individual clusters, particularly the largest. Therefore, the principal part of the curve of $F_i^2(Q)$ at large Q (i.e. $Q > 1/a$, a being the radius of the cluster) is given by the function [22] $2\pi(\rho_i - \rho_s)^2 S_i/Q^4$, where S_i is the surface area of the ith cluster. When $Q = 0$, $F_i^2(0) = V^2(\rho_i - \rho_s)^2$. Hence, equation (12) can be written as

$$I_1(Q) \propto \sum_i^\nu p_i(\rho_i - \rho_s)^2 \begin{cases} V^2 & Q = 0 \\ 2\pi S_i/Q^4 & Q > 1/a. \end{cases} \qquad (13)$$

The scattering from the rough surface of the clusters can be considered as many self-similar small islands on a two-dimensional surface (a two-dimensional fractal). Therefore the density correlation function $g(r) \propto r^{D-2}$, where $2 \leqslant D \leqslant 3$. Hence, the scattering intensity is proportional to $S_i Q^{-(1+D)}$, where this term is also valid at $D > 1/a$, because the surface area is limited by the radius of clusters. Equation (12) can be rewritten for large Q as

$$I_1(Q) = \sum_i 2\pi p_i(\rho_i - \rho_s)^2 S_i Q^{-(1+D)}. \qquad (14)$$

2.2. The second term—spinodal decomposition

Consider an inhomogeneous solution whose composition changes around an average composition c_0. The free-energy difference between the initially homogeneous solution and the inhomogeneous solution can be written

$$\Delta G = \int \left[\frac{\partial^2 f}{2\partial c^2} [c(r) - c_0]^2 + \kappa \{\nabla c(r)\}^2 \right] dr \qquad (15)$$

where f is the free-energy and κ is the gradient of the energy coefficient. If $\partial^2 f/\partial c^2 > 0$, the solution is stable to all infinitesimal fluctuations. On the other hand, if $\partial^2 f/\partial c^2 < 0$, the solution is in an unstable state, in which case spinodal decomposition occurs. The mathematical theory of spinodal decomposition, originally proposed by Hillert [23] and developed by Cahn and Hilliard [24] is based on a general diffusion equation containing terms in the gradient of the concentration. The solution of the equation has been given by Cahn in a linear form by means of a series of Fourier expansions of the concentration fluctuations, the ith component sinusoidal having a fixed wavenumber β_i, but with random directions and phase constant $\varphi(\beta_i)$, being of the form

$$c_i(r, t) - c_{0i} = A(\beta_i, t) \exp[\beta_i \cdot r + \varphi(\beta_i)] \qquad (16)$$

where

$$A(\beta_i, t) = A_0(\beta_i) \exp[w(\beta_i)t].$$

Summing over all possible solutions gives

$$c(r, t) - c_0 = \int A(\beta, t) \exp[\beta \cdot r + \varphi(\beta)] \, \mathrm{d}\beta. \tag{17}$$

The value of $A_0(\beta)$ is a slow function of β at $t = 0$ given by

$$A_0(\beta) = \exp[-w(\beta)t] \int [c(r, t) - c_0] \exp(i\beta \cdot r) \, \mathrm{d}r \tag{18}$$

where the $w(\beta)$ is an amplification factor determining the rate of growth or decay of the Fourier component and depending on the physical characteristics of the system, such as atomic mobility, energy gradient terms and external influences. $w(\beta)$ is positive only in the spinodal region. Cahn has shown that as the decomposition proceeds, in order to satisfy the generalized diffusion equation,

$$\partial c / \partial t = M(\partial f^2 / \partial c^2)\nabla^2 c - 2M\kappa \, \nabla^4 c \tag{19}$$

where M is an atomic mobility ($M > 0$). The solution to this equation gives

$$w(\beta) = -M[\partial^2 f(c) / \partial c^2]\beta^2 - 2M\kappa\beta^4 \qquad 0 < \beta < \beta_c \tag{20}$$

where β_c is the maximum wavenumber. The amplification factor $w(\beta)$ is positive in the spinodal region (see figure 1). Therefore, the maximum wavenumber β_c is given by

$$\beta_c^2 = -[\partial^2 f(c) / \partial c^2] / 2\kappa. \tag{21}$$
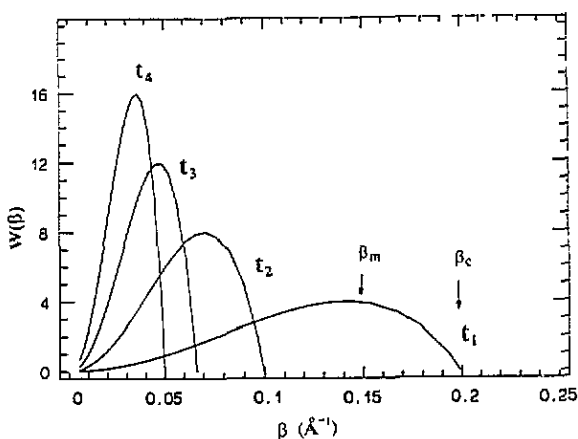

Figure 1. Diagram to illustrate schematically the behaviour of the amplification function $w(\beta, t)$ as predicted by Cahn's linear theory (the function $w(\beta, t)$ is normalized to unity). β_c is the maximum wavenumber and $\beta_m = \beta_c / \sqrt{2}$.

The spinodal wavenumber having maximum amplification in the system can be obtained from equation (20) as $\beta_m = \beta_c/\sqrt{2}$. Because the free energy $f(c)$ is a function of time t, β_c also changes with time as illustrated in figure 1. Therefore, the pair correlation function $G(r, t)$ can be written as

$$G(r, t) = N^{-1} \int [c(r', t) - c_0][c^*(r' - r, t) - c_0]\, dr' \tag{22}$$

$$= \sum_i \sum_j N^{-1} A(\beta_i, t) A^*(\beta_j, t) \int \exp[i(\beta_i - \beta_j) \cdot r' + \beta_j \cdot r + \varphi(\beta_i) - \varphi(\beta_j)]\, dr'.$$

As one knows that

$$\int \exp[i(\beta_i - \beta_j) \cdot r']\, dr' = (2\pi)^3 \delta(\beta_i - \beta_j) \tag{23}$$

all cross terms (i.e. $i \neq j$) are zero, which means that there is no interference between different sinusoidal wavevectors of the density fluctuation, and all the phase terms φ are cancelled. The pair correlation function can thus be expressed as the sum of all Fourier components of the density fluctuations, each component being weighted by the amplification factor $A^2(\beta, t)$, i.e.

$$G(r, t) = \sum_i 2\pi N^{-1} A^2(\beta_i, t) \exp(i\beta_i \cdot r). \tag{24}$$

Consider a system that is homogeneous on a large scale where the averaging over all possible directions of β_i gives

$$\langle \exp(i\beta_i \cdot r) \rangle = \sin(\beta_i r)/\beta_i r \tag{25}$$

and hence equation (24) can be written as

$$G(r, t) = \sum_i 2\pi N^{-1} A^2(\beta_i, t) \frac{\sin(\beta_i r)}{\beta_i r}. \tag{26}$$

In a real system, the long-wavelength fluctuations must break down at large scale as in other systems [25]. We therefore introduce an exponentially decaying term that has a correlation length ξ. The pair correlation function can now be written as

$$G'(r, t) = G(r, t) \exp(-r/\xi) = \sum_i 2\pi A^2(\beta_i, t) \sin(\beta_i r)(N\beta_i r)^{-1} \exp(-r/\xi). \tag{27}$$

Hence the total structure factor can be written as [26]

$$S(Q, t) = \int 4\pi r\, G'(r, t) \frac{\sin Qr}{Qr}\, dr$$

$$= \sum_i 8\pi^2 N^{-1} A^2(\beta_i, t) \int \frac{\sin Qr}{Q\beta_i} [\sin(\beta_i r) \exp(-r/\xi)]\, dr. \tag{28}$$

Since $\sin(Qr)\sin(\beta r)$ can be written as $[\cos(Q - \beta)r - \cos(Q + \beta)r]/2$, Fourier transformation of the function $\sin(\beta_i r) \exp(-r/\xi)$ gives $S(Q, t)$ in the following form:

$$S(Q, t) = \sum_i 4\pi^2 A(\beta_i, t)^2 (NQ\beta_i)^{-1} \left\{ \frac{\xi}{[1 + (Q - \beta_i)^2 \xi^2]} - \frac{\xi}{[1 + (Q + \beta_i)^2 \xi^2]} \right\}. \tag{29}$$

As can be seen, the total structure factor is a summation over a set of multi-Lorentzian terms and each term (or each Fourier component of β_i) satisfies the scaling relationship as discussed in the introduction.

$$S_i(Q, t) \propto \exp[2W(\beta_i, t)t]\xi^3 s[(Q/\beta_i), \beta_i\xi] \tag{30}$$

where $s(x, \alpha) = [1 + (x - 1)^2\alpha^2]^{-1}[1 + (x + 1)^2\alpha^2]$, which has a maximum when $\alpha = \beta_i\xi$ and $x = (Q/\beta_i)$. Finally, as an alternative, we can write an integrated form of equation (29) as

$$S(Q, t) \propto \int_0^{\beta_c} A^2(\beta, t)(Q\beta)^{-1} \left\{ \frac{\xi}{[1 + (Q - \beta)^2\xi^2]} - \frac{\xi}{[1 + (Q + \beta)^2\xi^2]} \right\} d\beta. \tag{31}$$

Thus the total coherent scattering intensity from the second term in equation (10) can be written as

$$I_2(Q, t) \propto \langle F(Q)\rangle^2 \int_0^{\beta_c} A^2(\beta, t)(Q\beta)^{-1} \left\{ \frac{\xi}{[1 + (Q - \beta)^2\xi^2]} - \frac{\xi}{[1 + (Q + \beta)^2\xi^2]} \right\} d\beta. \tag{32}$$

Here $\langle F(Q)\rangle^2 \neq P(Q)(= \langle F^2(Q)\rangle)$. They are equal when the system consists of a single particle size. For porous Vycor glass, the pores are produced by the spinodal decomposition process. Evidence suggests that the B_3O_2 cluster distribution is rather monodispersed. Therefore, we could ignore the variation of $F_i(Q)$ (i.e. the deviation of $\langle F(Q)\rangle^2$ from $\langle F^2(Q)\rangle$). Hence, $\langle F(Q)\rangle^2 = P(Q)$.

As can be seen, the integration of equation (32) is not possible, because the amplification factor $A(\beta, t) \propto \exp[w(\beta)t]$ has a complex exponential form. However, in the later stages (i.e. large t) of spinodal decomposition, the amplitudes of the sinusoidal waves have been weighted by $A(\beta, t)$ in a very narrow region centred around β_m. When $t \to \infty$, $A(\beta, t)$ becomes a delta function $\delta(\beta - \beta_m)$. Hence the component with wavenumber β_m dominates the scattering. Hence equation (32) can be simplified as

$$I_2(Q, \infty) \propto P(Q)(Q\beta)^{-1}\{\xi/[1 + (Q - \beta_m)^2\xi^2] - \xi/[1 + (Q + \beta_m)^2\xi^2]\}. \tag{33}$$

Figure 2 shows $S(Q, t)$ at a series of quenching times t, assuming that β_m increases as $t^{-1/6}$, as given by Binder and Stauffer [4]. The results are qualitatively similar to Monte Carlo simulations [7, 8] and experimental studies [1, 2]. Quantitative testing of this model would need to be carried out for a system undergoing spinodal decomposition to fit a series of data sets at different quenching times, especially in the early stages.

2.3. The third term—scattering from disordered systems—fractal geometry

Since the fractal concept was introduced by Mandelbrot [27], it has been successfully used to describe a wide range of disordered systems and irregular structures, such as branched polymers, percolation clusters, silica gel, colloid aggregates, cements and the rough surfaces of porous media. Porous Vycor glass (Corning 7930) has been proposed as a volume fractal with dimension 1.7 ± 0.12 on an inter-pore scale by Even *et al* [28] based on EET (electronic energy transfer) measurements. Recently, our SANS measurements have shown very clearly an extra scattering component in the very-low-Q region from the porous Vycor glass but only when the pores are partially saturated with water during desorption processes [29].
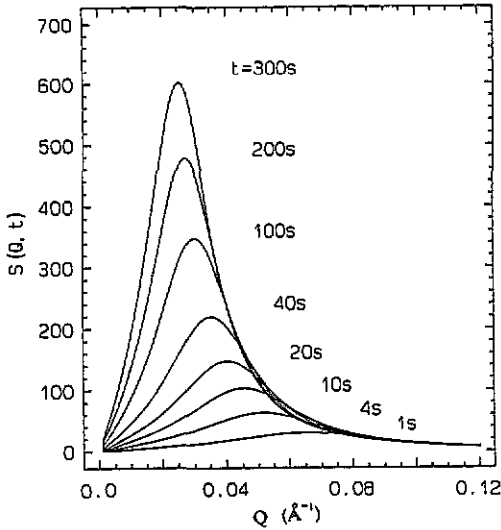
Figure 2. The dynamic scaling of the quenching process during spinodal decomposition. The function $S(Q, t)$ is calculated using equation (38) at various scaled times t.
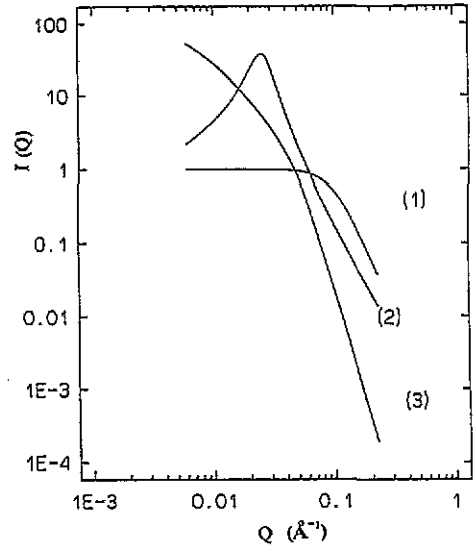
Figure 3. Typical scattering intensities from equation (36). (1) $I_1(Q)$ is the scattering intensity from all individual clusters; (2) $I_2(Q)$ is the scattering from the density fluctuation of spinodal decomposition; (3) $I_3(Q)$ is the intensity from a network of empty pores.

This component has a fractal dimensions in the range from 1.65 to 1.75. We believe that this feature can only be seen when the pores are being emptied by reducing the partial water vapour pressure, the effect being at its maximum when the remaining pores are filled with an H_2O/D_2O water mixture chosen to have a scattering length density to match the silica matrix. Here the distribution of empty pores, a percolating system, has its own correlation length. This extra scattering component can be described by the third term in equation (10), e.g.

$$I_3(Q) \propto \int g(r)b(Q,r)\frac{\sin Qr}{Qr}\, dr \simeq \langle F(Q)\rangle^2 c(1-c)\int G''(r)\frac{\sin Qr}{Qr}\, dr \tag{34}$$

where c is the fraction of the total number of empty pores and the function $G''(r)$ is frequently given as $(1 - Cr^{3-D})\exp(-r/\xi')$ [25]. The correlation length here is written as ξ' in order to distinguish it from the correlation length ξ of the spinodal decomposition. Fourier transformation of $G''(r)$ gives the third component of the scattering intensity

$$I_3(Q) \simeq P(Q)\{-\xi'^3/[1 + Q^2\xi'^2]^2$$
$$+ C\Gamma(5 - D)\xi'^{(5-D)}\sin[(5 - D)\tan^{-1}(Q\xi')]/Q[1 + Q^2\xi'^2]^{(5-D)/2}\}. \tag{35}$$

2.4. Summary

The total coherent scattering intensity can now be written as

$$I_{coh}(Q, t) \propto I_1(Q) + I_2(Q, t) + I_3(Q). \tag{36}$$

For a system undergoing spinodal decomposition, $I_3(Q)$ is zero, because $c(1 - c) = 0$. For the late stages of spinodal decomposition, the very narrow range of Fourier components around β_m has been well developed, as shown in figure 1. This also has been illustrated by Dozier *et al* [30] for Vycor using a 500-point nitrogen desorption technique, which shows the pore size distribution to be rather monodisperse. Therefore we can assume that $A(\beta)$ is a delta function, $\delta(\beta - \beta_m)$, so that the intensity is of the form

$$I_{coh}(Q, t) \propto P(Q, \beta_m) S_m(Q, t) \tag{37}$$

where

$$S_m(Q, t) \propto \{\xi/[1 + (Q - \beta_m)^2 \xi^2] - \xi/[1 + (Q + \beta_m)^2 \xi^2]\}(Q\beta_m)^{-1}. \tag{38}$$

When all spinodal wavenumbers are zero, $I_2(Q) = 0$, and equation (36) is reduced to the form of a normal fractal system given by

$$I_{coh}(Q) \propto \Gamma(5 - D)\xi'^{(5-D)} \sin[(5 - D)\tan^{-1}(Q\xi')]/Q[1 + Q^2\xi'^2]^{(5-D)/2} + I_1(Q). \tag{39}$$

This is similar to the equation used by Bale and Schmidt [31]. Figure 3 shows the three terms in equation (36). Curve (1) is the contribution from $I_1(Q)$, i.e. from the individual empty pores. Curve (2) is the 'structure factor' for the correlation function of pores, which originates from the spinodal decomposition process, and its intensity increases in proportion to the square of the fraction of emptied pores. Curve (3) describes the extra scattering that appears when pores are partially filled by water. Its intensity increases and then decreases because its amplitude is weighted by $c(1 - c)$.

3. Discussion

It is not our purpose, in this paper, to discuss the dynamic properties of the wavevector β (i.e. how these parameters vary with time, t) and the validity of the linear solution of Cahn's theory. Calculations of the dynamic structure factor $S(Q, t)$ using equation (36) require a model for the distribution function $w(\beta)$ which is associated with $\partial^2 f(c)/\partial c^2$, κ and M of the system. Cahn [21] states that κ varies slowly with varying temperature and composition. For the later stages of spinodal decomposition, a single wavevector β_m should give a good approximation for $S(Q, t)$, because the amplification factor $A(\beta, t)$ is close to a delta function $\delta(\beta - \beta_m)$. By fitting with this model, a number of parameters can be obtained from equation (38) that are all of obvious physical significance—for example the parameter β_m is associated with the positon of the peak in $S(Q, t)$, the correlation length ξ determined by the width at half height, and has a similar physical significance to the correlation length in liquid systems. If ξ increases linearly with λ_m (where $\lambda_m = 2\pi/\beta_m$), all curves at different quenching times could be overlapped by changing scales. In the more general case, the correlation length ξ is a function of λ_m, i.e. $\xi = n(t)\lambda_m$.

In figure 4, we demonstrate an example of the fitting process using this model for porous Vycor. The principal features of typical SANS data from dry Vycor in figure 4 are obtained using the D17 diffractometer at the ILL and LOQ at ISIS [32]. In order to fit this data, only the first two terms $I_1(Q)$ and $I_2(Q)$ in equation (36) need to be considered, because $c = 1$, so $I_3(Q) = 0$. The data for the dry sample fitted using this model gives $\beta_m = 0.0251$ Å^{-1} which corresponds to the density fluctuation wavelength $\lambda_m = 250$ Å, $\xi = 1020$ Å. It will be noted that the second term in $I(Q)$ produces an asymmetry in the peak very close to
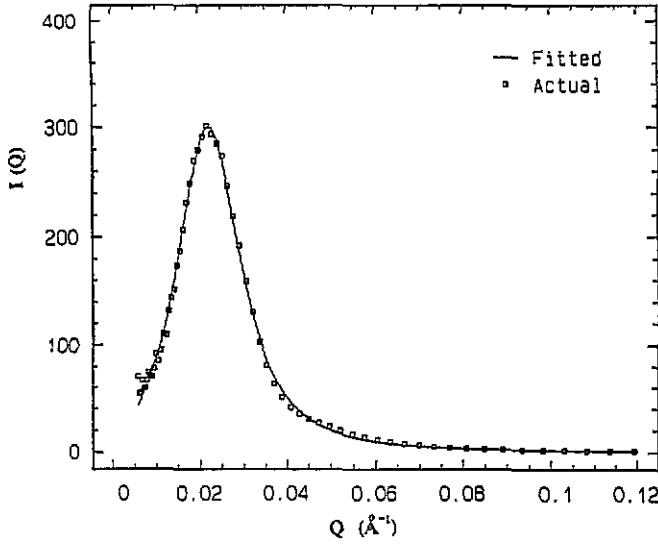
Figure 4. SANS intensity versus Q for dry solid porous Vycor (Corning 7930) with curve fitted using the model.
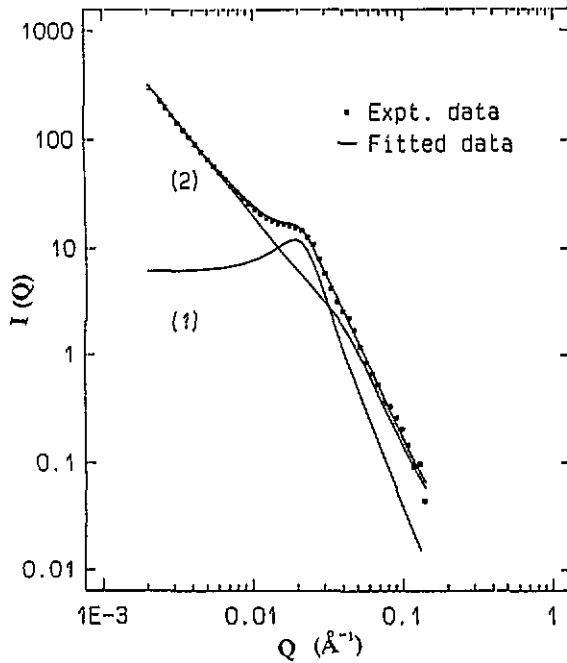

Figure 5. A log–log plot of $I(Q)$ versus Q for Vycor containing a water mixture with ratio of H_2O/D_2O 36:64 at a relative humidity of 70% during the desorption process. Smooth curves are fitted using the model; (1) is $I_1(Q) + I_2(Q)$ and (2) is $I_3(Q)$.

the observed data and that the fit is better than could be achieved with any previous models [15–17].

An interesting phenomenon occurs when porous Vycor is partially saturated with a matched D_2O/H_2O water mixture in a ratio of 64:36, which has been chosen to have the same scattering density as the Vycor matrix. A new scattering component appears in the very-low-Q region (see figure 5). This very-low-Q scattering component has a fractal-like power-law form, which results from the percolation network formed by the pores as they empty. This is the first diffraction evidence for the inter-pore scale 'percolation network' with fractal geometry as predicted by percolation theory [33, 34]; for full details, see [35]. Using this model, we can fit this extra component with the third term $I_3(Q)$. Figure 5 illustrates the fitting of the measured scattering intensity $I(Q)$ for the sample at 70% RH (relative humidity). As one can see, the fitted profiles (smoothed curves in figure 5) agree well with the experimental data. The fractal component covers a range of Q from $= 0.001$ to 0.05 Å^{-1}. This suggests that the empty pores are connected in a manner reminiscent of silica aerogels [36] or branching polymers, both of which systems show fractal geometry. The correlation length ξ' for the percolation clusters cannot be defined in the present experiment simply because of the limitation of the Q range. From the lowest Q data measured, the conclusion we draw is that the correlation length is larger than 1000 Å for higher-humidity samples, a distance equivalent to about five times the average pore separation distance.

In summary, the theory derives a dynamic structure factor $S(Q, t)$ based on Cahn's linear theory for a system showing phase separation in the unstable region in the early stages. Because the initial stages of phase separation are symmetric about c_0, the density fluctuation can be described as a series of superimposed sine waves with different wavelengths. As the phase separation continues, higher-order terms in the diffusion equation [37] will distort the solution and sharp interfaces may appear. We propose that the first term in equation (36) could describe these sharp interfaces, and even the rough surfaces in later stages of spinodal decomposition. Meanwhile any deviation during the desorption or adsorption processes can be described by the third term in equation (36) as a correction factor.

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