fringence as observed. This anisotropy could be due to the orientation of ester groups similar to the alignment of phenyl groups suggested to account for the positive photoelastic effect in polystyrene[10].

However, since the ester groups contribute much of the X-ray scattering from PMMA, changes in their orientation should have a quite visible effect on the scattering pattern[11]. In fact, undeformed and elastically deformed specimens give very similar patterns in the higher-angle region that comes from scattering within the chains.

Hence we conclude that the negative photoelasticity in PMMA is due to the 'local-field effect' but the theory needs to include the influence of correlation of segmental orientation before it can predict the observed values precisely.

Stein and Hong[12] have incorporated a similar modification into the theory of the stress optical coefficient of rubbers.

Further support for the local-field theory comes from LeGrand's findings[13] (which we have confirmed) that the strain optical coefficient of PMMA is almost independent of temperature over the range 20–70°C. The theory predicts that the birefringence at constant elastic strain should decrease slowly with increasing temperature, due to the lowering of refractive index caused by thermal expansion.

In the elastic strain region, the local-field effect does, of course, give a negative component of birefringence for all materials. For polymers, this term will only dominate for materials such as glassy PMMA where orientation of units

with highly anisotropic polarizibility does not occur during elastic deformation.

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Graph-like state of matter: 13. A caution on critical exponents

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There are two main different approaches to the modelling of the free energy ΔG of mixing a polymer solution: (a) the classical mean field approximation theories (for a review see Koningsveld[1]) and (b) the modern theories[2] based on continuum approximations to the singularities featured in the lattice-graph models of the Ising-type.

The latter (especially renormalisation group and SCF) theories seek to relate the subtleties of critical phenomena to analytic singularities of asymptotic continuum models, through critical exponents. According to scaling arguments, these exponents are interrelated by a hypothesis of universality[3] which should embrace phase equilibria in polymer solutions. The 'phenomenological' mean-field theories are content to operate within the framework of Gibbs, Maxwell and van der Waals now recognised as the essential lowest level of description. At this level the ΔG function extends through the metastable domain to spinodal loci. No analytical singularity is postulated at spinodal or even specifically at critical points, and accordingly suitable Taylor series are available if necessary.

Thus consider the following generalisation of the (mean-field) Flory-Huggins theory for a monodisperse solution in the usual notation (with $\Phi_o = 1 - \Phi$ = volume fraction of solvent):

$$\frac{\Delta G}{RT} = \Phi_o \ln\Phi_o + \Phi m^{-1}\ln\Phi + \Phi_o\Phi\,\frac{(\beta_o + \beta_1/T)}{(1 - \gamma\Phi)}; m = M/c$$

(1)

It has the advantage that all parameters ($\beta_o, \beta_1, \gamma, c = 117.76$) have a molecular interpretation[4]. The derived analytical spinodal curves ($T = T(\Phi)$ for $J \equiv \partial(\Delta G/RT)/\partial\Phi = 0$), fit extensive data on polystyrene/cyclohexane (PS/CH) only moderately. The data include 70 spinodal points for 11 PS samples in the range of molecular weight $5.1 \times 10^4 \leqslant M \leqslant 2.6 \times 10^6$, with the standard deviation $\sigma = 4.7 \times 10^{-3}$ of J from zero. For the historic theory ($\gamma = 0$) the misfit is severe ($\sigma = 2.2 \times 10^{-2}$), and attributed to the location of the critical and measurable spinodal points in the region of concentration $\Phi^* \simeq \lambda^{-1}$. In this region, the coils of volume $\lambda_0 m^{3/2} \equiv \lambda m$ ($\lambda_0 \approx 0.57$ for[5] PS/CH and m is the chain length taking solvent = 1), if prevented from overlapping, would just fill the solution volume. Flory[6] warned that the Flory–Huggins theory would break down there because the segment density becomes non-uniform (statistically heterogeneous). Accordingly, Koningsveld *et al.*[5] in their 'bridging theory' tried to span this concentration range by modelling the solution roughly as a pseudo two-phase

system, with different partition functions assigned to the dilute and concentrated phases. Poisson statistics were used to estimate the concentration of *segments* in non-overlapping domains. We simplify this treatment by using the same Poisson statistics to estimate the fraction of non-overlapping *chains*.

The reason is that we now have a conformational partition $Z(T)$ function for such an isolated chain[8]:

$$Z(T)/Z(T_\Theta) = z(z - 1)^{m-2}\exp(-m\bar{\beta} + \text{const. } m\ln m\bar{\beta}^2)$$

(2)

z being the co-ordination number of the lattice graph. Here $\bar{\beta}$ is the contact potential divided by RT, satisfactorily calibrated[8] by light scattering experiments of the expansion ratio at various T. This models a freely self-intersecting random-walk chain. The same equation, within the present approximation ($\bar{\beta}2 \sim 0$), is approached by the Flory—Huggins model as $\phi \to 0$:

$$Z(T)/Z(T_\Theta) = z(z - 1)^{m-2}\exp(-m.\text{const.}(\frac{1}{2} - \chi_1)) \quad (3)$$

In the absence of scattering data for $T < T_\Theta$, we merely equate $\bar{\beta}$ to const. $(1/2 - \chi_1)$, the contact potential ascribed by the Flory—Huggins theory. By virtue of the equivalence of equations (2) and (3), the only correction now required for statistical inhomogeneity in our Flory—Huggins-based model, which implements the two-phase approximation, is in the translational part of the partition function Z_{dil} of the fraction, P say, of isolated chains. We imagine the centre of an isolated chain to be constrained within a 'box' of volume equal to that of the coil. The Z_{dil} is reduced by a factor e per chain. (The reasoning resumbles that for the communal entropy factor e in classical cell theories[9] for the liquid state, as we will explain elsewhere). This greatly simplified bridging theory improves the fit of the above 70 spinodal points to $\sigma = 6.4 \times 10^{-4}$. If the factor e is replaced by a floating parameter K, optimisation yields $K = (e)^{0.96}$ with the negligible improvement $\sigma = 6.35 \times 10^{-4}$ to the fit, which supports the validity of the approach. So does the fact that, for this improved bridging theory, the 40-year-old second nearest neighbour correction of Huggins, dealing with longer-range correlations in the segment distribution, becomes very worthwhile for the first time, reducing σ further to 4.0×10^{-4}.

Accordingly, the additional terms added to $\Delta G/RT$ in (1) are (a) for the translational correction.

$$\Phi_0\Phi m^{-1}P \equiv \Phi_0\Phi m^{-1}\exp(-\lambda_0 m^{1/2}\Phi) \quad (4)$$

where $\lambda_0 \approx 0.57$ for PS/CH; and (b) for the Huggins correction[10], one finds

$$\frac{1}{\gamma}\left\{(1 - \gamma)\Phi\ln(1 - \gamma\Phi) - (1 - \gamma\Phi)\ln(1 - \gamma\Phi)\right\} \quad (5)$$

The resulting spinodal curve is obtained in closed form, analytic in Φ (for $0 < \gamma < 1$):

$$T = \beta_1 \Big/ \left\{\frac{(1 - \gamma\Phi)^3}{2(1 - \gamma)}\left[\Phi_0^{-1} + (\Phi m)^{-1} + m^{-1}P(\Phi_0\Phi\lambda^2\right.\right.$$
$$\left.\left. - 2 - 2\lambda\ (1 - 2\Phi)) - \frac{\gamma}{(1 - \gamma\Phi)}\right] - \beta_0\right\} \quad (6)$$

It is fitted to typical light scattering and (thermally stepped) PICS measurements in *Figure 1* for molecular weights between 5.1×10^4 and 2.61×10^6.

Parallel displacements of the calculated curves shown, which move their maxima slightly towards the Θ-point ($T_\theta = 306.2°K$, $\Phi = 0$), to optimize the fit further, are admissible because of the uncertainties in the molecular weight calibrations. The fits of almost all points shown are then better than 0.2K over the 18° range covered. As will be shown elsewhere, polydispersity effects, including the observed pattern of mutual intersection[7] of pairs of spinodal curves for samples of identical M_w but differing in M_z, are well modelled by the present bridging theory with appropriate minor generalization.

Discussion

Since from thermodynamics $(\partial T/\partial\Phi) = 0$ for the spinodal locus at the critical point, we have its Taylor expansion:

$$\frac{T_C - T}{T_C} = a_2(\Phi - \Phi_C)^2 + a_3(\Phi - \Phi_C)^3 \ldots \quad (7)$$

or inverting

$$\delta\Phi \equiv \Phi - \Phi_C = \frac{1}{a_2^{1/2}}\left(\frac{T_C - T}{T_C}\right)^{1/2} - \frac{a_3}{2a_2}\left(\frac{T_C - T}{T_C}\right)^{1/3}$$

$$\equiv (\epsilon/a_2)^{1/2} - a_3\,\epsilon/2a_2 \ldots \quad (8)$$

Thus if $\delta\Phi \sim \epsilon^\beta$, the critical exponent $\beta = 1/2$ for *any* spinodal function analytic at T_c (which is well known).

We compare the *spinodal* locus for $M = 1.56 \times 10^6$ (plot B) or 2.5×10^6 (plot A) with *binodal* measurements of Nakata *et al.*[20] (plot N). Binodals are easier to measure but hard to compute from a free energy function such as equations 1, 4 and 5 in the vincity of the critical point. In mean field theory, the binodal should asymptotically approach the corresponding spinodal curve at minus infinity. This prediction is plausibly supported by *Figure 2*. It is not safe to seek any counter-indication in the pattern of the last few points at X.

The line A' (*Figure 2*) displays the true limiting slope $\beta = 1/2$, which the theory approaches closely only in the region $\epsilon < 10^{-7}$ or so and, therefore, probably inaccessible even in principle because fluctuation effects intervene[11] seriously for samples of the size used. The basic mean-field theory allows the spinodal to return, at Y, close to the course of the asymptotic regression line A' ($\beta = 1/2$). In the intermediate range $10^{-7} < \epsilon < 10^{-2}$, the correction for statistical inhomogeneity is effective in displacing the spinodal locus from the line A'.

The important implication of *Figure 2* is this: over the two-decade range viz. $7 \times 10^{-5} < \epsilon < 5 \times 10^{-3}$ of the spinodal data (*Figure 1*) which furnished the optimized parameters for equation 4, this equation simulates, well within experimental error, the straight line A''. This line represents a fixed, non-limiting exponent, which agrees fortuitously closely with the *limiting* exponent ($\beta = 5/16 = 0.313$) for approach to the critical point of the 3-dimensional Ising model[3]. An analytic function can, of course, generate a non-limiting exponent over a finite range, constant to within arbitrarily small (but not zero) tolerance. The theoretical model furnishes such a function, which we are
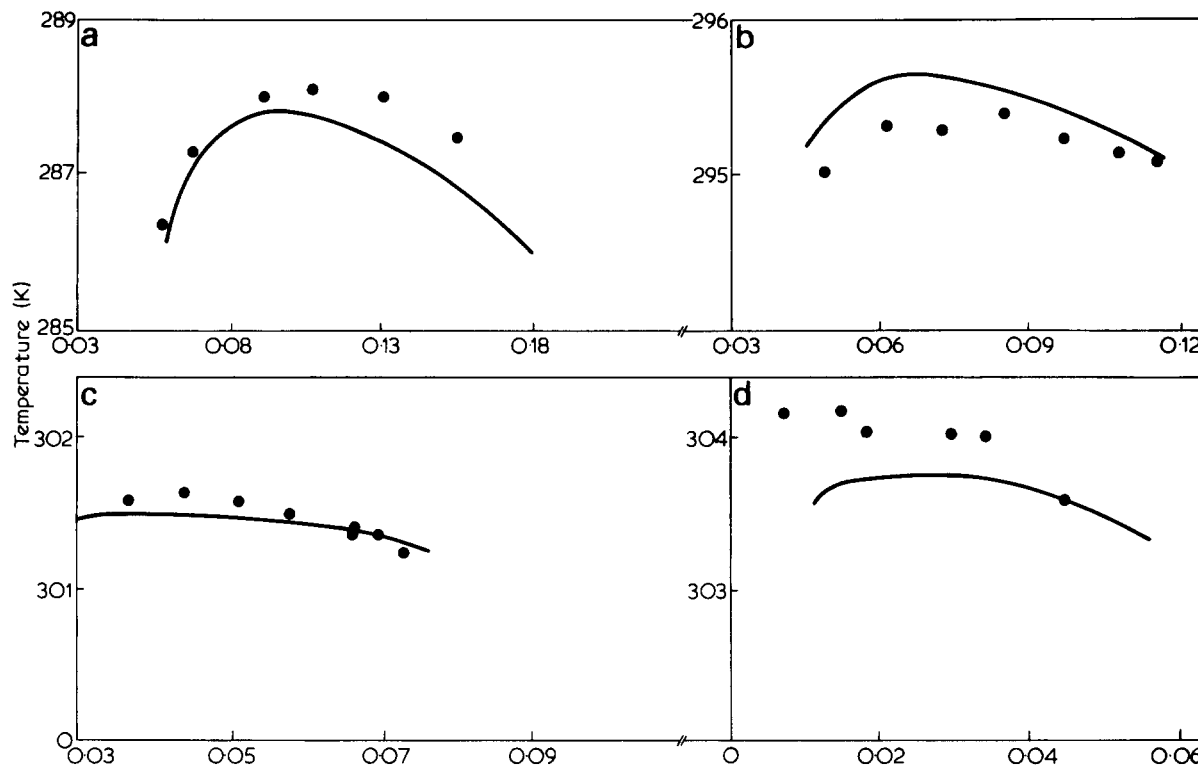
Figure 1   Curves from equation 6 (optimized parameters: $\beta_0 = 0.1717$, $\beta_1 = 100.53$, $\gamma = 0.4651$, $\lambda_0 = 0.6215$) fitted to experimental spinodal points on nominally monodisperse PS/CH solutions (cf. reference 7) of varying molecular weights: (a) 5.1×10^4; (b) 1.2×10^5; (c) 5.0×10^5; (d) 2.61×10^6
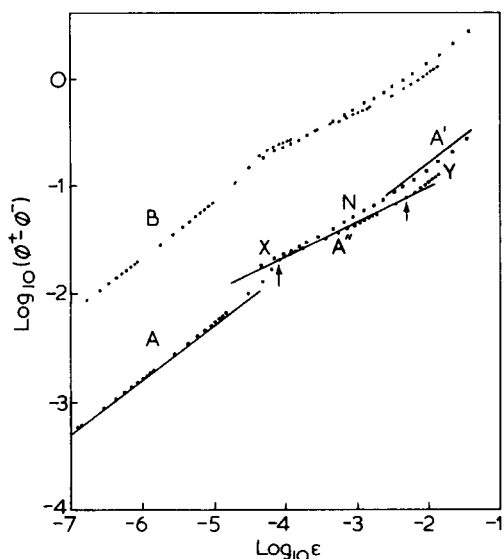

Figure 2   Isothermal differences $\Phi^+-\Phi^-$ on spinodal locus (circles), calculated from equation 6 (for parameter values see Figure 1) in comparison with the measured binodal (coexistence) points on PS/CH by Nakata et al.[20] (squares). Plot A: Molecular weight = 2.5×10^6 which gives (equation 6) $T_C = 30.50°C$, as stated by these authors. Plot B: Molecular weight = 1.56×10^6 as stated by these authors, which gives T_C about $29.81°C$. A': asymptotic regression line ($\beta = 0.5$); A'': linear part (regression line between arrow limits) simulating Ising-type exponent ($\beta = 0.313$) in experimental range near T_C; plot B is displaced one decade upwards

unable to contrive artificially! The shape of plot A implies significant contributions in the experimental range of at least two positive and two negative Taylor coefficients. Such contributions would require a rationalization of the pattern of convergence from the complex plane onto the positive and negative real axes of several roots of the partition func-

tion in the asymptotic continuum analysis of the I. The conventional plot of $(\Phi^+ - \Phi^-)$ against (ϵ), Figure 3, is very insensitive, since it compresses the non-limiting character of the correction for heterogeneity into the tiny intercept shown. A small but significant intercept is seen in a plot by Weinberger and Schneider[12] for the critical behaviour of Xenon.

In summary, we suggest:

(a) the quantitative comparison of experimental data with mathematical models is the business of statistics. No statistical tests are possible, on the basis of experiment, for the hypothesis that a function is analytic at a point. The suitability of models cannot, therefore, be decided on the criterion of analyticity;

(b) the singularities in Ising-type lattice models concern different physical situations (e.g. magnetic transitions in localized systems) from our mean-field theory which models statistical heterogeneity induced by diffusional mobility. The heterogeneity correction is at its maximum in a region not including the critical point (Figure 2). As a result, values of limiting exponents of the Ising model may be simulated, by the mean field theory, when roughly corrected for heterogeneity, throughout the experimental region;

(c) the general consistency of mean-field theories for mobile polymer systems is reinforced by other observations. In determining spinodals by Debye fluctuation scattering extending into the metastable region, the relevant Debye—Scholte[13] plots are found to be linear, reflecting the accuracy of the mean-field exponent unity, in preference to the non-classical[14] 5/4, over the experimental range[7]. For the liquid—gel transition at a gel point, Ising models seriously overestimate the intensity of ring-chain competition, as deduced both theoretically and experimentally[15]. As a result, classical exponents will prevail[16].

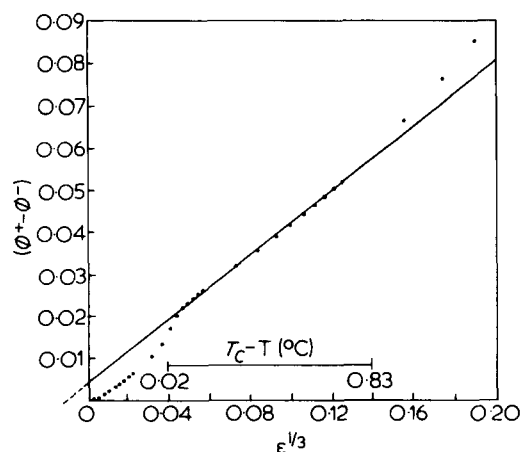The classical theories of gelation of Flory[17] and

Figure 3 Conventional test for 1/3 power law applied to theoretical spinodal, equation 6. For molecular weight, see plot A, *Figure 2*. Note small but finite intercept due to deviation from pseudo-linear course in the range $T_c \pm 0.03°C$

Stockmayer[18] represent a simpler graph-theoretical model than the Ising one: percolation on a tree rather than on a lattice graph. Only a tree-like model survives when we can average by integrating out, as happens generally in the graph-like state of matter, the random motions in all but one dimension[19]; and this is conducive to gratifying simplifications, without disturbing the beauty of the mathematical analysis of the Ising problem. Perhaps the only safe hypothesis of universality is that, without exception, each case must be examined on its merits.

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