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Thermodynamics of polymer solutions

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Abstract - Similarities and differences between the thermodynamics of macromolecular systems and small-molecule mixtures appear mainly in their miscibility behaviour. Liquid-liquid phase separation in polymer solutions is considered on the basis of the still usefull classic lattice model. The phase behaviour will mainly be governed by variations in chain-length (molecular weight distribution) and by disparity in size and shape between molecules and/or repeat units which implies differences in numbers of nearest neighbour contacts. Further statistical and empirical refinements of the model need to be included if a quantitative description of experimental data and prediction of other properties in a reasonably accurate manner is required. The system under consideration will be cyclohexane/poly(styrene) with moderate polymolecularity.
The influence of pressure, an important variable in polymer production and processing, can be dealt with by using the simple mean-field lattice-gas model. Here again, theory includes a number of semi-empirical parameters that enlarges as the system in hand becomes more complex. The predictive power of the molecular model needs to be tested against thermodynamic properties as we intend to demonstrate in the system n-alkane/poly(ethylene) with wide chain-length distribution.

INTRODUCTION

Partial miscibility is an important practical phenomenon in polymer science and engineering. Polymerisations frequently take place in solution, and demixing is not a rare phenomenon, even if the monomer serves as the solvent. Such liquid-liquid phase separations are to be avoided since they disturb the production process by the segregation of highly viscous phases. The cause of the relatively small resistance to demixing shown by polymer solutions is to be found in the long-chain structure of macromolecules. The blending and compounding of polymers reveals even more emphatically this sensitivity towards phase separation which, depending on application purposes, may well or not, have to be avoided. The mechanical properties of polymer blends, block copolymers and composites are, of course, enormously dependent on phase relationships and morphology. Theoretical models, as well as experimental techniques, have been and are still being developed. Basic thermodynamic relations on heterogeneous equilibria in mixtures of small molecules also apply to solvent/polymer and polymer/polymer systems. The most simple statistical-mechanical theory of Flory, Huggins and Staverman (FHS) only permits a qualitative description of the observed phenomena. Further statistical improvements and semi-empirical refinements that improve molecular theory over its mean-field nature in the description of reliable thermodynamic data on polymer systems is highly desirable. Such treatments will provide us with a deeper understanding of the molecular background of polymers themselves and of the demixing phenomena and will allow us to predict related thermodynamic properties more accurately.

As Van der Waals [1] already noticed, the difference in molecular size of the components in solvent/polymer systems is very large, which causes the miscibility gaps to become highly asymmetric, with the consolute states occuring at low mass fractions of polymer. An example is given in figure 1, where hexane and anilin have comparable sizes and masses and the miscibility gap is fairly symmetrical around a mass fraction of ½. The solvent diphenylether, however, differs in molar mass from the poly(ethylene)-sample by a factor of about 1000, and in this system the miscibility gap is confined to the extreme left (solvent-rich part) of the diagram, leaving the larger part of the composition range to homogeneous solutions.

Figure 1 is an arbitrarely selected example of a very familiar phenomenon. There is a maximum temperature (precipitation threshold) above which the system is completely miscible in all proportions. This type of demixing is called upper critical solution temperature (UCST) behaviour. The opposite also occurs, partial miscibility setting in when the temperature is raised. Then there is a minimum threshold temperature and the system is said to be of the lower critical solution temperature (LCST) type. An example of both LCST (n-hexane/poly(ethylene) and UCST behaviour (cyclohexane/poly(styrene)) is given in figure 2.

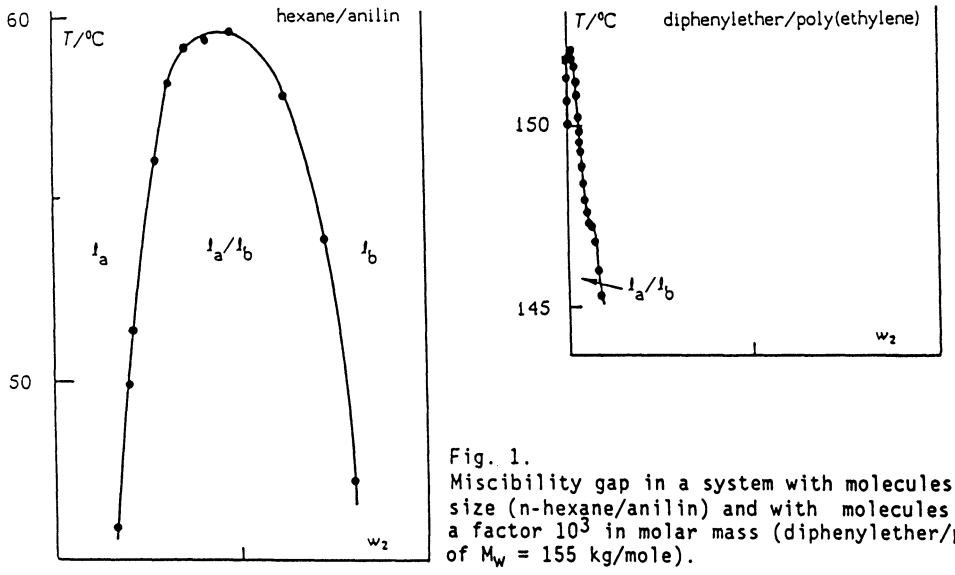

Fig. 1.
Miscibility gap in a system with molecules of comparable size (n-hexane/anilin) and with molecules differing by a factor 10^3 in molar mass (diphenylether/poly(ethylene) of M_w = 155 kg/mole).

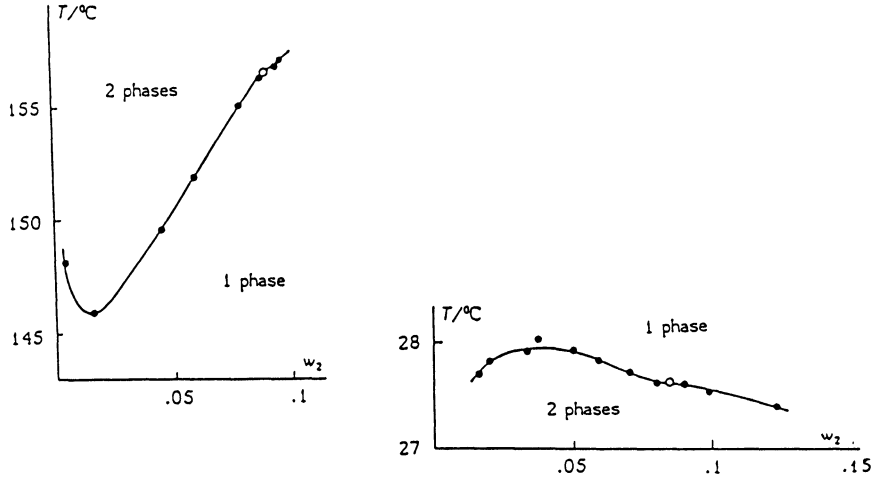

Fig. 2. Experimental cloud point curves (cloud point temperature versus weight fraction of polymer) and critical points (o). Top: n-hexane/poly(ethylene) [2] (M_w = 180 kg/mole; M_w/M_n = 23; M_z/M_w = 7); bottom: cyclohexane/poly(styrene) [3] (M_w/M_n = 1.07; M_z/M_w = 1.4).

Synthetic polymer samples practically always contain a large number homologues components differing in molar mass. Their solutions or mixtures are thus multicomponent systems and two-dimensional phase diagrams (e.g. temperature-composition diagrams as shown in figures 1 and 2) are, though very useful, in principle ambiguous and require great care in interpretation. Figure 3 represents the phase bounderies in a ternary system solvent (S), polymer 1 and polymer 2 (P_1, P_2; two homologous macromolecules differing in chain-length) as a function of temperature at constant pressure.

The binary systems SP_1 and SP_2 show complete and limited miscibility (this would imply that the molar mass in P_1 is smaller than in P_2). The line SX represents all systems containing a mixture X of components P_1 and P_2 and solvent S. For these systems SX is the composition axis. The plane TSX intersects the binodal surface, and the resulting curve, the cloud point curve (CPC), was called a 'quasi-binary section' of the ternary phase diagram. It is called CPC of mixture X in solvent S since in experimental determinations carried out by cooling or heating solutions of X of known concentrations in S, it is found by plotting the temperature of incipient phase separation (first cloudiness) against the concentration of the mixture X in S. Similar reasoning can be applied to the spinodal surface (thin line in figure 3), which is the limit for metastable equilibrium in the phase diagram. The spinodal touches the CPC and shares a common tangent plane with it at the critical point C_5 (for the mixture X in S) situated on the critical line CC'. It can also be seen from figure 3 that polymolecularity (e.g. the existence of a molecular weight distribution (MWD) in the polymer) causes the critical point to shift from the maximum to the right-hand side (more concentrated solution) of the CPC as is experimentally verified (see figure 2).

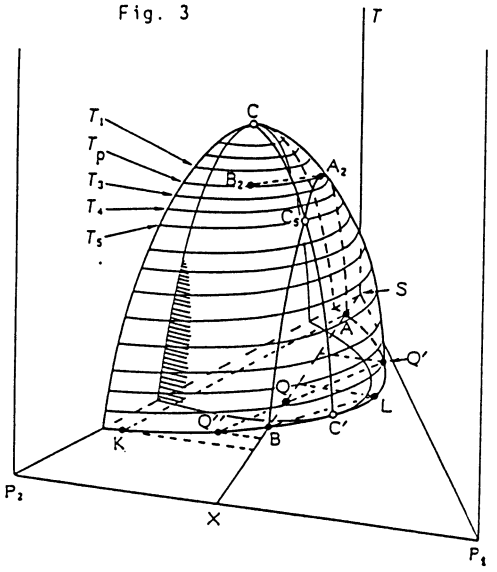

Fig. 3

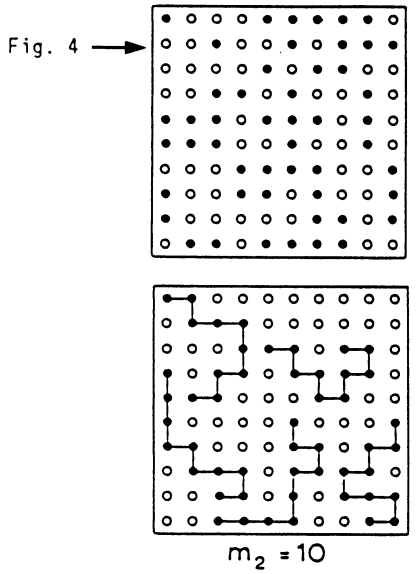

Fig. 4

Fig. 3. Miscibility or binodal surface in a strictly ternary system solvent (S), polymer 1 and 2 (P_1 and P_2), identical in chemical nature but differing in chain-length as a function of composition and temperature. Construction of cloud point curve AB and critical point C_5 for the mixture X of P_1 and P_2 in the solvent S. CC' is the critical line of the ternary system SP_1P_2. See text for detailed explanation.

Fig. 4. Schematical representation of a small molecule mixture (top) and a polymer solution (bottom) on a lattice.

Another important difference between macromolecular systems and small-molecule mixtures is that the concentration range of validity of the colligative limiting laws is much more restricted; except at very great dilutions, overlap an interpenetration of the domains of the coiled or rodlike macromolecules produces characteristically large deviations from the limiting behaviour. As chain-length is increased and the number of macromolecules in a given mass or volume decreases, the entropy of random mixing becomes smaller which can be accompanied by drastic changes in the miscibility behaviour of polymer solutions and polymer blends [4]. In section 2, we briefly explain the FHS molecular theory for polymer solutions and illustrate its application to and refinement in the description of the poly(styrene)/cyclohexane system by Nies et al. [5-7]. A more detailed description of hetereogeneous equilibria in polymer systems can be found in the recent litterature [8].

The influence of pressure on the miscibility behaviour of polymer solutions is both interesting and important. Although polymers have a negligible vapour pressure, we do not only have to deal with condensed phases. Many polymerisation processes take place in solution at elevated temperatures and/or pressures and vapour phases appear frequently. Momomers are often relatively volatile and may cause sizeable vapour pressures that have to be accounted for. We may recall the low-density poly(ethylene) production in compressed ethylene at high pressure and temperature. Solution polymerisation of ethylene in hydrocarbon solvents usually proceeds at elevated pressures. In both cases, the actual working conditions include temperature and pressure ranges in which the system is unstable as a homogeneous one-phase liquid or fluid and knowledge of phase relations is essential for controlling the production. Since the excess volume of mixing is zero in the statistical mechanical rigid-lattice considerations, the disadvantage of these models to describe pressure-effects is obvious. The need to describe and predict pressure effects on the miscibility behaviour of polymer solutions can be fulfilled in a satisfactory manner by using the simple mean-field lattice-gas (MFLG) model introduced by Trappeniers [9] and applied and developed by Kleintjens and Koningsveld [10, 11] to describe the phase behaviour of supercritical systems. Before discussing, we will illustrate in section 4 some general theoretical considerations related to the MFLG model and describe some applications in the system n-alkane/poly(ethylene). For a review of fluid phase separations in polymerising systems at elevated pressures we refer to the literature [12].

RIGID LATTICE MODEL: APPLICATION TO CYCLOHEXANE/POLY(STYRENE)

The rigid lattice model, developed independantly by Flory [13], Huggings [14] and Staverman [15, 16] still provides a usefull way of dealing with partial miscibility in condensed systems where pressure has no significant influence. In the FHS rigid lattice model, the mixture is represented by a number of regularly arranged lattice sites, each of fixed volume and definite coordination number (see figure 4). Only contacts between nearest-neighbours are accounted for in the enthalpy of mixing and the entropy of mixing is evaluated on the basis of regular solution theory.

We write for the Gibbs free energy ΔG of mixing n_1 moles of solvent with n_2 moles of polymer with a single molar mass M_2:

$$\frac{\Delta G}{NRT} = \frac{\phi_1}{m_1} \ln \phi_1 + \frac{\phi_2}{m_2} \ln \phi_2 + g\phi_1\phi_2 \qquad (1)$$

where RT has its usual meaning, g is the Van Laar interaction parameter, N is the total number of moles of lattice sites and ϕ_i are the relevant composition variables (volume fractions):

$$\phi_i = \frac{n_i m_i}{N}$$

m_i being the number of lattice sites occupied by molecule i. For polymer solutions, it is natural to define the site-volume as the molar volume of the solvent ($m_1 = 1$) so that

$$m_2 = \frac{M_2 \nabla_2}{M_1 \nabla_1}$$

where ∇_i is the specific volume of component i. The first two terms on the right-hand side of eq. 1 are the contributions from the combinatorial entropy in which we recognise the macromolecular analogues of the ideal solution free enthalpy for small-molecule mixtures. The smaller resistance towards partial miscibility in liquid mixtures containing macromolecules is due to the fact that the entropy of mixing is drastically reduced while the number of nearest-neighbour contacts per unit volume responsible for most of the g-term is scarcely smaller than in the small-molecule case (see also figure 4).

Experimental data suggest the interaction parameter g to be composed, in first approximation, out of an entropic contribution g_s in addition to the enthalpic term g_H [17-19];

$$g = g_s + \frac{g_H}{T} \qquad (2)$$

In a strictly binary system, i.e. a hypothetic monodisperse polymer in a solvent, one has

$$\left(\frac{\partial^2 \frac{\Delta G}{NRT}}{\partial \phi_2^2} \right)_{P,T} = 0 \quad \text{(spinodal)} \qquad (3)$$

$$\left(\frac{\partial^3 \frac{\Delta G}{NRT}}{\partial \phi_2^3} \right)_{P,T} = 0 \quad \text{(critical point)} \qquad (4)$$

Application of (3) and (4) to equations (1) and (2) leads to:

$$\frac{g_H}{T_c} = \frac{1}{2} - g_s + \left(m_2^{-\frac{1}{2}} + \frac{1}{2m_2}\right) \qquad (5)$$

Schultz and Flory [20] used equation (5) to find the parameters g_s and g_H, identifying the critical temperature T_c with the maximum threshold temperature. The predictive power of their treatment is therefore rather poor as is illustrated in figure 5, which shows the calculated spinodals for different molar masses [5-7] with the parameters from a Shultz-Flory plot for cyclohexane/poly(styrene) ($g_s = -0.27$; $g_H = 236$ K). It can be seen from figure 5 that the critical temperatures are obviously described well, but the critical concentrations and coexisting phase compositions are not.

Evidently, the parameter g must depend on concentration. Staverman already found in 1937 that the description of heats of mixing of small-molecule mixtures can be improved by taking into account the disparity in size and shape of the compounds [21]. Application to polymer solutions, leaving the rigid lattice model as an abstraction of real fluids yields the concentration-dependant interaction parameter g [5-7]

$$g = g_o + \frac{g_1}{(1 - \gamma\phi_2)} \qquad (6)$$

where g_1 summerizes the temperature dependance of g (for instance $g_1 = g_{10} + g_{11}/T$) and σ_2/σ_1 ($\gamma = 1 - \sigma_2/\sigma_1$) is the ratio of molecular surface areas of polymer segments and solvent molecules.

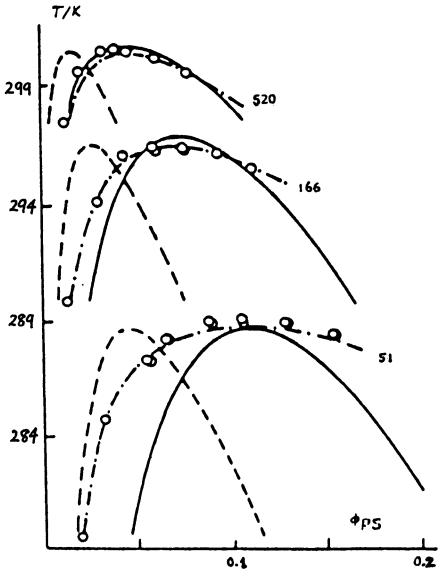

Fig. 5

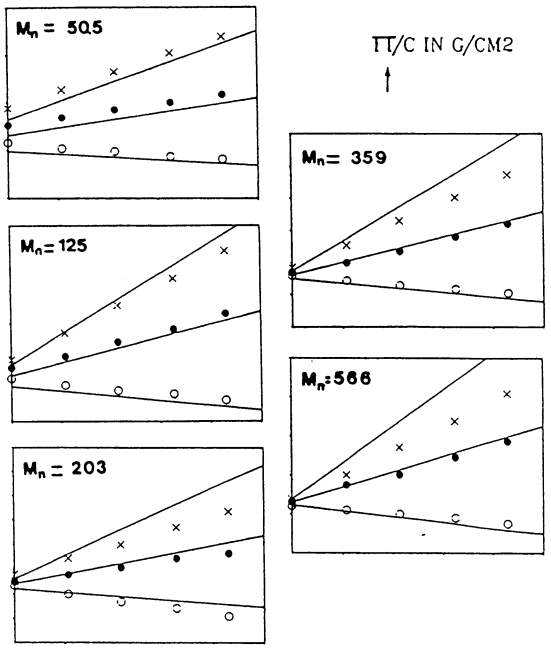

Fig. 6

Fig. 5. Spinodal points for the cyclohexane/poly(styrene) system for indicated values of the mass average molar mass (in kg/mole). Curves calculated on the basis of Shultz-Flory analysis (----), Staverman's approximation (——) and further theoretical developments by Nies et al (-.-.-) [5-7]. Data by Scholte [22] and Derham et al. [23].

Fig. 6. Reduced osmotic pressures Π/c (in g/cm^2) for the cyclohexane/poly(styrene) system for indicated values for the number average molar mass (in kg/mole) as a function of concentration and temperature (top, middle and bottom curves for 50, 40 and 30 °C, respectively) Data by Krigbaum [24], predictions using equation (6).

Fitting critical points [5-7] for various molar masses in the system cyclohexane/poly(styrene) with narrow MWD to equations (1), (3), (4) and (6) yields the parameter values listed below
g_o = -0.22; g_{10} = 0.57; g_{11} = 108 K; γ = 0.22

Note that the value found for σ_2/σ_1 is 0.78 and compares surprisingly well with the value calculated from Bondi's group contribution method, viz. 0.87. The calculated spinodals using equation (3) and the parameter values listed above show a much better agreement with the experimental data (figure 5). Both maximum separation temperature and concentration are now reproduced. This is not totally unexpected since in this approximation both critical temperatures and concentrations were used to determine the parameters. Yet, the experimental curves are still broader than the calculated ones, which requires further refinement of the model.

The shortcoming in describing the system cyclohexane/poly(styrene) with narrow MWD using Staverman's approximation can be emphasized by comparing the predicted osmotic pressures for different molar masses and temperatures to experimental data by Krigbaum [24] as is done in figure 6. The agreement between calculations and experimental data is quite good, deviations becoming larger at high temperatures as the molar mass is increased.

Two more aspects can be included in the rigid lattice model, namely the polymer coils being isolated at high dilution (non-uniform segment density) and the chains bending back ('back-biting') on themselves.
The first aspect has been dealt with by Stockmayer et al. [25, 26]. As we fail to quantitatively describe liquid-liquid phase equilibria in polymer solutions, where one of the phases is very dilute (isolated coils) and the other so concentrated that the coils overlap

extensively, Stockmayer remedies the situation. He writes the interaction function as a sum of two terms, one for each concentration range:

$$g = g^*(T, m_2)P + g^c \tag{7}$$

where g^c, representing the concentrated regime, may be expressed by eq. (6), and $g^*(T, m_2)$ quantifies the differences relevant for the dilute regime compared with the uniform density state. $g^*(T, m_2)$ is attinuated by the probability factor P

$$P = \exp(-\lambda_o m_2^{\frac{1}{2}}\phi_2) \tag{8}$$

where λ_o can be expressed in molecular parameters, obtainable from independant measurements [25, 26]. A detailed analysis [5-7] reveals the following semi-empirical expressions are needed to deal in a satisfactory manner with all available experimental data (i.e.; spinodal points, critical points, coexisting temperatures and compositions, χ-values from light scattering):

$$g^* = \left\{\beta_1 + \beta_2(T - \theta)\right\}(T - \theta)(1 - \frac{1}{m_2})/m_2 \tag{9}$$

$$g_o = a_1 + \frac{a_2}{m_2} + (a_3 + \frac{a_4}{m_2})(T - \theta) \tag{10}$$

where θ is the Flory-temperature. It is seen from figure 5 that the calculated spinodals using eqs (1), (3), (4), (7)-(10) are in overwhelming agreement with the experimental data.

It should be mentioned that the trend expressed in eq. (10) was predicted by Stavermans calculations of the effect back bending of the chain on itself has on the combinatorial entropy of mixing, particularly in poor solvents [27].

Although the number of parameters thus gathered is quite large (see list below) and the general form of the equations can be justified by molecular considerations the procedure needs to be justified by the predictive power it contains. Examples are shown in figures 7 and 8.

List of parameters obtained by Nies et al. [5-7]:
$g_{10} = -0.89$
$g_{11} = 490$ K
$\gamma = 0.29$
$a_1 = -0.003$
$a_2 = -2.10$
$a_3 = 0.00282$
$a_4 = 0.032$
$\beta_1 = -0.0281$
$\beta_2 = 0.00069$
$\lambda_o = 0.885$

In figure 7, it is witnessed that osmotic pressures, calculated on the basis of equations (7)-(10) pass trough Krigbaum's experimental results, within the specified accuracy (compare to the predictions using the 'second level' approximation in figure 6).

Figure 8 shows a ternary coexistence curve by Hashizume et al. [28] and the calculated binodal in the ternary mixture with the present level of approximation [5-7]. The agreement is fairly good, in view of the assumption that the ternary system can be treated as a simple superposition of two binary ones by replacement of the second term on the right-hand side of equation (1) by [29, 30]:

$$\frac{\phi_{21}}{m_{21}} \ln \phi_{21} + \frac{\phi_{22}}{m_{22}} \ln \phi_{22}$$

while $\phi_2 = \phi_{21} + \phi_{22}$. For the sake of comparison, we have added in figure 8 a calculated part of the binodal using the 'second level' approximation, based on eq. (6) where the agreement with experimental data is far from quantitative.

Note that the effect of polydispersity has been totally left out of consideration here since the experimental data used were carried out with polymers having a sharp-peaked MWD. The phase relationships discussed in this section can however also be studied numerically if the polymer constituents have any number of components [2]. The simplest FHS expression for the free enthalpy of mixing a 'real' binary polymer/solvent system could be written as:

$$\frac{\Delta G}{NRT} = \phi_1 \ln \phi_1 + \Sigma \frac{\phi_i}{m_i} \ln \phi_i + g\,\phi_1\phi_2 \tag{11}$$

where ϕ_i are now the volume fractions of polymer species i (whole polymer volume fraction is

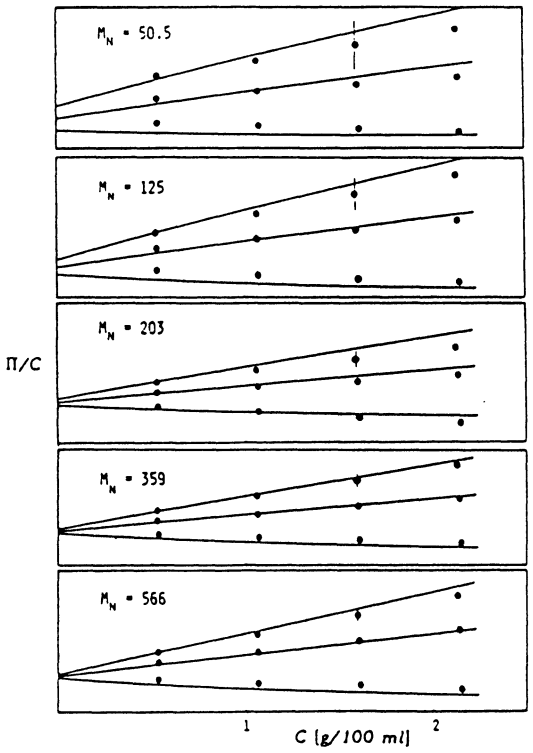

Fig. 7. As in fig. 6, predictions using equations (7)-(10) by Nies et al. [5-7].

$\phi_2 = \Sigma\ \phi_i$) and m_i is the number of lattice sites occupied by macromolecules i (measure of their chain-length). Without going further into detail, we show some cloud points curves in figure 9, calculated on the basis of equation (11) with g independant of ϕ_2 but temperature dependant. It illustrates the effect polymolecularity has on the location of the critical point as well as on the shape of the CPC, compared to a strictly binary system (see also figure 2). The molar mass distributions have equal M_w and M_w/M_n values but still differ in width, expressed as M_z/M_w. The calculated spinodals are therefore identical but CPC's appear to be very sensitive to the width parameter M_z/M_w which is associated with a quite different location of the TSX plane in figure 3. We note that the CPC may show a dent in the proximity of the critical point.

Fig. 8

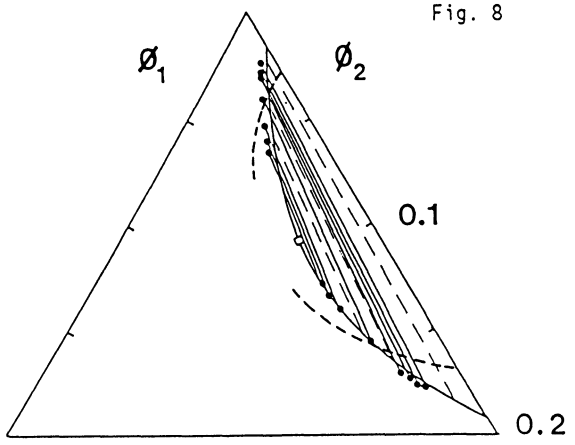

Fig. 9

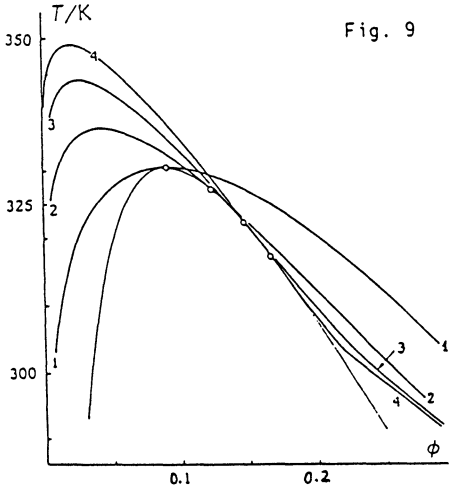

Fig. 8. Ternary phase relations (at a temperature of 19 °C) in the cyclohexane/poly(styrene) system. Molar masses of polymer constituents: 45 and 103 kg/mole. Data (•—•) by Hashizume et al. [28]. Curve represents highest level prediction of binodal (—), tie lines (- - -) and critical point (□) [5-7]. Dashed curve represents predicted part of the binodal using eq. (1) and (6).

Fig. 9. Cloud point curves calculated [8] on the basis of equation (11) (with g independant of composition) for various molecular weight distributions equal in M_w and M_w/M_n, but with increasing width (M_z/M_w value ranging from 1, curve 1, to 4.5, curve 4) ——: spinodal; 0: critical points.

MEAN-FIELD LATTICE-GAS MODEL: APPLICATION TO THE SYSTEM n-ALKANE/POLY(ETHYLENE)

The importance of pressure as a thermodynamic variable in controlling production processes and optimising polymerisation conditions has already been pointed out in the introduction. We may remind the example of the solution polymerisation of ethylene, carried out in mixtures of hydrocarbons, on the average roughly resembling n-hexane. Phase diagrams like the LCST curve, shown in figure 2 have been recorded for various (high-density) poly(ethylene) samples differing in molar mass, at varying pressures. Further information exists on the melting point of the polymer as a function of pressure and on boiling points and critical conditions of the solvent. As a consequence, the Bakhuis Roozeboom p, T, w_2 (w_2: weightfraction of polymer in the solvent) has an estimated appearance as shown in figure 10 [8], which reveals how preciously little is known about the system, nevertheless practically important.

Further, the asymmetrical phase diagram is normal for polymer solutions in contrast to small-molecule mixtures.

The influence of pressure (expansion or contraction upon mixing) cannot be dealt with within the scope of the FHS rigid lattice considerations, unless the g-function is adapted in a semi-empirical way [4, 31]. A simple and elegant alternative is provided by the mean-field lattice-gas model. This procedure has been shown to give adequate descriptions and predictions of the influence of pressure on thermodynamic properties of pure, polar or non-polar, compounds and mixtures of small molecules as well as macromolecular systems [10, 11, 32-34]. In this section, we briefly wish to explain the molecular background and statistical assumptions, underlying the MFLG treatment followed by a short demonstration of its adequacy in the description and prediction of the influence of pressure on liquid-liquid phase separation in the system n-alkane/poly(ethylene).

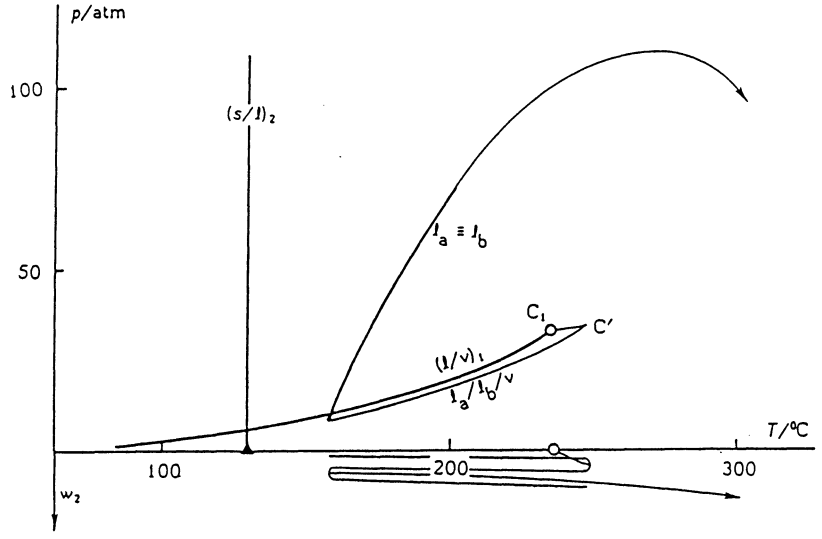

Fig. 10. Estimated p(T) and T(w_2) projections of the Bakhuis Roozeboom phase diagram for the system n-hexane/poly(ethylene). Heavy curves indicate the p(T) ranges for which experimental data exist. Light curves are estimations. Triple point poly(ethylene): ▲.

In the MFLG model, introduced by Trappeniers et al [9], each fluid, liquid or gas, is represented by a lattice in which the sites are either occupied or vacant (holes). It is assumed that only first nearest-neighbour contacts between molecules contribute to the internal energy. The number of these contacts is related to molecular suface areas following a suggestion by Staverman [21]. The entropy contribution to the free energy is calculated in a strictly regular solution approximation and usually empirical entropy correction parameters must be introduced. Besides temperature variations, one can also deal with pressure variations of the system because of the introduction of free volume. Molecules are allowed to occupy more than one site but the molar volume for each site, v_o, is taken constant, independant of pressure and temperature. We write for the Helmholtz free energy of 'mixing' ocupied sites (molecules 1) and vacant sites (holes o):

$$\frac{\Delta A}{N\phi RT} = \phi_o \ln \phi_o + \frac{\phi_1}{m_1} \ln \phi_1 + g\, \phi_o \phi_1 \qquad (12)$$

where the 'concentration' variable ϕ_1 is directly related to the density d (in g/cm^3) of the system (M_1 = molar mass in g/mole):

$$\phi_1 = \frac{d\, v_o m_1}{M_1}$$

Further, m_1 is the number of sites per molecule, N_ϕ is the total number of moles of lattice sites, and the interaction function g has the same form as equation (6):

$$g = \alpha_1 + \frac{\beta_{10} + \beta_{11}/T}{(1 - \gamma_1\phi_1)} \tag{13}$$

where β_{11} can be related to the interaction energy between molecules per unit contact surface, and $\gamma_1 = 1 - \sigma_1/\sigma_0$. α_1 and β_{10} are empirical entropy corrections for which a molecular origin has recently been formulated [35]. Thus, six adjustable parameters appear in eq. (12) and they all have a clear physical meaning.
Standard classical thermodynamic relations yield expressions for the MFLG equation of state (EOS), spinodal, critical condition and chemical potentials of the constituents [10]. We only recall here the EOS, derived with

$$p = -\left(\frac{\partial \Delta A}{\partial V}\right)_{T,\, n_1}$$

$$\frac{-pv_0}{RT} = \ln \phi_0 + \left(1 - \frac{1}{m_1}\right)\phi_1 + \phi_1^2\left\{\alpha_1 + \frac{\beta_1(1 - \gamma_1)}{Q^2}\right\} \tag{14}$$

where $Q = 1 - \gamma_1\phi_1$, $\beta_1 = \beta_{10} + \frac{\beta_{11}}{T}$ and the total volume V is given by

$$V = N_\phi v_0 = (n_0 + n_1 m_1)v_0 \tag{15}$$

with n_0 and n_1 the amounts of vacant and occupied sites in moles.

If equation (12) is used to describe a polymer species, the second term on the right-hand side must be replaced by $\Sigma\, \phi_i/m_i \ln \phi_i$ as in eq. (11) and as a result m_1 in eq. (14) will be related to the number average molecular weight m_n. In the spinodal and critical condition, m_1 will be replaced by m_w and m_w^2/m_z respectively.

It is worthwhile to mention here that in view of Frenkel's estimation [36] of an equilibrium hole volume of ca. 20 cm^3/mole, we hold on to this value for all pure substances, as well as for mixtures, thus avoiding the design of mixing rules. In figure 11, we show an example of the MFLG description of liquid/vapour equilibrium data and critical region in the pure substance n-hexane. As is witnessed by figure 12, macromolecular systems also fall within the scope of the MFLG model. The description of p-V-T-relations in molten linear poly(ethylene) of low molecular weight (M_n = 8000 g/mole) is in reasonable agreement with available experimental data at pressures below 500 bar.

Fig. 11

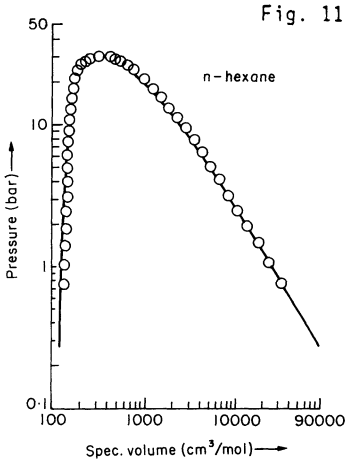

Fig. 12

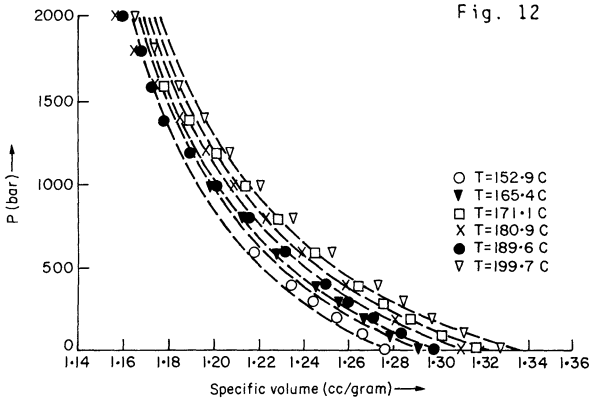

Fig. 11. MFLG description of gas-liquid equilibria and critical region in n-hexane (O: exp. data •: exp. critical point). Parameter values: see table on the following page.

Fig. 12. Experimental [37] and MFLG-calculated specific volumes for linear low molecular weight poly(ethylene) (M_n = 8000 g/mole) in the melt as a function of pressure and temperature. Parameter values: see table on the following page.

The relevant ΔA expression for the quasi-binary system n-alkane (1)/poly(ethylene) (2) contains, in addition to the pure component parameters, two extra parameters α_m and g_m (T) in the interaction term for the repeat units in the alkane and within the poly(ethylene):

$$\frac{\Delta A}{N_\phi RT} = \phi_o \ln \phi_o + \frac{\phi_1}{m_1} \ln \phi_1 + \Sigma \frac{\phi_{2,i}}{m_{2,i}} \ln \phi_{2,i} + \phi_o\phi_1 \left(\alpha_1 + \frac{\beta_1}{Q}\right) + \phi_o\phi_2 \left(\alpha_2 + \frac{\beta_2}{Q}\right)$$

$$+ \phi_1\phi_2 \left(\alpha_m + \frac{g_m(T)}{Q}\right) \qquad (16)$$

with $Q = 1 - \gamma_1\phi_1 - \gamma_2\phi_2$.

The overall volume fraction of the polymer $\phi_2 = \Sigma\phi_{2,i}$ is related to the weight fraction w_2 by

$$w_2 = \left\{1 + \frac{c_2}{c_1} \left(\phi_2{}^{o\,-1} - 1\right)\right\}^{-1}$$

where the binary volume fraction $\phi_2{}^o = \phi_2/(1 - \phi_o)$, $c_1 = m_1/M_1$ and $c_2 = m_2/M_n$.

We refer to the literature [10, 11, 32-34] for the derivation of EOS, spinodal and critical conditions and details on procedure for binary systems.
Since linear poly(ethylene) (LPE) and n-alkanes consist of identical repeat units, one might assume for both parameters of the mixture $\alpha_m = g_m(T) = 0$ [32]. This assumption seems at present too simplistic to even qualitatively describe recently measured cloud point curves for n-hexane/LPE of a known MWD at different pressures by calculated spinodals. However, figure 13 illustrates that it is possible to find parameters for the mixture which describe the measured LCST behaviour and it's pressure dependance fairly reasonable.

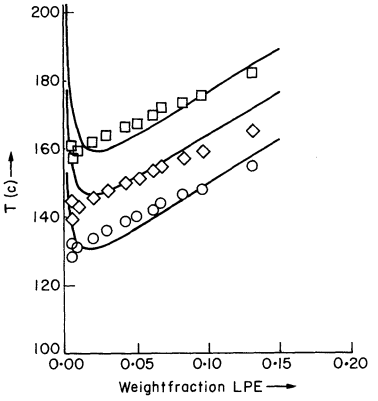

Fig. 13. Comparison of MFLG calculated spinodals (—) with experimental cloud point curves [38] in the system n-hexane/linear poly(ethylene) (LPE) at different pressures; 6 bar (O), 25 bar (◊) and 50 bar (□). Parameter values listed in table below.

TABLE of MFLG-parameters (v_o = 20 cm^3/mole)

Pure compounds:

	m_1	γ_1	α_1	β_1
n-hexane	4.3555	-3.5403	0.93441	-1.0443 + 673.34/T
n-octane	5.3817	-3.9691	0.89020	-0.93205 + 661.06/T
n-nonane	6.0469	-4.8307	0.89456	-1.0119 + 711.02/T
linear poly(ethylene)	454.89	0.17687	0.86853	-0.52627 + 260.25/T + 109500/T^2

Mixture of linear poly(ethylene)/n-alkane
α_m = 0.22499
$g_m(T)$ = 0.89485 - 395.22/T

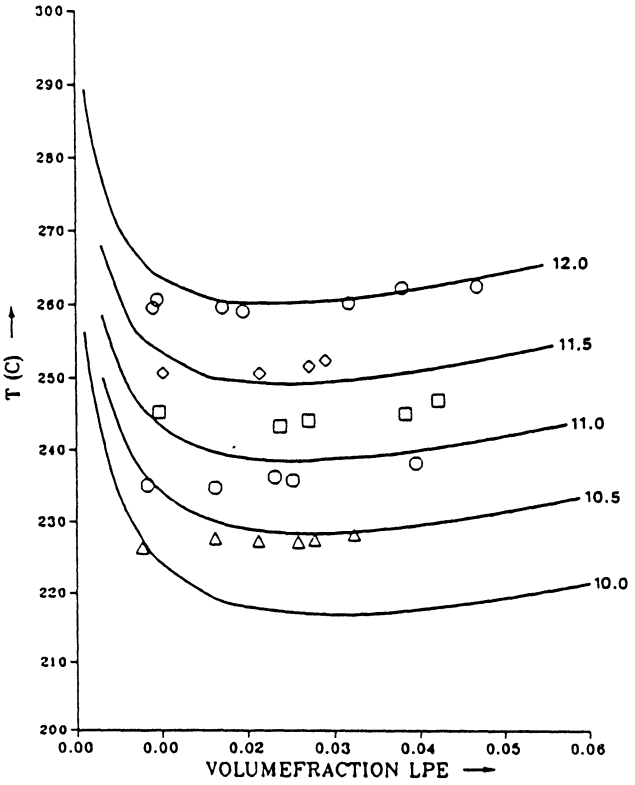

Fig. 14. Comparison of experimental cloud point curves [41] with predicted spinodals (—) at indicated pressures (in atm.) for the ternary system LPE (M_n = 36700; M_w = 49300 g/mole)/n-octane/n-nonane as a function of the mole fraction of nonane in the binary solvent mixture (O: x = 1.0, ◇: 0.726; □: 0.473; ○ : 0.240; △: x = 0.0).

It was recently demonstrated that extension of this treatment to ternary and multicomponent mixtures is straight-forward [39, 40]. To test the predictive power of the MFLG model, we compare in figure 14 predicted spinodals in the ternary system LPE/n-octane/n-nonane for different mole fractions in the binary solvent mixture with measured phase boundaries [41]. The agreement between experimental data and theoretical prediction is reasonable in view of the fact that interactions between alkanes were ignored and 'three body terms' left out of consideration.

CONCLUSION

In this paper, we have tried to underline the importance of liquid-liquid phase separation in polymer solutions in polymer science and engineering. The miscibility behaviour of polymer solutions also reveals the differences between such systems and small-molecule mixtures. It has further been demonstrated that pressure plays a non negligeable role in the synthesis and processing of polymers.

The rigid lattice model proves to be an adequate method in the theoretical description of phase separation phenomena. We have reviewed the description of thermodynamic properties of polymer solutions as far as the model would permit, taking cyclohexane/poly(styrene) as an example. Although the molecular origin of the many parameters thus appearing can be indicated roughly, their number is still excessive and the procedure resembles curve fitting of a primitive kind. Yet, it deserves a high level qualification because of its power of quantitative prediction. The influence of free volume, left out of consideration here, may be held responsible for a still too rough theoretical treatment.

Free volume can be taken into account by the simple mean-field lattice-gas model. The phase behaviour of polymer solutions, in particular the influence of pressure, can be described in a qualitative sence, using a moderate level of approximation (Stavermans surface contact

statistics) and with a small amount of parameters for the mixture. Description and prediction of phase equilibria in the system n-alkane/linear poly(ethylene) are far from quantitative and we are fully aware of the crudeness of comparing calculated spinodals with experimental cloud point curves. In view of this point, and considering the recent theoretical advances in deriving lattice equations of state [35, 42] the detailed description of the phase behaviour of series of n-alkanes, p-V-T-relations in different linear poly(ethylenes) and demixing phenomena in their mixtures is still a subject of current research [43].

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