Polymer Vol. 37 No. 5, pp. 825-830, 1996
Copyright © 1996 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0032-3861/96/$15.00+0.00

An analysis of the stability conditions of the Patterson and the Sanchez–Lacombe equation-of-state theories

Bernd Rudolf
Freiburger Materialforschungszentrum (FMF), and Institut für Makromolekulare Chemie, Albert-Ludwigs-Universität, Stefan-Meier-Strasse 21, 79104 Freiburg, Germany
(Received 30 December 1994; revised 5 April 1995)

The stability conditions of the Patterson theory and the Sanchez–Lacombe equation-of-state theory have been compared. It turned out that, for a certain special case, the free-volume part for both conditions can be put into analytically similar forms. Moreover, numerical calculations show that this special case is also a good approximation of the general case.

(Keywords: equation-of-state theory; Patterson theory; Sanchez–Lacombe theory)

INTRODUCTION

Numerical model calculations with the Patterson (PA) theory and the Sanchez–Lacombe (SL) equation-of-state (EOS) theory have revealed[1,2] that both theories yield similar results concerning the description of phase diagrams, the prediction of excess volumes and the influence of pressure on miscibility. Moreover, the cause of mixing and demixing, i.e. the influence of free volume and the effects of enthalpy, are predicted similarly by both models. Considering the fact that the foundations of the two models are entirely different, this seems surprising.

The PA theory is based on the Prigogine[3] corresponding-states theory, which is a cell model theory with a configurational partition function based on the Hirschfelder–Eyring partition function[4]. Flory *et al.*[5,6] gave a modified version of this theory, which we will call Prigogine–Flory (PF) theory.

From this starting point, Patterson *et al.*[7,8] derived a simpler EOS theory, which is formally identical with the Flory–Huggins theory, but whose interaction parameter also contains EOS contributions.

The EOS theory due to Sanchez and Lacombe[9,10] is a lattice-fluid theory. Formally it is similar to the Flory–Huggins theory, but a free-volume term is introduced via vacant lattice sites, thus making it an EOS theory. Its EOS does not satisfy a principle of corresponding states.

For the description of *PVT* data of polymers, both the PF (and therefore the PA theory) and the SL theory do not give good predictions of the behaviour for all pressure ranges[11,12]. They give better results for gases and supercritical fluids, which is probably due to their van der Waals-like potential energy dependence. If the *PVT* data are restricted to low pressures, however, they are described fairly well. Recently, the SL theory has also been successfully used for the description of the phase behaviour of homopolymer–copolymer blends[13].

THEORY

Patterson theory

In the PF theory, the quantities characterizing a liquid are the reduction parameters p^*, $v_s{}^*$ and T^*. They can be used to express the reduced pressure, volume and temperature, defined by:

$$\tilde{p} = \frac{p}{p^*} \quad \tilde{v} = \frac{v_s}{v_s^*} = \frac{v}{v^*} \quad \tilde{T} = \frac{T}{T^*} \tag{1}$$

Here p^* is the reduction pressure; T^* is the reduction temperature; v_s is the specific volume; v_s^* is the specific 'hard-core volume', i.e. the specific volume at 0 K; v and v^* are respectively the volume and the hard-core of a polymer segment. These relations are valid for both pure components and mixtures.

The reduced quantities are linked by the EOS. It is given by:

$$\frac{\tilde{p}\tilde{v}}{\tilde{T}} = \frac{\tilde{v}^{\frac{1}{3}}}{\tilde{v}^{\frac{1}{3}} - 1} - \frac{1}{\tilde{v}\tilde{T}} \tag{2}$$

and the reduction parametes are linked by:

$$p^* v^* = ckT^* \tag{3}$$

where $3c$ is the number of external degrees of freedom per segment.

For polymer mixtures, the quantities p^* and T^* are linked to those of the pure components, and an additional parameter X_{12}, the contact energy parameter, occurs. The sizes of the hard-core volumes for a segment can be chosen arbitrarily, and are assumed to be equal for both components, $v_1^* = v_2^* = v^*$. In the present work, the geometric mean of the value of the two monomeric units is chosen.

For $p = 0$, $\tilde{v}$ and $\tilde{T}$ are linked by the EOS. Both are a measure of the free volume of the liquid. They can be calculated from the thermal expansion coefficient α at $p = 0$[5].

$$\tilde{v}^{1/3} - 1 = \frac{\alpha T}{3(1 + \alpha T)} \tag{4}$$

and from the EOS at $p = 0$:

$$\tilde{T} = \frac{(\tilde{v}^{1/3} - 1)}{\tilde{v}^{4/3}} \tag{5}$$

For a binary mixture, the difference of free volume of the component is characterized by:

$$\tau = 1 - \frac{T_1^*}{T_2^*} \tag{6}$$

The paramters v_s^* and T^* can be dertermined from $\tilde{v}$, $\tilde{T}$ and v_s. Morover, p^* is obtained from:

$$p^* = \frac{\alpha}{\kappa}\tilde{v}^2 T \tag{7}$$

The stability condition of the PA theory is now given by:

$$2\chi < \frac{1}{r_1\Phi_1} + \frac{1}{r_2\Phi_2} \tag{8}$$

with the number r_i of segments per chain of component i, and the corresponding volume fraction Φ_i. (The segment and surface fractions appearing in the PF theory are set equal to the volume fractions.) Equation (8) is formally identical to the stability condition of Flory–Huggins theory. However, in this case, the χ parameter also takes into account non-combinatorial contributions. It consists of an interactional and free-volume contribution and reads[8]:

$$\chi = \frac{U_1\nu^2}{RT} + \frac{C_{p1}}{2R}\left(\tau + \frac{\kappa_1 p}{\alpha_1 T}\pi\right)^2 \tag{9}$$

where the first term represents the interactional part χ_i, and the second the free-volume part χ_f. Here α_1 and κ_1 are the expansion coefficient and compressibility of component 1 at pressure p respectively; U_1 is the internal energy of component 1; ν^2 is a measure of the relative weakness of the 1–2 contact to the average of 1–1 and 2–2 contacts; and C_{p1} is the configurational heat capacity of component 1. For the PF theory they are given by:

$$U_1 = -\frac{P_1^* V_1^*}{\tilde{v}_1} \tag{10}$$

$$\nu^2 = \frac{X_{12}}{P_1^*} \tag{11}$$

$$C_{p1} = \frac{p_1^* V_1^*}{T_1^*}\tilde{C}_{p1} \tag{12}$$

where V_1^* is the molar hard-core volume, X_{12} the contact energy parameter of the PF theory and:

$$\tilde{C}_{p1}^{-1} = \left(1 - \frac{2}{3}\tilde{v}_1^{-1/3}\right) - \frac{2\left(1 - \tilde{v}_1^{-1/3}\right)}{1 + \tilde{p}\tilde{v}_1^2} \tag{13}$$

Finally, π is given by:

$$-\pi = 1 - \frac{P_1^*}{P_2^*} \tag{14}$$

The meaning of π is not as obvious as that of τ. However, we note that for the special case of $c_1 = c_2$, it can be deduced from equation (3) that $\pi = -\tau$. Moreover, the second part in the brackets of equation (9) can be expressed as:

$$\frac{\kappa p}{\alpha T} = \frac{\tilde{p}\tilde{v}^2}{1 + \tilde{p}\tilde{v}^2} \tag{15}$$

Sanchez–Lacombe theory

The SL theory is a lattice-fluid theory. Besides occupied lattice sites, it also comprises holes, i.e. vacant lattice sites. A binary system is formally treated as a three-component system, where the third component is represented by the holes. Hole–hole and hole–mer interactions are assigned a zero energy, to that there remains only one interaction parameter χ_{SL}—as in the Flory–Huggins theory. As in the PF theory, a liquid is characterized by three reduction parameters p^*, v_s^* and T^*. Again v_s^* is the specific hard-core volume, which in this case represents the specific volume of the occupied lattice sites.

In analogy to equation (1), reduced quantities can be defined according to:

$$\tilde{p} = \frac{p}{p^*} \quad \tilde{v} = \frac{v_s}{v_s^*} = \frac{N_0 + rN}{rN} \quad \tilde{T} = \frac{T}{T^*} \tag{16}$$

with the number N_0 of vacancies, and $rN = r_1N_1 + r_2N_2$ the number of occupied lattice sites. N_i is the number of molecules of component i, r_i the corresponding number of mers per chain and $N = N_1 + N_2$ the total number of polymer chains.

The EOS of this model is given by:

$$\frac{1}{\tilde{v}^2} + \tilde{p} + \tilde{T}\left[\ln\left(1 - \frac{1}{\tilde{v}}\right) + \left(1 - \frac{1}{r}\right)\frac{1}{\tilde{v}}\right] = 0 \tag{17}$$

and the reduction parameters are connected by

$$p^* v^* = kT^* \tag{18}$$

Again, the quantities p^* and T^* of a mixture are related to those of the pure components, and the interaction parameter χ_{SL}. However, the volume v^* of a lattice site is fixed; it cannot be chosen arbitrarily in this model. It turns out to have only about 10–20% of the volume of a monomer unit. The size of the sites of a mixture is an average of those of the pure components, and depends on composition. Hence, the number r_i of lattice sites occupied by one molecule in the mixture also differs from the number r_i° of occupied sites in the pure system.

For vanishing pressure and infinite chain length, the reduced variables $\tilde{v}$ and $\tilde{T}$ are linked by the EOS. As for the PF theory, both quantities are a measure of free volume, and can be calculated from the thermal expansion coefficient for $p = 0$[14].

$$\alpha T = \frac{1}{\tilde{T}/(1 - 1/\tilde{v}) - 2} \tag{19}$$

and the EOS at $p = 0$:

$$\frac{1}{\tilde{v}^2} + \tilde{T}\left[\ln\left(1 - \frac{1}{\tilde{v}}\right) + \frac{1}{\tilde{v}}\right] = 0 \tag{20}$$

However, these equations cannot be solved explicitly for the desired variables, so they have to be solved numerically. From $\tilde{v}$, $\tilde{T}$ and v_s, v_s^* and T^* can be obtained and p^* is obtained from:

$$p^* = \frac{\alpha}{\kappa}\tilde{v}^2 T \tag{21}$$

The intermolecular energy U of the system can be expressed as:

$$U = -rN\frac{\epsilon^*}{\tilde{V}} \tag{22}$$

with

$$\epsilon^* = \Phi_1\epsilon_{11}^* + \Phi_2\epsilon_{22}^* + \Phi_1\Phi_2 kT\chi_{SL} \tag{23}$$

and

$$\chi_{SL} = (\epsilon_{11}^* + \epsilon_{22}^* - 2\epsilon_{12}^*)/kT \tag{24}$$

where ϵ_{ij}^* is the mean interaction energy of a mer of component i with its neighbouring mer of component j. χ_{SL} is the analogue of the χ parameter of the original Flory–Huggins theory and Φ_i is the hard-core volume fraction.

U can be put in the form:

$$U = -\frac{p^* V^*}{\tilde{v}} \tag{25}$$

which is formally the same as for the PF theory.

The stability condition obtained from this theory is given by[10,14]:

$$\frac{1}{\tilde{v}}\{2[(\Phi_1 + v\Phi_2)\chi_{SL} + (1 - v)\lambda_{12}] + \tilde{T}\Psi^2 p^*\kappa \\ (\Phi_1 + v\Phi_2)\} < \frac{1}{r_1^0\Phi_1} + \frac{v}{r_2^0\Phi} \tag{26}$$

with

$$\lambda_{12} = \frac{1}{\tilde{T}_1} - \frac{1}{\tilde{T}_2} + (\Phi_1 - \Phi_2)\chi_{SL} \tag{27}$$

$$\Psi = \frac{\lambda_{12}}{\tilde{v}} - \frac{v}{(\Phi_1 + v\Phi_2)^2}\left(\frac{1}{r_1^0} - \frac{1}{r_2^0}\right) \\ + \frac{\tilde{p}\tilde{v}}{\tilde{T}}\frac{(v - 1)}{(\Phi_1 + v\Phi_2)} \tag{28}$$

and the ratio

$$v = \frac{v_1^*}{v_2^*} \tag{29}$$

which for $v \neq 1$ corresponds to the introduction of a surface area effect[10].

This stability condition for the SL theory can be formulated similarly to the one of PA theory[1]. In analogy to the χ parameter of the PA theory, a parameter Λ consisting of three parts an be defined:

$$\Lambda = \Lambda_\chi + \Lambda_s + \Lambda_f \tag{30}$$

with

$$\Lambda_\chi = \frac{1}{\tilde{v}}(\Phi_1 + v\Phi_2)\chi_{SL}$$

$$\Lambda_s = \frac{1}{\tilde{v}}(1 - v)\lambda_{12} \tag{31}$$

$$\Lambda_f = \frac{1}{2\tilde{v}}\tilde{T}\Psi^2 p^*\kappa(\Phi_1 + v\Phi_2)$$

The stability condition then assumes the form:

$$2\Lambda < \frac{1}{r_1^0\Phi_1} + \frac{v}{r_2^0\Phi_2} \tag{32}$$

The first term Λ_χ is an interactional term, the second term Λ_s arises from the surface area effect, hence it is also an interactional term, and Λ_f is due to the introduction of free volume. As can be seen, λ_{12} and χ_{SL} have the same temperature dependence. Therefore, it is clear that both interactional terms have the same temperature dependence; they are proportional to $1/(\tilde{v}T)$. The same temperature dependence is exhibited by the interactional term of the PA theory. However, in contrast to the χ parameter of the PA theory, the parameter Λ depends on composition and on the chain lengths of the components.

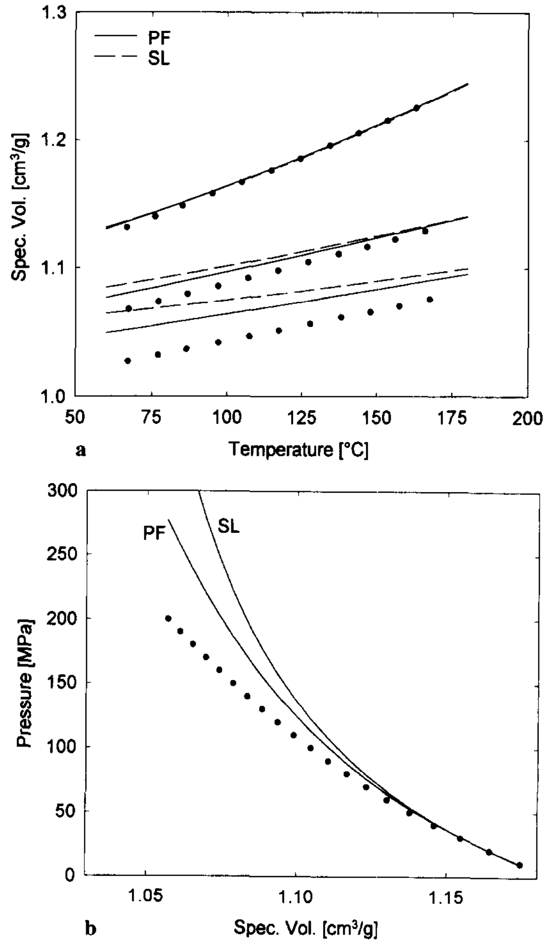

Figure 1 Description of *PVT* data (●) of low-molecular-weight polyisoprene (PI) by EOS theories: (a) v_s vs. T; (b) p vs. v_s. SL theory (—): $p^* = 383$ MPA, $v_s^* = 1.0405\,\mathrm{cm^3\,g^{-1}}$, $T^* = 631.2\,\mathrm{K}$. PF theory (—): $p^* = 469.7$ MPa, $v_s^* = 0.9396\,\mathrm{cm^3\,g^{-1}}$, $T^* = 6713\,\mathrm{K}$ (refs 1, 2)

DESCRIPTION OF *PVT*-DATA BY THE PF AND SL THEORY

In *Figure 1a*, the specific volume of a low-molecular-weight polyisoprene ($M_n = 2600 \text{ g mol}^{-1}$, $M_w/M_n = 1.08$) as a function of temperature is shown for pressures of 0, 100 and 200 MPa (downwards) respectively. The dots represent experimental data, the full lines are calculated with PF theory and the dashed lines are calculated with SL theory. The reduction parameters were calculated at $p = 0$ with equations (4) and (5) and equations (19) and (20) respectively. Their determination is described more fully in ref. 1. In *Figure 1a* it can be seen that for low pressures the data are described well by both theories. For lower temperatures v_s is predicted somewhat too high; for higher temperatures it fits the data very well. This means that the expansion coefficient for lower temperatures is predicted too low. The value given by SL theory is even lower than that given by PF theory. However, for higher temperatures it is the converse, the coefficient of expansion predicted by SL theory is higher than that predicted by PF theory.

For higher pressures the experimental and calculated data disagree. The deviation from experimental data is much higher for SL theory than for PF theory. This can also be seen from *Figure 1b*, where pressure vs. specific volume is shown at 125°C. Again, for low pressures the agreement between experiment and theory is fairly good. The higher the pressure, the higher is the deviation from experiment, but the description of PF theory is superior to the one of SL theory.

However, one can state that both theories exhibit the same principal behaviour concerning the description of *PVT* data.

RESULTS

At first glance, Λ (in particular Λ_f) seems to be entirely different from the corresponding expression of χ. Therefore, the similarities exhibited by numerical calculations seem surprising.

To gain deeper insight, we consider Λ_f for the special case of $\Phi_1 = \Phi_2$, $v = 1$ and $r_1^0 = r_2^0$. Then λ_{12} and Ψ reduce to:

$$\lambda_{12} = \frac{1}{T}(T_1^* - T_2^*) \tag{33}$$

$$\Psi = \frac{\lambda_{12}}{\tilde{v}} \tag{34}$$

and hence Λ_f reads:

$$\Lambda_f = \frac{p^*\kappa}{\tilde{v}^3 T 2T^*}(T_1^* - T_2^*)^2 \tag{35}$$

The goal is now to show that it is possible to get equation (35) into a form that is similar to the free-volume term of the PA χ parameter. To this end, we consider the heat capacity C_p of a system with volume V and energy U, which is given by:

$$C_p = \left[\left(\frac{dU}{dV}\right)_T + p\right]\alpha V \tag{36}$$

Differentiating the energy given by equation (25) with respect to V, and inserting the result into equation (36) yields:

$$C_p = \frac{\alpha p^* V^*}{\tilde{v}}(1 + \tilde{p}\tilde{v}^2) \tag{37}$$

As in the case of the PA theory, we assume that $V^* = N_A v^*$ is the molar hard-core volume. Equation (18) then yields:

$$p^* V^* = RT^* \tag{38}$$

(N_A is the Avogadro number and R the gas constant). Moreover, the relation:

$$\frac{\kappa p}{\alpha T} = \frac{\tilde{p}\tilde{v}^2}{1 + \tilde{p}\tilde{v}^2} \tag{39}$$

is valid, which is the same as equation (15) in PF theory. From this:

$$p^*\kappa = \frac{\alpha \tilde{v}^2 T}{1 + \tilde{p}\tilde{v}^2} \tag{40}$$

is obtained. By solving equation (37) for α and inserting into equation (40), the following result can be obtained:

$$\frac{p^*\kappa}{\tilde{v}^3 T} = \frac{C_p}{RT^*}\frac{1}{(1 + \tilde{p}\tilde{v}^2)^2} = \frac{C_p}{RT^*}\left(1 - \frac{\kappa p}{\alpha T}\right)^2 \tag{41}$$

Inserting into equation (35), this yields for Λ_f:

$$\Lambda_f = \frac{C_p}{2R}\left(\frac{T_1 - T_2^*}{T^*}\right)^2\left(1 - \frac{\kappa p}{\alpha T}\right)^2 \tag{42}$$

Compared with χ_f from the PA theory, it can be seen

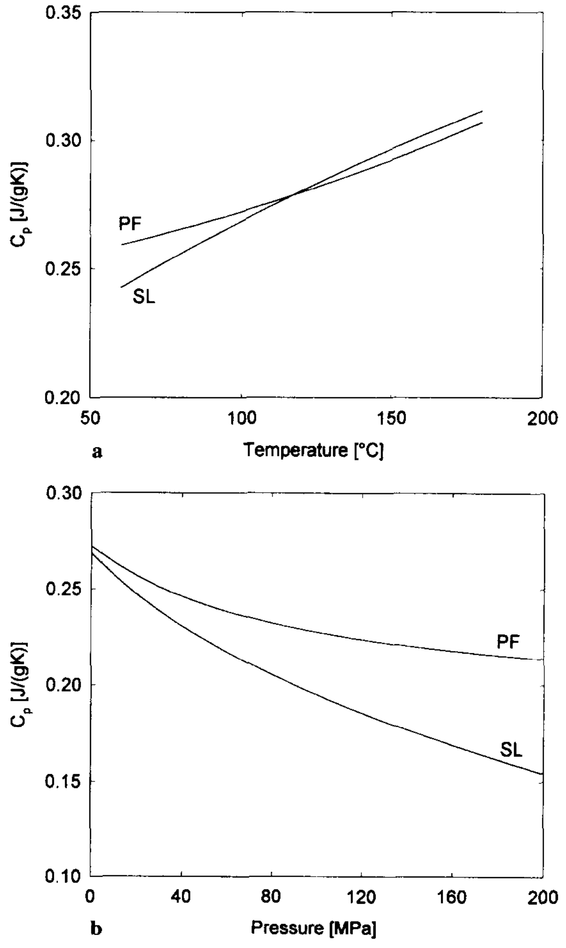

Figure 2 Specific heat capacity of PI predicted by SL and PF theory: (a) as a function of temperature; (b) as a function of pressure

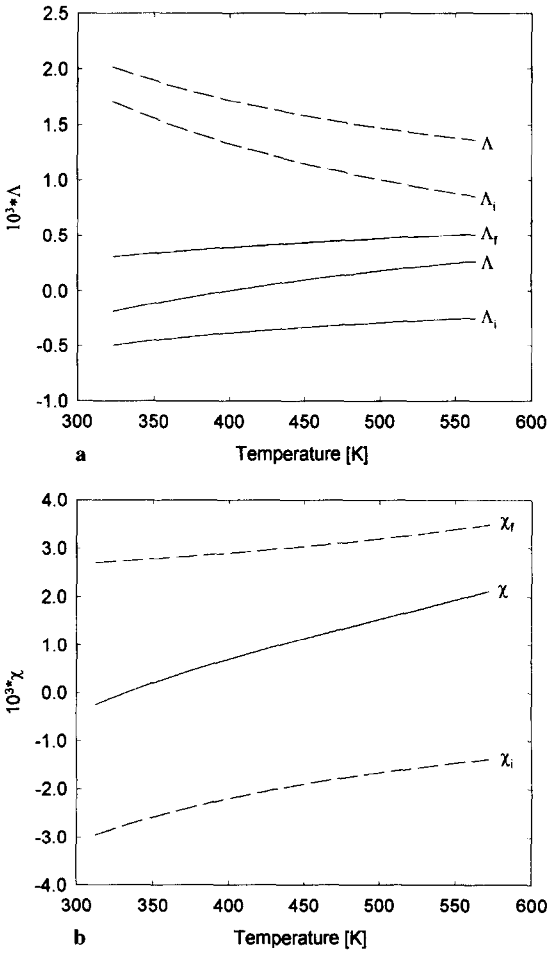

Figure 3 Temperature dependence of the various contributions of (a) Λ and (b) χ for a compatible system (see text). SL theory (a): $p_1^* = 428.1\,\mathrm{MPa}$, $v_{s1}^* = 0.9232\,\mathrm{cm^3\,g^{-1}}$, $T_1^* = 796.3\,\mathrm{K}$ (PS); $p_2^* = 417.6$ MPa, $v_{s2}^* = 0.862\,\mathrm{cm^3\,g^{-1}}$, $T_2^* = 760.8\,\mathrm{K}$ (PCHMA); $\chi_{SL} T +$ 0.57633 K. PF theory (b): $p_1^* = 522.6\,\mathrm{MPa}$, $v_{s1}^* = 0.8356\,\mathrm{cm^3\,g^{-1}}$, $T_1^* = 8508\,\mathrm{K}$; $p_2^* = 511.4$ MPa, $v_{s2}^* = 0.7791\,\mathrm{cm^3\,g^{-1}}$, $T_2^* = 8115\,\mathrm{K}$; $X_{12} = -0.1\,\mathrm{J\,cm^{-3}}$ (refs 1, 2)

that for the case $\pi = -\tau$ in the PA theory both free-volume terms look in fact very similar; τ in the PA theory corresponds to $(T_1^* - T_2^*)/T^*$ in the SL theory. Another difference is the fact that C_p and the state variables appearing in the free-volume terms of SL theory (equation (42)) refer to the 50/50 mixture, whereas those of the PA theory refer to component 1. The latter is due to the fact that χ from the PA theory is derived from a series expansion about $\tilde{T}_1$. However, since the principal behaviour of the v–T and p–v curves is the same for both models and for all compositions, the same should be true for α, κ and C_p.

The heat capacity of the SL theory can be expressed similarly to the one of PF theory.

$$C_p = \frac{p^* V^*}{T^*} \tilde{C}_p \tag{43}$$

where $\tilde{C}_p$ is given by:

$$\tilde{C}_p = \frac{(1 + \tilde{p}\tilde{v}^2)^2}{\tilde{v}\tilde{T}\{\tilde{v}\tilde{T}[1/(\tilde{v} - 1) + 1/r] - 2\}} \tag{44}$$

The heat capacities predicted by the two theories as a function of temperature (at $p = 0$) and pressure (at $T = 100°\mathrm{C}$) are shown in *Figures 2a* and *2b* respectively. The C_p values given in equations (12) and (43) respectively are molar heat capacities, i.e. they refer to one mole of segments. However, the sizes of the lattice sites of the two theories are different. So, in order to be able to compare the results of both models, the specific heat capacities are calculated.

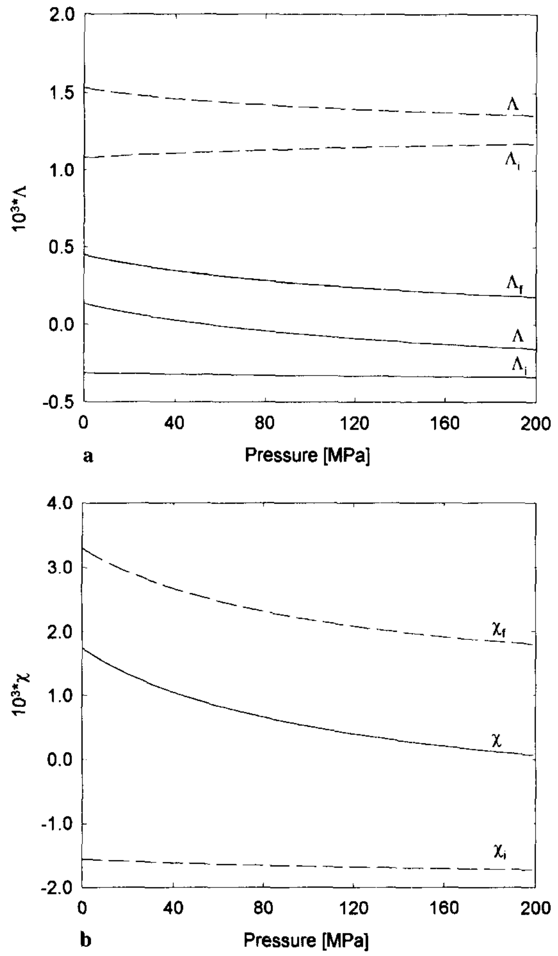

Figure 4 Pressure dependence of the various contributions of (a) Λ and (b) χ (see text). The same parameters are used as in *Figure 3*

Since the expansion coefficient predicted by SL theory is lower for low temperatures and higher for high temperatures than predicted by PF theory, the same is true for the heat capacity. SL theory also predicts a greater influence of pressure on heat capacity than PF theory. However, as one expects, the principal behaviour is predicted to be the same by both theories. Therefore the temperature and pressure dependences of Λ_f and χ_f should be very similar.

DISCUSSION

In order to be able to derive equation (42), some assumptions were necessary. Now, we want to examine how the results change when these assumptions are relaxed. One of the assumptions was that both components have equal chain lengths in their pure states; another one was the neglect of the surface area effect.

First we note that only the reciprocal of the chain lengths r_i° enters into the equations. Therefore, for sufficiently long chains, it is a good approximation to neglect this term. Moreover, for vanishing or low pressures, the value of v is not important either. Hence, the essential difference to the PA theory which remains is the concentration dependence of Λ_f. However, the PA theory is derived from a series expansion, where higher-order terms are neglected. By keeping these higher-order terms, the χ parameter of PA theory would be concentration-dependent as well.

According to the statements above, for low pressure the exact and the approximate value of Λ_f should be very similar. This is demonstrated in *Figure 3a*, where Λ for a compatible polymer pair (polystyrene (PS), $M_n = 230\,000\,\mathrm{g\ mol^{-1}}$, $M_w/M_n = 1.11$ and poly(cyclohexyl methacrylate) (PCHMA), $M_n = 114\,000\,\mathrm{g\ mol^{-1}}$, $M_w/M_n = 1.26$) is shown as a function of temperature for $p = 0$ and $\Phi_2 = 0.5$. The dashed lines represent the curves for $v = 1$ and $r_1{}^\circ = r_2{}^\circ$, and the full lines give the exact values. It can be seen that the approximate and the exact Λ_f basically coincide.

For the case of $v = 1$, the interactional parts $\Lambda_i = \Lambda_\chi + \Lambda_s$ of Λ ($\Lambda_s = 0$ for $v = 1$) can be put in a form that formally corresponds to that of χ_i. However, the results obtained in this way differ appreciably from the exact values, as can be seen from *Figure 3a*. They differ not only in magnitude, but also in sign. Therefore, their predictions would be totally different, in this case complete immiscibility would be predicted. This means that the surface area effect must not be neglected.

The χ parameter for the same system is shown in *Figure 3b*. All three curves show a similar behaviour as the corresponding exact Λ. Therefore, only when the surface area effect in SL theory is included does it yield the same results as PA theory, where no surface area effects have been considered. Its influence on the free-volume term, however, is negligible.

The influence of pressure on Λ is shown in *Figure 4a*. Again, the dashed lines give the results for $v = 1$ and $r_1^0 = r_2^0$, and the full lines give the exact value. It can be seen that even for higher pressures the exact and the approximate value of Λ_f agree. The value of v obtained for this system is $v = 1.0211$. However, calculations show that, even for values which differ appreciably from 1, the picture hardly changes.

Therefore, the expression in equation (42), derived for a special case, is except for the neglect of the concentration dependence, a good approximation. However, this concentration dependence only leads to other symmetries of the phase diagrams; it does not change the principal behaviour. Finally, *Figure 4b* shows the pressure dependence of χ, which is similar to that of the corresponding Λ.

CONCLUSIONS

It could be shown that for a special case the free-volume term of the stability condition of the SL theory can be put into an analytically similar form as the free-volume part of the PA theory. Moreover, numerical calculations have shown that this special case is a good approximation for the more general case. The pressure- and temperature-dependent quantities appearing in this term can all be expressed by reduced state variables.

Now, the description of *PVT* behaviour of polymers is—at least qualitatively—very similar by both the SL and the PF theory. Therefore, the fact that the pressure and temperature dependences of the free-volume term are predicted to be similar by both models is not surprising any more.

The dependence of the interactional parts on temperature and pressure is also similar for both models. However, the neglect of the surface area effect, which can be made in the free-volume part of SL theory, must not be made in the interactional part. It would completely change the behaviour. This is what one expects, because the energy of a system is influenced by the number of interactions per mer. The fact that the pressure and temperature dependences of the interactional term are predicted similarly by both models might be expected, since both terms are proportional to $1/\tilde{v}T$.

REFERENCES

1 Rudolf, B. and Cantow, H.-J. *Macromolecules* submitted

2 Rudolf, B. and Cantow, H.-J. *Macromolecules* submitted

3 Prigogine, I. 'The Molecular Theory of Solutions', North-Holland, Amsterdam, 1959

4 Eyring, H. and Hirschfelder, J. O. *J. Phys. Chem* 1937, **41**, 249

5 Flory, P. J., Orwoll, R. A. and Vrij, A. *J. Am. Chem. Soc.* 1964, **86**, 3507

6 Flory, P. J. *J. Am. Chem. Soc.* 1965, **87**, 1833

7 Patterson, D. *J. Polym. Sci. (C)* 1968, **16**, 3379

8 Patterson, D. and Delmas, G. *Trans. Faraday Soc.* 1969, **65**, 708

9 Sanchez, I. C. and Lacombe, R. H. *J. Phys. Chem.* 1976, **80**, 2352

10 Lacombe, R. H. and Sanchez, I. C. *J. Phys. Chem.* 1976, **80**, 2568

11 Dee, G. T. and Walsh, D. J. *Macromolecules* 1988, **21**, 811

12 Dee, G. T. and Walsh, D. J. *Macromolecules* 1988, **21**, 815

13 Gan, P. P., Paul, D. R. and Padwa, A. R. *Polymer* 1994, **35**, 1487

14 Sanchez, I. C. in 'Polymer blends' (Eds D. R. Paul and S. Newman), Academic Press, New York, 1978, Ch. 3