

# Influence of the lattice site size in cell model theories on the prediction of thermodynamic properties of polymers and their mixtures

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Model calculations with the equation of state theories of Prigogine and Simha *et al.* were performed to investigate the influence of the lattice site size on the predicted thermodynamic properties. In these theories, as well as in some other equation of state theories, this quantity can be chosen arbitrarily, but it turns out that some properties of the theories depend appreciably on that choice. The theory of Simha *et al.* contains an equilibrium condition which serves to determine the fraction of occupied lattice sites. This condition contains the quantity  $3c/r$ , where  $3c$  is the number of degrees of freedom per chain, and  $r$  the number of segments per chain. It is common practice to set this quantity equal to unity, thus fixing the lattice site size. In the present work, it is also investigated how different choices for the lattice site size alter the description of pressure–volume–temperature (PVT) data of polymers. It turns out that for the theory of Simha *et al.*, the reduction parameters of the polymers strongly depend on this choice, but the description of PVT behaviour and the prediction of free volume is almost independent of this choice. The prediction of phase behaviour of binary blends, however, can completely change when different choices for this quantity are made. It turns out that this change occurs in a way very similar to that of the Prigogine theory, in spite of the fact that the reduction parameters of the latter do not change. It seems that only the ratio of the lattice site volumes is important, not, however, their absolute size. © 1997 Elsevier Science Ltd.

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## INTRODUCTION

When working with the cell model theories which are based on the Hirschfelder–Eyring<sup>1</sup> partition function, one is dealing with the problem of how to fix the size of a lattice site. Usually, in the theories which are applied mostly nowadays (i.e. the theory of Flory *et al.*<sup>2</sup>, the modified cell model of Dee and Walsh<sup>3,4</sup>, and also in the lattice fluid theory of Sanchez and Lacombe<sup>5,6</sup> (SL)), for the sake of simplicity the hard core volume for multi-component systems is chosen to be the same for all components. (In SL theory the sizes are usually different for the pure components, but a simple mixing rule is applied to have the same lattice site size for both components in the mixture.) If certain rules are obeyed, in these cell models the descriptions or predictions of the thermodynamic behaviour of polymer blends do not depend on this choice. Moreover, the equation of state (EOS) and its parameters do not depend on this choice either.

In the case of the cell model of Prigogine<sup>7</sup> and the Simha–Somcynsky<sup>8–10</sup> (SS) theory, a mixing rule is applied to determine the hard-core volume  $v^*$  of a lattice site of the mixture from those of the pure components. This mixing rule is derived from the use of a 6-12 Lennard–Jones potential and at the same time serves to determine the average interaction energy  $\varepsilon^*$  between the chain segments. It is given by the following two equations:

$$\begin{aligned} \varepsilon^* v^{*2} &= X_1^2 \varepsilon_{11}^* v_{11}^{*2} + 2X_1 X_2 \varepsilon_{12}^* v_{12}^{*2} + X_2^2 \varepsilon_{22}^* v_{22}^{*2} \\ \varepsilon^* v^{*4} &= X_1^2 \varepsilon_{11}^* v_{11}^{*4} + 2X_1 X_2 \varepsilon_{12}^* v_{12}^{*4} + X_2^2 \varepsilon_{22}^* v_{22}^{*4} \end{aligned} \quad (1)$$

where  $\varepsilon_{ij}^*$  is the interaction energy between chain segments of component  $i$  and  $j$ ,  $v_{ii}^* = v_i^*$  is the hard-core volume of a segment of component  $i$ ,  $v_{12}^*$  is an average of the two pure components' segmental hard-core volume and the  $X_i$  are site fractions of component  $i$ .

This mixing rule does not tell one, however, how to fix the lattice sites of the pure components. When all the  $v_{ij}^*$  are equal, however (e.g. by simply fixing them, or by first averaging the  $v_i^*$  for the mixture — depending on the theory under consideration), the two equations coincide and a simple mixing rule is obtained. It was already shown before that, in this case, the cell model theories and the SL and SS theories give very similar results<sup>11–13</sup>. In the present work, we want to show that by choosing the size of the lattice sites in the same way for SS and Prigogine theory, both theories give similar results as well. In the following, we will see how different choices of segment size alter the reduction parameters, the predicted number of degrees of freedom in SS theory and the prediction of phase behaviour (spinodal) of binary polymer blends for both theories.

## THEORY

The Helmholtz free energy  $F$  of the EOS theory of Prigogine is given by<sup>7</sup>:

$$\begin{aligned} \frac{F}{N} &= -ckT[\ln v^* + 3 \ln(\bar{v}^{1/3} - 2^{-1/6})] \\ &+ \frac{qz\varepsilon^*}{2} \left[ \frac{1.011}{\bar{v}^4} - \frac{2.409}{\bar{v}^2} \right] \end{aligned} \quad (2)$$

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From equation (2) the following EOS can be derived

$$\frac{\bar{p}\bar{v}}{\bar{T}} = \frac{\bar{v}^{1/3}}{\bar{v}^{1/3} - 2^{-1/6}} + \frac{2}{\bar{T}\bar{v}^2} \left[ \frac{1.011}{\bar{v}^2} - 1.2045 \right] \quad (3)$$

which is independent of the size of the lattice site. In equations (2) and (3),  $N$  is the number of polymer chains,  $3c$  is the number of degrees of freedom per chain,  $\bar{v} = v_{sp}/v_{sp}^*$  is the reduced volume ( $v_{sp}$  and  $v_{sp}^*$  are specific volume and specific hard-core volume respectively)  $\bar{p} = p/p^*$  and  $\bar{T} = T/T^*$  are reduced pressure and temperature,  $p^*$  and  $T^*$  are reduction pressure and reduction temperature, respectively. They are defined by

$$p^* = \frac{qz\varepsilon^*}{rv^*} \quad T^* = \frac{qz\varepsilon^*}{ck} \quad (4)$$

Since equation (3) is independent of  $v^*$ , these reduction parameters as well as  $v_{sp}^*$  do not depend on  $v^*$  either. This means that the same is true for the hard-core volume  $Mv_{sp}^* = rv^*$  per chain ( $M =$  mass per chain,  $r =$  number of segments per chain). For  $c$  the following relation holds

$$c = \frac{p^*rv^*}{kT^*} \quad (5)$$

hence  $c$  is also independent of the chosen size of  $v^*$ . Therefore, upon changing  $v^*$ , the quantities  $r$ ,  $qz = r(z - 2) + 2$  ( $z =$  coordination number, a value of  $z = 12$  will be used) and  $\varepsilon^*$  change correspondingly to keep the reduction parameters constant.

In the term containing the potential energy in equation (2),  $qz$  is used to sum over all contributions from one chain. This is to take account of the end effects, and is only important for very short chains. If this end effect is neglected and instead of  $qz$  one uses simply  $r(z - 2)$ ,  $\varepsilon^*$  would be directly proportional to  $v^*$  (the same is true for the theory of Flory *et al.* and the theory of Dee and Walsh, where  $rs$  is used,  $s$  being a measure of molecular surface). For sufficiently long chains, however, the difference between  $qz$  and  $r(z - 2)$  is very small. It can, however, be seen that the potential energy expression is independent of the choice of lattice site size. However, due to the term  $\ln v^*$ , the free energy expression depends on that choice (Since most thermodynamic quantities are derived from  $F$  by differentiation, this usually does not matter).

The foundations of SS theory are similar to those of the Prigogine theory. The lattice includes however also vacant sites. The Helmholtz free energy is then given by<sup>8-10</sup>

$$\begin{aligned} \frac{F}{N} = & rkT \left[ \frac{(1-y)}{y} \ln(1-y) + \frac{1}{r} \ln y \right] \\ & - ckT \left[ \ln v^* + 3 \ln((y\bar{v})^{1/3} - 2^{-1/6}y) \right] \\ & + \frac{yqz\varepsilon^*}{2} \left[ \frac{1.011}{(y\bar{v})^4} - \frac{2.409}{(y\bar{v})^2} \right] \end{aligned} \quad (6)$$

and leads to the following EOS, consisting of two equations

$$\frac{\bar{p}\bar{v}}{\bar{T}} = \left[ 1 - 2^{-1/6}y(y\bar{v})^{-1/3} \right]^{-1} + \frac{2y}{\bar{T}(y\bar{v})^2} \left[ \frac{1.011}{(y\bar{v})^2} - 1.2045 \right] \quad (7)$$

$$\begin{aligned} & \frac{r}{3c} \left[ \frac{r-1}{r} + \frac{1}{y} \ln(1-y) \right] - \frac{2^{-1/6}y(y\bar{v})^{-1/3} - \frac{1}{3}}{1 - 2^{-1/6}y(y\bar{v})^{-1/3}} \\ & - \frac{y}{6\bar{T}(y\bar{v})^2} \left[ 2.409 - \frac{3.033}{(y\bar{v})^2} \right] = 0 \end{aligned} \quad (8)$$

where  $y$  is the fraction of occupied lattice sites. It can be seen that the first term of equation (6) (due to the combinatorial energy) depends on the size of the lattice sites, for the free volume term and the potential energy term the same holds as in Prigogine theory. Also the reduction parameters are defined in the same way (equation (4)). Moreover, for  $c$  the same relation (equation (5)) as in Prigogine theory holds.

As mentioned above, when using the EOS of this theory, one is dealing with two equations. One is the actual EOS (equation (7)), which also depends on  $y$ , the fraction of occupied lattice sites. To obtain  $y$ , an additional equation (equation (8)) is required. This is obtained by the condition that in thermodynamic equilibrium  $y$  will adjust itself so as to minimise the free energy.

This equilibrium condition (equation (8)), however, depends not only on the reduced variables of state, but also on the number of segments per chain  $r$  and the quantity  $3c/r$  where  $3c$  is the number of degrees of freedom per chain. These quantities are in general different for different polymers, therefore, this EOS generally does not satisfy a principle of corresponding states. However, it is common practice to set the quantity  $3c/r$  equal to one. Moreover, for polymers of sufficiently long chain lengths, the corresponding term (first term in first bracket on the l.h.s. of equation (8)) in the equilibrium condition is equal to unity. In this case, the EOS obeys a principle of corresponding states. This means that there is a unique functional relationship  $f$  between the reduced variables of state, i.e.  $f(\bar{p}, \bar{v}, \bar{T}) = 0$ . The reduction parameters for different substances obtained in this way, show similar tendencies as those found for other EOS theories. This means, for example, that for all these theories  $p^*$  depends in a similar way on the expansion coefficient and compressibility, and  $T^*$  depends in a similar way on the expansion coefficient and is independent of compressibility. Similarly the quantity  $\tau = 1 - T_1^*/T_2^*$  defined by Patterson<sup>14</sup> gives information about free volume differences of two polymers.

By fixing the quantity  $3c/r$ ,  $v^*$ , the hard-core volume of a chain segment and thus the size of the segment itself is fixed as well. This means that, in contrast to other cell model theories, it cannot be chosen arbitrarily. When choosing  $3c/r = 1$ , this chain segment is in general much smaller than a monomer unit. However, instead of fixing  $3c/r$ , we can assign a certain value to  $v^*$  and substitute a corresponding expression for  $3c/r$  (via equation (5)). Then, however, the equilibrium condition will generally be different for different substances, implying that the functional relationship between the reduced variables of state is also different. This essentially means that they obey different EOSs.

For other EOS theories where the segment size can be chosen arbitrarily, the choice of  $v^*$  does not influence the EOS or the reduction parameters. For SS theory, however, it is expected that this choice influences the values of the reduction parameters. From equation (5) it can be seen that  $c$  should be independent of the size of the lattice site. For SS theory it turns out, however, due to the dependence of the reduction parameters on the lattice site size, that this is not the case.

To deal with mixtures, we need the free energy of mixing. For the Prigogine theory it is given by

$$\begin{aligned} \frac{\Delta F}{N} = & kT[x_1 \ln \Phi_1 + x_2 \ln \Phi_2] \\ & + kT \left\{ x_1 c_1 \left[ \ln \frac{v_1^*}{\bar{v}^*} + 3 \ln \left( \frac{\bar{v}_1^{1/3} - 2^{-1/6}}{\bar{v}^{1/3} - 2^{-1/6}} \right) \right] \right. \\ & \left. + x_2 c_2 \left[ \ln \frac{v_2^*}{\bar{v}^*} + 3 \ln \left( \frac{\bar{v}_2^{1/3} - 2^{1/6}}{\bar{v}^{1/3} - 2^{-1/6}} \right) \right] \right\} \\ & + \frac{qz\varepsilon^*}{2} \left[ \frac{1.011}{\bar{v}^4} - \frac{2.409}{\bar{v}^2} \right] - \frac{x_1 q_1 z \varepsilon_1^*}{2} \left[ \frac{1.011}{\bar{v}_1^4} - \frac{2.409}{\bar{v}_1^2} \right] \\ & - \frac{x_2 q_2 z \varepsilon_2^*}{2} \left[ \frac{1.011}{\bar{v}_2^4} - \frac{2.409}{\bar{v}_2^2} \right] \end{aligned} \quad (9)$$

where  $x_i = N_i/N$  ( $N = N_1 + N_2$ ) is the mole fraction of component  $i$ ,  $qz$  is calculated from  $qz = r(z - 2) + 2$  where  $r$  is calculated from the condition that the hard-core volume of the mixture is equal to the sum of the hard-core volumes of the components.

$$rNv^* = r_1 N_1 v_1^* + r_2 N_2 v_2^* \quad (10)$$

By using the definition for  $r$  which is usually applied ( $r = x_1 r_1 + x_2 r_2$ ), the hard-core volume is not conserved upon mixing, unless  $v_1^* = v_2^*$ . The  $\Phi_i$  are the hard-core volume fractions defined by

$$\Phi_i = \frac{r_i N_i v_i^*}{r_1 N_1 v_1^* + r_2 N_2 v_2^*} \quad (11)$$

(it should be noted that the  $r_i$  are the number of segments per chain in the pure state, in the mixture it is given by  $r_i v_i^*/v^*$ ). This means that  $\Phi_i$  defined by equation (11) and expressed via quantities of the mixtures reduces to the usual expression which is used to calculate the combinatorial entropy).

It can be seen that for  $v_1^* = v_2^*$  the free energy of mixing is indeed independent of the size of  $v_i^*$ . (Apart from the factor  $qz\varepsilon^*$ , which due to the non-proportionality between  $\varepsilon^*$  and  $v^*$ , depends on that choice. Again, however, for sufficiently long chains this can be neglected.) For the case of  $v_1^* \neq v_2^*$  only the ratio  $v_1^*/v_2^*$  is important, not, however, the absolute values of the  $v_i^*$  (again for sufficiently long chains).

The free energy of mixing of SS theory is given by

$$\begin{aligned} \frac{\Delta F}{N} = & kT \left[ x_1 \ln \Phi_1 + x_2 \ln \Phi_2 + \frac{r(1-y)}{y} \ln(1-y) + \ln y \right] \\ & - x_1 kT \left[ \frac{r_1(1-y_1)}{y_1} \ln(1-y_1) + \ln y_1 \right] \\ & - x_2 kT \left[ \frac{r_2(1-y_2)}{y_2} \ln(1-y_2) + \ln y_2 \right] \\ & + x_1 c_1 kT \left[ \ln \frac{v_1^*}{\bar{v}^*} + 3 \ln \left( \frac{((y_1 \bar{v}_1)^{1/3} - 2^{-1/6} y_1)}{(y \bar{v})^{1/3} - 2^{-1/6} y)} \right) \right] \\ & + x_2 c_2 kT \left[ \ln \frac{v_2^*}{\bar{v}^*} + 3 \ln \left( \frac{((y_2 \bar{v}_2)^{1/3} - 2^{-1/6} y_2)}{(y \bar{v})^{1/3} - 2^{-1/6} y)} \right) \right] \\ & + \frac{yqz\varepsilon^*}{2} \left[ \frac{1.011}{(y \bar{v})^4} - \frac{2.409}{(y \bar{v})^2} \right] - \frac{x_1 y_1 q_1 z \varepsilon_1^*}{2} \left[ \frac{1.011}{(y_1 \bar{v}_1)^4} \right. \\ & \left. - \frac{2.409}{(y_1 \bar{v}_1)^2} \right] - \frac{x_2 y_2 q_2 z \varepsilon_2^*}{2} \left[ \frac{1.011}{(y_2 \bar{v}_2)^4} - \frac{2.409}{(y_2 \bar{v}_2)^2} \right] \end{aligned} \quad (12)$$

Even if both  $v_i^*$  are chosen to be equal ( $v_1^* = v_2^*$ ), the free energy of mixing equation (12) depends on the size of the  $v_i^*$ . This is due to the terms stemming from the combinatorial entropy of mixing holes and chain segments (the logarithmic terms containing  $(1-y)$ ).

From the expressions for the free energy of mixing,  $\Delta F$  (equations (9) and (12) respectively), the spinodal can be calculated by a numerical procedure described previously<sup>13</sup>.

For discussing the miscibility of polymer blends, it is very popular to use the Flory-Huggins  $\chi$  parameter. When the  $v_i$  in the mixing rule equation (1) are set equal, one can derive an expression for the  $\chi$  parameter from the EOS theories by simply equating the residual free energy of the Flory-Huggins theory (i.e. without the combinatorial entropy) and the corresponding EOS theory. For the general case  $v_1^* \neq v_2^*$  this is not as simple.

However, Patterson and Delmas derived an approximate expression by series expansion of the residual free energy of mixing<sup>15</sup>. It is predicted by this expression that different sizes of the lattice sites give an additional contribution to  $\chi$ .

$$\begin{aligned} \chi = & \frac{c_1}{s_1} \left[ \left( -\frac{\tilde{U}_1}{\bar{T}_1} \right) v^2 + \frac{\tilde{C}_{p1}}{2} \left( \tau + \frac{p\kappa_1}{T\alpha_1} \pi \right)^2 \right. \\ & \left. + \frac{\tilde{C}_{p1} p \kappa_1}{T^2 \alpha_1^2} \left( \frac{39}{4} \rho^2 + \frac{3}{2} \rho \delta \right) \right] \end{aligned} \quad (13)$$

where

$$v^2 = (9\rho^2 - 2\theta) \quad (14)$$

with

$$\theta = \frac{1}{\varepsilon_{11}^*} \left[ \varepsilon_{12}^* - \frac{1}{2}(\varepsilon_{11}^* + \varepsilon_{22}^*) \right] \quad (15)$$

and

$$\rho = \frac{R_{22}^*}{R_{11}^*} - 1 \quad (16)$$

$R_{ii}^*$  is the 'hard-core radius' of a segment of type  $i$ . Expressing this via the  $v_i^*$  yields

$$\rho = \left( \frac{v_2^*}{v_1^*} \right)^{1/3} - 1 \quad (17)$$

Hence, for  $v_1^* = v_2^*$ ,  $\rho$  vanishes. The quantities  $\tau$  and  $\pi$  are defined by

$$\tau = 1 - \frac{T_1^*}{T_2^*} \quad \text{and} \quad -\pi = 1 - \frac{p_1^*}{p_2^*} \quad (18)$$

respectively. It can already be seen from equation (13), that the parameter  $\rho$  and hence the ratio  $v_1^*/v_2^*$  has an influence on  $\chi$ .

$\delta$  is defined as

$$\delta = \frac{\varepsilon_{22}^*}{\varepsilon_{11}^*} - 1 \quad (19)$$

$\tilde{U}_1$  and  $\tilde{C}_{p1}$  are the reduced internal energy and heat capacity of component 1 respectively. For the Prigogine theory they are given by

$$\tilde{U}_1 = \frac{1}{2} \left[ \frac{1.011}{\bar{v}_1^4} - \frac{2.409}{\bar{v}_1^2} \right] \quad (20)$$

and

$$\tilde{c}_{p1}^{-1} = -\tilde{T}^2 \left[ \frac{\tilde{v}^{1/3}}{3(\tilde{v}^{1/3} - 2^{-1/6})} - \frac{\tilde{v}^{2/3}}{3(\tilde{v}^{1/3} - 2^{-1/6})^2} \right. \\ \left. + \frac{4.818}{\tilde{T}\tilde{v}^2} - \frac{8.088}{\tilde{T}\tilde{v}^4} - \frac{\tilde{p}\tilde{v}}{\tilde{T}} \right] / \left[ \frac{2.409}{\tilde{v}^2} - \frac{2.022}{\tilde{v}^4} + \tilde{p}\tilde{v} \right]^2 \quad (21)$$

$\alpha_1$  and  $\kappa_1$  are thermal coefficient of expansion and compressibility of component 1. The first term on the r.h.s. of equation (13) represents the interactional part  $\chi_i$  of  $\chi$ , whereas the second and third term represent the free volume contributions  $\chi_f$ . Usually, when equation (13) is applied, the segmental hard-core volumes of both components are set equal, and it is used in connection with the EOS theory of Flory *et al.* It can be seen, that for  $\rho = 0$  the expression equation (13) simplifies considerably. Moreover, in that case  $2\theta = -X_{12}/p_1^*$ , where  $X_{12}$  is the exchange energy parameter of Flory's theory<sup>16</sup>. This is the form of the Patterson theory which is usually applied.

#### Determination of the reduction parameters

We showed before that by calculating reduction parameters from the experimental coefficient of thermal expansion  $\alpha$ , the compressibility  $\kappa$  and the specific volume at  $p = 0$ , the results of different EOS theories are comparable<sup>11-13</sup>. When these parameters are determined by fitting the EOS to PVT data the results obtained by the different theories are not so similar. Therefore, in the present work we will also calculate them.

How to calculate them for Prigogine theory is outlined in Ref. 17. There, the determination of the reduction parameters was actually performed for the modified cell model. By setting the quantity of that theory which was introduced to decouple the free volume term from the geometry (usually called  $q$ ) to unity, however, the corresponding equations for the Prigogine theory are obtained. For SS theory it can be accomplished in the following way:

$\alpha$  and  $\kappa$  are given by

$$\alpha T = \frac{\tilde{T}}{\tilde{v}} \left[ \frac{A_2 A_6 - A_3 A_5}{A_1 A_5 - A_2 A_4} \right] \quad (22)$$

and

$$\kappa p = \frac{\tilde{p}}{\tilde{v}} \left[ \frac{A_5 A_7}{A_1 A_5 - A_2 A_4} \right] \quad (23)$$

respectively. The  $A_i$  appearing in equations (22) and (23) are given in the appendix.  $\tilde{v}$  and  $\tilde{T}$  can be determined by solving simultaneously the EOS and the equation for  $\alpha$  at  $p = 0$ .  $y$  is determined from the equilibrium condition. From this  $v_{sp}^*$  and  $T^*$  can be calculated. From equations (22) and (23) the following expression for  $p^*$  is derived

$$p^* = \frac{\alpha T}{\kappa} \frac{1}{\tilde{T}} \left[ \frac{A_5 A_7}{A_2 A_6 - A_3 A_5} \right] \quad (24)$$

As discussed above, when determining the SS reduction parameters the question arises how to fix  $v^*$  or equivalently the quantity  $3c/r$ . Nies and Stroeks<sup>18,19</sup> have performed fits of the SS-EOS to PVT data, where they set a chain segment equal to a monomer unit. It is not surprising that the reduction parameters differ from those obtained with the condition  $3c/r = 1$ <sup>20</sup>. Calculating, however, the number of degrees of freedom  $3c$  per polymer chain from these different parameters, it is found that the results also differ.

$c$  calculated from the parameters where a chain segment is equal to a monomer unit is greater than that calculated from the parameters determined by the condition  $3c/r = 1$ . This means that the prediction of the theory concerning the flexibility of polymer chains depends on the choice of the size of a polymer segment.

In the present work, the reduction parameters were calculated by first setting  $3c/r = 1$ . From equation (5), it is obvious, that the segment size is fixed after fixing the ratio  $c/r$ . This segment size is usually much smaller than the monomeric unit. From equation (5), however, the number of degrees of freedom of an arbitrarily chosen part of the chain, for example a monomer unit, can be calculated. This value can then be inserted into the equilibrium condition, and the reduction parameters can be recalculated. From these new parameters  $c/r$  is calculated once more, and again inserted into equation (8). This is repeated until consistency is achieved, i.e. the value of  $c/r$  calculated from the reduction parameters is equal to the one previously inserted into the equilibrium condition. In general, this procedure converges after about 5-6 iterations.

## EXPERIMENTAL

For our discussions we will perform model calculations on two binary polymer systems which were already described before by using other EOS theories<sup>11-13</sup>. One of the systems is polystyrene ( $M_n = 2100$  g mole<sup>-1</sup>,  $M_w/M_n = 1.08$ ) combined with polyisoprene ( $M_n = 2600$  g mole<sup>-1</sup>,  $M_w/M_n = 1.08$ ) (PS 2.1/PI 2.6), the other system is polystyrene ( $M_n = 230\,000$  g mole<sup>-1</sup>,  $M_w/M_n = 1.11$ ) with poly(cyclohexyl methacrylate) ( $M_n = 114\,000$  g mole<sup>-1</sup>,  $M_w/M_n = 1.26$ ) (PS 230/PCHMA 114). PS 2.1/PI 2.6 exhibits UCST behaviour with a critical temperature of about 115°C, and PS 230/PCHMA 114 is an LCST system whose critical temperature is about 240°C. The corresponding experimental phase diagrams can be found in Ref. 10. Expansion coefficients, compressibilities and specific volumes were determined from PVT measurements.

## RESULTS

### Reduction parameters

Since reduction parameters generally turn out to depend almost linearly on temperature, they have to be averaged suitably. This is done over the temperature range where both components of a blend are well above their glass transition. For PS/PI this corresponds to calculating the parameters at a temperature of 125°C, for PS/PCHMA it is 200°C<sup>10</sup>.

The reduction parameters obtained for Prigogine theory are shown in Table 1. For SS theory the calculations were performed for four different sizes of segments. First, with the condition  $3c/r = 1$ , then by setting  $v_f^*$  equal to the hard-core volume of a monomer unit, and by fixing the segmental hard-core volume to 60 cm<sup>3</sup> mole<sup>-1</sup> and 100 cm<sup>3</sup> mole<sup>-1</sup> respectively.

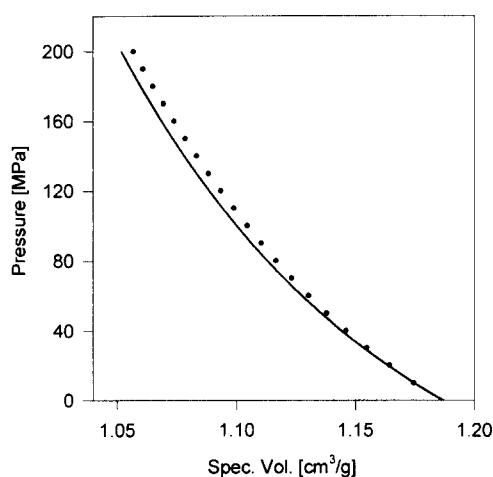
Table 2 shows the results of these calculations. It can be

**Table 1** Reduction parameters of Prigogine theory for the polymers used

Polymer	$p^*$ (MPa)	$v_s$ (cm <sup>3</sup> g <sup>-1</sup> )	$T^*$ (K)
PS 2.1	627.1	0.8825	4042
PI 2.6	506.6	1.0205	3853
PS 230	590.4	0.9055	4846
PCHMA 114	558.4	0.8453	4647

**Table 2** Reduction parameters of SS theory for the polymers used, obtained by different choices for  $3c/r$ 

Way of fixing $3c/r$	$p^*$ (MPa)	$v_{sp}^*$ (cm <sup>3</sup> g <sup>-1</sup> )	$T^*$ (K)	$V_s^*$ (cm <sup>3</sup> mole <sup>-1</sup> )	$V_m^*$ (cm <sup>3</sup> mole <sup>-1</sup> )	$c/d$
PS 2.1						
$3c/r = 1$	753.5	0.9361	10345	38.06	97.35	0.8489
$r = d$	755.3	0.9245	8351	96.15	96.15	1.0457
$V_s^* = 60$ cm <sup>3</sup> mole <sup>-1</sup>	753.5	0.9296	9100	60	96.68	0.9626
$V_s^* = 100$ cm <sup>3</sup> mole <sup>-1</sup>	755.3	0.9233	8308	100	96.02	1.0498
PI 2.6						
$3c/r = 1$	614.5	1.0789	9695	43.73	73.37	0.5592
$r = d$	617.1	1.0696	8373	72.73	72.73	0.6446
$V_s^* = 60$ cm <sup>3</sup> mole <sup>-1</sup>	615.5	1.073	8790	60	72.96	0.6147
$V_s^* = 100$ cm <sup>3</sup> mole <sup>-1</sup>	618.6	1.0654	7906	100	72.45	0.6859
PS 230						
$3c/r = 1$	708.2	0.9608	12426	48.64	99.92	0.6852
$r = d$	709.9	0.9501	10292	98.81	98.81	0.8196
$V_s^* = 60$ cm <sup>3</sup> mole <sup>-1</sup>	708.8	0.9564	11515	60	99.46	0.7362
$V_s^* = 100$ cm <sup>3</sup> mole <sup>-1</sup>	709.9	0.9500	10272	100	98.80	0.8211
PCHMA 114						
$3c/r = 1$	675.2	0.8949	11757	48.26	150.34	1.0383
$r = d$	680.7	0.8811	9196	148.02	148.02	1.3177
$V_s^* = 60$ cm <sup>3</sup> mole <sup>-1</sup>	676.7	0.8908	10878	60	149.65	1.1195
$V_s^* = 100$ cm <sup>3</sup> mole <sup>-1</sup>	679.3	0.8842	9685	100	148.55	1.2529

**Figure 1** Pressure versus specific volume for PI 2.6. The dots represent experimental values, the lines are calculated with the different sets of the reduction parameters for SS theory. It can be seen that all the four lines practically coincide.

seen that the numerical values of the reduction parameters differ appreciably for the different segment sizes. For  $p^*$  and  $v_{sp}^*$  the changes are not as large as for  $T^*$ .

Figure 1 shows pressure versus specific volume of PI 2.6 at 125°C. The dots are experimental, and the lines give the theoretical values of SS theory calculated for all four sets of reduction parameters. It can be seen that the four curves practically coincide. Moreover, calculations show that also volume versus temperature and occupied site fraction  $y$  as a function of pressure and temperature are basically equal.

Table 2 also contains  $V_s^*$ , the molar volume of the chain segments and  $V_m^*$ , the corresponding molar volume of the monomeric unit. The latter seems to be almost independent of the size of  $v^*$ . Taking into account the fact that the occupied site fraction is also independent of the size of  $v^*$ , this means that the free volume predicted by the theory does not depend on the choice of  $v^*$ .

In order to directly compare the predicted number of degrees of freedom, we calculate the quantity  $c/d$  ( $d$  = degree of polymerisation), the number of degrees of freedom per monomeric unit. It is given in the last column of Table 2. It can be seen that the larger the segment size is chosen, the higher is the prediction for  $c/d$ , i.e. a greater

chain flexibility is predicted. It can also be seen that the chains of the low molecular weight PS are predicted to be more flexible than those of the high molecular weight PS. This is partially due to the different expansion coefficients, but also due to the fact that the reduction parameters are temperature dependent. This in turn implies, that  $c$  is temperature dependent as well. It turns out that  $c$  decreases with increasing temperature. Since the reduction parameters for PS 2.1 were evaluated at a lower temperature than those for PS 230 a higher value for  $c$  is expected.

#### Phase behaviour

To describe the phase behaviour of polymer blends, in addition to the pure component parameters, the quantities  $\varepsilon_{12}^*$  and  $v_{12}^*$  are required.  $v_{12}^*$  is usually taken as the average

$$v_{12}^* = [(v_1^{*1/3} + v_2^{*1/3})/2]^3 \quad (25)$$

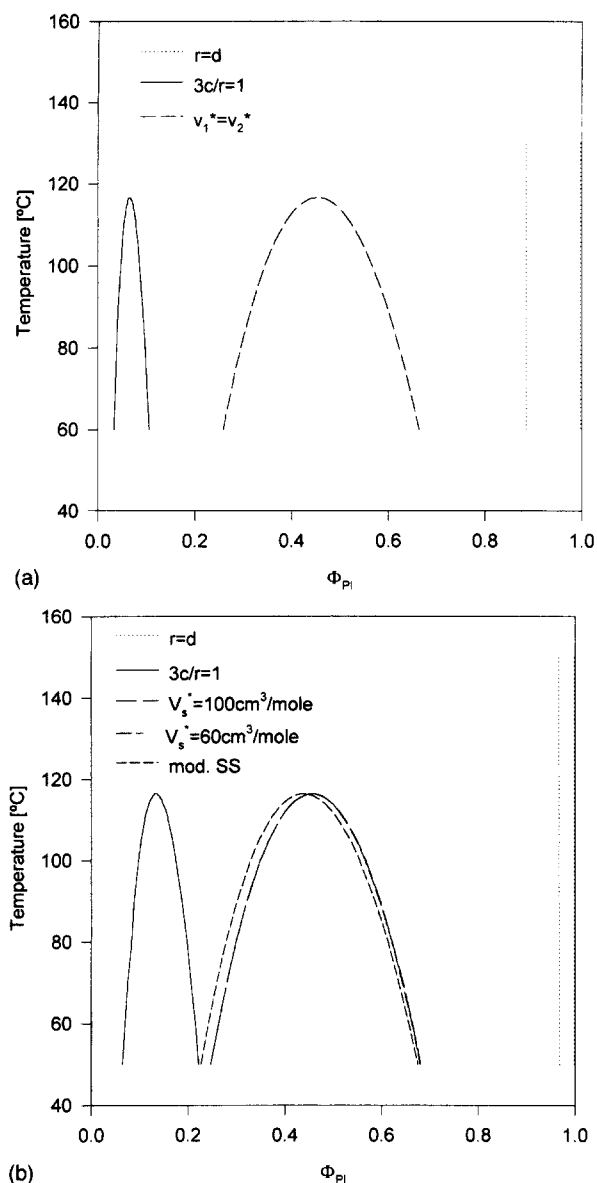
of the pure components. Following Sanchez and Lacombe<sup>6</sup>, for  $\varepsilon_{12}^*$  we will use the Berthelot relationship and introduce a parameter  $\zeta$  as a measure of deviation from this relationship. Thus

$$\varepsilon_{12}^* = \zeta(\varepsilon_{11}^* \varepsilon_{22}^*)^{1/2} \quad (26)$$

$\zeta$  is then determined by adjusting it in such a way that the calculated and the experimental critical temperatures in phase diagrams are equal. Usually  $\zeta$  does not deviate too much from unity, and the larger  $\zeta$ , the more favourable it is for miscibility.

To discuss the influence of different sizes of the lattice sites for the two components, we use the parameter  $\rho$  (equation (16)) introduced by Patterson.

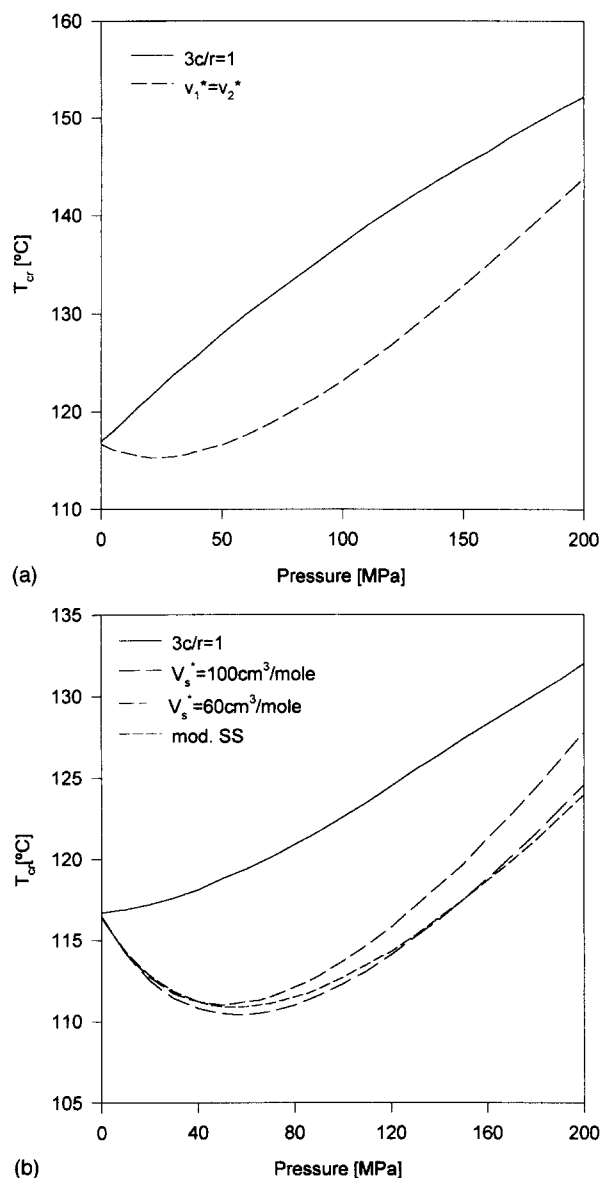
Figure 2a shows spinodals calculated by the Prigogine theory for the system PS/PI. The dashed curve is the result obtained when setting  $v_1^* = v_2^*$  and  $\zeta = 1.00158$ . When the  $v_i^*$  are set equal to their respective values of the monomeric units ( $r_i = d_i$ , this corresponds to  $\rho = -0.09$ ) and  $\zeta$  does not differ too much from unity complete immiscibility is predicted. Upon increasing  $\zeta$ , miscibility on the PS-rich side of the phase diagram is predicted, but not however for high PI contents. Even for  $\zeta = 2$ , which is a very large value, on the PI-rich side still almost complete immiscibility is predicted. This is shown as a dotted line in Figure 2a. For the sake of comparison with SS theory, we also include the phase diagram which is calculated with  $v_i^*$  values that are



**Figure 2** Spinodals of PS 2.1/PI 2.6 calculated for different choices of lattice site sizes: (a) Prigogine theory, (b) SS theory.

determined by fixing  $3clr = 1$  (corresponding to  $\rho = 0.0567$ ). It was calculated with  $\zeta = 1.0785$  and is shown as a solid line in Figure 2a. It is very small and completely asymmetric, in contrast to experiment. The only reasonable phase diagram is predicted for the case when the segmental hard-core volume is chosen equal for both components.

The corresponding curves obtained by SS theory are shown in Figure 2b. As mentioned above, even for the case of  $v_1^* = v_2^*$  the free energy of mixing depends on the size of the  $v_i^*$  values. Therefore, the spinodals were calculated for a molar hard-core segment volume  $V_s^*$  of  $60 \text{ cm}^3 \text{ mole}^{-1}$  and  $100 \text{ cm}^3 \text{ mole}^{-1}$  respectively. It turns out that these two curves are basically identical. However, different values of  $\zeta$  were required to obtain these diagrams. For  $V_s^* = 60 \text{ cm}^3 \text{ mole}^{-1}$  and  $V_s^* = 100 \text{ cm}^3 \text{ mole}^{-1}$ ,  $\zeta = 1.001997$  and  $\zeta = 1.00182$  respectively were used. It should also be kept in mind that the reduction parameters of SS theory depend on the chosen size of  $v_i^*$ . So for both curves different reduction parameters were used, therefore the similarity of the curves seems surprising. The curves obtained are shown as medium and long dashes for the case of  $V_s^* = 60 \text{ cm}^3 \text{ mole}^{-1}$  and  $V_s^* = 100 \text{ cm}^3 \text{ mole}^{-1}$  respectively.

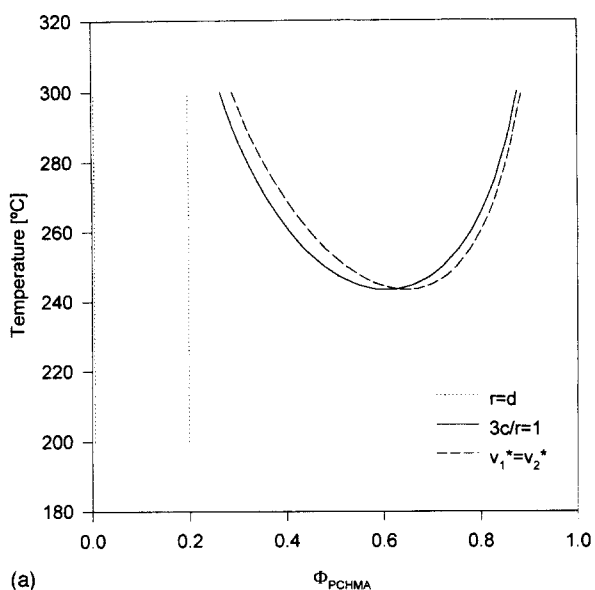


**Figure 3** Pressure dependence of the critical temperature of PS 2.1/PI 2.6 calculated for different choices of lattice site sizes: (a) Prigogine theory, (b) SS theory.

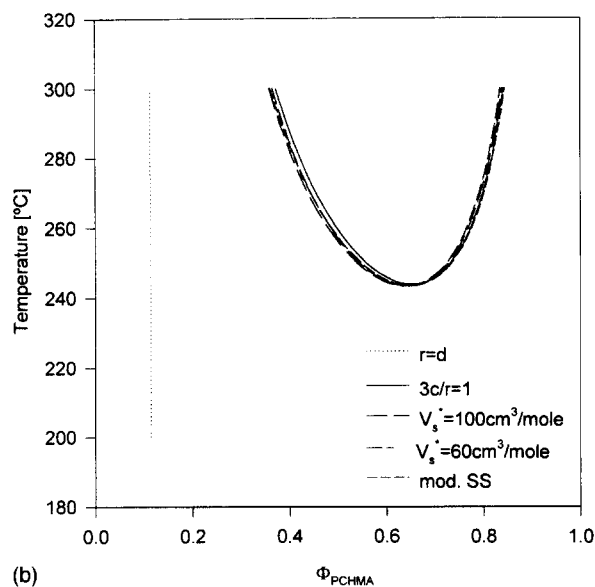
The curve obtained by setting the segment size equal to a monomer unit (corresponding to  $\rho = -0.0889$ ) is shown as dotted line. As for the Prigogine theory, it is not possible to obtain a phase diagram whose critical temperature equals the experimental one. Rather, immiscibility is predicted for  $\zeta$  not too different from unity, and for large  $\zeta$  only on the PI-rich side immiscibility results. The curve in Figure 2b was calculated with  $\zeta = 2$ . Finally, the spinodal obtained by using the reduction parameters calculated with the condition  $3c/r = 1$  (corresponding to  $\rho = 0.0474$ ) is shown as a solid line. It was calculated with a value of  $\zeta = 1.0212$ .

Figure 3a and 3b finally show the predicted pressure dependence of the critical temperature for the different cases for Prigogine and SS theory respectively. It can be seen that for both theories in the case of fixing the segment size by setting  $3c/r = 1$ , a monotonic increase of the critical temperature is predicted. For the case of  $v_1^* = v_2^*$  both theories first predict a decrease of critical temperature with pressure, but on further pressure increase the critical temperature increases as well.

The spinodals calculated for PS/PCHMA using the Prigogine theory are shown in Figure 4a. Again, the



(a)



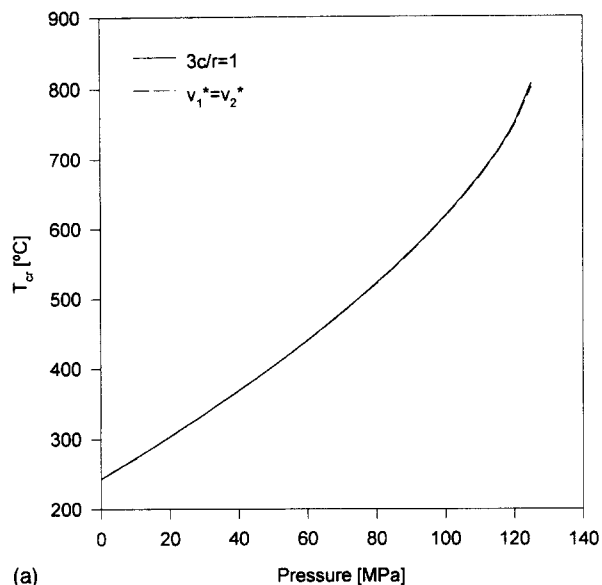
(b)

**Figure 4** Spinodals of PS 230/PCHMA 114 calculated for different choices of lattice site sizes: (a) Prigogine theory, (b) SS theory.

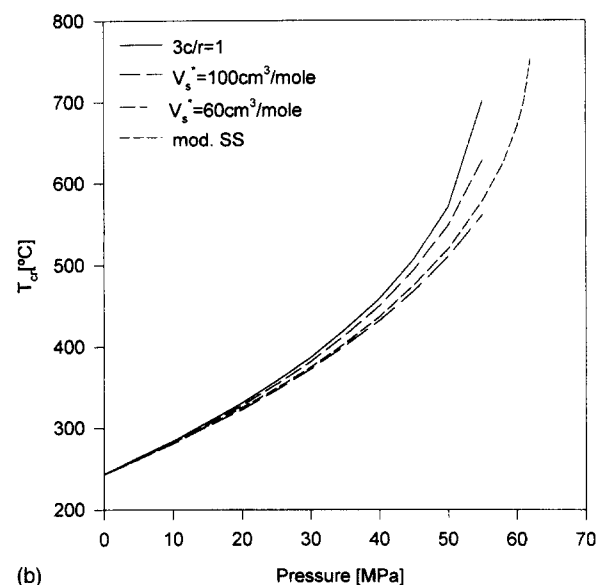
dashed curve gives the result when setting  $v_1^* = v_2^*$ . This curve was obtained by using a value of  $\zeta = 1.000485$ . As for the system PS/PI, it is not possible to describe the experimental phase behaviour when the segmental hard-core volumes are set equal to the monomer hard-core volumes (corresponding to  $\rho = 0.1466$ ). The phase diagram obtained using a value of  $\zeta = 1.5$  is shown as a dotted line.

Finally, fixing the hard-core volumes by the condition  $3c/r = 1$  yields the solid curve in Figure 4a. It was calculated with  $\zeta = 1.0004589$ . For this system, the hard-core volumes obtained from the condition  $3c/r = 1$  are very similar ( $\rho = 0.0046$ ). Therefore, the phase diagrams and the corresponding  $\zeta$  obtained from this condition and from  $v_1^* = v_2^*$  are similar as well.

The spinodal curves obtained for this system using SS theory are shown in Figure 4b. Again, the calculations for the case of equal hard-core volume was performed for  $V_s^* = 60 \text{ cm}^3 \text{ mole}^{-1}$  and  $V_s^* = 100 \text{ cm}^3 \text{ mole}^{-1}$ . In this case, however, the results differ slightly. For  $V_s^* = 60 \text{ cm}^3 \text{ mole}^{-1}$  the corresponding curve is shown as short dashes (using  $\zeta = 1.0004294$ ), for  $V_s^* = 100 \text{ cm}^3 \text{ mole}^{-1}$  it is shown as long dashes (using  $\zeta = 1.000422$ ). The curve obtained from



(a)



(b)

**Figure 5** Pressure dependence of the critical temperature of PS 230/PCHMA 114 calculated for different choices of lattice site sizes: (a) Prigogine theory, (b) SS theory.

setting a segment equal to a monomer unit is shown as dotted line ( $\rho = 0.1442$ ,  $\zeta = 1.5$ ), that obtained by using the  $3c/r = 1$  parameter as solid lines ( $\rho = -0.0026$ ,  $\zeta = 1.000599$ ). Again, it should be kept in mind, that for different segment sizes different reduction parameters result.

In Figure 5a and 5b, the pressure dependence of the critical temperature is shown for Prigogine and SS theory respectively. Prigogine theory predicts almost the same pressure dependence for both cases. For higher pressures, the critical temperature  $T_{cr}$  tends to infinity, which means that from a certain pressure complete miscibility is predicted. For the case of  $3c/r = 1$ , the increase of  $T_{cr}$  at higher pressures is slightly faster; however, the difference is very small. For SS theory similar tendencies are predicted, the difference between the different cases is much bigger however. Even for the cases of  $V_s^* = 60 \text{ cm}^3 \text{ mole}^{-1}$  and  $V_s^* = 100 \text{ cm}^3 \text{ mole}^{-1}$  the curves differ.

Recently, we have found that a modification of the SS theory<sup>13</sup> gives results which are qualitatively similar to those of other EOS theories, i.e. the theories of Patterson

et al., Sanchez and Lacombe and Dee and Walsh. A difference between the SS theory and the other investigated theories is the mixing rule for  $\varepsilon^*$  and  $v^*$ . SS theory uses equation (1), whereas the other theories use a simpler mixing rule which is derived from equation (1) under the assumption that the  $v_{i1}^*$  and  $v_{i2}^*$  are equal. Upon introduction of this simplified mixing rule into the SS theory, similar predictions are obtained as from the other theories. For these investigations reduction parameters were used which were determined with the condition  $3c/r = 1$ , hence the functional relationship between the reduced variables of state was the same for all components.

Now, it turns out that the results of the original SS theory are similar to those of this modified SS theory when the segmental hard-core volumes of both components are equal or similar. This is not only true for the case when the reduction parameters, and hence the  $v_i^*$ , were determined by the condition  $3c/r = 1$ , as is the case for PS/PCHMA. For this system, the corresponding segmental hard-core volumes determined by this condition are very similar for both components, therefore, the similar description of the phase diagrams might be expected. It is, however, also true when the  $v_i^*$  of the components determined by the condition  $3c/r = 1$  differ appreciably as for PS/PI. By setting  $v_i^*$  equal for both components in the original SS theory, similar results are obtained as for the modified SS theory. The reduction parameters, however, differ for the two cases, so the similarities in the predicted behaviour seem surprising.

The results obtained with this modified SS theory are shown in Figure 2b and 4b as short dashes.

Comparing the results obtained from Prigogine theory and those of SS theory, it is again found that they are — at least qualitatively — very similar. For both theories the results obtained depend strongly on the chosen value of  $\rho$ .

Also other thermodynamic quantities are dependent on  $\rho$ . Figure 6 for example shows the excess volume for a PS/PI 50/50 (wt.%) mixture at  $p = 0$  as a function of  $\rho$ . It was calculated by using  $\zeta = 1.00158$  (determined for  $\rho = 0$ ) and keeping it constant, varying only  $\rho$ . In the vicinity of vanishing and small positive  $\rho$ , the excess volume is negative, outside of this region it is positive and increases strongly with increasing magnitude of  $\rho$ . This curve was

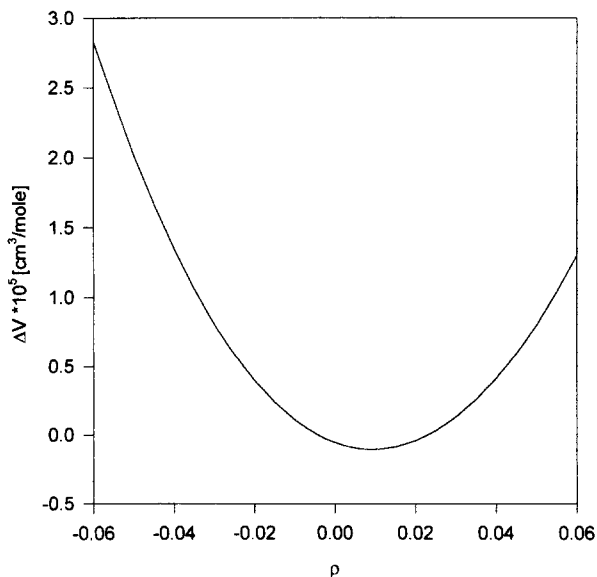


Figure 6 Calculated excess volume for a 50/50 wt.% mixture of PS 2.1/PI 2.6 at  $p = 0$  as a function of  $\rho$  (see text).

calculated with the Prigogine theory; however, SS theory yields qualitatively similar results, the magnitude of the predicted excess volume being larger.

Another example is shown in Figure 7, the energy of mixing  $\Delta E$  for the same blend (the last three terms of the free energy of mixing equations (9) and (12) respectively) as a function of  $\rho$ . The solid curve is calculated with Prigogine theory, using the  $\zeta$  value corresponding to  $\rho = 0$ . The dots are calculated from SS theory also using the  $\zeta$  value corresponding to  $\rho = 0$  (with  $V_s^* = 100 \text{ cm}^3 \text{ mole}^{-1}$ ), but the reduction parameters corresponding to that of  $\rho$ .

For  $\rho = 0$ , the results obtained by using the parameters for  $V_s^* = 60 \text{ cm}^3 \text{ mole}^{-1}$  and those for  $V_s^* = 100 \text{ cm}^3 \text{ mole}^{-1}$  (also using the corresponding  $\zeta$ ) differ only by about 2% in spite of the fact that the parameters differ appreciably.

It should be pointed out that using different values for  $\zeta$

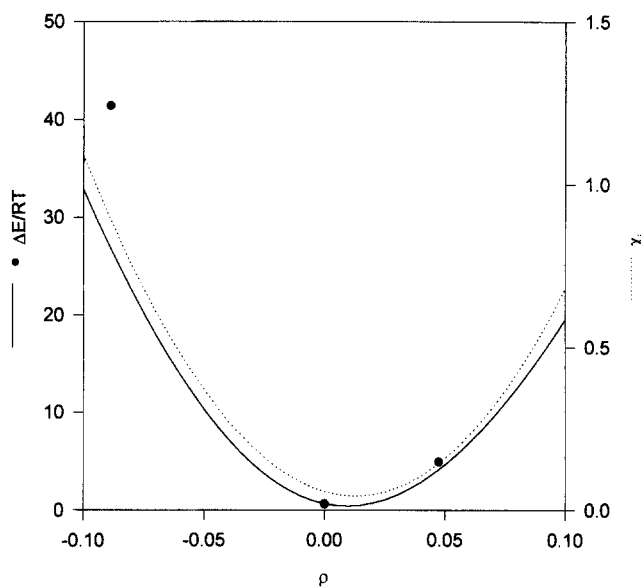


Figure 7 Calculated energy of mixing for a 50/50 wt.% mixture of PS 2.1/PI 2.6 at  $p = 0$  as a function of  $\rho$ . Full line calculated by Prigogine theory, dots calculated by SS theory. The dotted line gives the interactional part  $\chi_1$  of the  $\chi$  parameter.

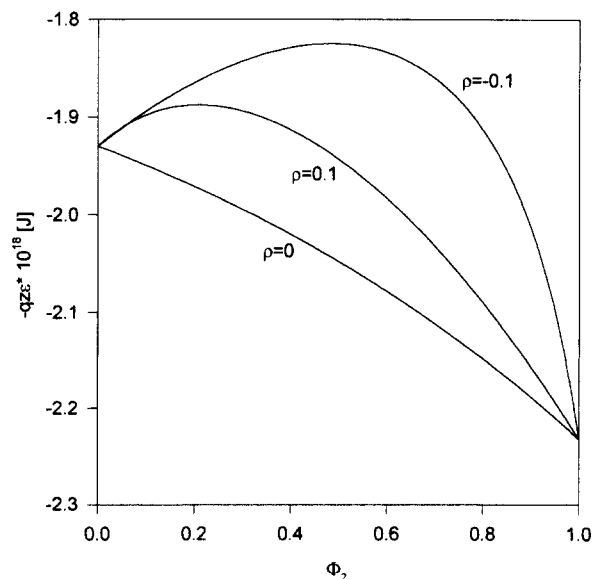


Figure 8  $-qz\varepsilon^*$  of PS 2.1/PI 2.6 as a function of composition for various values of  $\rho$ .



(as long as  $\zeta$  does not differ too much from 1) does not alter the shape of the curve very much. The change in  $\Delta E$  is mainly due to changes in  $\rho$ . This increase in  $\Delta E$  with increasing magnitude of  $\rho$  is the reason for the predicted immiscibility in that range of  $\rho$ . This, in turn, is a consequence of the mixing rule equation (1). *Figure 8* shows the quantity  $-qz\epsilon^*$  as a function of  $\Phi_2$  for different values of  $\rho$ . In the vicinity of  $\rho \approx 0$  this quantity has its lowest values, whereas for other values of  $\rho$  it is much higher. For positive  $\rho$  the maximum difference to the  $\rho = 0$  curve lies more on the  $\Phi_1$ -rich side, whereas for negative  $\rho$  it lies more on the  $\Phi_2$ -rich side. Since  $\bar{v}_i$ ,  $y_i$  and the  $q_i z \epsilon_i^*$  of the pure components are (almost) independent of the chosen lattice site size, this difference between the values of  $qz\epsilon^*$  for  $\rho = 0$  and the values for  $\rho$  different from 0 is the reason for the predicted form of the  $\Delta E$  versus  $\rho$  curves. Moreover, the position of the maximum difference in *Figure 8* accounts for the above found symmetry of the phase diagrams. It should be noted, that these results were obtained by only using equation (1). So, this mixing rule together with the chosen value of  $\rho$  governs the predicted miscibility behaviour of the theories.

A physical reason for this unusual behaviour might be a 'surface area effect' similar to that introduced by Sanchez and Lacombe<sup>6</sup>. The number of interactions per mer in the pure state and in the mixed state differ if the lattice site volumes of the components differ. Therefore, the energy of the mixed system might be very different from the sum of the energy of the pure components, thus leading to large excess energies.

#### *Influence of $\rho$ on the $\chi$ parameter*

Now we want to see the influence of  $\rho$  on the  $\chi$  parameter. The interactional part  $\chi_i$  (cf. equation (13)) is also shown in *Figure 7* as a dotted curve. It can be seen that it is quite similar to the  $\Delta E$  curve. As one can directly see from equation (13), the first free volume term does not depend on  $\rho$ . At vanishing pressure, the second free volume term also vanishes. At higher pressures, however, its magnitude can be larger than that of the first free volume term. The phase diagrams calculated with Patterson theory using this  $\chi$  parameter does not have the same symmetry as the corresponding Prigogine phase diagram. This is because this  $\chi$  parameter is not concentration dependent, therefore the symmetry is mainly governed by the chain lengths of the components as in the Flory-Huggins theory.

## DISCUSSION

Results of SS and Prigogine and other EOS theories are usually found to be not only quantitatively different, but also qualitatively. These differences however are not intrinsic due to the different nature of the theories, but only due to different choices of the lattice site sizes that are usually made. Simha *et al.* fix the lattice site of the pure components by setting  $3c/r = 1$ , Nies and Stroeks use a monomeric unit, whereas in the other theories the size is simply chosen to be equal for both components. However, neither the condition  $3c/r = 1$  nor  $v_1^* = v_2^*$  is made on a physical basis. They are only made for convenience, to simplify the calculations. There is no physical justification for either of these choices.

It turns out, however, that the properties of the theories depend very strongly on these choices. From the calculations presented above, it must be concluded that for a value of  $\rho$  which is too different from zero, it is generally not possible to get a reasonable description of phase behaviour.

Thus, as long as there are no physically justified criteria for choosing the size of the lattice sites, it seems most reasonable to choose  $v_1^* = v_2^*$  and then calculate the average interaction energy. It would, however, be desirable to have a theory where no such lattice site size has to be fixed.

It seems likely that all the cell model theories and also the lattice fluid theory give similar thermodynamic predictions not only when the  $v_i^*$  of the two components are equal, but also generally when the same mixing rule is applied. As shown above, this mixing rule can appreciably change the concentration dependence of  $qz\epsilon^*$ , and this can dominate the predicted behaviour of the system. If the same mixing rule is applied for all theories, this concentration dependence is the same. Also, the free volume terms are similar for all cell model theories, and even the corresponding term of SL theory can be cast into a form<sup>21</sup> which is similar to that of the Patterson theory. The latter stems from a series expansion of the cell model theories. Moreover, the magnitude of the contribution due to the combinatorial entropy of 'mixing' holes and segments in SS theory is usually very small and does not influence the behaviour so much.

Therefore, since the energetical and the free volume terms are so similar, it can now be understood why theories which at first sight seem completely different predict, in fact, very similar thermodynamic behaviour, as long as the same mixing rule applies.

It should be noted that the introduction of different potentials yields different mixing rules, so that for  $v_1^* \neq v_2^*$  indeed, different theories can yield different results.

In SL theory the lattice site size of the pure components is fixed. However, a mixing rule is applied so that in the mixture both components' lattice sites have equal size. This is done before the average interaction energy between the chain segments is calculated. This means that for the latter also the simplified mixing rule applies. For this theory it is not possible, however, to introduce a potential. But in principle one could also introduce a different mixing rule for the  $v_i^*$ , so that the theory would give different predictions.

For SS theory, one might expect different results for different choices of  $v_i^*$ , since the reduction parameters are different in that case. However, the terms that are important contain only quantities like  $\bar{v}$  and  $y$ , which have been shown to be independent of  $v_i^*$ .

## CONCLUSIONS

Using different theories, it has already been shown before that they give qualitatively similar results when the  $v_i^*$  are set equal for both components so that the simplified mixing rule applies. Now we have shown that also for the more general case of  $v_1^* \neq v_2^*$  the predictions of the theories are very similar. For a given mixing rule,  $\rho$  seems to be the key variable that fixes the properties of the theory. However, so far there seems to be no way of fixing this quantity on a physical basis. It is mainly chosen for convenience to simplify the equations. This might be one of the key problems to find EOS theories which give a more appropriate description of experiment. Perhaps, if a physically justified way to fix  $v_i^*$  could be found, the poor predictive power of the theories could be improved. As seen above, this choice influences the predictions of thermodynamic properties like energy of the system, excess volumes, symmetry of phase diagrams etc. When  $\rho$  is too different from 0 it can completely dominate the predicted phase behaviour. Usually, when fixing the  $v_i^*$  it is not

thought about how this influences these thermodynamic properties, although it was already clear from the expression equation (13) for the  $\chi$  parameter that  $\chi$  (and hence  $\Delta F$ ) depends on  $\rho$ .

Another problem with these theories is the accuracy of the determination of the reduction parameters. The predicted phase diagram depends very sensitively on them. This, however, is no principal problem.

#### ACKNOWLEDGEMENTS

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#### APPENDIX A:

The quantities  $A_i$  appearing in equations (22) and (23) are given as follows:

$$A_1 = \frac{\tilde{p}}{\tilde{T}} + \frac{1}{3} \frac{2^{-1/6} y^{2/3} \tilde{v}^{-4/3}}{(1 - 2^{-1/6} y (y\tilde{v})^{-1/3})^2} + \frac{8.088y^2}{\tilde{T}(y\tilde{v})^5} - \frac{4.818y^2}{\tilde{T}(y\tilde{v})^3}$$

$$A_2 = \frac{6.066}{\tilde{T}(y\tilde{v})^4} - \frac{2.409}{\tilde{T}(y\tilde{v})^2} - \frac{2}{3} \frac{2^{-1/6} (y\tilde{v})^{-1/3}}{(1 - 2^{-1/6} y (y\tilde{v})^{-1/3})^2}$$

$$A_3 = \frac{2y}{\tilde{T}^2 (y\tilde{v})^2} \left[ \frac{1.011}{(y\tilde{v})^2} - 1.2045 \right] - \frac{\tilde{p}\tilde{v}}{\tilde{T}^2}$$

$$A_4 = \frac{2.409y^2}{3\tilde{T}(y\tilde{v})^3} - \frac{2.022y^2}{\tilde{T}(y\tilde{v})^5} + \frac{1}{3} \frac{2^{-1/6} y^{2/3} \tilde{v}^{-4/3}}{(1 - 2^{-1/6} y (y\tilde{v})^{-1/3})^2} + \frac{2^{-1/6} y (y\tilde{v})^{-1/3} - 1/3}{(1 - 2^{-1/6} y (y\tilde{v})^{-1/3})^2} \left[ \frac{1}{3} 2^{-1/6} y^{2/3} \tilde{v}^{-4/3} \right]$$

$$A_5 = \frac{r}{3c} \left[ -\frac{1}{y^2} \ln(1-y) - \frac{1}{y(1-y)} \right] + \frac{2.409}{6\tilde{T}(y\tilde{v})^2}$$

$$- \frac{9.099}{6\tilde{T}(y\tilde{v})^4} - \frac{2}{3} \frac{2^{-1/6} (y\tilde{v})^{-1/3}}{(1 - 2^{-1/6} y (y\tilde{v})^{-1/3})^2}$$

$$- \frac{2^{-1/6} y (y\tilde{v})^{-1/3} - 1/3}{(1 - 2^{-1/6} y (y\tilde{v})^{-1/3})^2} \left[ \frac{2}{3} 2^{-1/6} (y\tilde{v})^{-1/3} \right]$$

$$A_6 = \frac{1}{6\tilde{T}^2 (y\tilde{v})^2} \left[ 2.409 - \frac{3.033}{(y\tilde{v})^2} \right]$$

$$A_7 = \frac{\tilde{v}}{\tilde{T}}$$

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