(37) Stromberg, R. R.; Grant, W. H.; Passaglia, E. *J. Res. Natl. Bur. Stand., Sect. A* **1964**, *68*, 391.
(38) Flory, P. J.; Vrij, A. *J. Am. Chem. Soc.* **1963**, *85*, 3548.
(39) Gomez, M. A.; Fatou, J. G.; Bello, A. *Eur. Polym. J.* **1986**, *22*, 661.
(40) Sanchez, A.; Marco, C.; Fatou, J. G.; Bello, A. *Makromol. Chem.* **1987**, *188*, 1205.
(41) Cortazar, M.; Guzman, G. M. *Makromol. Chem.* **1982**, *183*, 721.
(42) Guttman, C. M.; DiMarzio, E. A.; Hoffman, J. D. *Polymer* **1981**, *22*, 597.
(43) Guttman, C. M.; DiMarzio, E. A.; Hoffman, J. D. *Polymer* **1981**, *22*, 1466.
(44) Guttman, C. M.; DiMarzio, E. A. *Macromolecules* **1982**, *15*, 525.
(45) Mansfield, M. L. *Macromolecules* **1983**, *16*, 914.
(46) Lacher, R. C.; Bryant, J. L.; Howard, L. N. *J. Chem. Phys.* **1986**, *85*, 6147.
(47) Fatou, J. G.; Mandelkern, L. *J. Phys. Chem.* **1965**, *69*, 417.
(48) Maxfield, J.; Mandelkern, L. *Macromolecules* **1977**, *10*, 1141.
(49) Hoffman, J. D. *SPE Trans.* **1964**, *4*, 315.
(50) Suzuki, T.; Kovacs, A. J. *Polym. J. (Tokyo)* **1970**, *1*, 82.
(51) Buchanan, D. R.; Miller, R. L. *J. Appl. Phys.* **1966**, *37*, 4003.
(52) Balta Calleja, F. J.; Hosemann, R.; Wilke, W. *Makromol. Chem.* **1966**, *92*, 25.
(53) Khoury, F. *Faraday Discuss. Chem. Soc.* **1979**, *No. 68*, 404.
(54) Sadler, D. M. *Polymer* **1983**, *24*, 1401.
(55) Mansfield, M. L., submitted for publication in *Macromolecules*.
(56) Hoffman, J. D.; Miller, R. L.; Mansfield, M. L., submitted for publication.
(57) Lauritzen, J. I., Jr.; Hoffman, J. D. *J. Res. Natl. Bur. Stand., Sect. A* **1960**, *64*, 73.
(58) Hoffman, J. D. *Macromolecules* **1986**, *19*, 1124. Hoffman, J. D.; Miller, R. L., submitted for publication.
(59) Mansfield, M. L., submitted for publication.
(60) **Note Added in Proof.** It has recently been pointed out to us by Professors J. Skolnick and R. Yaris of Washington University, St. Louis, that the presence of a certain amount of the constraint release mechanism would cause a tendency for β to vary more nearly as $1/n_z$ rather than $1/n_w$. (The constraint release mechanism accounts for the fact that the chains forming the reptation tube of a particular molecule in a pure polymeric liquid are themselves reptating.) As noted, our data analysis suggests that the fit with $1/n_z$ as depicted in Figure 4 is somewhat better than that with $1/n_w$. Thus it would appear that while the simple steady-state reptation model with $y \simeq 1$ certainly holds with respect to its main features in the present application, there is a hint in the results that some constraint release may occur despite the rapidity with which the chains are drawn onto the crystal.

Multicomponent Forms of Polymer Solution Theories

Charles J. Glover* and William A. Ruff†

Department of Chemical Engineering, Texas A&M University,
College Station, Texas 77843-3122. *Received November 12, 1987;*
Revised Manuscript Received February 29, 1988

ABSTRACT: Equation-of-state polymer solution theories provide a rational means of describing polymer solution vapor/liquid equilibrium and liquid/liquid equilibrium for multicomponent systems. These theories require a relatively small number of parameters to describe solution behavior but are quite complex and cumbersome for manipulation and calculation. This work presents an efficient mathematical framework for manipulating these equations for the purpose of deriving solution thermodynamic properties such as species activities or chemical potentials. Writing the equations in matrix form and obtaining an expression for the excess free energy provide a route to species activities which is relatively clean and compact. The resulting multicomponent equation for species activities for the Flory equation of state theory, the simplified Flory theory, and the Sanchez and Lacombe lattice fluid theory can all be obtained in a similar way and have similar forms. The compact form allows easy comparison of different theories and also provides a convenient form for coding computer calculations of solution behavior.

Introduction

The theories of Flory[1] and of Huggins,[2] based upon an incompressible lattice structure, provide the basic framework for more recent equation of state theories. This Flory–Huggins theory allows for combinatorial effects and energetic interactions between molecules and has been used widely to calculate the thermodynamic properties of polymer solutions. It succeeds in providing a rough representation of solvent activities in nonpolar polymer solutions with one adjustable parameter per binary pair interaction. It has also been fairly successful at approximating liquid–liquid phase equilibria and predicting upper critical solution temperature (UCST) of binary, nonpolar polymer solutions.[3]

Equation-of-state theories such as those by Flory[4] and by Sanchez and Lacombe[5] have extended the foundation for these types of equations by beginning with a partition function which can be used to rigorously derive equations of state and other thermodynamic relations such as species activities. The Flory theory is based upon earlier work by Prigogine,[6,7] and the Sanchez–Lacombe theory is based upon a fluid lattice, that is, one which allows for holes or unoccupied cells of the lattice in addition to cells occupied by molecular segments. The theories are successful in predicting both UCST and LCST behavior. Furthermore, they are not restricted to single-polymer systems, and, in principle, may be applied to nonpolymeric liquid solutions and multiple-polymer solutions as well. In this latter context, they have been used to aid in understanding polymer compatibility in polymer blends. Additionally, the Sanchez–Lacombe equation of state is capable of describing fluids in both the liquid and vapor states.

While these theories have the advantage, in multicomponent systems, of requiring a small number of adjustable parameters, they do suffer from the difficulty of being quite complex and unwieldy. For multicomponent systems the number of terms in the equations becomes very large, and organizing and manipulating the terms to obtain expressions for the various thermodynamic relations and computing the quantities by using these relations are quite difficult and complex.

The objective of this paper is to present a matrix approach to deriving and manipulating the multicomponent solution theory equations. This approach is both simplified in method and compact in form. In addition, this paper provides a convenient and unified review, summary,

---

* Author to whom correspondence may be sent.
† Present address: Texaco Research, P.O. Box 1608, Port Arthur, TX 77641.

and comparison of three equation-of-state (EOS) theories that have appeared in the literature. Finally, the end-use equations for species activities (for activity coefficients) are derived and presented in their full multicomponent form for the three EOS solution theories.

These theories start with a statistical–mechanical partition function, Z, from which can be calculated the thermodynamic properties of interest. Presented below is, first, a general procedure for an approach which may be followed, given a specific partition function, to obtain polymer solution activities, activity coefficients, and other relations. This general procedure includes an outline of the procedure and certain mathematical definitions and relations which are useful in the applications. Second, examples of the procedure's use are presented for three equation-of-state solution theories.

General Procedure

Outline. The derivation of the activity equations for a specific solution theory follows the six-step procedure given below.

1. Select the partition function to be used for the pure components, e.g., $Z = Z(T,V;\text{pure component parameters})$ or $Z = Z(T,p;\text{pure component parameters})$.

2. Use the same partition function for the mixture as for the pures but introduce binary interaction energy parameters. The composition is expressed in terms of the number of moles or molecules of each species present. Also, mixture properties for the partition function are written in terms of the pure component parameters (properties), binary parameters, and composition through mixing rules.

3. Introduce mixing rules.

4. Determine the equation of state fot the partition function chosen. Since the partition function is the same for each species and for the mixture, the EOS is the same for each, in form, differing only by the actual numbers used for the various properties. The EOS is found by minimizing the Helmholtz or Gibbs free energy, depending on whether the partition function depends on V or p, respectively ($A = -kT \ln Z(T,V)$ and $G = -kT \ln Z(T,p)$).

5. Determine the excess functions[8] A^{E} (if $Z = Z(T,V)$) or G^{E} (if $Z = Z(T,p)$):

$$A^{\mathrm{E}} = A_{\mathrm{mix}} - \sum_i x_i A_i - kT \sum_i x_i \ln x_i \qquad (1)$$

or

$$G^{\mathrm{E}} = G_{\mathrm{mix}} - \sum_i x_i G_i - kT \sum_i x_i \ln x_i \qquad (2)$$

6. Determine $\partial(NA^{\mathrm{E}})/\partial N_i$ or $\partial(NG^{\mathrm{E}})/\partial N_i$, which gives $kT \ln \gamma_i$ (N = total system moles or molecules). Along the way, the EOS is used to simplify the final expression.

An alternate procedure followed in the literature (in place of steps 5 and 6) is as follows:

5′. Determine the partial molar properties $\bar{A}_i$ ($= [\partial(NA_{\mathrm{mix}})\partial N_i]_{T,V,N_j}$) or $\bar{G}_i$ ($=[\partial(NG_{\mathrm{mix}})/\partial N_i]_{T,p,N_j}$).

6′. Then $kT \ln \gamma_i = \bar{A}_i - A_i - kT \ln x_i$ or $kT \ln \gamma_i = \bar{G}_i - G_i - kT \ln x_i$. This procedure involves much more algebra, however.

Also, note that $\ln a_i = \ln (\gamma_i x_i)$, so the species activities (and chemical potentials) can be obtained from the relations determined in step 6.

Useful Notation. For working with the multicomponent equations, we introduce several matrix definitions.

1. Define 1^{T} to be a row vector with each element equal to unity and with the number of elements equal to the number of species, n.

2. Define $\mathbf{N}$ to be an $n \times n$ diagonal matrix of the number of molecules (or moles, as appropriate) of each species. With these first two definitions, $N = \sum_i N_i = 1^{\mathrm{T}}\cdot\mathbf{N}\cdot 1$ = total number of molecules in the system.

3. Each theory defines a composition fraction (volume fraction, segment fraction, site fraction), and in addition there are mole fractions. For example, for the Flory theory we define a diagonal matrix of site fractions $\hat{\theta}$ so that $\sum_i \theta_i = 1^{\mathrm{T}}\cdot\hat{\theta}\cdot 1 = 1$. As another example, mole fractions are $\mathbf{x} = \mathbf{N}/N$ and $1^{\mathrm{T}}\cdot\mathbf{x}\cdot 1 = 1^{\mathrm{T}}\cdot\mathbf{N}\cdot 1/N = N/N = 1$.

4. Other diagonal matrices will be used for the various species properties. For example, $\mathbf{M}$ is a diagonal matrix of the species molecular masses.

5. Each theory describes the total system mer–mer interaction energy per segment in terms of quantities which are characteristic of the individual pair interactions and sums these binary interactions, weighted according to the appropriate composition fractions. For the Flory theory we define $\hat{\eta}$ to be the $n \times n$ symmetric matrix of these binary interactions (η_{ij}) for the system. The mixture interaction (η, a scalar) then is

$$\eta = 1^{\mathrm{T}}\cdot\hat{\theta}\cdot\hat{\eta}\cdot\hat{\theta}\cdot 1 = \sum_i \sum_j \theta_i \theta_j \eta_{ij} \qquad (3)$$

6. We also define $\mathbf{U}_i$ to be an $n \times n$ diagonal matrix with only one non-zero element, a 1 in the ith diagonal position. Note that $1^{\mathrm{T}}\cdot\mathbf{U}_i$ and $\mathbf{U}_i\cdot 1$ are the ith row and column unit vectors, respectively, and that $1^{\mathrm{T}}\cdot\mathbf{U}_i\cdot 1 = 1$ for all $\mathbf{U}_i$.

Useful Relations. A number of identities are useful for obtaining thermodynamic relations from the multicomponent polymer solution theory formulations.

1. Given a set of functions, $f_j(x_1,x_2,...,x_n)$, for the various species, j, a function NG formed as a linear combination of the fs with the mole fractions ($\mathbf{x}$ and $\mathbf{f}$ are diagonal matrices)

$$NG = N\sum_j x_j f_j(\mathbf{x}) = N 1^{\mathrm{T}}\cdot\mathbf{x}\cdot\mathbf{f}\cdot 1 \qquad (4)$$

is differentiated with respect to N_i to give

$$\frac{\partial NG}{\partial N_i} = \left(\frac{\partial N}{\partial N_i}\right)G + N1^{\mathrm{T}}\cdot\left(\frac{\mathbf{U}_i}{N} - \frac{\mathbf{x}}{N}\right)\cdot\mathbf{f}\cdot 1 + N1^{\mathrm{T}}\cdot\mathbf{x}\cdot\left(\frac{\partial \mathbf{f}}{\partial N_i}\right)\cdot 1 = f_i(\mathbf{x}) + 1^{\mathrm{T}}\cdot\mathbf{N}\cdot\left(\frac{\partial \mathbf{f}(\mathbf{x})}{\partial N_i}\right)\cdot 1 = f_i(\mathbf{x}) + 1^{\mathrm{T}}\cdot\mathbf{x}\cdot\left(\frac{\partial \mathbf{f}(\mathbf{x})}{\partial x_i}\right)\cdot 1 - 1^{\mathrm{T}}\cdot\mathbf{x}\cdot\left(\frac{\partial \mathbf{f}}{\partial(\mathbf{x}\cdot 1)}\right)\cdot\mathbf{x}\cdot 1 \qquad (5)$$

These relations appear when obtaining activity coefficients as described in step 6 of the general procedure outline. Note that when differentiating $\mathbf{f}$ with respect to the x_i that this is a partial derivative holding the other x_j constant. Because $\sum_i x_i = 1$, we cannot perform this differentiation experimentally, but we can do it mathematically. The actual differentiation is with respect to moles, which is physically meaningful. As long as the sum $\sum_k (\partial f_j/\partial x_k)_{x_m} (\partial x_k/\partial N_i)_{N_l}$ is formed, then the derivative $[(\partial f_j)/(\partial N_i)]_{N_l}$ is obtained. In matrix form, $[\partial x/\partial N_i]_{Nl} = (\mathbf{U}_i - \mathbf{x})/N$, giving the first equality in eq 5. The last term in eq 5 is written in summation form as $\sum_i \sum_j x_i x_j (\partial f_i/\partial x_j)$.

2. The mixture interaction is differentiated with respect to moles, treating the η_{ij} as independent of composition, to give the scalar

$$\left(\frac{\partial \eta}{\partial N_i}\right)_{N_j} = \frac{\partial(1^{\mathrm{T}}\cdot\hat{\theta}\cdot\hat{\eta}\cdot\hat{\theta}\cdot 1)}{\partial N_i} = 2 1^{\mathrm{T}}\cdot\hat{\theta}\cdot\hat{\eta}\cdot\left(\frac{\partial(\hat{\theta}\cdot 1)}{\partial N_i}\right) \qquad (6)$$

with the second equality resulting from the fact that $\hat{\eta}$ is symmetric. Then, because

$$\frac{\partial(\hat{\theta}\cdot\mathbf{1})}{\partial N_i} = \hat{\theta}\cdot\left(\mathbf{N}^{-1}\cdot\mathbf{U}_i - \mathbf{I}\frac{\theta_i}{N_i}\right)\cdot\mathbf{1} \qquad (7)$$

eq 6 becomes

$$\left(\frac{\partial\eta}{\partial N_i}\right)_{N_j} = (2\mathbf{1}^{\mathrm{T}}\cdot\hat{\theta}\cdot\hat{\eta}\cdot\mathbf{U}_i\cdot\mathbf{1} - 2\eta)\frac{\theta_i}{N_i} \qquad (8)$$

3. An identity for part of this last result is particularly useful

$$2\mathbf{1}^{\mathrm{T}}\cdot\hat{\theta}\cdot\hat{\eta}\cdot\mathbf{U}_i\cdot\mathbf{1} = \eta_{ii} + tr(\hat{\theta}\cdot\hat{\eta}) - \mathbf{1}^{\mathrm{T}}\cdot\mathbf{U}_i\cdot\Delta\hat{\eta}\cdot\hat{\theta}\cdot\mathbf{1} \qquad (9)$$

where $\Delta\eta_{ij} \equiv \eta_{ii} + n_{jj} - 2\eta_{ij}$. Note that $\Delta\eta_{ii} = 0$ and that $\Delta\hat{\eta}$ is symmetric. Also, $tr(\hat{\theta}\cdot\hat{\eta}) = \eta + \mathbf{1}^{\mathrm{T}}\cdot\hat{\theta}\cdot\Delta\tilde{\eta}\cdot\hat{\theta}\cdot\mathbf{1}/2$ so that

$$2\mathbf{1}^{\mathrm{T}}\cdot\hat{\theta}\cdot\hat{\eta}\cdot\mathbf{U}_i\cdot\mathbf{1} = \eta_{ii} + \eta + \tfrac{1}{2}(\mathbf{1}^{\mathrm{T}}\cdot\hat{\theta}\cdot\Delta\hat{\eta}\cdot\hat{\theta}\cdot\mathbf{1}) - \mathbf{1}^{\mathrm{T}}\cdot\mathbf{U}_i\cdot\Delta\hat{\eta}\cdot\hat{\theta}\cdot\mathbf{1} \qquad (10)$$

Application to Solution Theories

This section presents the development, following this outline and the matrix approach, of the multicomponent species activity equations for three specific equation-of-state solution theories: the Flory theory, the simplified Flory theory, and the Sanchez–Lacombe lattice fluid theory. For the Flory and Sanchez and Lacombe theories, the development is presented in the six parts which correspond to the general procedure of the outline.

Flory Theory. The polymer solution theories of Flory[4] and Patterson[9] were derived from the initial work of Prigogine.[6,7] Each borrowed the concept of a cell model type partition function which required the separation of internal and external degrees of freedom. Internal degrees of freedom were associated with intramolecular chemical bond forces, whereas external degrees of freedom depended only on intermolecular forces. The derivation introduced the concepts of hard-core and free volumes to account for local liquid structure and, thus, volume changes on mixing. The form of the partition function provided a mathematically simple equation of state and was easily generalized to mixtures. These theories are often characterized as corresponding states theories since they yield reduced equations of state which are functions only of the reduced temperature, pressure, and volume.

1. For pure polymer liquid species i consisting of N r-mers, the partition function is written as a function of temperature and volume and is given by

$$Z(T,V) = (\text{constant})v_i^{*r_iN_ic_i}(\tilde{v}_i^{1/3} - 1)^{3r_iN_ic_i}\exp\left(-\frac{E_{0i}}{kT}\right) \qquad (11)$$

When writing equations for a pure species, the subscripts normally are omitted. In this paper they are included to avoid confusion with mixture equations that will follow. Quantities without subscripts are used to indicate mixture values. Note that $r_iN_iv_i$ is the total system volume for the pure component i.

The total system interaction energy, taken to be van der Waals in form (proportional to v^{-1}) and expressed per mer intermolecular contact site, is

$$-E_{0i} = r_iN_is_i\left(\frac{\eta_i}{2v_i}\right) \qquad (12)$$

where $rNs/2$ represents the number of pair interactions and η_i/v_i is the energy/(contact site pair) for a mer–mer interaction. It is customary to write this system energy in terms of a characteristic energy per segment, ϵ_i^*

$$-E_{0i} = \frac{r_iN_i}{\tilde{v}_i}\left(\frac{s_i\eta_i}{2v_i^*}\right) = \frac{r_iN_i}{\tilde{v}_i}\epsilon_i^* \qquad (13)$$

Table I
Relations between the Molecular and EOS Parameters for the Flory Theory

parameters		
molecular	EOS	relation
r		
v^*	v_{sp}^*	$rv^* = Mv_{\mathrm{sp}}^*$
ϵ^*	p^*	$r\epsilon^* = Mp^*v_{\mathrm{sp}}^*$
c	T^*	$rc = \dfrac{Mp^*v_{\mathrm{sp}}^*}{kT^*}$

Then, a characteristic temperature and pressure are defined by using this characteristic energy and are used to calculate reduced temperatures and pressures:

$$T_i^* = \frac{\epsilon_i^*}{c_ik}; \qquad \tilde{T}_i = \frac{T}{T_i^*} \qquad (14)$$

$$p_i^* = \frac{\epsilon_i^*}{v_i^*} = \frac{s_i\eta_i}{2v_i^{*2}}; \qquad \tilde{p}_i = \frac{p}{p_i^*} \qquad (15)$$

For each pure component, then, there are four fundamental molecular parameters related to three equation-of-state parameters through three equations, given in Table I. For a pure component, the EOS parameters can be obtained experimentally. However, these three parameters cannot be used to obtain a unique set of molecular parameters. In mixtures, the Flory theory sets all hard-core segment volumes (v^*) equal.

2. For a mixture with N total molecules, the mixture partition function is

$$Z = Z(T,V,\mathbf{N}) = (\text{constant})Z_{\mathrm{comb}}v^{*rNc}(\tilde{v}^{1/3} - 1)^{3rNc}\exp\left(-\frac{E_0}{kT}\right) \qquad (16)$$

This is the same partition function as was defined for each of the pure components with the exception of the combinatorial term, which is taken to be the same as the classical Flory–Huggins term:

$$\ln Z_{\mathrm{comb}} = \mathbf{1}^{\mathrm{T}}\cdot\mathbf{N}\cdot\ln\hat{\psi}\cdot\mathbf{1} \qquad (17)$$

where $\ln\hat{\psi}$ is *defined* to be the diagonal ($n \times n$) matrix containing the $\ln\psi_i$ values. Also, for this mixture partition function, v^*, r, c, and E_0 are values for the mixture and are defined by the mixing rules.

3. Mixing rules express average properties for the mixture in terms of the pure component values. Table II gives the mixing rules for the Flory theory. The hard-core segment volumes for the species in the mixture are taken to be equal. The mixture-average segments per molecule, degrees of freedom per segment, and surface area or contact sites per segment are calculated as the total in the mixture divided by the total number of segments in the mixture. The interaction matrix, $\hat{\eta}$, is symmetric, containing the pure component interactions, η_i, as the diagonal elements and unlike pair interactions, η_{ij}, as the off-diagonal elements. In this work, as is typical in the literature, we assume that $\hat{\eta}$ is independent of composition. Also, the characteristic energy, temperature, and pressure for the mixture are related to each other in the same way as these quantities are related for each of the pure components.

For the Flory theory, both segment-fraction and site-fraction compositions are defined. In our formulation, diagonal segment fraction and site fraction arrays are defined according to $\hat{\psi} = \mathbf{r}\cdot\mathbf{N}/rN$ and $\hat{\theta} = \mathbf{r}\cdot\mathbf{N}\cdot\mathbf{s}/rNs$. Hence, the ith diagonal elements of $\hat{\psi}$ and $\hat{\theta}$ are $\psi_i = r_iN_i/rN$ and $\theta_i = r_iN_is_i/rNs$, which are the fraction of segments and sites, respectively, in the total mixture that

Table II
Mixing Rules for the Flory Theory

$$v^* = v_1^* = v_2^* = \ldots = v_n^*$$

$$r \equiv \frac{\sum r_i N_i}{\sum N_i} = \frac{\mathbf{1}^{\mathrm{T}}\cdot\mathbf{r}\cdot\mathbf{N}\cdot\mathbf{1}}{N}; \quad \text{i.e., } rN = \mathbf{1}^{\mathrm{T}}\cdot\mathbf{r}\cdot\mathbf{N}\cdot\mathbf{1}$$

$$c \equiv \frac{\sum r_i N_i c_i}{\sum r_i N_i} = \frac{\mathbf{1}^{\mathrm{T}}\cdot\mathbf{r}\cdot\mathbf{N}\cdot\mathbf{c}\cdot\mathbf{1}}{rN}; \quad \text{i.e., } rNc = \mathbf{1}^{\mathrm{T}}\cdot\mathbf{r}\cdot\mathbf{N}\cdot\mathbf{c}\cdot\mathbf{1}$$

$$s \equiv \frac{\sum r_i N_i s_i}{\sum r_i N_i} = \frac{\mathbf{1}^{\mathrm{T}}\cdot\mathbf{r}\cdot\mathbf{N}\cdot\mathbf{s}\cdot\mathbf{1}}{rN}; \quad \text{i.e., } rNs = \mathbf{1}^{\mathrm{T}}\cdot\mathbf{r}\cdot\mathbf{N}\cdot\mathbf{s}\cdot\mathbf{1}$$

$$-E_0 \equiv \frac{rNs\eta}{2v}, \text{ where } \eta \equiv \mathbf{1}^{\mathrm{T}}\cdot\hat{\theta}\cdot\hat{\eta}\cdot\hat{\theta}\cdot\mathbf{1}; \quad \hat{\theta} \equiv \frac{\mathbf{r}\cdot\mathbf{N}\cdot\mathbf{s}}{rNs}, \text{ the site fractions}$$

$$\epsilon^* = \frac{s\eta}{2v^*}; \quad T^* = \frac{\epsilon^*}{ck}; \; p^* = \frac{\epsilon^*}{v^*}$$

are contributed by species i.

4. The equation of state is obtained from the partition function by the relation

$$p = -\left(\frac{\partial NA}{\partial V}\right)_{T,N_i} = kT\left(\frac{\partial \ln Z(T,V)}{\partial V}\right)_{T,N_i} \tag{18}$$

In this differentiation, $rNv = V$, and the well-known result, obtained for the pures as well as for the mixture, is

$$\frac{\tilde{p}\tilde{v}}{\tilde{T}} = \frac{\tilde{v}^{1/3}}{\tilde{v}^{1/3} - 1} - \frac{1}{\tilde{v}\tilde{T}} \tag{19}$$

The characteristic EOS parameters v_{sp}^*, p^*, and T^* are evaluated by fitting eq 19 to experimental pressure–volume–temperature (PVT) data.[3,4,10] Bondi's correlations[11] can be used to generate reasonable approximations to limited PVT data. Values of p^*, T^*, and v_{sp}^* are tabulated by Bonner and Prausnitz[10] for many common polymers and solvents.

Defining site fractions introduces segment–surface ratios s_i/s_j, which can be estimated from crystallographic or other geometric considerations[12,13] or via the group contribution format of Bondi.[11] Comparison with actual polymer solution thermodynamic measurements indicates that neither method is entirely satisfactory.[14-17] Alternatively, s_i/s_j can be treated as an additional adjustable-fit parameter.[14,18]

5. The excess Helmholtz function,[8] A^{E} $(=A - \sum_i x_i A_i - kT\sum_i x_i \ln x_i)$, is

$$\frac{NA^{\mathrm{E}}}{kT} = \left[\frac{E_0}{kT} - 3rNc \ln (v^{1/3} - v^{*1/3}) + \mathbf{1}^{\mathrm{T}}\cdot\mathbf{N}\cdot\ln \hat{\psi}\cdot\mathbf{1} - \ln (\text{const})\right] - \sum_i \left[\frac{E_{0i}}{kT} - 3r_iN_ic_i \ln (v_i^{1/3} - v^{*1/3}) - \ln (\text{const})\right] - \mathbf{1}^{\mathrm{T}}\cdot\mathbf{N}\cdot\ln \mathbf{x}\cdot\mathbf{1} \tag{20}$$

6. The activity for a species i can be obtained through the activity coefficient of i, obtained by differentiating the above expression with respect to moles of i

$$\left(\frac{\partial NA^{\mathrm{E}}/kT}{\partial N_i}\right)_{T,V,N_j} = \ln \gamma_i = \left(\frac{\partial E_0/kT}{\partial N_i}\right) - \sum_j \left(\frac{\partial (E_{0j}/kT)}{\partial N_i}\right) - 3\left(\frac{\partial [rNc \ln (v^{1/3} - v^{*1/3})]}{\partial N_i}\right) + 3r_ic_i \ln (v_i^{1/3} - v^{*1/3}) - r_ic_i\left(\frac{\tilde{p}_i\tilde{v}_i}{\tilde{T}_i} + \frac{1}{\tilde{v}_i\tilde{T}_i}\right) + \mathbf{1}^{\mathrm{T}}\cdot\mathbf{N}\cdot\frac{\partial}{\partial N_i}[\ln \hat{\psi} - \ln \mathbf{x}]\cdot\mathbf{1} + \ln \psi_i - \ln x_i \tag{21}$$

This result can be expressed in terms of EOS parameters and interaction energies. Obtaining the result, made considerably easier by the matrix formulations, nevertheless requires considerable manipulation and substitution. These steps are summarized in Table III. Substitution E makes use of eq 10. Substitution F in Table III comes from combining D and E and collecting $\psi_i rNc\tilde{v}^{1/3}/[N_i(\tilde{v}^{1/3} - 1)]$ and $-\psi_i rNs\eta/(2vkTN_i)$ through the EOS. The multicomponent matrix form of the Flory theory equation for species i activity then is

$$\ln a_i = \ln \psi_i + \mathbf{1}^{\mathrm{T}}\cdot\hat{\psi}\cdot(\mathbf{I} - M_i v_{i\mathrm{sp}}^* \mathbf{M}^{-1}\cdot\mathbf{v}_{\mathrm{sp}}^{*-1})\cdot\mathbf{1} + \frac{M_i p_i^* v_{i\mathrm{sp}}^*}{kT}\left[3\tilde{T}_i \ln \frac{(\tilde{v}_i^{1/3} - 1)}{(\tilde{v}^{1/3} - 1)} + \tilde{\rho}_i - \tilde{\rho} + \tilde{p}_i(\tilde{v} - \tilde{v}_i)\right] + \frac{M_i v_{i\mathrm{sp}}^* \tilde{\rho}}{kT}\left[\mathbf{1}^{\mathrm{T}}\cdot\mathbf{U}_i\cdot\left(\frac{s_i\Delta\hat{\eta}}{2v^{*2}}\right)\cdot\hat{\theta}\cdot\mathbf{1} - \tfrac{1}{2}\mathbf{1}^{\mathrm{T}}\cdot\hat{\theta}\cdot\left(\frac{s_i\Delta\hat{\eta}}{2v^{*2}}\right)\cdot\hat{\theta}\cdot\mathbf{1}\right] \tag{22}$$

Flory's theory conventionally is written in terms of X_{ij} parameters, and accordingly we define an asymmetric $\mathbf{X}$ (energy density) as

$$\mathbf{X} \equiv \frac{\mathbf{s}\cdot\Delta\hat{\eta}}{2v^{*2}} \tag{23}$$

For example, $X_{12} = s_1\Delta\eta_{12}/(2v^{*2})$; $X_{21} = s_2\Delta\eta_{21}/(2v^{*2}) = s_2X_{12}/s_1$. In terms of these $\mathbf{X}$ parameters, the interaction energy terms in eq 22 are

$$\frac{M_i v_{i\mathrm{sp}}^* \tilde{\rho}}{kT}\left[\mathbf{1}^{\mathrm{T}}\cdot\mathbf{U}_i\cdot\mathbf{X}\cdot\hat{\theta}\cdot\mathbf{1} - \tfrac{1}{2}\mathbf{1}^{\mathrm{T}}\cdot\hat{\psi}\cdot\mathbf{X}\cdot\hat{\theta}\cdot\mathbf{1}\frac{\theta_i}{\psi_i}\right] \tag{24}$$

because

$$\hat{\theta}\cdot\frac{s_i\Delta\hat{\eta}}{2v^{*2}} = \left(\frac{\mathbf{r}\cdot\mathbf{N}}{rN}\right)\cdot\left(\frac{\mathbf{s}\cdot\Delta\hat{\eta}}{2v^{*2}}\right)\frac{rN}{rNs}s_i = \hat{\psi}\cdot\mathbf{X}\frac{\theta_i}{\psi_i} \tag{25}$$

By allowing for free volume effects and molecular contact surface area dissimilarities, the Flory EOS theory provides an improved representation of polymer solution thermodynamics beyond the scope of the original lattice theory. This advantage, however, is at the expense of a considerably more complex form and the need for pure component characteristic parameters. Successful application of the theory requires accurate values of these parameters.[12,15] Nevertheless, it embodies the essence of the lattice theory by incorporating the same formulation for combinatorial contributions. The improved theory usually succeeds in predicting thermodynamic behavior where the lattice theory fails. For example, although it qualitatively predicts the simultaneous occurrence of both the UCST and LCST, the predicted value of the LCST is usually inaccurate.[3] McMaster[19] reported that relatively small changes in values of the thermal expansion coefficients produced significant changes in the predicted LCST for binary polymer systems.

The theory has been successfully applied to nonpolar solutions.[12] Using gas chromatography, Bonner et al.[20] reported significant improvement over the lattice theory for correlating polymer thermodynamics. Pouchlý and Patterson[13] presented evidence in favor of the theoretical consideration of interaction between molecular surfaces of the components.

Simplified Flory Theory. A simplified version of Flory's theory has been presented by Bonner and Brockmeier,[21] following Bonner and Prausnitz[10] by assuming that all of the segment–surface values (s) are equal. If this is true, then

$$\hat{\theta} = \frac{\mathbf{r}\cdot\mathbf{N}\cdot\mathbf{s}}{rNs} = \frac{\mathbf{r}\cdot\mathbf{N}s}{rNs} = \frac{\mathbf{r}\cdot\mathbf{N}}{rN} = \hat{\psi} \tag{26}$$

Table III
Substitutions Used in Obtaining the Flory Theory Result

substitution	
A	$\mathbf{1}^{\mathrm{T}}\cdot\mathbf{N}\cdot\left(\dfrac{\partial \ln \mathbf{x}}{\partial N_i}\right)\cdot\mathbf{1} = \mathbf{1}^{\mathrm{T}}\cdot\dfrac{\mathbf{N}}{N}\cdot\mathbf{x}^{-1}\cdot(\mathbf{U}_i - \mathbf{x})\cdot\mathbf{1} = 1 - 1 = 0$
B	$\mathbf{1}^{\mathrm{T}}\cdot\mathbf{N}\cdot\left(\dfrac{\partial \ln \hat{\psi}}{\partial N_i}\right)\cdot\mathbf{1} = \mathbf{1}^{\mathrm{T}}\cdot\mathbf{N}\cdot\left(\mathbf{N}^{-1}\cdot\mathbf{U}_i - \mathbf{I}\dfrac{\psi_i}{N_i}\right)\cdot\mathbf{1} = 1 - \dfrac{r_i}{r} = 1 - \dfrac{\mathbf{1}^{\mathrm{T}}\cdot\mathbf{r}\cdot\mathbf{r}^{-1}\cdot\mathbf{N}\cdot\mathbf{1}}{rN}r_i = \mathbf{1}^{\mathrm{T}}\cdot\hat{\psi}\cdot(\mathbf{I} - r_i\boldsymbol{r}^{-1})\cdot\mathbf{1}$
C	$\dfrac{\partial}{\partial N_i}\left(\Sigma_j\dfrac{E_{0j}}{kT}\right) = \dfrac{\partial}{\partial N_i}\left(\Sigma_j\dfrac{-r_jp_j^*\tilde{v}_j^{-1}v^*N_j}{kT}\right) = -\dfrac{2r_ip_i^*\tilde{\rho}_iv^*}{kT}$
D	$\dfrac{\partial}{\partial N_i}[3rNc \ln (v^{1/3} - v^{*1/3})] = 3r_ic_i \ln [v^{*1/3}(\tilde{v}^{1/3} - 1)] - \dfrac{rNc\tilde{v}^{1/3}}{(\tilde{v}^{1/3} - 1)}\dfrac{\psi_i}{N_i}$, obtained by using $\left(\dfrac{\partial(rNc)}{\partial N_i}\right) = r_ic_i$ and $\dfrac{\partial}{\partial N_i} \ln (v^{1/3} - v^{*1/3}) = -\dfrac{\tilde{v}^{1/3}\psi_i}{3(\tilde{v}^{1/3} - 1)N_i}$ where $\left(\dfrac{\partial v^{1/3}}{\partial N_i}\right) = \dfrac{\partial}{\partial N_i}\left(\dfrac{rNv}{rN}\right)^{1/3} = \left[\dfrac{\partial}{\partial N_i}\left(\dfrac{V}{rN}\right)^{1/3}\right]_{T,V,N_j} = -\dfrac{v^{1/3}}{3}\dfrac{\psi_i}{N_i}$
E	$\dfrac{\partial}{\partial N_i}\left(\dfrac{E_0}{kT}\right) = -\left[\dfrac{\partial}{\partial N_i}\dfrac{(rNs)(rN)}{2VkT}(\mathbf{1}^{\mathrm{T}}\cdot\hat{\theta}\cdot\hat{\eta}\cdot\hat{\theta}\cdot\mathbf{1})\right]_{T,V,N_j} =$ $-\left(\dfrac{r_is_i\eta}{v} + \dfrac{(rNs)\eta}{v}\dfrac{\psi_i}{N_i} + 2\dfrac{rNs}{v}[\mathbf{1}^{\mathrm{T}}\cdot\hat{\theta}\cdot\hat{\eta}\cdot\mathbf{U}_i\cdot\mathbf{1} - \eta]\dfrac{\theta_i}{N_i}\right)\dfrac{1}{2kT} = -\dfrac{rNs}{2kTv}\left(-\dfrac{\theta_i}{N_i}\eta + \dfrac{\psi_i}{N_i}\eta + 2\mathbf{1}^{\mathrm{T}}\cdot\hat{\theta}\cdot\hat{\eta}\cdot\mathbf{U}_i\cdot\mathbf{1}\dfrac{\theta_i}{N_i}\right) =$ $-\dfrac{rNs}{2vkT}\left[\dfrac{\psi_i}{N_i}\eta + \dfrac{\theta_i}{N_i}(\eta_i + \tfrac{1}{2}\mathbf{1}^{\mathrm{T}}\cdot\hat{\theta}\cdot\Delta\hat{\eta}\cdot\hat{\theta}\cdot\mathbf{1} - \mathbf{1}^{\mathrm{T}}\cdot\mathbf{U}_i\cdot\Delta\hat{\eta}\cdot\hat{\theta}\cdot\mathbf{1})\right]$
F	$\dfrac{\partial}{\partial N_i}\left(\dfrac{E_0}{kT}\right) - 3\dfrac{\partial}{\partial N_i}[rNc \ln (v^{1/3} - v^{*1/3})] = -3r_ic_i \ln [v^{*1/3}(\tilde{v}^{1/3} - 1)] +$ $\dfrac{r_ip_i^*v^*}{kT}\tilde{p}_i\tilde{v} - \dfrac{r_iv^*}{kT\tilde{v}}\left[\dfrac{s_i\eta_i}{2v^{*2}} + \tfrac{1}{2}\mathbf{1}^{\mathrm{T}}\cdot\hat{\theta}\cdot\dfrac{s_i\Delta\hat{\eta}}{2v^{*2}}\cdot\hat{\theta}\cdot\mathbf{1} - \mathbf{1}^{\mathrm{T}}\cdot\mathbf{U}_i\cdot\dfrac{s_i\Delta\hat{\eta}}{2v^{*2}}\cdot\hat{\theta}\cdot\mathbf{1}\right]$

and the first equality of the second line of relation E in Table III is

$$\frac{\partial}{\partial N_i}\left(\frac{E_0}{kT}\right) = -\frac{r_iv^*}{kT\tilde{v}}\left[2\mathbf{1}^{\mathrm{T}}\cdot\hat{\psi}\cdot\frac{s\hat{\eta}}{2v^{*2}}\cdot\mathbf{U}_i\cdot\mathbf{1}\right] \qquad (27)$$

Combining this with the other relations, as for the full Flory theory, gives

$$\ln a_i = \ln \psi_i + \mathbf{1}^{\mathrm{T}}\cdot\hat{\psi}\cdot(\mathbf{I} - M_iv_{i\mathrm{sp}}^*\cdot\mathbf{M}^{-1}\cdot\mathbf{v}_{\mathrm{sp}}^{*-1})\cdot\mathbf{1} + \frac{M_ip_i^*v_{i\mathrm{sp}}^*}{kT}\left[3\tilde{T}_i \ln \frac{(\tilde{v}_i^{1/3} - 1)}{(\tilde{v}^{1/3} - 1)} + \tilde{\rho}_i - \tilde{p}_i\tilde{v}_i\right] + \frac{rNc\tilde{v}^{1/3}}{(\tilde{v}^{1/3} - 1)}\frac{\psi_i}{N_i} - \frac{M_iv_{i\mathrm{sp}}^*\tilde{\rho}}{kT}\left(2\mathbf{1}^{\mathrm{T}}\cdot\hat{\psi}\cdot\frac{s\hat{\eta}}{2v^{*2}}\cdot\mathbf{U}_i\cdot\mathbf{1}\right) \qquad (28)$$

Similar to the full Flory theory, $\psi_irNc\tilde{v}^{1/3}/[N_i(\tilde{v}^{1/3} - 1)]$ is replaced through the EOS. The final equation for this simplified theory, then, is

$$\ln a_i = \ln \psi_i + \mathbf{1}^{\mathrm{T}}\cdot\hat{\psi}\cdot(\mathbf{I} - M_iv_{i\mathrm{sp}}^*\mathbf{M}^{-1}\cdot\mathbf{v}_{\mathrm{sp}}^{*-1})\cdot\mathbf{1} + \frac{M_ip_i^*v_{i\mathrm{sp}}^*}{kT}\left[3\tilde{T}_i \ln \frac{(\tilde{v}_i^{1/3} - 1)}{(\tilde{v}^{1/3} - 1)} + \tilde{\rho}_i + \tilde{p}_i(\tilde{v} - \tilde{v}_i)\right] + \frac{M_iv_{i\mathrm{sp}}^*\tilde{\rho}}{kT}(\mathbf{1}^{\mathrm{T}}\cdot\hat{\psi}\cdot\mathbf{P}^*\cdot\hat{\psi}\cdot\mathbf{1} - 2\mathbf{1}^{\mathrm{T}}\cdot\hat{\psi}\cdot\mathbf{P}^*\cdot\mathbf{U}_i\cdot\mathbf{1}) \qquad (29)$$

where $\mathbf{P}^* = s\hat{\eta}/(2v^{*2})$. Also, we can define a scalar characteristic pressure for the mixture $p^* = \mathbf{1}^{\mathrm{T}}\cdot\hat{\psi}\cdot\mathbf{P}^*\cdot\hat{\psi}\cdot\mathbf{1}$. Note that in their result, Bonner and Brockmeier do not include the $\tilde{p}_i\tilde{v}$ term, which is small at low pressures.

The simplifying assumption of equal contact area for all segments in solution makes this version more restrictive in its description of polymer solution thermodynamics than the original Flory theory. Predictions of the two versions are analogous, of course, except for those situations where unequal interaction sites between components become a major contributing factor.[13,14,17]

Sanchez and Lacombe Lattice Fluid Theory. Another EOS approach to polymer solution thermodynamics is the lattice fluid model of Sanchez and Lacombe.[5] Although the theory used the formalism of the Flory–Huggins theory by applying a lattice to enumerate configurations, the distinctive difference was that empty lattice sites or free volume effects were taken into account. Thus, this "hole" theory allowed for a compressible lattice and, therefore, volume changes on mixing, which were previously excluded in the original lattice theory.

The development led to a statistical mechanical partition function which, unlike the cell model type partition function of the Flory theory, did not require the distinction and separation of internal and external degrees of freedom. In addition, except for polymers of sufficiently high molecular mass, the lattice fluid equation of state did not satisfy a simple corresponding states principle.

1. For this model, the partition function for pure species i is written as

$$Z_i(T,p) = \left(\frac{1}{f_0}\right)^{N_0}\left(\frac{\omega_i}{f_i}\right)^{N_i}\exp\left(-\frac{E_i + pV_i}{kT}\right) \qquad (30)$$

In these and subsequent equations for this theory, when concerned with a pure species only (as opposed to a mixture), Sanchez and Lacombe use no subscripts and use r for the (segment)/(molecule) (as opposed to r°). However, in the mixture the segments per molecule may be different for a species from its value in the pure state. In the mixture, then, Sanchez and Lacombe use r_i to indicate the

Table IV
Relations between the Molecular and EOS Parameters for the Sanchez–Lacombe Theory

parameters		
molecular	EOS	relations
r	v_{sp}^*	$rv^* = Mv_{\mathrm{sp}}^*$
v^*	p^*	$v^* = \dfrac{kT^*}{p^*}$
ϵ^*	T^*	$\epsilon^* = kT^*$

Table V
Mixing Rules for the Sanchez–Lacombe Theory

$$r_i v^* = r_i^\circ v_i^* \quad \text{or} \quad \mathbf{r}\mathbf{v}^* = \mathbf{r}^\circ\cdot\mathbf{v}^*$$

$$r = \frac{rN}{N} = \frac{1^{\mathrm{T}}\cdot\mathbf{r}\cdot\mathbf{N}\cdot 1}{N} = \frac{1^{\mathrm{T}}\cdot\mathbf{r}^\circ\cdot\mathbf{N}\cdot 1}{N}$$

$$V = N_0 v^* + V^* = (N_0 + rN)v^* = rNv$$

$$(V^* = rNv^* = 1^{\mathrm{T}}\cdot\mathbf{r}\cdot\mathbf{N}v^*\cdot 1 = 1^{\mathrm{T}}\cdot\mathbf{r}^\circ\cdot\mathbf{N}\cdot\mathbf{v}^*\cdot 1)$$

$$E = -rN\tilde{\rho}\epsilon^*; \quad p^* \equiv \frac{\epsilon^*}{v^*}; \quad T^* \equiv \frac{\epsilon^*}{k}$$

mixture value for species i and r_i° to indicate the pure value for species i. To avoid confusion, we have included the subscript and superscript notation in the pure-state definitions.

The total system energy, E_i, is calculated as (mer–mer interaction energy) × (number of pair interactions) × (probability that two cells are occupied by mers):

$$E_i = -(\epsilon_i)\left[\frac{z_i}{2}(N_0 + r_i^\circ N_i)\right](f_i^2) = -r_i^\circ N_i \tilde{\rho}_i \epsilon_i^* \qquad (31)$$

where $\epsilon_i^* = z_i\epsilon_i/2$. Characteristic EOS parameters and reduced properties are defined according to

$$T_i^* = \frac{\epsilon_i^*}{k}; \qquad \tilde{T}_i = \frac{T}{T_i^*} \qquad (32)$$

$$p_i^* = \frac{\epsilon_i^*}{v_i^*}; \qquad \tilde{p}_i = \frac{p}{p_i^*} \qquad (33)$$

For this theory, each pure component can be described by using three molecular parameters or three EOS parameters, related by three equations (Table IV). Both sets of parameters can be obtained uniquely from pure component data.

2. For a mixture with N total molecules, the mixture partition function is

$$Z(T,p,N) = \left(\frac{1}{f_0}\right)^{N_0}\left(\frac{\omega_1}{f_1}\right)^{N_1} \cdots \left(\frac{\omega_n}{f_n}\right)^{N_n} \exp\left(-\frac{E + pV}{kT}\right) \qquad (34)$$

3. Mixing rules for the lattice fluid theory are given in Table V. These rules concern hard-core segment volumes, the number of segments per molecule, the total volume of the mixture, and the mixture interaction energy.

The Sanchez and Lacombe theory defines a hard-core segment volume for the mixture, as does Flory's, but allowing this volume to be the same for each species in the mixture requires that r for each species be different in the mixture from its value in the pure state. The hard-core volume occupied by an entire molecule (not segment) in the mixture must, however, be the same as in the pure state. This fact, and the concept of holes in the lattice, lead to the first rule in Table V.

The second rule defines a mixture average number of segments per molecule in terms of the species values in the mixture and in the pure state. The number of segments or cells occupied by molecules in solution is required to be the same as the total for the individual pure states, preserving the number of pair interactions. From this definition, segment fractions can be defined, both in terms of mixture segments per molecule values, $\hat{\psi} \equiv \mathbf{r}\cdot\mathbf{N}/rN$, and in terms of unmixed (pure state) segments per molecule values, $\hat{\psi}^\circ \equiv \mathbf{r}^\circ\cdot\mathbf{N}/rN$. Note that even though $1^{\mathrm{T}}\cdot\hat{\psi}\cdot 1 = 1^{\mathrm{T}}\cdot\hat{\psi}^\circ\cdot 1 = 1$, it still holds that $\hat{\psi} \neq \hat{\psi}^\circ$; i.e., the individual r_iN_i terms are not equal to the corresponding $r_i^\circ N_i$ terms, but the sums $\sum r_iN_i$ and $\sum r_i^\circ N_i$ are equal.

The third rule states that the (total volume of the mixture) = (volume of the vacant sites) + (hard core volume of the molecules). Then a reduced volume is defined for the mixture, as well as the fraction of cells occupied by holes and by each of the species in the mixture:

$$\tilde{v} = \frac{v}{v^*} = \frac{rNv}{rNv^*} = \frac{(N_0 + rN)}{rN} = \frac{1}{\tilde{\rho}} \qquad (35)$$

$$f_0 = \frac{N_0}{N_0 + rN} = 1 - \tilde{\rho}; \qquad N_0 = rN(\tilde{v} - 1)$$

$$f_i = \frac{r_iN_i}{N_0 + rN} = \frac{\psi_i rN}{N_0 + rN} = \psi_i\tilde{\rho} \qquad (36)$$

For the pure state, analogous equations hold where values are for the pure species and the segment fraction is unity.

The relation for the total interaction energy in the mixture is analogous to that for a pure component and serves to define ϵ^* for the mixture. As will be discussed later in this paper, Sanchez and Lacombe have suggested two forms for ϵ^* in terms of the individual species interactions. One form assumes pairwise additivity of the elements of an interaction energy matrix $\hat{\epsilon}^*$ ($\epsilon^* = 1^{\mathrm{T}}\cdot\hat{\psi}\cdot\epsilon^*\cdot\hat{\psi}\cdot 1$), where the ϵ_{ij}^* are assumed composition independent; the other assumes pairwise additivity of the elements of an interaction $\mathbf{P}^*$ matrix ($p^* = 1^{\mathrm{T}}\cdot\hat{\psi}\cdot\mathbf{P}^*\cdot\hat{\psi}\cdot 1$), where the P_{ij}^* are assumed composition independent. In terms of ϵ^*, $E = -rN\tilde{\rho}\epsilon^*$; in terms of p^*, $E = -rN\tilde{\rho}p^*v^*$.

4. The EOS for this theory is obtained from the Gibbs free energy by using the thermodynamic relations

$$V = \left(\frac{\partial NG}{\partial p}\right)_{T,N_i} = -kT\left(\frac{\partial \ln Z}{\partial p}\right)_{T,N_i} \qquad (37)$$

Defining $\tilde{G} = G/r\epsilon^*$ gives for the Sanchez–Lacombe theory

$$\tilde{G} = -\tilde{\rho} + \tilde{p}\,\tilde{v} + \tilde{T}\left[(\tilde{v} - 1)\ln(1 - \tilde{\rho}) + \frac{1}{r}\ln\frac{\tilde{\rho}}{\omega}\right] \qquad (38)$$

in which $\tilde{v}$ is in turn a function of $\tilde{p}$ and $\tilde{T}$. Now, in terms of reduced quantities, eq 37 becomes $(\partial\tilde{G}/\partial\tilde{p})_{\tilde{T}} = \tilde{v}$, which in terms of eq 38 is

$$\tilde{v} = \left(\frac{\partial\tilde{G}}{\partial\tilde{p}}\right)_{\tilde{T},\tilde{v}} + \left(\frac{\partial\tilde{G}}{\partial\tilde{v}}\right)_{\tilde{T},\tilde{p}}\left(\frac{\partial\tilde{v}}{\partial\tilde{p}}\right)_{\tilde{T}}$$

$$= \tilde{v} + \left(\frac{\partial\tilde{G}}{\partial\tilde{v}}\right)_{\tilde{T},\tilde{p}}\left(\frac{\partial\tilde{v}}{\partial\tilde{p}}\right)_{\tilde{T}} \qquad (39)$$

from which it is clear that $(\partial\tilde{G}/\partial\tilde{v})_{\tilde{T},\tilde{p}}\ 0$. Performing this differentiation on eq 38 and setting it equal to zero give the EOS for this theory as

$$\tilde{\rho}^2 + \tilde{p} + \tilde{T}[\ln(1 - \tilde{\rho}) + (1 - 1/r)\tilde{\rho}] = 0 \qquad (40)$$

For a pure component, the quantities in the equations above are for the pure species, including r_i°, and for the mixture they are all mixture properties.

Sanchez and Lacombe,[5,15] using a nonlinear least-squares fit of experimental PVT data to the EOS, tabulated the characteristic molecular parameters for low molecular weight and polymeric fluids, respectively. For polymers where PVT data were limited, the parameters were estimated from one-point experimental values of density, thermal expansion coefficient, and either thermal pressure coefficient or isothermal compressibility. Note that these pure component parameters have different values from the Flory theory values. Also, since there are only three molecular parameters related to the three EOS parameters, the molecular parameters for this EOS theory can be evaluated uniquely.

5. The excess Gibbs function,[8] G^{E} ($=G - \sum_i x_i G_i - kT\sum_i x_i \ln x_i$), becomes

$$\begin{aligned} \frac{NG^{\mathrm{E}}}{kT} = {} & \Bigg[\frac{\mathrm{E} + pV}{kT} + rN(\tilde{v} - 1)\ln(1 - \tilde{\rho}) + \\ & \mathbf{1}^{\mathrm{T}}\cdot\mathbf{N}\cdot\ln\hat{\psi}\tilde{\rho}\cdot\mathbf{1}\Bigg] - \mathbf{1}^{\mathrm{T}}\cdot\mathbf{N}\cdot\ln\mathbf{x}\cdot\mathbf{1} - \Bigg[\sum_j \frac{E_j + pV_j}{kT} + \\ & \sum_j r_j{}^{\circ}N_j(\tilde{v}_j - 1)\ln(1 - \tilde{\rho}_j) + \mathbf{1}^{\mathrm{T}}\cdot\mathbf{N}\cdot\ln\hat{\rho}\cdot\mathbf{1}\Bigg] \end{aligned} \tag{41}$$

In this result, the $\ln(1 - \tilde{\rho})$ terms come from $\ln f_0$ for the mixture and for the pure components; the $\ln \psi_j\tilde{\rho}$ and $\ln \tilde{\rho}_j$ terms come from $\ln f_j$ in the mixture and $\ln f_j$ for the pure components. The $\ln \omega_i$ terms arising from the mixture and pure component $\ln Z$ values cancel because ω_i is the same in the mixture as in the pure state.

6. Differentiating this result with respect to N_i gives the activity coefficient of species i

$$\begin{aligned} \ln \gamma_i = {} & \frac{\partial}{\partial N_i}\Bigg[\frac{E + pV}{kT} + rN(\tilde{v} - 1)\ln(1 - \tilde{\rho}) - \\ & \sum_j \frac{E_j + pV_j}{kT}\Bigg] + \mathbf{1}^{\mathrm{T}}\cdot\mathbf{N}\cdot\frac{\partial}{\partial N_i}\ln(\tilde{\rho}\hat{\psi})\cdot\mathbf{1} + \ln(\tilde{\rho}\psi_i) - \\ & r_i{}^{\circ}(\tilde{v}_i - 1)\ln(1 - \tilde{\rho}_i) - \ln\tilde{\rho}_i - \ln x_i \end{aligned} \tag{42}$$

Analogous to the Flory result, this equation can be expressed in terms of pure component and mixture EOS parameters and interaction energies. For this theory, a result in terms of molecular parameters can also be obtained. The relations for obtaining this final form (in addition to relation A of Table III) are summarized in Table VI. Equation E of this table uses eq 10. The $\partial\tilde{\rho}/\partial N_i$ terms in relations A through E cancel through the mixture EOS. The Sanchez and Lacombe multicomponent equation for the case of pairwise additivity of p^* and in terms of molecular parameters is

$$\begin{aligned} \ln a_i = {} & \ln \psi_i + \mathbf{1}^{\mathrm{T}}\cdot\hat{\psi}\cdot(\mathbf{I} - r_i\mathbf{r}^{-1})\cdot\mathbf{1} + \frac{r_i{}^{\circ}}{\tilde{T}_i}\Bigg(\tilde{p}_i - \tilde{\rho} + \\ & \tilde{p}_i(\tilde{v} - \tilde{v}_i) + \tilde{T}_i\Bigg[(\tilde{v} - 1)\ln(1 - \tilde{\rho}) - \\ & (\tilde{v}_i - 1)\ln(1 - \tilde{\rho}_i) + \frac{1}{r_i{}^{\circ}}\ln\frac{\tilde{\rho}}{\tilde{\rho}_i}\Bigg]\Bigg) + \\ & r_i{}^{\circ}\tilde{\rho}\Bigg[\mathbf{1}^{\mathrm{T}}\cdot\mathbf{U}_i\cdot\frac{\Delta\mathbf{P}^* v_i{}^*}{kT}\cdot\hat{\psi}\cdot\mathbf{1} - \tfrac{1}{2}\mathbf{1}^{\mathrm{T}}\cdot\hat{\psi}\cdot\frac{\Delta\mathbf{P}^* v_i{}^*}{kT}\cdot\hat{\psi}\cdot\mathbf{1}\Bigg] \end{aligned} \tag{43}$$

In terms of EOS parameters this is

$$\begin{aligned} \ln a_i = {} & \ln \psi_i + \mathbf{1}^{\mathrm{T}}\cdot\hat{\psi}\cdot(\mathbf{I} - r_i\mathbf{r}^{-1})\cdot\mathbf{1} + \frac{M_i v_{i\mathrm{sp}}{}^* p_i{}^*}{kT}\Bigg(\tilde{p}_i - \tilde{\rho} + \\ & \tilde{p}_i(\tilde{v} - \tilde{v}_i) + \tilde{T}_i[(\tilde{v} - 1)\ln(1 - \tilde{\rho}) - (\tilde{v}_i - 1)\ln(1 - \tilde{\rho}_i)] + \\ & \ln\frac{\tilde{\rho}}{\tilde{\rho}_i}\Bigg) + \frac{M_i v_{i\mathrm{sp}}{}^*}{kT}\tilde{\rho}[\mathbf{1}^{\mathrm{T}}\cdot\mathbf{U}_i\cdot\Delta\mathbf{P}^*\cdot\hat{\psi}\cdot\mathbf{1} - \tfrac{1}{2}\mathbf{1}^{\mathrm{T}}\cdot\hat{\psi}\cdot\Delta\mathbf{P}^*\cdot\hat{\psi}\cdot\mathbf{1}] \end{aligned} \tag{44}$$

Following Flory, Sanchez and Lacombe also define a set of dimensionless parameters $\mathbf{X}_i \equiv \Delta\mathbf{P}^* v_i{}^*/kT$ so that the energy terms in eq 43 are

$$r_i{}^{\circ}\tilde{\rho}[\mathbf{1}^{\mathrm{T}}\cdot\mathbf{U}_i\cdot\mathbf{X}_i\cdot\hat{\psi}\cdot\mathbf{1} - \tfrac{1}{2}\mathbf{1}^{\mathrm{T}}\cdot\hat{\psi}\cdot\mathbf{X}_i\cdot\hat{\psi}\cdot\mathbf{1}] \tag{45}$$

In some of their papers, Sanchez and Lacombe have invoked pairwise additivity of ϵ^* instead of p^*, $\epsilon^* = \mathbf{1}^{\mathrm{T}}\cdot\hat{\psi}\cdot\hat{\epsilon}^*\cdot\hat{\psi}\cdot\mathbf{1}$. Then they obtained results with the multicomponent form

$$\begin{aligned} \ln a_i = {} & \ln \psi_i + \mathbf{1}^{\mathrm{T}}\cdot\hat{\psi}\cdot(\mathbf{I} - r_i\mathbf{r}^{-1})\cdot\mathbf{1} + \frac{r_i{}^{\circ}}{\tilde{T}_i}\Bigg(\tilde{p}_i - \tilde{\rho} + \tilde{p}_i(\tilde{v} - \\ & \tilde{v}_i) + \tilde{T}_i\Bigg[(\tilde{v} - 1)\ln(1 - \tilde{\rho}) - (\tilde{v}_i - 1)\ln(1 - \tilde{\rho}_i) + \\ & \frac{1}{r_i{}^{\circ}}\ln\frac{\tilde{\rho}}{\tilde{\rho}_i}\Bigg]\Bigg) + \frac{r_i{}^{\circ}\tilde{\rho}}{kT}\Bigg[\epsilon_i{}^* + \epsilon^*\left(2\frac{v_i{}^*}{v^*} - 1\right) - \\ & \frac{2v_i{}^*}{v^*}\mathbf{1}^{\mathrm{T}}\cdot\hat{\psi}\cdot\hat{\epsilon}^*\cdot\mathbf{U}_i\cdot\mathbf{1}\Bigg] \end{aligned} \tag{46}$$

Note that in the Flory theory and in the Sanchez and Lacombe p^* additive theory it is possible to eliminate the η (for Flory) and p^* (for Sanchez and Lacombe) terms from the final result. However, in the Sanchez and Lacombe ϵ^* additive theory, defining $\Delta\hat{\epsilon}^*$ does not eliminate the ϵ^* term, making this form less convenient. Sanchez and Lacombe also state that the p^* additive form is more quantitative than the ϵ^* form.[22]

The lattice fluid theory of Sanchez and Lacombe provides a better representation of polymer themodynamics by a simple generalization of the original Flory–Huggins lattice model. Free volume effects were included by introducing vacant lattice sites. The statistical mechanical development allowed molecular contact surface dissimilarities between components to be incorporated implicitly by the judicious choice of mixing rules. Combinatorial contributions to the solution thermodynamics, however, retained the original Flory–Huggins formulation.

The lattice fluid theory qualitatively, and often quantitatively, describes the many known types of fluid-phase behavior. Its ability to predict mixture miscibility limits (i.e., UCST and LCST) and closed immiscibility loops was systematically treated by Lacombe and Sanchez.[22] Predicted results for heats and volume changes on mixing also compared favorably with experimental determinations.

Comparison of the Theories. The equations for the activity of a species in solution for the Flory, simplified Flory, and lattice fluid (p^* additive form) theories are summarized in Table VII. The matrix form of these equations facilitates comparing these results. In each case combinatorial contributions are handled in the same way (at least in the activity equations) and appear in the first two terms of each of these equations. The last terms of the Flory and Sanchez and Lacombe equations account for deviations of the unlike pair interaction energies from the arithmetic average of the interaction energies for each of these two components in the pure state. Although the form of these terms in these two theories is identical, their treatment of segment surface effects is not. The Flory theory uses site fractions rather than segment fractions, thereby accounting for differences in the contact sites (per segment) between the different species; the Sanchez–Lacombe theory does not allow explicitly for these differences, but rather allows for them implicitly through the holes in the lattice. The middle collection of terms comes from a variety of sources: differentiating pure and mixture energy terms, the equation of state substitution, (for the Flory

Table VI
Substitutions Used in Obtaining the Sanchez–Lacombe Result

substitution	
A	$-\frac{\partial}{\partial N_i}\sum_j \frac{E_j + pV_j}{kT} = \frac{\partial}{\partial N_i}\sum_j\left[\frac{r_j^\circ N_j\tilde{\rho}_j\epsilon_j^*}{kT} - \frac{pr_j^\circ N_j v_j^*}{\tilde{\rho}_j kT}\right] = \frac{r_i^\circ}{\tilde{T}_i}(\tilde{\rho}_i - \tilde{p}_i\tilde{v}_i)$
B	$1^{\mathrm{T}}\cdot\mathbf{N}\cdot\frac{\partial}{\partial N_i}\ln\tilde{\rho}\hat{\psi}\cdot 1 = 1^{\mathrm{T}}\cdot\mathbf{N}\cdot\left[\left(\frac{\partial\ln\hat{\psi}}{\partial N_i}\right)+\left(\frac{\partial\ln\tilde{\rho}\mathbf{I}}{\partial N_i}\right)\right]\cdot 1 =$ $1^{\mathrm{T}}\cdot\hat{\psi}\cdot(\mathbf{I} - r_i\mathbf{r}^{-1})\cdot 1 + \frac{N}{\tilde{\rho}}\left(\frac{\partial\tilde{\rho}}{\partial N_i}\right)$ where $\left(\frac{\partial\ln\hat{\psi}}{\partial N_i}\right) = \hat{\psi}^{-1}\cdot\frac{\partial}{\partial N_i}\left(\frac{\mathbf{r}v^*\cdot\mathbf{N}}{rNv^*}\right) = \hat{\psi}^{-1}\cdot\frac{\partial}{\partial N_i}\left(\frac{\mathbf{r}^\circ\cdot\mathbf{v}^*\cdot\mathbf{N}}{rNv^*}\right) =$ $\hat{\psi}^{-1}\cdot\left[\frac{\mathbf{r}^\circ\cdot\mathbf{v}^*\cdot\mathbf{U}_i}{rNv^*} - \frac{\mathbf{r}^\circ\cdot\mathbf{v}^*\cdot\mathbf{N}}{(rNv^*)^2}r_i^\circ v_i^*\right] = \hat{\psi}^{-1}\cdot\left[\frac{\mathbf{r}\cdot\mathbf{U}_i}{rN} - \hat{\psi}\frac{\psi_i}{N_i}\right] = \left(\mathbf{N}^{-1}\cdot\mathbf{U}_i - \frac{\psi_i}{N_i}\mathbf{I}\right)$
C	$\frac{\partial}{\partial N_i}[rN(\tilde{v}-1)\ln(1-\tilde{\rho})] = r_i^\circ(\tilde{v}-1)\ln(1-\tilde{\rho}) - \frac{rN}{\tilde{\rho}^2}\left(\frac{\partial\tilde{\rho}}{\partial N_i}\right)\ln(1-\tilde{\rho}) - \frac{rN}{\tilde{\rho}}\left(\frac{\partial\tilde{\rho}}{\partial N_i}\right)$ since $\frac{\partial}{\partial N_i}(rN) = r_i^\circ$ and $\left(\frac{\partial\tilde{v}}{\partial N_i}\right) = \left(\frac{\partial\tilde{\rho}^{-1}}{\partial N_i}\right)$
D	$\left[\frac{\partial}{N_i}\left(\frac{pV}{kT}\right)\right]_{T,p,N_j} = \frac{\partial}{\partial N_i}\left(\frac{prNv^*\tilde{v}}{kT}\right) = \left[r_i^\circ v_i^* p_i^*(\tilde{p}_i\tilde{v}) - \frac{prNv^*}{\tilde{\rho}^2}\left(\frac{\partial\tilde{\rho}}{\partial N_i}\right)\right]\frac{1}{kT}$
E	$\frac{\partial}{\partial N_i}\left(\frac{E}{kT}\right) = \frac{\partial}{\partial N_i}\left(\frac{-rN\tilde{\rho}v^*p^*}{kT}\right) = -[r_i^\circ v_i^*\tilde{\rho}p^* + rNv^*\left(\frac{\partial\tilde{\rho}}{\partial N_i}\right)p^* + rNv^*\tilde{\rho}\frac{\partial}{\partial N_i}(1^{\mathrm{T}}\cdot\hat{\psi}\cdot\mathbf{P}^*\cdot\hat{\psi}\cdot 1]\frac{1}{kT} =$ $-\frac{r_i^\circ\tilde{\rho}}{kT}[p^*v_i^* + p^*v^*\frac{rN}{r_i^\circ\tilde{\rho}}\left(\frac{\partial\tilde{\rho}}{\partial N_i}\right) + 2\frac{rNv^*}{r_i^\circ}(1^{\mathrm{T}}\cdot\hat{\psi}\cdot\mathbf{P}^*\cdot\mathbf{U}_i\cdot 1 - \mathrm{p}^*)\frac{\psi_i}{N_i} =$ $-\frac{r_i^\circ\tilde{\rho}}{kT}\left[p_i^*v_i^* + p^*v^*\frac{rN}{r_i^\circ\tilde{\rho}}\left(\frac{\partial\tilde{\rho}}{\partial N_i}\right) + v_i^*(\tfrac{1}{2}1^{\mathrm{T}}\cdot\hat{\psi}\cdot\Delta\mathbf{P}^*\cdot\hat{\psi}\cdot 1 - 1^{\mathrm{T}}\cdot\mathbf{U}_i\cdot\Delta\mathbf{P}^*\cdot\hat{\psi}\cdot 1)\right]$

Table VII
Summary of the Activity Equations

theory	$\ln a_i$
Flory	$\ln\psi_i + 1^{\mathrm{T}}\cdot\hat{\psi}\cdot(\mathbf{I} - M_iv_{i\mathrm{sp}}^*\mathbf{M}^{-1}\cdot\mathbf{v}_{\mathrm{sp}}^{*-1})\cdot 1 + \frac{M_ip_i^*v_{i\mathrm{sp}}^*}{kT}\left[3\tilde{T}_i\ln\frac{(\tilde{v}_i^{1/3}-1)}{(\tilde{v}^{1/3}-1)} + \tilde{p}_i - \tilde{p} + \tilde{p}_i(\tilde{v} - \tilde{v}_i)\right] +$ $\frac{M_iv_{i\mathrm{sp}}\tilde{p}}{kT}\left[1^{\mathrm{T}}\cdot\mathbf{U}_i\cdot\left(\frac{s_i\Delta\hat{\eta}}{2v^{*2}}\right)\cdot\hat{\theta}\cdot 1 - \tfrac{1}{2}1^{\mathrm{T}}\cdot\hat{\theta}\cdot\left(\frac{s_i\Delta\hat{\eta}}{2v^{*2}}\right)\cdot\hat{\theta}\cdot 1\right]$
simplified Flory	$\ln\psi_i + 1^{\mathrm{T}}\cdot\hat{\psi}\cdot(\mathbf{I} - M_iv_{i\mathrm{sp}}^*\mathbf{M}^{-1}\cdot\mathbf{v}_{\mathrm{sp}}^{*-1})\cdot 1 + \frac{M_ip_i^*v_{i\mathrm{sp}}^*}{kT}\left[3\tilde{T}_i\ln\frac{(\tilde{v}_i^{1/3}-1)}{(\tilde{v}^{1/3}-1)} + \tilde{p}_i + \tilde{p}_i(\tilde{v} - \tilde{v}_i)\right] +$ $\frac{M_iv_{i\mathrm{sp}}^*\tilde{p}}{kT}(1^{\mathrm{T}}\cdot\hat{\psi}\cdot\mathbf{P}^*\cdot\hat{\psi}\cdot 1 - 21^{\mathrm{T}}\cdot\hat{\psi}\cdot\mathbf{P}^*\cdot\mathbf{U}_i\cdot 1)$
Sanchez–Lacombe	$\ln\psi_i + 1^{\mathrm{T}}\cdot\hat{\psi}\cdot(\mathbf{I} - r_i\mathbf{r}^{-1})\cdot 1 +$ $\frac{M_iv_{i\mathrm{sp}}^*p_i^*}{kT}\left(\tilde{p}_i - \tilde{p} + \tilde{p}_i(\tilde{v} - \tilde{v}_i) + \tilde{T}_i[(\tilde{v}-1)\ln(1-\tilde{\rho}) - (\tilde{v}_i - 1)\ln(1-\tilde{\rho}_i)] + \ln\frac{\tilde{\rho}}{\tilde{\rho}_i}\right) +$ $\frac{M_iv_{i\mathrm{sp}}^*}{kT}\tilde{\rho}[1^{\mathrm{T}}\cdot\mathbf{U}_i\cdot\Delta\mathbf{P}^*\cdot\hat{\psi}\cdot 1 - \tfrac{1}{2}1^{\mathrm{T}}\cdot\hat{\psi}\cdot\Delta\mathbf{P}^*\cdot\hat{\psi}\cdot 1]$

theory) differentiating the free volume term in the partition function, and (for the Sanchez–Lacombe theory) the terms which represent unoccupied sites of the lattice. With the exception of the manner in which these two theories account for free volume, these middle terms are identical.

These formulations of the solution theories provide a convenient framework for numerical calculations of multicomponent polymer solutions and, consequently, for quantitative comparisons of the relative contributions of the various terms in different theories. As an example, we have applied these equations in a parameter estimation technique using perturbation gas chromatography in ternary systems. We have also used these equations to obtain the multicomponent equations for analyzing osmotic pressure second virial coefficient and preferential adsorption data in multicomponent systems. In these cases the equations were reported in summation form rather than matrix form.

Acknowledgment. Support of this work by the National Science Foundation, Grant CPE-8111272, is greatfully acknowledged.

Notation

A	Helmholtz free energy per molecule
$\bar{A}$	partial molar Helmholtz free energy
a_i	activity of component i in solution
$3c$, $3c_i$	number of external degrees of freedom for the mixture ($3c$) or for pure species i ($3c_i$), per segment
E_0, E_{0i}	total system interaction energy for the mixture (E_0) or for pure species i (E_{0i}), for the Flory theory
E, E_i	total system interaction energy for the mixture (E) or for pure species i (E_i), for the Sanchez–Lacombe theory
f_i	fraction of lattice sites occupied by species i for the Sanchez–Lacombe theory, or a set of functions of the mole fractions, eq 22
f_0	fraction of lattice sites which are vacant, Sanchez–Lacombe theory
G	Gibbs free energy per molecule
G^E	excess Gibbs free energy, eq 6
$\tilde{G}$	partial molar Gibbs free energy
$\mathbf{I}$	identity matrix
k	Boltzmann's constant
M_i	mass average molecular mass of component i
$\mathbf{M}$, M_i	$n \times n$ diagonal matrix ($\mathbf{M}$) of the molecular masses of species i (M_i)
N	total number of molecules in the system
N_0	number of vacant lattice sites in the Sanchez–Lacombe theory
n	number of species in solution
$\mathbf{N}$, N_i	$n \times n$ diagonal matrix ($\mathbf{N}$) of the number of molecules of each species i (N_i) in solution
p	absolute pressure
$\tilde{p}$	mixture reduced pressure, $\tilde{p} = p/p^*$
p^*	characteristic pressure for a mixture
$\mathbf{P}^*$, P_{ij}^*	$n \times n$ symmetric matrix ($\mathbf{P}^*$) of the characteristic binary interaction pressures (energy per volume) (P_{ij}^*) for the simplified Flory theory or for the Sanchez–Lacombe theory; $P_{ii}^* = p_i^*$, the pure component characteristic pressure
$\Delta\mathbf{P}^*$, ΔP_{ij}^*	$n \times n$ symmetric matrix of the lattice fluid interaction parameters ($\Delta P_{ij}^* = P_{ii}^* + P_{jj}^* - 2P_{ij}^*$)
$\tilde{p}_i$	reduced pressure for component i, $\tilde{p}_i = p/p_i^*$
p_i^*	characteristic pressure of component i
$\mathbf{r}$, r_i	$n \times n$ diagonal matrix ($\mathbf{r}$) of the number of segments per molecule for species i (r_i), for the Flory theory
$\mathbf{r}^\circ$, r_i°	$n \times n$ diagonal matrix ($\mathbf{r}^\circ$) of the number of segments per molecule for species i in the pure state, for the Sanchez–Lacombe theory
r	average number of segments per molecule for the mixture
$\mathbf{s}$, s_i	$n \times n$ diagonal matrix ($\mathbf{s}$) of the number of intermolecular contact sites per segment for species i (s_i), for the Flory theory
s	average number of contact sites per segment for the mixture for the Flory theory
T	absolute temperature
$\tilde{T}$	mixture reduced temperature, $\tilde{T} = T/T^*$
$\tilde{T}_i$	reduced temperature for species i, $\tilde{T}_i = T/T_i^*$
T^*	characteristic temperature for the mixture, defined by the mixing rules in Table I (Flory Theory) or Table III (lattice fluid theory)
T_i^*	characteristic temperature for species i
$\mathbf{U}_i$	$n \times n$ diagonal matrix with only one non-zero element, a 1 in the ith diagonal position
V	total system volume
$\tilde{v}$	mixture reduced volume
v^*	mixture characteristic volume per segment
v_i	volume per segment for species i
$\tilde{v}_i$	reduced volume for species i, $\tilde{v}_i = v_i/v_i^*$
$\mathbf{v}^*$, v_i^*	$n \times n$ diagonal matrix ($\mathbf{v}^*$) of the pure species characteristic volumes per segment v_i^*, $r_i v_i^* = M_i v_{isp}^*$
$\mathbf{v}_{sp}^*$, v_{isp}^*	$n \times n$ diagonal matrix ($\mathbf{v}_{sp}^*$) of the characteristic close-packed volumes per unit mass for species i (v_{isp}^*), $M_i v_{isp}^* = r_i v_i^*$
$\mathbf{X}$, X_{ij}	$n \times n$ matrix ($\mathbf{X}$) of the Flory interaction parameters, X_{ij}
$\mathbf{x}$, x_i	$n \times n$ diagonal matrix ($\mathbf{x}$) of the mole fractions of species i (x_i)
Z	statistical mechanical partition function
z_i	coordination number for the lattice
$\mathbf{1}$	n-dimensional column vector with each element equal to unity

Subscripts

i, j	species i or j
mix	mixture value

Greek Letters

γ_i	activity coefficient of species i
ϵ_i	binary interaction energy per segment for the Sanchez–Lacombe theory
$\hat{\epsilon}^*$, ϵ_{ij}^*	$n \times n$ symmetric matrix ($\hat{\epsilon}^*$) of the segment pair characteristic interaction energies (ϵ_{ij}^*) for the Sanchez–Lacombe theory
ϵ^*	average characteristic interaction energy per segment for the mixture, Sanchez–Lacombe theory
η_i/v_i	energy per segment pair interaction for pure species i for the Flory theory
$\hat{\eta}$, η_{ij}	$n \times n$ symmetric matrix ($\hat{\eta}$) of the Flory theory segment pair interactions, η_{ij}
η	the total mixture interaction (a scalar) calculated by eq 20
$\Delta\hat{\eta}$, $\Delta\eta_{ij}$	$n \times n$ matrix ($\Delta\hat{\eta}$) of the $\Delta\eta_{ij}$ values, $\Delta\eta_{ij} = \eta_{ii} + \eta_{jj} - 2\eta_{ij}$, $\eta_{ii} = \eta_i$
$\hat{\theta}$, θ_i	$n \times n$ diagonal matrix ($\hat{\theta}$) of the site fractions of species i, $\theta_i = r_i N_i s_i / (\sum r_j n_j s_j)$
μ_i	chemical potential of species i
$\tilde{\rho}$	reduced density for the mixture, $\tilde{\rho} = 1/\tilde{v}$
$\tilde{\rho}_i$	reduced density of species i, $\tilde{\rho}_i = 1/\tilde{v}_i$
$\ln \hat{\tilde{\rho}}$	$n \times n$ diagonal matrix of the $\ln \tilde{\rho}_i$ values
$\hat{\psi}$, ψ_i	$n \times n$ diagonal matrix ($\hat{\psi}$) of segment fractions of species i, $\psi_i = r_i^\circ N_i / (\sum r_j^\circ N_j)$
$\ln \hat{\psi}$	$n \times n$ diagonal matrix of the $\ln \psi_i$ values
$\hat{\psi}^\circ$, ψ_i°	$n \times n$ diagonal matrix ($\hat{\psi}^\circ$) of the pure-state segment fractions of species i for the Sanchez–Lacombe theory, $\psi_i^\circ = r_i^\circ N_i / (\sum r_j^\circ N_j)$
ω_i	number of configurations available to a segment of pure species i in the close-packed state

References and Notes

(1) Flory, P. J. *J. Chem. Phys.* **1942**, *10*, 51.
(2) Huggins, M. L. *Ann. N.Y. Acad. Sci.* **1942**, *43*, 1.
(3) Bonner, D. C. *J. Macromol. Sci., Rev. Macromol. Chem.* **1975**, *C13*, 263.
(4) Flory, P. J. *J. Am. Chem. Soc.* **1965**, *87*, 1833.
(5) Sanchez, I. C.; Lacombe, R. H. *J. Phys. Chem.* **1976**, *80*, 2352.
(6) Prigogine, I.; Trappeniers, N.; Mathot, V. *Discuss. Faraday Soc.* **1953**, *15*, 93.
(7) Prigogine, I.; Trappeniers, N.; Mathot, V. *J. Chem. Phys.* **1953**, *21*, 559.
(8) Van Ness, H. C.; Abbott, M. M. *Classical Thermodynamics of Non Electrolyte Solutions*; McGraw-Hill: New York, 1982; Chapter 5.
(9) Patterson, D. *Rubber Chem. Technol.* **1967**, *40*, 1.
(10) Bonner, D. C.; Prausnitz, J. M. *AIChE J.* **1973**, *19*, 943.
(11) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 3, 441.
(12) Eichinger, B. E.; Flory, P. J. *Trans. Faraday Soc.* **1968**, *64*, 2035.
(13) Pouchlý, J.; Patterson, D. *Macromolecules* **1976**, *9*, 574.
(14) Wedgeworth, J. B.; Glover, C. J. *Macromolecules* **1987**, *20*, 2268.
(15) Sanchez, I. C.; Lacombe, R. H. *Macromolecules* **1978**, *11*, 1145.
(16) Olabisi, O.; Robeson, L. M.; Shaw, M. T. *Polymer-Polymer Miscibility*, Academic: New York, 1979; Chapter 2.

(17) Horta, A.; Fernández-Piérola, I. *Macromolecules* **1981**, *14*, 1519.
(18) Ruff, W. A.; Glover, C. J.; Watson, A. T.; Lau, W. R.; Holste, J. C. *AIChE J.* **1986**, *32*, 1954.
(19) McMaster, L. P. *Macromolecules* **1973**, *6*, 760.
(20) Bonner, D. C.; Maloney, D. P.; Prausnitz, J. M. *Ind. Eng. Chem., Process Des. Dev.* **1974**, *13*, 91.
(21) Bonner, D. C.; Brockmeier, N. F. *Ind. Eng. Chem., Process Des. Dev.* **1977**, *16*, 180.
(22) Lacombe, R. H.; Sanchez, I. C. *J. Phys. Chem.* **1976**, *80*, 2568.

Critical Experimental Test of the Flory–Rehner Theory of Swelling

N. A. Neuburger and B. E. Eichinger*

Department of Chemistry, BG-10, University of Washington, Seattle, Washington 98195.
Received January 12, 1988; Revised Manuscript Received March 24, 1988

ABSTRACT: Differential swelling measurements performed on two poly(dimethylsiloxane) (PDMS) networks are reported. The two elastomers are closely similar to one another except for the chemical structures of the cross-links, which are quite different. The samples were swollen in benzene and in cyclohexane at 20 °C and at 30 °C. The reduced dilation moduli of the two samples parallel one another in a given solvent at a fixed temperature, but they reveal solvent and temperature dependences that are not encompassed by any known theory. The results demonstrate conclusively that the assumption of separability of mixing and elastic free energies is incorrect and that the Flory–Rehner theory of swelling is in need of modification.

Introduction

For the past 40 years, the phenomenon of swelling has been used to analyze the physical properties of elastomers. The criterion for swelling equilibrium was first recognized by Frenkel[1,2] and was later developed by Flory and Rehner[3,4] into a general theory. Flory–Rehner theory is based on two peculiar properties of elastomers, which distinguishes them from other typical solids: They absorb large amounts of solvent without dissolving, and they undergo large deformations with correspondingly small stresses. The major hypothesis of Flory and Rehner is that the free energy change on swelling an elastomer consists of two contributions, which they assumed to be separable and additive. These are the free energy of mixing, ΔG_{m}, and the free energy of elastic deformation, ΔG_{el}. Thus, the free energy change accompanying the absorption of a diluent was assumed to be given by

$$\Delta G = \Delta G_{\mathrm{m}} + \Delta G_{\mathrm{el}} \qquad (1)$$

The general theories of mixing and of rubber elasticity are well-known. Polymer solution theory was developed independently by Flory[5] and Huggins.[6-8] They calculated the enthalpy of mixing by counting the number of polymer–solvent contacts, and the entropy of mixing by counting the number of different configurations possible for the polymer–solvent system. There are several theories of elasticity, the most familiar of these being due to Wall and Flory[9-13] and to James and Guth.[14-19] Both of these theories treat the elastomer as an assembly of randomly coiled chains linked together into a coherent network by chemical bonds.

The virtue of swelling is that it is a relatively simple method for characterizing elastomers. According to eq 1 and depending on the applicable theory of ΔG_{el}, measurements conducted at swelling equilibrium will directly yield the modulus of elasticity. With somewhat more effort than that needed for swelling equilibrium measurements, the solvent activity can be varied so as to swell the elastomer to different extents. This allows one to probe the elastic energy function in domains of deformation not readily accessible in ordinary stress–strain measurements. In view of these facts, elastomer swelling deserves careful consideration, both as a characterization technique and as a basis to test elasticity theory.

Vapor sorption techniques enable one to vary the solvent activity, as was shown in the seminal work of Gee, Herbert, and Roberts.[20] They conducted experiments that allowed them to control the vapor pressure of the solvent, and the amount of the solvent that the polymer absorbed was determined by using a sensitive microbalance housed in a vacuum system. Similar experiments were later conducted by Yen and Eichinger[21,22] using an improved experimental apparatus. Later still, Brotzman and Eichinger[23-25] conducted experiments on siloxane networks using the same apparatus. The primary purpose of each of these studies was to probe the elastic theories. However, what they all found was an elastic free energy function that could not be explained with any of the current theories. Even more disconcerting, both Yen and Brotzman found the elastic free energy function to be solvent dependent, thus calling to question the basic assumptions inherent in eq 1. This fact, and the fact that the elastic free energy function shows anomalous behavior, has led to the opinion that the major premise of the theory of swelling of networks, namely, the hypothesis that the elastic and mixing free energies are separable, is questionable.

At the present time, the status of the Flory–Rehner theory is still unresolved. From the experiments recounted above it appears that the theory is in need of modification. There is at least one possibility for the breakdown of the theory, as was first noted by Gee et al.[20] It is possible that the interaction of the solvent with the cross-links is different from that with the midchain segments. If this is the case, the elastic modulus could appear to be solvent dependent because inappropriate account had been taken of the cross-link–solvent mixing term. Calculations[24] to estimate the magnitude of the cross-link–solvent interaction on the swelling measurements showed that this is an unlikely source of the apparent breakdown of the Flory–Rehner theory. To settle this experimentally, we have conducted swelling measurements on two closely similar model networks that have cross-links with quite different structures. If a cross-link–solvent mixing term is important, this experiment should discover it.

0024-9297/88/2221-3060$01.50/0