Quasi-Chemical Approximation for Nonrandomness in the Hole Theory of Polymeric Fluids. 1. Equation of State Behavior of Pure Components

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ABSTRACT: The effect of nonrandomness is introduced in the Holey Huggins hole theory (a modified version of the Simha-Somcynsky theory) based on the quasi-chemical approximation of Guggenheim. The resulting nonrandomness not only is dependent on the energetic interactions but also is determined by the so-called free volume contributions typical of cell and hole theories. The observed influence of free volume is in some respects unexpected. Furthermore, the theory offers an accurate description of experimental equation of state data of polymers and small molecules. A comparison with the random mixing analogue of the present theory shows that the introduction of the quasi-chemical approximation improves the accuracy of the description of experimental data.

I. Introduction

In recent years there has been sustained interest in the development and refinement of equation of state theories of polymeric fluids. Since the first successful equation of state theory of Prigogine[1] and Flory, Orwoll, and Vrij,[2] many different kinds of such theory have been proposed, among which there are cell theories, the lattice-fluid theory, the lattice-gas theory, and hole theories.[3-8] Originally, in these theories the energy and entropy were calculated assuming randomness of, e.g., polymer segments and solvent molecules (and also holes in the lattice-gas theory and hole theories). However, in certain circumstances, this assumption is certainly not valid. For instance, when there exist strong dipole-dipole interactions or other kinds of strong interaction between two different kinds of polymer segments, unlike segments would have a strong propensity to be adjacent to one another, resulting in a nonrandom mixing of the segments. Thus, if one wants to obtain a more appropriate and hopefully more precise theory for polymer fluids, the nonrandomness of the system should not be neglected. Consequently, more recently, the effect of nonrandomness has received considerable attention. For instance, Renuncio and Prausnitz[9] proposed a phenomenological equation based on the intuitive notion of "local composition" to account for nonrandomness. This method, which was later improved by Brandani,[10] is simple but lacks a statistical-mechanical basis. Panayiotou and Vera[11] used Guggenheim's quasi-chemical approach[12] to obtain explicit expressions for the local surface fractions, which were combined with the formalism of the Flory, Orwoll, and Vrij (FOV) theory to account for nonrandomness in polymer solutions. More recently, Li et al.[13] proposed an improvement in the Flory corresponding states theory for polymer solutions. In their work, nonrandomness is taken into account by inserting factors in the equations which determine the number of contact pairs. Doing so, equations identical to those proposed by Guggenheim are obtained. Thus, the influence of the free volume, typical of cell theories, is not considered.

The quasi-chemical approximation was applied by different authors to discuss the influence of preferential interactions among molecules and groups constituting the molecules.[14-18] A general discussion of the use of the quasi-chemical approximation has been given by Wilczek-Vera and Vera.[18] General quasi-chemical equations and the corresponding expressions for the free energy, the chemical potentials, the equation of state, and the internal energy were derived, and the relevance of these equations for group contribution methods was discussed. It was also stressed that the ultimate success of a quasi-chemical theory is primarily determined by the model used to describe the limiting random system.

In this work, we apply the quasi-chemical approximation to the Holey Huggins (HH) hole theory[8] to study the influence of nonrandomness on the equation of state behavior of single components. The HH theory is a modified version of the Simha-Somcynsky theory.[6] It is known that the Simha-Somcynsky (SS) theory allows for a good description and/or prediction of equation of state behavior and relevant properties of molecular fluids as well as miscibility behavior of polymer solutions and mixtures. With the modified version of the SS theory (i.e., the HH theory), even very complicated thermodynamic properties, such as the subtle influence of pressure on phase behavior, can be predicted.[19] However, both SS and HH theory are only valid for "conventional" molecular fluids, i.e., fluids without strong dipole-dipole interaction or other kinds of specific interactions.

At present, we are trying to extend the applicability of the HH theory to systems possessing specific interactions. Hereby, an important step is to introduce nonrandomness in the theory, which will be accomplished by the quasi-chemical approximation. However, the resulting quasi-chemical equations are considerably different from Guggenheim's, due to the introduction of the free volume contribution. Also the resulting equation of state is different from those given by the HH theory, indicating that nonrandomness affects the equation of state behavior as well as the miscibility behavior. So far as the agreement between theory and experiment is concerned, the present theory is better than the HH and SS theories. Furthermore, the present theory can be easily extended to more complicated systems. Especially, for the systems with specific interactions, we are confident that the present hole theory will provide a firm basis for further systematic development.

In this series of papers, we will introduce our theory along with some of its applications. In the first paper, we

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present the theory for pure components. In a subsequent contribution, the theory will be extended to polymer solutions and mixtures. The application of the present theory to random copolymer systems will be the subject of succeeding papers.

II. Theory

Consider a system of N s-mers occupying a lattice with N_h empty sites or holes. As in the HH theory, the most important structural parameter is the contact fraction q of the s-mers, defined by

$$q = Nzq_c/(Nzq_c + zN_h) \tag{1}$$

where $zq_c = s(z-2)+2$ is the number of external contacts of one s-mer and z is the coordination number of the lattice. The contact fraction q, which is a measure for the number of intersegmental contacts the s-mers can make, is related to the occupied site fraction by

$$q = (1-\alpha)y/(1-\alpha y) \tag{2}$$

where $\alpha = \gamma(1-1/s)$ and $\gamma = 2/z$. When nonrandom mixing of segments and holes is considered, another microscopic parameter X, which accounts for the fraction of segment–hole contacts, is needed. If we designate the total number of contact pairs by Q

$$Q = \frac{1}{2}z(Nq_c + N_h) = \frac{1}{2}Nq_c z/q \tag{3}$$

then QX is the number of segment–hole or hole–segment contacts, whereas the number of segment–segment contacts is $Q(q-X)$ and the number of hole–hole contacts is $Q(1-q-X)$.

(a) Partition Function. According to Guggenheim,[12] the configurational partition function of the system is given by

$$Z(N,y,V,T) = \sum_{\{X\}} Z_X(N,y,V,T,X) \tag{4}$$

where $Z_X(N,y,V,T,X)$ is the partition function of the subsystem with a certain fixed value of X; V and T are the volume and temperature of the system, respectively. For hole theories, Z_X can be factorized into three contributions[6,8]

$$Z_X = g l_f^{3sNc_s} \exp(-E_0/kT) \tag{5}$$

where g is the combinatorial factor arising from mixing holes with polymer segments, E_0 is the internal energy, and l_f is the segmental free length of an s-mer with $3c_s$ external degrees of freedom per segment. Following Guggenheim, the combinatorial factor g is taken to be

$$g = N_{HH} \frac{[Q(q-X^*)]![(QX^*)!]^2[Q(1-q-X^*)]!}{[Q(q-X)]![(QX)!]^2[Q(1-q-X)]!} \tag{6}$$

where X^* is the value of X in the case of random mixing and N_{HH} is a normalization factor which gives the value of g for the random mixing case. According to the HH theory, the logarithm of N_{HH} reads

$$\ln(N_{HH}) = -\frac{\ln(y)}{s} - \frac{1-y}{y}\ln(1-y) + \frac{1-\alpha y}{\gamma y}\ln(1-\alpha y) \tag{7}$$

The internal energy E_0 is given by

$$E_0 = Q(q-X)\epsilon_c \tag{8}$$

In the above equation ϵ_c is the volume-dependent contact energy of a pair of segments, which is assumed to obey a Lennard-Jones 6–12 potential:

$$\epsilon_c = \epsilon^*[A(\omega/v^*)^{-4} - 2B(\omega/v^*)^{-2}] \tag{9}$$

where ω ($=yv = yV/Ns$) is the cell volume, v is the volume per segment, and ϵ^* and v^* are the maximum attraction energy and corresponding segmental volume as defined in the SS and HH theories. The constants A and B are taken to be $A = 1.011$ and $B = 1.2045$, valid for a face-centered cubic lattice.[20]

The segmental free length l_f is taken to be

$$\begin{aligned} l_f &= (1-X/q)l_s + (X/q)l_g \equiv \tilde{l}_f v^{*1/3} \\ l_s &= (\tilde{\omega}^{1/3} - 2^{-1/6})v^{*1/3} = \tilde{l}_s v^{*1/3} \\ l_g &= \tilde{\omega}^{1/3} v^{*1/3} = \tilde{l}_g v^{*1/3} \end{aligned} \tag{10}$$

where l_s and l_g are solidlike and gaslike free lengths and $\tilde{\omega} = \omega/v^*$ is the reduced cell volume.

In eq 10, X/q is the fraction of segment–hole contacts with respect to the total number of external contacts of the segments and $(1-X/q)$ is the remaining fraction of segment–segment contacts. It may be shown that if random mixing of segments with holes is assumed, i.e., if X takes the value of X^*, eq 10 reduces to the expression for the segmental free length defined in the HH theory

$$l_f = ql_s + (1-q)l_g \tag{11}$$

(b) Maximization of Z_X. To evaluate the partition function $Z(N,y,V,T)$, the summation on the right-hand side of eq 4 is replaced by its maximum term. If we denote the value of X in the maximum term by $\bar{X}$, we have

$$Z(N,y,V,T) = Z_X(N,y,V,T,\bar{X}) \tag{12}$$

where $\bar{X}$ is determined by

$$\left.\frac{\partial \ln(Z_X)}{\partial X}\right|_{N,y,V,T} = 0 \tag{13}$$

When eqs 5–10 are combined with eq 13, we obtain an explicit equation for $\bar{X}$, viz.

$$\bar{X}^2\eta_e^{\,2} = (q-\bar{X})(1-q-\bar{X})\eta_s \tag{14}$$

where

$$\eta_e = \exp\left(\frac{-\epsilon_c}{2kT}\right)$$

$$\eta_s = \exp\left(\frac{6c_s\beta}{z(1-\alpha)[1-\beta(1-X/q)]}\right) = \exp\left(\frac{2^{-1/6}(6c_s)}{z(1-\alpha)\tilde{l}_f}\right)$$

$$\beta = 2^{-1/6}\tilde{\omega}^{-1/3}$$

On the other hand, if we let $\eta_e = \eta_s = 1$ in eq 14, or, in other words, if l_f and E_0 are no longer functions of X and the system assumes a state of complete randomness, we obtain the equation for X^*, viz.

$$(X^*)^2 = (q-X^*)(1-q-X^*) \tag{15}$$

Equation 15 is exactly the same as Guggenheim's equation for X^* and leads to the same solution

$$X^* = q(1-q) \tag{16}$$

It is worth mentioning that eq 14 is different from Guggenheim's original quasi-chemical equation, because the free volume contribution as well as the configurational energy contribution is incorporated in determining $\bar{X}$. Besides, both η_e and η_s in eq 14 are volume dependent,

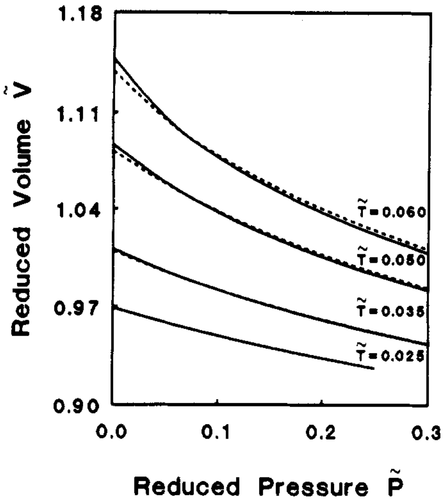

Figure 1. Reduced volume vs reduced pressure at the indicated reduced temperatures according to the HH theory (- - -) and the present theory (—) for a polymer (s = 1000). The results for monomers (s = 1) are similar.

whereas in Guggenheim's original treatment, the quasi-chemical equation is volume independent. Furthermore, it should be noted that in the present theory q is not a constant but is pressure and temperature dependent.

(c) Approximate Partition Function Z_{conf}. By employing the maximum term approximation, the configurational partition function of the system is given by

$$Z_{\text{conf}} = g(N,y,\bar{X})[l_f(V,N,y,\bar{X})]^{3Nsc_s} \times \exp[-E_0(V,N,y,\bar{X})/kT] \quad (17)$$

where we have given the explicit functional relationship of each factor on the right-hand side of the equation.

It is more convenient to express Z_{conf} in its logarithm form. Combination of eqs 6–11 with eq 17 yields

$$\ln (Z_{\text{conf}})/(Ns) = -\frac{\ln (y)}{s} - \frac{1-y}{y}\ln (1-y) + \frac{1-\alpha y}{\gamma y} \times \ln (1-\alpha y) - \frac{z(1-\alpha)}{2q}[2q \ln (q) + 2(1-q) \ln (1-q) - (q-\bar{X}) \ln (q-\bar{X}) - 2\bar{X} \ln (\bar{X}) - (1-q-\bar{X}) \ln (1-q-\bar{X})] + 3c_s \ln \left[(1-\bar{X}/q)(\tilde{\omega}^{1/3} - 2^{-1/6}) + \frac{\bar{X}\tilde{\omega}^{1/3}}{q}\right] + c_s \ln (v^*) - \frac{z(1-\alpha)}{2qkT}(q-\bar{X})\epsilon^*(A\tilde{\omega}^{-4} - 2B\tilde{\omega}^{-2}) \quad (18)$$

It is interesting to compare eq 18 with the corresponding result of the HH theory. It may be seen that the first three terms on the right-hand side of eq 18, which account for the combinatorial entropy of random mixing polymer segments with holes, are exactly the same as those in the partition function of the HH theory. The terms in the square brackets are extra contributions due to nonrandom mixing, which cancel when $X = X^*$. The last term is the contribution of the internal energy, and the remaining terms come from the free volume contribution. They are quite similar in form to the corresponding terms in the HH theory and become identical when X takes the value X^*.

(d) Helmholtz Free Energy and Equation of State. The Helmholtz free energy of the system is given by

$$A = -kT \ln Z_{\text{conf}} \quad (19)$$

Following Simha and Somcynsky,[6] the structural parameter q (and henceforth y) in the configuration partition function Z_{conf} is determined according to the minimization condition

$$\left.\left(\frac{\partial A}{\partial y}\right)\right|_{N,T,V} = 0 \quad (20)$$

and the equation of state is given by

$$P = -\left.\left(\frac{\partial A}{\partial V}\right)\right|_{N,T} = -\left.\left(\frac{\partial A}{\partial V}\right)\right|_{N,T,y} + \left.\left(\frac{\partial A}{\partial y}\right)\right|_{N,T,V}\left.\left(\frac{\partial y}{\partial V}\right)\right|_{N,T} \quad (21)$$

In reduced form, the free energy and the equation of state may be written as

$$\frac{A}{nsRT} = \frac{\ln (y)}{s} + \frac{1-y}{y}\ln (1-y) - \frac{1-\alpha y}{\gamma y}\ln (1-\alpha y) - \frac{z(1-\alpha)}{2q}[2q \ln (q) + 2(1-q) \ln (1-q) - (q-\bar{X}) \ln (q-\bar{X}) - 2\bar{X} \ln (\bar{X}) - (1-q-\bar{X}) \ln (1-q-\bar{X})] - c_s \ln [\tilde{\omega}v^*(1-\beta(1-\bar{X}/q))]^3 + \frac{c_s(1-\bar{X}/q)}{2\tilde{T}}(A\tilde{\omega}^{-4} - 2B\tilde{\omega}^{-2}) \quad (22)$$

$$\tilde{P}\tilde{v}/\tilde{T} = \frac{1}{1-\beta(1-\bar{X}/q)} + \frac{2}{\tilde{T}}(1-\bar{X}/q)(A\tilde{\omega}^{-4} - B\tilde{\omega}^{-2}) + [m_2 + m_3 + m_4/\tilde{T}]v\frac{\partial \bar{X}}{\partial \tilde{v}} \quad (23)$$

where

$$m_2 = -\frac{\dfrac{6\beta}{1-\beta(1-\bar{X}/q)} + \dfrac{A\tilde{\omega}^{-4} - 2B\tilde{\omega}^{-2}}{\tilde{T}}}{2q}$$

$$m_3 = \frac{3\beta}{q[1-\beta(1-\bar{X}/q)]}$$

$$m_4 = \frac{A\tilde{\omega}^{-4} - 2B\tilde{\omega}^{-2}}{2q}$$

In the above expressions, n is the number of moles of s-mers, and the reduced pressure, specific volume, and temperature are defined as

$$\tilde{P} = P/P^* \qquad \tilde{v} = v/v^* \qquad \tilde{T} = T/T^*$$

with $P^* = z(1-\alpha)\epsilon/v^*$, $v^* = v^*/m_0$, and $T^* = z(1-\alpha)\epsilon^*/c_sR$. ϵ^* and v^* are defined per mole of segments.

The derivative $(\partial\bar{X}/\partial\tilde{v})$, which is obtained at constant y, N, and T, can be derived either analytically or numerically. In the present work it was obtained analytically from eq 14, giving

$$\frac{\partial\bar{X}}{\partial\tilde{v}}\left[2\bar{X}\eta_e^{\,2} + \eta_s\left(\bar{X}(1-2\bar{X}) + \frac{(q-\bar{X})(1-q-\bar{X})[2^{-1/6}(6c_s)(l_g - l_s)]}{z(1-\alpha)q\bar{l}_f^{\,2}}\right)\right] = \frac{4\bar{X}^2\eta_e^{\,2}\epsilon^*}{kT\tilde{v}}[B\tilde{\omega}^{-2} - A\tilde{\omega}^{-4}] \quad (24)$$

III. Results and Discussion

(a) Universal *PVT* Surface. The reduced isotherms for a polymer molecule (s = 1000) are shown in Figure 1 along with the corresponding results of the HH theory. It may be seen that at low reduced temperatures, the difference between the present theory and the HH theory is almost negligible, while at higher reduced temperatures,

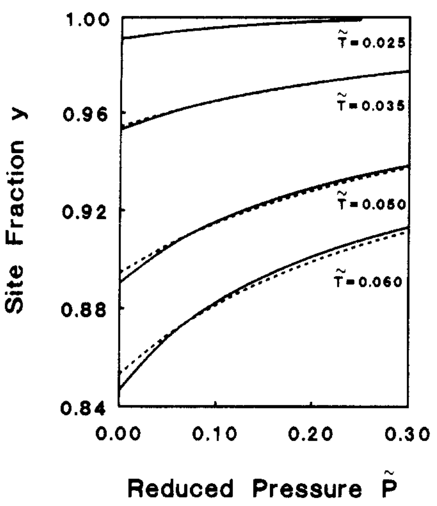

Figure 2. Occupied site fraction y vs reduced pressure at the indicated reduced temperatures according to the HH theory (- - -) and the present theory (—) for a polymer ($s = 1000$).

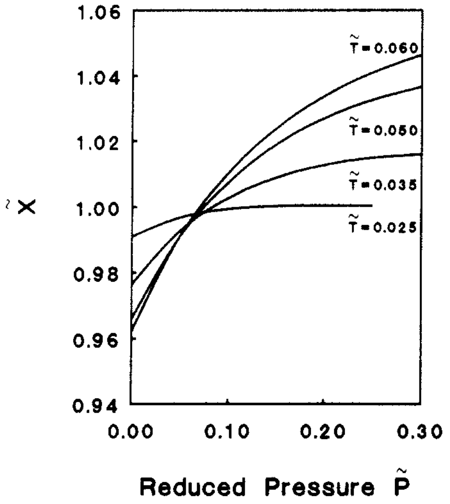

Figure 3. Reduced structural parameter $\tilde{X}$ vs reduced pressure at the indicated temperatures for an $s = 1000$-mer.

the two theories have different universal *PVT* surfaces with slightly different curvatures, indicating a higher compressibility due to nonrandom effects. For small molecules ($s = 1$) the differences between the HH and the present theory are very similar compared to the result shown in Figure 1. In Figure 2 the occupied site fraction y is plotted vs reduced pressure. At high reduced temperatures, the present theory suggests a lower occupied fraction at low reduced pressures, whereas the HH theory gives lower values of y at higher reduced pressures. Again, at low reduced temperatures, the difference between the two theories diminishes. In Figure 3, the behavior of the reduced structural variable $\tilde{X} = X/X^*$; i.e., the segment–hole contact fraction in the case of the nonrandom mixing relative to the random mixing value X^* is shown. Since this new parameter plays an important role in the present theory, we will discuss it in some detail. First of all, we will inspect the pressure dependence. In the region of low reduced pressure, the value of $\tilde{X}$ is smaller than that of X^*, implying that segment–segment contacts are favored. In the region of higher reduced pressure, however, $\tilde{X}$ is larger than X^*, indicating an increased number of segment–hole contacts. To understand this result, we have to consider the structure of the quasi-chemical equation (14), which determines the value of $\tilde{X}$ in some detail. By comparing eq 14 with the corresponding equation for X^* (eq 15), one finds two extra factors η_e and η_s. The former is just the correction factor originally introduced by Guggenheim,[12] except that now it is volume dependent and henceforth also pressure dependent. This factor is energetic in nature and favors more segment–segment contacts in the present case. The factor η_s, originating from the free volume contribution, is entropic in nature. This factor is also volume and pressure dependent but favors segment–hole contacts. In the quasi-chemical equation (eq 14), this factor stands for the difference between our quasi-chemical treatment and Guggenheim's original method. Now that we have two competing factors, it may be easily seen that the magnitude of $\tilde{X}$ is determined by the ratio η_e^2/η_s. When $\eta_e^2/\eta_s > 1$, $\tilde{X}$ is smaller than 1 and thus X is always smaller than X^*, which means that if the energetic factor η_e prevails over the entropic factor η_s, the present theory predicts more segment–segment contacts than the original HH theory. On the contrary, when $\eta_e^2/\eta_s < 1$, i.e., when the entropic factor dominates, $\tilde{X}$ is always larger than 1, indicating that more segment–hole contacts are favored. A trivial case is $\eta_e^2/\eta_s = 1$, which leads to $X = X^*$. Numerical calculation shows that at low reduced pressure η_e^2 is usually larger than η_s and thus X is usually smaller than X^*. As pressure increases, η_s increases rapidly due to the decrease of reduced free length $\tilde{l}_f$, as is readily seen from its exponential form. On the other hand, η_e increases more slowly than η_s, because the intersegmental interaction energy changes less compared to $\tilde{l}_f$. Hence at high enough reduced pressure, the entropic contribution eventually prevails over the energetic contribution, resulting in the change of the magnitude of X from $X < X^*$ to $X > X^*$. Another interesting feature is

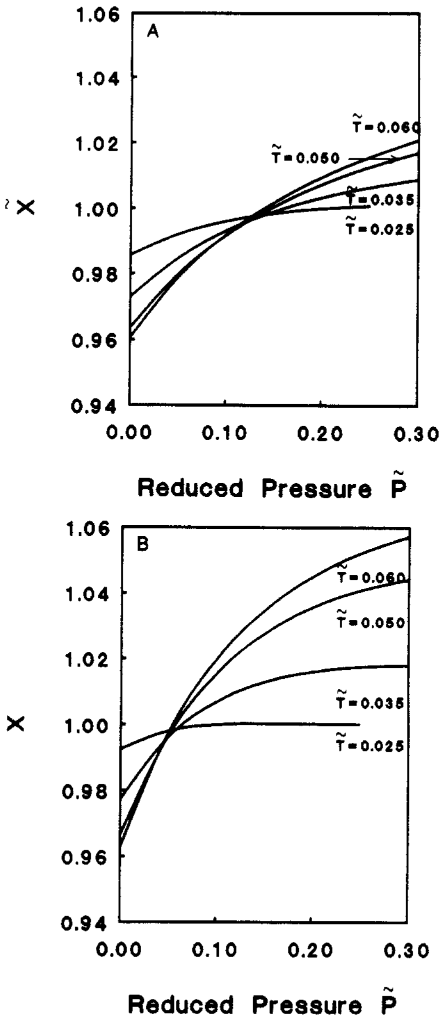

Figure 4. Reduced structural parameter $\tilde{X}$ vs reduced pressure at the indicated temperatures for an $s = 1000$-mer as a function of the external degrees of freedom c_s [(A) $c_s = 0.5$; (B) $c_s = 1.3$].

Table I
Molecular and Scaling Parameters for Polystyrene[21] for the Present Theory and the SS and HH Theories

PS	ϵ^* (J/mol)	$v^* \times 10^{-6}$ (m^3/mol)	c_s	m_0 (kg/mol)	s	p^* (bar)	v^* (cm^3/g)	T^* (K)
present theory	7052.7	89.754	0.8766	0.104	490	7144.6	0.9496	9680.3
HH theory	6690.9	98.460	0.8531	0.104	490	6796.6	0.9468	9438.1
SS theory	6968.8	99.54	0.7694	0.104	490	7002.6	0.9572	10899.2

the temperature dependence of $\bar{X}$. In Figure 3 one finds that at low reduced pressure, $\bar{X}$ decreases as temperature increases, whereas at higher reduced pressure, $\bar{X}$ increases with increasing temperature. In both cases, $\bar{X}$ tends to deviate more from X^* at elevated temperatures. This is unexpected at first sight since, according to Guggenheim's original approach, one may anticipate that $\bar{X}$ should become closer to X^* upon raising the temperature. The reason for this "extraordinary" behavior again lies in the free volume contribution. From the definition of η_e and η_s, one finds that both of them decrease with increasing temperature. But this change is not directly responsible for the temperature dependence of $\bar{X}$. A more decisive factor is the change of the occupied site fraction y (or, equivalently, the external contact fraction q). It should be noted that in hole theories, the value of y is determined by the minimization of the free energy of the system. Thus, although the quasi-chemical equation for $\bar{X}$ (eq 14) is formally quite similar to Guggenheim's original expression (except for the extra factor η_s), the underlying physics is rather different, since now q is a pressure- and temperature-dependent parameter rather than a constant. Generally speaking, q decreases with increasing temperature and decreasing pressure. Bearing this in mind, we can proceed to analyze the temperature dependence of $\bar{X}$. It may be seen that in the low-pressure region, where the energetic factor plays a major role, when more holes emerge as a result of elevated temperature, the quasi-chemical correction makes it possible for more segments to be adjacent to each other (relative to the random mixing case) and henceforth reduces the number of segment–hole contacts. On the contrary, in the high-pressure region, where the free volume contribution dominates and more segment–hole contacts are favored, $\bar{X}$ increases with increasing number of holes introduced by the elevated temperature. Finally, the value of $\bar{X}$ is quite sensitive to the change of the flexibility of the polymer chains as is evident in Figure 4. However, the influence of the change in $\bar{X}$ on the reduced *PVT* surface is surprisingly small. By comparing Figure 1 with Figure 2, one finds that the change in reduced *PVT* surface is mainly caused by the difference in the value of the occupied site fraction y. This gives also an indication that equation of state data probably do not suffice to test the merits of a theory since *PVT* data are almost equally well described by a random mixing and a nonrandom mixing theory.

Table II
Molecular Parameters for PpClS,[22] LPE,[23] and PoMeS[21] According to the Present Theory and the HH Theory[a]

	ϵ^* (J/mol)	$v^* \times 10^{-6}$ (m^3/mol)	c_s	m_0 (kg/mol)	χ^2
PpClS					
present theory	11121.8	1.0779	1.6732	0.1386	302
HH theory	9535.9	1.0787	1.4356	0.1386	337
LPE					
present theory	3533.1	0.29612	0.64173	0.028	318
HH theory	3157.5	0.29566	0.58234	0.028	360
PoMeS					
present theory	8134.4	1.1383	1.1066	0.1182	1.7
HH theory	8181.9	1.1352	1.0611	0.1182	7.6

[a] The last column summarizes the relative sum of squares χ^2, defined according to eq 25. This quantity is a measure for the agreement between the experimental and the computed equation of state data.

(b) Comparison with Experiments. The present theory is used to extract molecular parameters from the experimental equation of state data of several homopolymers. For all the polymers under consideration (including polystyrene (PS),[21] poly(*p*-chlorostyrene) (PpClS),[22] poly(*o*-methylstyrene) (PoMeS),[21] and linear polyethylene (LPE),[23] the description of the experimental data is better than with the original HH and SS theories. The molecular parameters and scaling parameters for PS are summarized in Table I along with the results of the HH and SS theories. The molecular parameters for three other polymers obtained with the present theory and the HH theory are shown in Table II, where χ^2 is defined by

$$\chi^2 = \sum [(P_{\rm exp} - P_{\rm theory})/\sigma_P]^2 + [(T_{\rm exp} - T_{\rm theory})/\sigma_T]^2 + [(V_{\rm exp} - V_{\rm theory})/\sigma_V]^2 \quad (25)$$

The above summation is performed over all data points, and σ_P, σ_T, and σ_V represent the standard deviations of the relevant parameters. A comparison of the values of χ^2 for each component obtained with the present theory and the HH theory shows that the present theory offers an improved description of the components considered.

It may be seen that, compared to the HH and SS theories, the values of the interaction parameters ϵ^* and v^* according to the present theory are larger, indicating a deeper and wider potential bowl. The same is true for the Prigogine parameter c_s, indicating that more degrees of freedom are volume dependent.

IV. Conclusions

If one is interested in an accurate description of experimental *PVT* data with a limited set of molecular parameters, the present theory offers improved results compared to the original HH and SS theories. As expected, the improvement is not dramatic since both the SS and HH theories already provide descriptions often well within the experimental accuracy. Nevertheless it is our opinion that the theoretical effort is justified since the improvements are obtained without the need for extra adjustable parameters: the new parameter $\bar{X}$ is obtained from the maximization of the partition function. Although only limited differences are noticeable in the equation of state, i.e., the ultimate macroscopic behavior, the consequences for the microscopic model s-mers are quite important. It is clear that even for the systems with only dispersive interactions considered here, nonnegligible deviations from randomness are observed. Therefore, from a theoretical point of view the differences are important. Naturally, the observed effects of nonrandomness will also influence the mixture behavior, since it is well known that pure component characteristics govern, e.g., the lower critical miscibility behavior.

Presently we are studying the relevance of the quasi-chemical approximation in the evaluation of the partition function Z. This is accomplished by a comparison of analytical calculations and Monte Carlo simulation results for a lattice–fluid model for single-component and multicomponent systems. Preliminary calculations show that the quasi-chemical approximation results in a quantitative prediction of, e.g., the equation of state behavior and segmental contacts computed in an exact manner from MC simulations. Random mixing approximations fail completely in predicting or even describing these data. These and more detailed results will be communicated in the near future.

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