A theory for compressible binary lattice polymers: Influence of chain conformational properties

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A theory for compressible binary lattice polymers: Influence of chain conformational properties

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The influence of long-range chain connectivity on the thermodynamic properties of athermal compressible single component and binary polymer mixtures is studied for the lattice model both theoretically and by Monte Carlo simulations. Theoretical expressions for the thermodynamic properties are derived based on the chain insertion probabilities. The chain conformations enter the theoretical insertion probabilities by the number of intramolecular contacts. The distribution of the number of intramolecular contacts of a single athermal chain is taken as input, of which the dependence on density is predicted by the theory. The theory successfully predicts the Monte Carlo simulation data for the equation of state of pure components and mixtures. Also microscopic details on the different types of self-contacts and cross contacts in the mixtures are accurately predicted. © *1998 American Institute of Physics.* [S0021-9606(98)52535-4]

I. INTRODUCTION

The interest in the lattice model in polymer science can be retraced to Flory and Huggins more than half a century ago. Their independent works resulted in the celebrated theoretical Flory Huggins (FH) expression for the free enthalpy of mixing of a polymer solution:[1–4] At the same time Flory pointed to the inadequacies of the lattice model for the real off-lattice fluid state, thereby relativizing the importance of refinements to the primitive FH result which carry details of the model.[2] Although the limits of the lattice model for understanding the liquid state have over the years been unravelled in more detail, it has persistently attracted attention. Especially the advent of molecular simulation techniques, becoming feasible with modern computer facilities, renewed the interest in the lattice model. In the framework of statistical mechanics and properly accounting for finite-size effects simulations essentially provide the exact properties of a model.[5,6] Thus by comparing theory and simulations it is possible to study the approximations invoked in theoretical investigations. From these comparative studies it is now clear that the different refinements of the primitive FH theory indeed lead to improved predictions of the thermodynamic properties of the lattice model.[7–12]

One of the first systematic studies of the lattice model by Monte Carlo (MC) computer simulations was pursued by Sariban and Binder who investigated symmetric binary polymer mixtures on a cubic lattice with a constant fraction of vacancies.[9–12] A variety of properties was investigated in these simulations. Of interest to the present contribution we report their study of liquid–liquid coexistence as a function of chain length, temperature, and vacancy fraction. In addition to this sheer thermodynamic data also the average number of the different types of contacts in the mixture was collected in the simulations. The simulation results were compared to the FH and Guggenheim expressions for the lattice model.[2,4,13]

The FH free enthalpy density equals the sum of the internal energy, given by a van Laar–Hildebrand expression, and the combinatorial entropy derived for the athermal systems. Thus the influence of the interactions on the entropy is completely ignored and a random mixing of all segments is assumed. In addition the chain connectivity is fully ignored and the FH expression is given in terms of the occupied site or volume fraction. It should be mentioned that Huggins already predicted an entropy correction to the FH result, including the influence of the nearest-neighbor covalent bonds of each segment. The Huggins correction is most naturally formulated employing the external contact fraction, so excluding the covalent bonds making up the linear chains from participating in intersegmental contacts.

The next important theoretical advancement was established by Guggenheim. Employing his quasichemical approximation, Guggenheim incorporated the influence of the segmental interactions on the free enthalpy, thus removing the random mixing assumption adopted by Flory and Huggins. Sariban and Binder clearly showed that the Guggenheim expression is substantially better than the simple FH theory. At the same time they exposed the main shortcomings of the investigated theories. For the relatively short chain lengths studied in the simulations the real (simulated) coexistence curves clearly have a nonparabolic shape due to a nonclassical critical scaling behavior.[9] In contrast, the theoretical coexistence curves have a parabolic shape associated with their mean-field character.[13] A second deficiency of the FH and Guggenheim theories was found for the different types of segmental contacts. In the simulation a significant number of intramolecular or self-contacts was found; such contacts are completely ignored in the theories. Further de-

tailed studies of the equation of state and miscibility behavior of compressible symmetric binary mixtures in combination with the segmental contacts demonstrated the influence of the intramolecular contacts on the thermodynamic results and it was anticipated that a theory incorporating the intramolecular contacts might further improve the agreement with MC simulation.[14]

An important theoretical advancement for the lattice model is provided by the lattice cluster theory (LCT) of Freed and co-workers.[15,16] These authors molded the lattice partition function in a double expansion in terms of the inverse lattice coordination number and inverse temperature. The zeroth-order term in this expansion is the simple FH result and the higher-order contributions constitute systematic corrections over the simple FH result. Several applications of the LCT, e.g., to mixtures of chemically different polymers[17] and mixtures of linear and branched chain molecules,[18] have indicated the relevance of these theoretical refinements. In the case of athermal linear chains the LCT provides slightly better predictions of the compressibility factor than the Guggenheim approximation[7,8] (for athermal chains the Guggenheim theory reduces to the Huggins combinatorial entropy expression). For the chain lengths actually investigated the difference between the Guggenheim and LCT theory was only minor but was anticipated to increase in favor of the latter for longer chain lengths.[8] Despite the importance of the LCT theory also some drawbacks should be mentioned. For instance, as a function of chain length, peculiar critical behavior was found in the isomorphic conditions of liquid–liquid coexistence of an incompressible polymer solution and the vapor–liquid coexistence of a compressible pure component.[8,19,20] Further, as the LCT theory relies on a truncated expansion in the inverse lattice coordination number and inverse temperature it is unable to fully account for the long-range consequences of the excluded volume effects typical of chainlike fluids.

Another approach to deal with the influence of the detailed molecular architecture on the thermodynamic behavior of polymer solutions and blends was put forward by Gujrati.[21,22] In a series of papers this author presented an approximate theory of lattice polymers of a variety of architectures such as linear homopolymers, branched structures star polymers, and dendrimers. The actual lattice is approximated by an infinite tree (Bethe lattice) of the same coordination number as the actual lattice. This approximation to the lattice is then solved exactly. Closed expression were derived for the entropy, free energy, and the phase diagram of polymer solution and blends on fully occupied lattices.[21] Furthermore, an effective Flory–Huggins χ parameter was derived, being a complex function of composition, chain length, and temperature, which is in agreement with experimental results.[22]

Another line of approach, i.e., the integral equation theory of polymers fluids, was investigated by Curro, Schweizer, and collaborators.[23,24] Integral equation theories were initially developed for simple monoatomic fluids to study the microscopic structure of fluids.[25] These liquid state theories, employing correlation functions, were extended to simple molecular fluids in the reference interaction site model (RISM) theory by Chandler and co-workers.[26,27] The RISM theory makes it feasible to predict the intermolecular correlations among segments or interaction sites on different molecules from information from the intramolecular correlations, which are set by the molecular architecture, between segments of the same molecule. The application of the RISM theory to flexible chain molecules (polymer-RISM or PRISM) was initiated by Curro and Schweizer to study the microscopic structure of polymer single components and mixtures.[23,24] For flexible macromolecules, the intramolecular structure is not *a priori* known and it must be expected to depend on the intermolecular correlations which according to the (P)RISM theory are determined by the intramolecular correlations. Hence a complicated interdependence between inter- and intra-molecular correlations exists and, in principle, both types of correlations must be calculated self-consistently. The first attempts to establish this self-consistency have been published only recently and are still a matter of further investigation.[28–31] Based on the detailed information concerning the correlations in the fluid, the thermodynamic properties can be derived employing exact statistical mechanical relationships.[25,27,32] Unfortunately, and this is a major drawback of all integral equation theories, these calculations are plagued with so-called thermodynamic inconsistencies which are related to the necessary approximations involved in the calculation of the theoretical correlations.[25]

Another interesting approach incorporating the conformational degrees of freedom of the chain molecules in the thermodynamics is due to Szleifer.[33] He considered the chain molecule as a whole in the environment made up by the total system. Note that in the usual FH theory, the influence of the environment is only considered on the segmental level. In evaluating the expression for the partition function, the conformation and translational or configurational degrees of freedom are decoupled. The translational part is assumed to be given by the Flory–Huggins combinatorial entropy and the influence of the conformational degrees of freedom is limited to the internal energy.[33] Hence for athermal chains the simple FH combinatorial entropy is recovered.

In a more recent theoretical development, Weinhold *et al.* achieved a coupling between translational and conformational degrees of freedom for athermal lattice chains.[34] They derived the total entropy in combinatorial and conformational contributions. For the combinational entropy a Huggins–Guggenheim-type expression was used, depending on the average number of intramolecular contact which is determined by the conformational degree of freedom.[34] The authors found chain dimensions and chemical potentials calculated with this new theory in reasonable agreement with MC simulation data.[34]

In the present contribution the influence of the excluded volume of the chain molecule is also investigated. We also start from the notion of intramolecular self-contacts and use this concept to formulate a new theory for athermal systems. It will be shown that the intramolecular contacts require the introduction of a new composition variable excluding such contacts and hence fundamentally change the functional dependence of the combinatorial entropy. In Sec. II we provide

some general statistical mechanics relationships and present the derivation of the new theory and expressions for several thermodynamic properties. These results are also placed in relation to other existing theories. In Sec. III the employed MC simulation algorithms are discussed. In Sec. IV the results for athermal pure components as well as mixtures are discussed. Finally, Sec. V summarizes the important results and gives directions for future investigations involving interacting systems.

II. THEORY

A. Partition functions, insertion probabilities, and thermodynamics

The present discussion considers the thermal properties, at temperature T, of a binary mixture containing N_A s_A-mers, N_B s_B-mers, and N_h holes on a lattice of N_L sites, each of volume v^*. Thus each $A(B)$ molecule is modeled as a linear sequence of $s_A(s_B)$ consecutive sites on the lattice. For the following general discussion of thermodynamics and statistical mechanics it is convenient to define the following variables

Total number of molecules N: $\quad N = N_A + N_B$,

Number average chain length s:

$$s = (s_A N_A + s_B N_B)/N,$$

Occupied site fraction y:

$$y = sN/N_L = sN/(sN + N_h),$$

Chemical composition $\phi_B (= 1 - \phi_A)$:

$$\phi_A = s_A N_A / sN, \quad \phi_B = s_B N_B / sN.$$

The partition function Q of the binary mixture is defined by[25,35]

$$Q(N_A, N_B, N_L, T) = \frac{1}{N_A! N_B! 2^N} \sum_{\{\Lambda_N\}} \exp[-\beta U(\Lambda_N)]$$

$$= \frac{1}{N_A! N_B!} Z(N_A, N_B, N_L, T) \qquad (1)$$

with $\beta = 1/k_B T$ the reciprocal of the temperature multiplied by the Boltzmann constant; Λ_N is an allowed configuration of the N chain molecules on the lattice; $U(\Lambda_N)$ is the internal energy of the system in configuration Λ_N; the sum runs over all allowed configurations. The factorials in Eq. (1) correct for the indistinguishability of the molecules of components A and B. The factor $1/2^N$ corrects for the indistinguishability of the chain ends. The normal kinetic contributions to the partition function are not shown since they do not contribute to the density and composition dependence of the thermal properties discussed in this paper.

A configuration Λ_N is specified by the positions of all segments on the lattice which agree with the constraints of (i) at most single occupancy of lattice sites and (ii) the connectivity of the segments in each chain molecule. In lattice theories, it is customary to consider only nearest-neighbor interactions and the internal energy of the configuration Λ_N can be written as

$$U(\Lambda_N) = -(\mathscr{N}_{AA}(\Lambda_N)\epsilon_{AA} + \mathscr{N}_{BB}(\Lambda_N)\epsilon_{BB}$$

$$+ \mathscr{N}_{AB}(\Lambda_N)\epsilon_{AB}) \qquad (2)$$

with $\mathscr{N}_{ij}(\Lambda_N)$ the number of contact pairs of the type ij in the configuration Λ_N carrying a corresponding contact energy $-\epsilon_{ij}$. All contacts involving empty lattice sites are assigned a zero contact energy. The athermal case is found by putting all $\epsilon_{ij} = 0$.

The partition function Q offers a direct route to the Helmholtz free energy[25,35]

$$\beta A(N_A, N_B, N_L, T) = -\ln Q(N_A, N_B, N_L, T). \qquad (3)$$

An alternative route is provided by the insertion probabilities of both components, $P_A(N_A, N_B, N_L, T)$ and $P_B(N_A, N_B, N_L, T)$, which are defined by the following ratios of partition functions[13,36,37]

$$P_A(N_A, N_B, N_L, T) = \frac{Z(N_A + 1, N_B, N_L, T)}{Z(N_A, N_B, N_L, T)Z(1, 0, N_L, T)}$$

$$= \frac{Z(N_A, +1, N_B, N_L, T)}{Z(N_A, N_B, N_L, T)N_L Z_A}, \qquad (4a)$$

$$P_B(N_A, N_B, N_L, T) = \frac{Z(N_A, N_B + 1, N_L, T)}{Z(N_A, N_B, N_L, T)Z(0, 1, N_L, T)}$$

$$= \frac{Z(N_A, N_B + 1, N_L, T)}{Z(N_A, N_B, N_L, T)N_L Z_B}. \qquad (4b)$$

The last equalities in Eqs. (4) are obtained if one realizes that the partition functions of a single chain on the lattice can be written as the product of an intramolecular contribution $Z_A(Z_B)$ and the total number of lattice sites N_L. More specifically, for a single A chain

$$Z(1, 0, N_L, T) = \frac{1}{2} \sum_{\{\Lambda_1\}} \exp[-\beta U_1(\Lambda_1)]$$

$$= \frac{N_L}{2} \sum_{\{\Lambda_{1'}\}} \exp[-\beta U_1(\Lambda_{1'})] = N_L Z_A \quad (5)$$

with $\Lambda_{1'}$ the allowed configurations of the chain with the first segment fixed. The summation appearing in the second equality is the intramolecular partition function of the chain. The first segment can be positioned on each lattice site and N_L identical terms Z_A are obtained.

Equations (4) are called chain insertion probabilities. This interpretation stems from the possibility to rearrange Eqs. (4) as ensemble averages over all configurations of a single s_j-mer, the $(N_j + 1)$th molecule, in the mixture of all other molecules.[5,38]

The insertion probabilities were originally introduced by Guggenheim in the study of incompressible lattice mixtures.[13] More recently, Hall and co-workers employed the insertion probabilities to derive continuum space analogs of the Flory and the Flory–Huggins lattice theories, the so-called generalized Flory and Flory-dimer theories.[36,37]

Clearly the chemical potentials of both components are related to the intrinsic insertion probabilities according to

$$\beta\mu_A(N_A,N_B,N_L,T) = \beta(A(N_A+1,N_B,N_L,T)$$

$$-A(N_A,N_B,N_L,T))$$

$$= -\ln\left[\frac{Z(N_A+1,N_B,N_L,T)}{Z(N_A,N_B,N_L,T)(N_A+1)}\right]$$

$$= -\ln[Z_A P_A(N_A,N_B,N_L,T)N_L/$$

$$(N_A+1)], \tag{6a}$$

$$\beta\mu_B(N_A,N_B,N_L,T) = \beta(A(N_A,N_B+1,N_L,T)$$

$$-A(N_A,N_B,N_L,T))$$

$$= -\ln\left[\frac{Z(N_A,N_B+1,N_L,T)}{Z(N_A,N_B,N_L,T)(N_B+1)}\right]$$

$$= -\ln[Z_B P_B(N_A,N_B,N_L,T)N_L/$$

$$(N_B+1)]. \tag{6b}$$

In the thermodynamic limit, i.e., $N_L,N_A,N_B\rightarrow\infty$ and $sN/N_L=y$ and $s_B N_B/sN=\phi_B$, the chemical potentials and all other intensive thermodynamic functions of state are independent of the extension of the system and depend only on the intensive variables y, ϕ_B, and T. Hence in this limit also the right-hand sides of Eqs. (6) can only be functions of these intrinsic variables and one can define limiting chain insertion probabilities according to

$$p_A(y,\phi_B,T) = \lim_{\substack{N_L,N_A,N_B\rightarrow\infty \\ sN/N_L=y, s_B N_B/sN=\phi_B}} P_A(N_A,N_B,N_L,T),$$

$$\tag{7a}$$

$$p_B(y,\phi_B,T) = \lim_{\substack{N_L,N_A,N_B\rightarrow\infty \\ sN/N_L=y, s_B N_B/sN=\phi_B}} P_B(N_A,N_B,N_L,T).$$

$$\tag{7b}$$

Consequently, in the thermodynamic limit, the expressions for the chemical potentials become

$$\beta\mu_A(y,\phi_B,T) = -\ln[s_A p_A(y,\phi_B,T)Z_A/(\phi_A y)], \tag{8a}$$

$$\beta\mu_B(y,\phi_B,T) = -\ln[s_B p_B(y,\phi_B,T)Z_B/(\phi_B y)]. \tag{8b}$$

Furthermore, the chain insertion probabilities can be used to determine the Helmholtz free energy. Applying the definitions of the insertion probabilities, Eqs. (4), recursively to Eq. (1), the partition function can be written as a product of chain insertion probabilities, i.e., the mixture is built up by inserting the chain molecules one at a time. For example, if the N_A molecules are inserted before the N_B molecules, one finds

$$Q(N_A,N_B,N_L,T) = \frac{Z_A^{N_A}Z_B^{N_B}N_L^N}{N_A!N_B!}\prod_{l=1}^{N_A-1} P_A(l,0,N_L,T)$$

$$\times\prod_{m=1}^{N_B-1} P_B(N_A,m,N_L,T). \tag{9}$$

On the other hand, if the order of insertion is reversed one obtains

$$Q(N_A,N_B,N_L,T) = \frac{Z_A^{N_A}Z_B^{N_B}N_L^N}{N_A!N_B!}\prod_{l=1}^{N_A-1} P_A(l,N_B,N_L,T)$$

$$\times\prod_{m=1}^{N_B-1} P_B(0,m,N_L,T). \tag{10}$$

Unfortunately, the approximate nature of available theoretical expressions for the insertion probabilities (such as the Huggins approximation discussed in the sequel) may make the partition function dependent on the particular order of insertion.[37] The thermodynamic functions, being state functions, must be independent of this order. A possible way to prevent this problem is to average over all distinct ways of constructing the mixture. However, this is a formidable task as, in total, there are $N!/N_A!N_B!$ distinct ways of inserting the chains.

In an alternative insertion scheme, the molecules can be introduced in sequences such that after the addition of a sequence the composition remains fixed at the macroscopic composition ϕ_B. To illustrate this principle consider a mixture of overall composition $\phi_B=1/3$ and both components having equal chain lengths, i.e., $s_A=s_B$. Then, the partition function $Z(N_A,N_B,N_L,T)$ can be written as

$$Z(N_A,N_B,N_L,T) = \left\{\frac{Z(N_A,N_B,N_L,T)}{Z(N_A-1,N_B,N_L,T)}\frac{Z(N_A-1,N_B,N_L,T)}{Z(N_A-1,N_B-1,N_L,T)}\frac{Z(N_A-1,N_B-1,N_L,T)}{Z(N_A-2,N_B-1,N_L,T)}\right\}\cdots$$

$$\times\left\{\frac{Z(l,m,T)}{Z(l-1,m,N_L,T)}\frac{Z(l-1,m,N_L,T)}{Z(l-1,m-1,N_L,T)}\frac{Z(l-1,m-1,N_L,T)}{Z(l-2,m-1,N_L,T)}\right\}\cdots$$

$$\times\left\{\frac{Z(2,1,N_L,T)}{Z(1,1,N_L,T)}\frac{Z(1,1,N_L,T)}{Z(1,0,N_L,T)}\frac{Z(1,0,N_L,T)}{Z(0,0,N_L,T)}\right\}, \tag{11}$$

where the molecules are introduced in the order $\cdots\{ABA\}\{ABA\}\cdots$ and the different typical sequences are grouped by the curly brackets.

Equation (11) can be rewritten employing the chain insertion probabilities P_A and P_B defined in Eqs. (4), yielding

$$Z(N_A,N_B,N_L,T) = Z_A^{N_A} Z_B^{N_B} N_L^N$$

$$\times \{P_A(N_A-1,N_B,N_L,T)P_B(N_A-1,N_B-1,N_L,T)P_A(N_A-2,N_B-1,N_L,T)\}\cdots$$

$$\times \{P_A(l-1,m,N_L,T)P_B(l-1,m-1,N_L,T)P_A(l-2,m-1,N_L,T)\}\cdots$$

$$\times \{P_A(1,1,N_L,T)P_B(1,0,N_L,T)P_A(0,0,N_L,T)\}. \tag{12}$$

Another expression for the partition function can be obtained from Eq. (11) if the intermediate partition functions Z in a typical sequence are cancelled, yielding the result

$$Z(N_A,N_B,N_L,T) = \left\{\frac{Z(N_A,N_B,N_L,T)}{Z(N_A-2,N_B-1,N_L,T)}\right\}\cdots\left\{\frac{Z(l,m,N_L,T)}{Z(l-2,m-1,N_L,T)}\right\}\cdots\left\{\frac{Z(2,1,N_L,T)}{Z(0,0,N_L,T)}\right\}, \tag{13a}$$

$$Z(N_A,N_B,N_L,T) = Z_A^{N_A} Z_B^{N_B} N_L^N \times P_{\text{seq}}(N_A,N_B,N_L,T)\cdots P_{\text{seq}}(l,m,N_L,T)\cdots P_{\text{seq}}(2,1,N_L,T). \tag{13b}$$

Equation (13b) serves to define the insertion probability of a typical sequence, $P_{\text{seq}}(l,m,N_L,T)$. The insertion probability of a typical sequence can be rearranged as an ensemble average over all configurations of a typical sequence in the mixture of all other remaining molecules. From this it can be appreciated that both the typical sequence and the remaining mixture possess the same overall composition ϕ_B. Although $P_{\text{seq}}(l,m,N_L,T)$ operates at constant overall composition it still depends on the finite size of the system. However, in the thermodynamic limit we can define a *limiting insertion probability of a typical sequence* that only depends on the intensive variables y and ϕ_B

$$p_{\text{seq}}(y,\phi_B,T) = \lim_{\substack{N_L,l,m\to\infty \\ (s_A l + s_B m)/N_L = y \\ s_B m/(s_A l + s_B m) = \phi_B}} P_{\text{seq}}(l,m,N_L,T). \tag{14}$$

Furthermore, in the thermodynamic limit the limiting sequence insertion probability can also be related to the limiting chain insertion probabilities at constant overall composition ϕ_B. Combining Eqs. (12), (13b), (14), and (7) we find

$$p_{\text{seq}}(y,\phi_B) = \lim_{\substack{N_L,l,m\to\infty \\ (s_A l + s_B m)/N_L = y \\ s_B m/(s_A l + s_B m) = \phi_B}} P_{\text{seq}}(l,m,N_L)$$

$$= \lim_{\substack{N_L,l,m\to\infty \\ (s_A l + s_B m)/N_L = y \\ s_B m/(s_A l + s_B m) = \phi_B}} \{P_A(l-1,m,N_L)P_B(l-1,m-1,N_L)P_A(l-2,m-1,N_L)\}$$

$$= \lim_{\substack{N_L,l,m\to\infty \\ (s_A(l-1) + s_B m)/N_L = y \\ s_B m/(s_A(l-1) + s_B m) = \phi_B}} P_A(l-1,m,N_L)$$

$$\times \lim_{\substack{N_L,l,m\to\infty \\ (s_A(l-1) + s_B(m-1))/N_L = y \\ s_B(m-1)/(s_A(l-1) + s_B(m-1)) = \phi_B}} P_B(l-1,m-1,N_L)$$

$$\times \lim_{\substack{N_L,l,m\to\infty \\ (s_A(l-2) + s_B(m-1))/N_L = y \\ s_B(m-1)/(s_A(l-2) + s_B(m-1)) = \phi_B}} P_A(l-2,m-1,N_L)$$

$$= p_A(y,\phi_B)p_B(y,\phi_B)p_A(y,\phi_B) = (p_A(y,\phi_B)^{2/3} p_B(y,\phi_B)^{1/3})^{N_{\text{seq}}} = p_e(y,\phi_B)^{N_{\text{seq}}}, \tag{15}$$

where N_{seq} is the number of molecules in a typical sequence (in this particular example $N_{\text{seq}}=3$).

In the last equality we define the *limiting effective chain insertion probability* $p_e(y,\phi_B,T)$. The effective chain insertion probability $p_e(y,\phi_B,T)$ can be thought of as the chain insertion probability of a molecule of an *effective component*, determined by the composition of the mixture.

Although Eqs. (11)–(15) are derived for the particular example, $\phi_B=1/3$ and $s_A=s_B$, the above discussion can be repeated for any set N_A, N_B, N_L. The limiting insertion probability of a typical sequence is still given by Eq. (14) whereas the relation between $P_{\text{seq}}(l,m,N_L,T)$ and the limiting chain insertion probabilities becomes

$$p_{\text{seq}}(y,\phi_B,T) = \{p_A(y,\phi_B,T)^{N_A/N} p_B(y,\phi_B,T)^{N_B/N}\}^{N_{\text{seq}}}$$

$$= \{p_A(y,\phi_B,T)^{s\phi_A/s_A} p_B(y,\phi_B,T)^{s\phi_B/s_B}\}^{N_{\text{seq}}}$$

$$= p_e(y,\phi_B,T)^{N_{\text{seq}}}. \tag{16}$$

The simple relation, Eq. (16), between the insertion probability of the separate chains and of a typical sequence is only obtained in the thermodynamic limit. It was already mentioned that after the addition of each typical sequence the composition remains at the overall composition ϕ_B. However, in general, in a finite system it will be impossible to unravel P_{seq} in separate chain insertion probabilities at the overall composition ϕ_B. This is again easily illustrated for the example $\phi_B = 1/3$. For example, the factor $P_{seq}(2,1,N_L,T)$ in Eq. 13(b), the insertion of these three molecules is expressed in separate chain insertion probabilities in Eq. (12). Clearly, the introduction of the sequence $\{ABA\}$ occurs at instantaneous compositions $\phi'_B = 0.0$ (first A molecule), $\phi'_B = 0.0$ (B molecule), $\phi'_B = 0.5$ (second B molecule), respectively. Hence in general it is impossible to insert the separate molecules at constant overall composition ϕ_B. Nevertheless, in the following we will approximate the factors $P_{seq}(l,m,N_L,T)$ in a finite system by the limiting insertion probability $p_{seq}(y,\phi_B,T)$, given by Eq. (16).

Using the insertion factor of the effective component, defined in Eq. (16), the partition function, Eq. (1), is in approximation given by

$$Q(N_A,N_B,N_L,T) = \frac{Z_A^{N_A} Z_B^{N_B} N_L^N}{N_A! N_B!} \prod_{i=1}^{N-1} p_e(y'(i),\phi_B,T)$$
(17)

with $y'(i)$ the density of the mixture upon introducing the typical sequence i.

Combining Eqs. (3) and (17), and making use of the Stirling approximation, $N! = (N/e)^N$, the Helmholtz free energy can be written as

$$\beta A = N_A \ln(\phi_A y) + N_B \ln(\phi_B y)$$
$$- \sum_{i=1}^{N-1} \ln[p_e(y'(i),\phi_B,N_L,T)]$$
$$- N_A \ln(es_A Z_A) - N_B \ln(es_B Z_B).$$
(18)

The last two terms in Eq. (18) are linear in composition and do not contribute to the thermodynamic properties discussed in the following and are therefore omitted in the sequel.

Considering the intensive Helmholtz free energy per segment, and replacing the summation by an integral, we arrive at the following expressions

$$\beta A/sN = (\phi_A/s_A)\ln(\phi_A) + (\phi_B/s_B)\ln(\phi_B) + (1/s)\ln(y)$$
$$- (N_L/s^2 N) \int_1^{N-1} \ln[p_e(y'(i),\phi_B,N_L,T)]$$
$$\times d(si/N_L),$$
(19a)

$$\beta A/sN = (\phi_A/s_A)\ln(\phi_A) + (\phi_B/s_B)\ln(\phi_B) + (1/s)\ln(y)$$
$$- (1/sy) \int_0^y \ln[p_e(y',\phi_B,T)]dy'.$$
(19b)

Finally the equation of state can be derived from Eq. (19) by direct differentiation with respect to the volume at constant temperature and composition, or by making use of the thermodynamic identity

$$pV = N_A \mu_A + N_B \mu_B - A.$$
(20)

Both routes lead to the same result, i.e.,

$$\beta pV/sN = \beta pv*/y = (1 - \ln(p_e))/s$$
$$+ (1/sy) \int_0^y \ln[p_e(y',\phi_B,T)]dy'.$$
(21)

Equations (8), (19), and (21) provide relations between the insertion probabilities and the thermodynamic properties considered in this work. The expressions for the Helmholtz free energy and the equation of state, derived by Dickmann and Hall for pure components, can be recovered from Eqs. (19) and (21) by setting $\phi_B = 1$ or $\phi_B = 0$. Hence it should be noted that also for pure components Eqs. (19) and (21) are only approximate as the limiting insertion probabilities are also assumed to be valid for finite systems.

B. Theoretical expressions for the insertion probabilities of athermal chains

Further progress depends on the development of accurate expressions for the insertion probabilities. It was already mentioned that the limiting chain insertion probabilities as defined in Eqs. (7) are a measure for the success of introducing a test chain in the mixture. For athermal chains, i.e., $\epsilon_{AA} = \epsilon_{BB} = \epsilon_{AB} = 0$, each allowed configuration of the test chain is equally probable and the insertion probability is independent of temperature.

To illustrate the concept, the insertion probabilities typical for the well-known Flory and Huggins approximations will be derived. In particular the Huggins approximation will serve as a reference to obtain a more accurate approximation for the insertion probabilities. Both Flory and Huggins derived independently expressions for the entropy of mixing polymer and solvent on a fully occupied lattice.[2,4] The equivalence of the incompressible polymer solution and the compressible polymer melt was exploited to discuss the equation of state and its influence on miscibility of compressible polymer systems.[7,14] In this contribution the Flory and Huggins approximations will be discussed for a compressible binary polymer mixture.

In the Flory approximation it is assumed that each segment can be inserted independently of the other segments in the chain.[13,36] Consequently, the chain insertion probability can be written as the product of these segmental contributions. The insertion factor of an independent segment (which is the ensemble average over all configurations of the mixture and the test segment) is equal to the fraction of free lattice sites, $(1-y)$, and the insertion probabilities of a complete j chain ($j = A$ or B)

$$p_j(y,\phi_B,T) = p_j(y) = (1-y)^{s_j} \quad \text{and} \quad p_e = (1-y)^s.$$
(22)

The chain insertion probability depends only on density and chain length whereas the effective chain insertion probability depends on composition only through the number average chain length s.

In Eq. (22) the insertion problem is oversimplified by completely ignoring the chain connectivity. In particular, for

a middle segment two of its z contact positions are taken by covalent bonds. For an end segment one contact position participates in a covalent bond. In fact, the contact positions of a segment involved in covalent bonds are unavailable for contacts with other segments and it is useful to distinguish between covalent and other (external) contacts of a molecule. This distinction leads to the definition of *external contact fractions*[7,13,14]

$$q_A = \frac{N_A(s_A(z-2)+2)}{N_A(s_A(z-2)+2)+N_B(s_B(z-2)+2)+N_h z}$$

$$= \frac{\phi_A(1-\alpha_A)y}{(1-\alpha y)}, \tag{23a}$$

$$q_B = \frac{\phi_B(1-\alpha_B)y}{(1-\alpha y)}, \tag{23b}$$

$$q = q_A + q_B = \frac{(1-\alpha)y}{(1-\alpha y)} \tag{23c}$$

with N_h the number of vacancies on the lattice, α the fractional number of covalent contacts per segment, $\alpha = \alpha_A \phi_A + \alpha_B \phi_B$, $\alpha_j = \gamma(1-1/s_j)$ ($j=A$ or B), and $\gamma=2/z$. The numerator of Eq. (23a) denotes the number of intersegmental contact positions of the N_A chains of type A and the denominator is the total number of contact positions of chain molecules and vacancies. A similar expression, Eq. (23b), is valid for type B molecules. The fraction of intersegmental contacts, irrespective of being of type A or B, is given by Eq. (23c).

Huggins derived an expression for the entropy of mixing of an incompressible lattice polymer solution, based on the difference between covalent and external contact positions.[4] The chain insertion probability according to Huggins is also obtained by sequentially inserting the chain segments. As in the Flory approximation, the probability to insert the first segment is equal to the fraction of free lattice sites, $(1-y)$. To insert the second segment it suffices to find a free contact place, on the first segment. The average probability that a contact position of the first segment is already involved in an external contact pair with other segments in the mixture is equal to the external contact fraction q. The average is over all configurations of the molecules already inserted and all configurations of the segment. This estimate of the average probabilities implicitly assumes that the contact positions on each segment can form independently of each other contact pairs; this is called noninterference of pairs. Hence the probability that a chosen contact position is free equals $(1-q)$. The insertion of the third and subsequent segments is treated in a similar manner; also for these segments it is assumed that the probability to find a free contact place is equal to $(1-q)$. Thus the excluded volume of the chain, resulting from connectivity effects propagated along the chain, is not accounted for. These approximations result in the following expressions for the insertion probabilities

$$p_A = (1-y)(1-q)^{s_A-1} = \frac{(1-y)^{s_A}}{(1-\alpha y)^{s_A-1}},$$

$$p_B = (1-y)(1-q)^{s_B-1} = \frac{(1-y)^{s_B}}{(1-\alpha y)^{s_B-1}}, \tag{24}$$

$$p_e = \frac{(1-y)^s}{(1-\alpha y)^{s(\phi_A(s_A-1)/s_A+\phi_B(s_B-1)/s_B)}} = \frac{(1-y)^s}{(1-\alpha y)^{s-1}}.$$

In addition to the density and chain length dependence already observed in the Flory approximation, the insertion probabilities acquire an extra composition dependence by virtue of the parameter α.

More recently, Bawendi, Freed, and Mohanty developed the lattice cluster (LC) theory offering systematic corrections to the Flory result.[15,16] Although the Huggins correction is not a combination of those systematic corrections, it provides a substantial improvement over the Flory result. For instance, the equation of state of athermal lattice polymers obtained from Monte Carlo (MC) simulations is predicted more accurately by the Huggins approximation than by the Flory expression.[7] For moderate chain lengths both the LC theory and the Huggins approximation are virtually indistinguishable. However, the quality of the Huggins prediction deteriorates with increasing chain length and the higher-order lattice cluster theory offers room for further systematic improvement.[8] Nevertheless, the Huggins expression can be considered to be an effective and rather accurate expression which was confirmed in further investigations, including interacting lattice polymers and binary polymer mixtures.[7,14]

The interpretation of the Huggins approximation, given in the derivation of Eq. (24), provides also an opportunity to define an improved insertion probability. Recall the parameter α introduced with the definition of the external contact fraction. The quantity $z\alpha_j$ is the number of covalent contacts of a segment, averaged over all s_j segments in the chain. Hence the quantity $z(1-\alpha_j)$ is the average number of free contact positions of a segment. It was shown that a drawback of the Huggins expression is the ignorance of self-contacts, intrinsically related to the excluded volume of the chain.[9–12,14] It should be mentioned that also in the Guggenheim free enthalpy expression, the external contact fractions are used and, hence the same drawbacks apply to this theory. In addition to the covalent contacts, a chain molecule possesses also *intramolecular* contacts which are not able to participate in *intermolecular* contacts. For the moment, suppose that the average number of intramolecular contacts (covalent and noncovalent) of a segment in an s_j-mer is given by $z\omega_j$ [the average is over all configurations of the mixture and the complete s_j-mer and as before ($j=A$ or B)]. It is then possible to define *intermolecular contact fractions*

$$\theta_A = \frac{N_A s_A z(1-\omega_A)}{N_A s_A z(1-\omega_A)+N_B s_B z(1-\omega_B)+N_h z}$$

$$= \frac{\phi_A(1-\omega_A)y}{(1-\omega y)},$$

$$\theta_B = \frac{\phi_B(1-\omega_B)y}{(1-\omega y)}, \tag{25}$$

$$\theta = \theta_A + \theta_B = \frac{(1-\omega)y}{(1-\omega y)} \quad \text{and} \quad \theta_h = 1 - \theta$$

with $\omega = \omega_A \phi_A + \omega_B \phi_B$.

It is now possible to formulate chain insertion probabilities, which account for the occurrence of intramolecular contacts, irrespective of the covalent or noncovalent character. Again, the probability to insert the first segment is equal to $(1-y)$. The next segment can only be added at a free contact place of the first segment. The probability that a contact place in the mixture is involved in an intermolecular contact pair is θ. Hence the probability that a contact position is free equals $(1-\theta)$. Taking the same reasoning for the subsequent segments the following chain insertion probabilities are obtained

$$p_A = (1-y)(1-\theta)^{s_A-1} = \frac{(1-y)^{s_A}}{(1-\omega y)^{s_A-1}},$$

$$p_B = (1-y)(1-\theta)^{s_B-1} = \frac{(1-y)^{s_B}}{(1-\omega y)^{s_B-1}}, \quad (26)$$

$$p_e = \frac{(1-y)^s}{(1-\omega y)^{s-1}}.$$

In Eqs. (26), the effect of the chain excluded volume on the nearest-neighbor surrounding of the segment is accounted for, provided that the parameter ω_j is known. This is a difficult problem by itself as ω_j depends on density and chain length. In the following theoretical analysis we will also use the probability distribution of ω_j, denoted by $P_{\omega_j}(\Omega,y)$; the probability that, on average, a segment of the s_j-mer has $z\Omega$ intramolecular contact positions. It is easily seen that ω_j can be obtained from $P_{\omega_j}(\Omega,y)$

$$\omega_j = \frac{\Sigma_\Omega \Omega P_{\omega_j}(\Omega,y)}{\Sigma_\Omega P_{\omega_j}(\Omega,y)}. \quad (27)$$

For the single chain, i.e., $(y=0)$, the probability distribution $P_{\omega_j}(\Omega,y=0)$ is easily extracted from a lattice simulation. It suffices to generate a proper sample of the allowed self-avoiding walks (SAW's) of the s_j-mer and to inspect each chain configuration for the total number of intramolecular contacts. From this, the intramolecular contacts per segment are then easily calculated. For higher chain lengths, it may be necessary to use sophisticated simulation schemes, such as the biased MC algorithm.[39] For the chain lengths considered in this paper, the chain configurations can be produced by straightforward generation of a sufficient number of SAW's on the lattice. For 30- and 16-mers $P_{\omega_j}(\Omega,y=0)$ is shown in Fig. 1 (simulation details are found in the section on simulations).

The distribution $P_{\omega_j}(\Omega,y)$ at density y can also be obtained from a simulation. Moreover, if such a simulation is available, other properties of the system are easily extracted. Therefore we seek an approximate expression to predict the density dependence of ω_j. The zero-density probabilities, $P_{\omega_j}(\Omega,y=0)$, reflect the distribution of the allowed single chain configurations according to their intramolecular surroundings $z\Omega$. The relative importance of these different in-
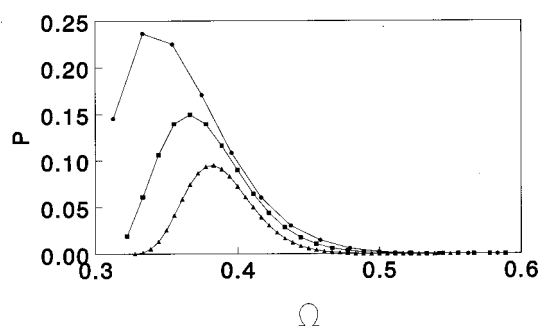

FIG. 1. Zero-density probability distribution $P_{\omega_j}(\Omega,y=0)$ for an athermal 16-mer (●), a 30-mer (■), and a 60-mer (▲). Line pieces are drawn for convenience.

tramolecular surroundings is altered by the density. An estimate of the influence of the density is accomplished along the following lines. The insertion probability p_j refers to the absorption of a chain in a mixture quantified by its density y and the average number of intramolecular segmental contacts $z\omega$. Of course, once assimilated, the test chain acquires these mixture characteristics. From Eq. (26), the Flory contribution $(1-y)^{s_j}$ can be isolated which permits an alternative interpretation for p_j. Equations (26) can be viewed as the Flory insertion of independent segments (irrespective of their intramolecular configuration) and the factor $1/(1-\omega y)^{(s_j-1)}$ which constitutes a measure for the conditional probability that the segments are present with the correct average intramolecular organization. To this last factor, each segment contributes a factor $1/(1-\omega y)^{((s_j-1)/s_j)}$. Invoking the noninterference of pairs, one can push the interpretation even further and define the contribution of a single intramolecular contact position

$$\left[\frac{1}{(1-\omega y)^{(s_j-1)/s_j}} \right]^{1/z\omega}. \quad (28)$$

Recapitulating, Eq. (28) is a measure for the conditional probability to find an intramolecular contact position in the mixture specified by ω and y. On the other hand, $P_{\omega_j}(\Omega,y)$ is the conditional probability that a chain-segment in the mixture possesses $z\Omega$ intramolecular contact positions. A measure for the probability that a chain has the surrounding $z\Omega$, in the mixture specified by ω and y, can be calculated from Eq. (28). Each of the $z\Omega$ intramolecular contacts of a segment carries a factor, given by Eq. (28). The conditional probability for a complete chain is obtained by subsequent insertion of the s_j independent segments. Putting everything together gives

$$\left(\left[\frac{1}{(1-\omega y)^{(s_j-1)/s_j}} \right]^{z\Omega/z\omega} \right)^{s_j}. \quad (29)$$

Equation (29) provides a measure for the influence of density on the probability of a chain to have $z\Omega$ intramolecular contacts per segment. The probability distribution $P_{\omega_j}(\Omega,y)$ can then be calculated according to

$$P_{\omega_j}(\Omega,y) = C_N P_{\omega_j}(\Omega,y=0) \left(\frac{1}{(1-\omega y)^{\Omega/\omega}} \right)^{s_j-1}, \quad (30)$$
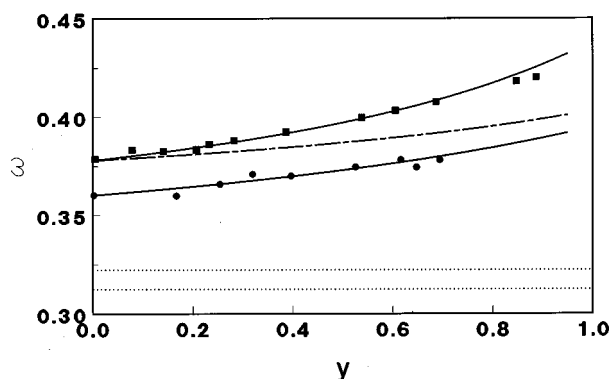
FIG. 2. The fraction of average intramolecular contacts per segment for athermal 16-mers (●) and athermal 30-mers (■) as a function of density y. Solid lines indicated the predictions according to Eq. (30). The dotted lines indicate the value of ω used in the NRM theory. The dash-dotted line is the prediction for athermal 30-mers according to the theory of Weinhold *et al.* (Ref. 34).

where we have introduced a normalization factor C_N which needs not to be known as it cancels in the calculation of ω_j by means of Eq. (27).

The average segmental surrounding of a segment at any density can now be calculated from the simulation data of the single chain, Eqs. (30) and (27). Note that the ω_j's are also present on the right-hand side of Eq. (30) and the ω_j's are obtained iteratively. The predictions for ω_j are compared to simulation data in Fig. 2 and are discussed in Sec. IV.

Equations (26) and (30) are the main theoretical results for athermal chains. The probability distribution $P_{\omega_j}(\Omega, y)$ can be calculated via Eq. (30) from the distribution $P_{\omega_j}(\Omega, y=0)$, obtained from the single chain simulation. Combined with the available relations between the insertion probabilities and thermodynamic properties [Eqs. (8), (19), and (21)] a complete theory for athermal lattice chains is provided. For instance, the Helmholtz free energy of the athermal mixture becomes

$$\beta A/sN = (\phi_A/s_A)\ln(\phi_A) + (\phi_B/s_B)\ln(\phi_B) + (1/s)\ln(y)$$
$$- (1/sy)\int_0^y \ln[(1-y')^s/(1-\omega y')^{s-1}]dy'.$$

$$(31)$$

The equation of state is given by

$$\beta pV/sN = \beta pv^*/y$$
$$= (1 - \ln(p_e))/s + (1/sy)\int_0^y \ln[(1-y')^s/$$
$$(1-\omega y')^{s-1}]dy'$$

$$(32)$$

with ω defined by Eqs. (30) and (27).

The complicated density dependence of the insertion probabilities prevents further analytical formulation of the integrals.

III. MONTE CARLO SIMULATIONS

To verify the proposed theoretical approach we performed Monte Carlo (MC) simulations on a cubic lattice providing thus independent results for the same molecular model as used in the theoretical development. Simulations for homogeneous systems of chain lengths $s = 20$, 30, and 60 were performed in the NpT ensemble. Since these simulations are described in detail in a previous publication we only point out the differences related to the evaluation of the intramolecular contacts.[7,14] All details such as the number of chains in the systems, the size of the lattice, etc., are the same as in previous publications.[7,14] To evaluate the effect of chain connectivity we did not analyze the total spatial pair distribution function in the coils but concentrated on nearest-neighbor contacts. Specifically, we distinguished in the simulations between intra- and inter-molecular self-contacts. This is the route to obtain the parameter ω, expressing the average intramolecular surroundings of a segment, introduced in the theoretical section.

In addition to the multichain simulations mentioned above we performed also single chain simulations. Theoretical considerations presented in previous sections rely on the knowledge of the connectivity in the athermal single chain, from which the values for higher concentrations can be predicted. We performed single chain simulations composed of athermal segments by two methods and obtained the desired factor ω and its distribution. In the first method, growing the relatively short chains, we created configurations with no chain overlap. Second, we also used the dynamic Monte Carlo method employed in the multichain systems, where different self-avoiding configurations are created by configurational moves from a previous chain configuration. Both methods yielded identical results for the parameter ω and the distribution $P_\omega(\Omega, y=0)$ indicating the correctness of the simulation algorithms.

IV. RESULTS AND DISCUSSION

A. Pure components

In Fig. 1 the probability distribution $P_{\omega_j}(\Omega, y=0)$, the probability at zero density that on average a segment in an athermal s-mer has $z\Omega$ intramolecular contacts (either covalent bonds or intramolecular contacts), is depicted for a 16-mer (●), a 30-mer (■), and a 60-mer (▲). These MC simulation data, collected as explained in Sec. III, are required to calculate the average number of intramolecular contacts of an athermal chain at any thermodynamic state according to Eq. (30).

The distributions presented in Fig. 1 are bounded from above and below, the minimum number of intramolecular contacts equals the number of covalent bonds, i.e., $\Omega_{\min} = \alpha_j = \gamma(1-1/s)$, and the maximum value of Ω evidently equals 1. Clearly, this upper bound is very unlikely to occur and is not sampled at all in the finite simulation runs involving 10^6 distinct conformations. The lower bound may substantially contribute to the distribution although the importance of this state decreases with chain length. Furthermore, it can be observed that the most probable value for Ω shifts to larger values with increasing chain length. Earlier theo-

ries, such as the NRM theory,[7] only operated with this lower limiting value Ω_{min} in the calculations. As will become clear in the subsequent discussion, this is an important factor for the remaining discrepancies between theory and simulation observed for the NRM and similar theories.

The simulation data collected for the athermal single chains can immediately be put to use in the calculation of the intramolecular contacts of athermal chains at any density in the melt, see Eqs. (27) and (30). These theoretical predictions (solid lines) are shown in Fig. 2 and compared to MC simulation data for 16-mers (●) and 30-mers (■). At zero density ($y=0$) the calculated and MC results are, by definition, in exact agreement since in this case we are merely calculating the average value of ω according to Eq. (27) over the zero-density distribution $P_{\omega_j}(z\Omega, y=0)$. Despite the simple arguments leading to Eq. (30), it is also clear from Fig. 2 that the predicted nonzero density results are in excellent agreement with the MC simulation data. Both theory and simulation show that the fraction of intramolecular contacts increases with density. Naturally, this increase is intimately connected, although not expressed quantitatively, to the contraction of the average chain dimensions with density. As conjectured in the Flory ideality hypothesis,[40] and quantified in, e.g., renormalization group theories, the dimensions of the single chain will change from a self-avoiding walk at low density to a Gaussian random walk at high densities.[41] These conformational changes are a result of the more efficient screening of intra- and inter-molecular interactions with density and are accompanied by a decrease in the coil dimensions.

As a reminder the value of ω employed in the NRM theory, i.e., $\omega = \alpha$, is shown in Fig. 2 by the dotted lines (α increases with chain length). It becomes clear that the number of covalent bonds is a poor (under)estimate for the total number of intramolecular contacts. Furthermore, since α is independent of density it is unable to capture the subtle changes with density found for the true ω. One may anticipate that properties depending directly or indirectly on the intramolecular contacts will be poorly predicted by the NRM theory. In the sequel, several examples of this will be presented.

At this point a comparison with the recent theory of Weinhold et al. is at place.[34] These authors presented a theoretical derivation of the total entropy of an athermal polymer solution, composed of combinatorial and conformational parts. Also in their theory a coupling between conformational and translational degrees of freedom is established. This coupling results in a concentration dependence of the intramolecular contacts of the chain molecule, which are directly connected to its conformational properties. Making use of the similarity between an athermal incompressible polymer solution and an athermal compressible pure component the density dependence of the number of intramolecular contacts for athermal 30-mers according to their theory is depicted by the dash-dotted line in Fig. 2. Clearly, the predicted density dependence of this theory is too weak. This is in agreement with their results on the variation of the radius of gyration and the solvent chemical potential in athermal incompressible solutions.[34]
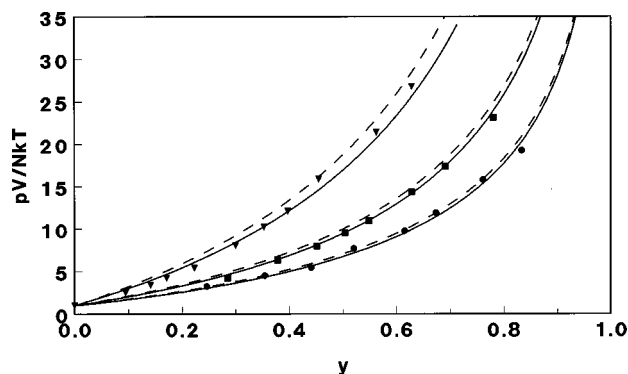

FIG. 3. Compressibility factor pV/NkT as a function of packing fraction y for different chain lengths $s=20$, (●); $s=30$, (■); and $s=60$, (▼). Full lines represent the ω theory and long dashed lines the NRM theory.

In Fig. 3 the compressibility factor pV/NkT for athermal s-mers is plotted as a function of density. The theoretical predictions of the new theory (solid lines) are compared to MC simulation data (symbols). In addition, the NRM theory, presented in previous publications, serves as a reference.[7] As already discussed in some detail and confirmed in Fig. 3, the NRM theory gives a quantitative prediction of the compressibility factor of 20-mers (●) and 30-mers (■). However, it was already anticipated that the accuracy of the prediction should deteriorate with increasing chain length.[8] Therefore we present additional simulation data for athermal 60-mers (▼). In Fig. 3 it can indeed be observed that the NRM predictions overestimate these new MC results. On the other hand, the predictions according to the new theory (solid lines) are in excellent agreement with the MC data for all investigated chain lengths. Actually, for all chain lengths the new predictions are systematically lower than the NRM predictions. Hence for a given temperature, pressure, and chain length the new theory predicts in all cases a slightly higher density. For these athermals the physical explanation is quite clear. The insertion probability depends on the average number of intramolecular contacts of the chain molecules according to Eq. (26). At a given density and chain length the insertion of a molecule in an environment with a higher number of intramolecular contacts is easier than in an environment with a smaller number of intramolecular contacts. Whence, in order to reach a certain density a lower pressure is required or, alternatively, at a given pressure the density can become higher if the molecules have a larger number of intramolecular contacts. In the new theory the number of intramolecular contacts of chain segments exceeds the number of covalent bonds, i.e., the minimal number of intramolecular contacts used in the NRM theory. This higher value of ω leads to a higher insertion probability and hence to a higher density at a selected pressure and temperature.

B. Mixtures

The deficiencies related to the use of a homogeneous segment distribution in the NRM theory are most clearly demonstrated for mixtures. (The deficiencies of theories operating with a homogeneous density assumption become clear in the prediction of the different type of contacts. In
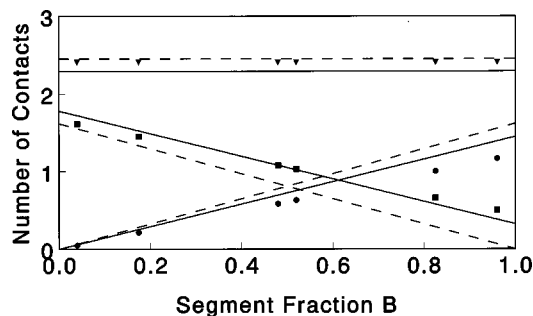
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FIG. 4. Number of contacts of A segments as a function of composition for athermal mixtures ($e_{AA} = e_{BB} = e_{AB} = 0$) at the reduced pressure $\tilde{p} = 0.16$: AA contacts (■), AB contacts (●), and Ah contacts (▼). The full lines represent the ω theory prediction and dashed lines the NRM theory.

such theories, the number of intramolecular self-contacts, due to the chain connectivity, are ignored, which results in an underestimation of the total number of self-contacts and an accompanying overestimation of the cross contacts.)

A simple but nevertheless very illustrative example is provided by a (hypothetical) binary mixture in the athermal limit ($e_{AA} = e_{BB} = e_{AB} = 0$) where both components have equal chain lengths. In the case of equal chain lengths, chosen here to be $s_A = s_B = s = 30$, the equation of state is truly independent of composition (A and B are indistinguishable) and identical to that of a single component with the same chain length. In Fig. 3 it is demonstrated that the athermal equation of state is accurately predicted by the new as well as the NRM theory.[7] However, a detailed comparison of the different contacts in the mixture clearly reveals the deficiencies of the NRM theory. In Fig. 4 the different types of contacts of A segments are shown as a function of the mixture composition given by ϕ_B. The NRM predictions at a reduced pressure $\tilde{p} \equiv pv*/kT = 0.16$ are depicted by the dashed lines. The number of contacts involving vacancies (▼) is predicted quite accurately, in agreement with the quality of prediction of overall density. However, the situation is different for the contacts involving other segments. For instance, the number of (AA) contacts (■) is predicted to decrease with ϕ_B and in (nearly) pure B the number of (AA) contacts equals zero. However, the simulation shows a decrease in (AA) contacts to a limiting value at $\phi_B = 1$, which is due to the chain connectivity. Even at infinite dilution, A segments remain surrounded by intramolecular A segments that result in a nonzero number of (AA) contacts in (almost) pure B. The number of (AB) contacts (●), starting in pure A from zero, is predicted to increase with ϕ_B. The simulation shows the same limiting behavior since (AB) contacts only involve intermolecular contacts that vanish if one of the components is infinitely diluted. The value of (AB) contacts with increasing ϕ_B is overestimated, which is a direct consequence of the inaccurate limiting behavior of the (AA) contacts and the constraint on the total number of contacts a type A segment can make. The latter is for a 30-mer, $s_A = 30$, given by

$$AA + AB + Ah = (s_A(z-2)+2)/s_A$$

$$= z(1-\alpha_A) = 4.066\ 67. \tag{33}$$

Figure 4 applies equally well to B contacts if the following changes are made $\phi_B \rightarrow \phi_A$, $(AA) \rightarrow (BB)$, $(AB) \rightarrow (BA)$, and $(Ah) \rightarrow (Bh)$. From this comparison it is clear that the assumption of a homogeneous segment distribution is not really fulfilled.

Turning our attention to the new theory, it can be observed that all types of contacts are accurately predicted. For contacts involving different molecules, i.e., AB and Ah contacts, the predictions are quite similar for both the NRM and the new theory. It might appear that the NRM theory provides a somewhat better prediction of the Ah contacts. However, both predictions are well within the accuracy of the MC simulation data and the slightly worse result for the new theory may be attributed to this ''experimental'' uncertainty. The new theory clearly performs better than the NRM theory in the prediction of the AA contacts, involving both intra- and inter-molecular contributions. Evidently, the new theory correctly accounts for the limiting behavior of the AA contacts in pure B. This limiting behavior is completely due to the intramolecular contacts which are taken care of by the parameter ω in the theory. Clearly, the improved prediction of the AA contacts also leads to an improved prediction of the AB contacts as the total number of contacts (excluding covalent bonds) remains fixed by the constrained, Eq. (33).

V. CONCLUSIONS

Starting from the definition of the insertion probabilities a new theory for athermal compressible binary mixtures was defined. Due to the approximate nature of theoretical expressions for the insertion probability the partition function and the thermodynamic state functions may depend on the particular order of insertion. We therefore have defined a practically useful insertion order which assures that the intensive thermodynamic state functions are functions of the appropriate thermodynamic variables, i.e., density, temperature, and composition. Based upon this insertion order, approximate relations between the chain insertion probabilities, the Helmholtz free energy, and the equation of state have been derived. Subsequently, theoretical expressions for the insertion probabilities were derived which depend on the presence of intramolecular self-contacts related to the long-range excluded volume of the chain molecules. These theoretical developments automatically resulted in a dependence on density, i.e., the environment of the chain molecule, of the intramolecular contacts. Equations (26) and (30) are the main theoretical results for athermal chains. From Eq. (30), the influence of density on the distribution $P_{\omega_j}(\Omega, y)$ can be obtained. Employing Eq. (27) the average molecular environment, expressed in ω_j, can be computed. The insertion probability at any density can be found by employing ω_j in Eq. (26). The Helmholtz free energy and the equation of state can be calculated by inserting $p_e(y)$ in Eqs. (19) and (21), respectively.

Employing the new theory, predictions for the equation of state of athermal pure components and binary mixtures were provided and compared to MC simulation results. Furthermore, detailed microscopic information on the different types on segmental contacts were collected in the MC simu-

lations and compared to the theoretical predictions. It was found that the new theory successfully predicts all presented data. For example, the compressibility factor of athermal chains is accurately predicted even for the highest investigated chain lengths ($s = 60$). The predictions of the new theory were systematically better than those of the NRM theory and are even better than those provided by the LCT theory for linear chains.[42] An extensive comparison of the new theory to the LCT theory and some other theoretical approaches will be the subject of a forthcoming publication.[42]

The effects of the intramolecular self-contacts are most clearly demonstrated for mixtures. The most clarifying example is provided by the predicted nonzero number of homocontacts even for the most asymmetric mixture compositions. In conclusion, the present theory has been shown to be very accurate in comparison with MC simulation data. In a forthcoming publication the theory will be extended to interacting system. The introduction of nearest-neighbor segmental interaction will result in a substantially richer thermodynamic behavior, e.g., the possible occurrence of vapor–liquid coexistence in a pure component and the occurrence of liquid–liquid coexistence in a binary mixture. This will allow for a more detailed and demanding test of the theory. The new theory also opens the way to the thermodynamics of more complex chain architectures such as branched chains, etc. Furthermore, the theory is equally applicable to compressible polymers solutions by assigning a chain length of unity to one of the chain molecules.

ACKNOWLEDGMENTS

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