Multicomponent Hard-Sphere Heterochain Fluid: Equations of State in a Continuum Space

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ABSTRACT: Simple analytical equations of state have been derived for a mixture of heterochain molecules differing among themselves in both the chain length and primary structure. A model for a polymer chain has been constructed as a sequence of freely jointed tangent hard spheres, whose diameters are not necessarily identical. The statistical mechanical methods previously reported in the literature, namely, a polymeric analog of the Percus-Yevick approximation and the first-order thermodynamic perturbation theory (TPT) of polymerization, have been generalized. According to either of those approaches, the equation of state and residual thermodynamic potentials for the chain fluid are the sum of two terms of which one characterizes a system of disconnected monomers and the other one reflects the effect of monomer bonding in the chain. The specificity of the theories in question shows up in the representation of a second (bonding) term. The quantitative discrepancy in the predictive power of these theories tends to diminish with decreasing packing fraction of the system. As has been found, a version of perturbative theory recently developed by Freed for a homopolymer liquid and the TPT of polymerization lead to essentially the same result in their respective low-order approximations. The general results obtained have been exemplified by a binary copolymer-in-solvent system. The copolymer primary structure has been accounted for in the thermodynamic formulas through a weight-average fraction of available chain unit diads, and the chain-length distribution, through a number-average degree of polymerization. Given the packing fraction, the only necessary molecular parameter in the derived expressions is the ratio of hard-sphere diameters for monomer units and the solvent molecules.

Introduction

At present, the equilibrium properties of excluded-volume polymer chains are well enough understood. Major achievements in this field bear upon the renormalization group and scaling theories which were instrumental in proposing a number of universal (independent of the local chain structure) predictions of the polymer behavior on a scale significantly larger over the Kuhn segment length, in the case of dilute and semidilute solutions. However, those theories have proved to be of little use when applied to concentrated solutions and melts, where the local properties of polymer chains, manifest on the scale of elementary chain unit, come to the foreground. As a polymer system becomes more dense, its polymeric features become less pronounced owing to the predominant role of intermolecular interactions vis-à-vis intramolecular ones and to the increased importance of chain-packing effects. These effects are mainly governed by short-range repulsion forces operative between monomers (which, to a first approximation, may be regarded as impenetrable hard cores). Therefore, a well-posed statistical mechanical theory of dense systems must, wherever possible, take into account the proper volume of monomer units as well as the sequential order of units in the chain, if the system under study is a copolymer.

Until recently, the theoretical study of equilibrated polymeric liquids in a real (off-lattice) space has not been a matter of special interest. This was particularly true in regard to copolymer systems. It has been our intention to discuss in this paper some of the modern methods which provide the possibility of an adequate description of copolymeric systems.

Since a dense system of chain molecules and usual liquid share a number of common features, one can gain a profitable intelligence from the vast knowledge acquired in the study of liquid state.

The data of long enough standing in molecular physics have provided a good reason to believe that many of the equilibrium properties—and primarily structural ones—of low molecular weight fluids can be satisfactorily treated within the framework of models that take into account only the repulsive portion of molecular interaction potential. The real molecules are thus modeled by hard convex bodies and, in the simplest case, by hard spheres.[1] In the theory of liquids, this concept plays a role much the same as that of an ideal gas in the theory of gases. It is implied that the attractive forces, especially at high temperature, are less important than the repulsion forces and can be accounted for as a perturbation of a "hard-body" reference model. In other words, the proper volume of molecules is a factor of prime importance in an interpretation of the behavior of low molecular weight fluids.

In an attempt to extend this concept to polymeric liquids, we shall arrive, in a natural manner, at the visualization of the model chain as a sequence of tangent hard particles, in the simplest case, hard spheres. These spheres correspond thus to the elementary units of a polymer chain. The chain fluid modeled in such a manner may be treated by the methods currently employed for atomic fluids, however, with an essential constraint added: these methods must take into account the connectivity of monomers within a particular chain. The available data show that such an approach may provide satisfactorily accurate (sometimes, in analytical form) equations of state for chain molecules.

One of the pioneering works in the field was that of Dickman and Hall[2] who have studied a monodisperse system of chains composed of identical tangent hard spheres within the framework of a continuous analog of the Flory and Huggins lattice mean field theories. These authors have shown that it was possible, remaining even within of a mean field approximation, to improve significantly the equation of state in comparison with the classical lattice model; this conclusion was borne out by Monte Carlo simulation data. Schweizer and Curro[3,4] have constructed a theory of polymer melts and blends starting from the Ornstein-Zernike integral equation generalized to molecular fluids (so-called reference interaction site model). This theory enables one to find intermolecular

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site–site pair distribution functions provided that the intramolecular functions for monomer–monomer distributions have been defined in a certain manner. To find the intramolecular correlation functions, the authors made use of the Flory theorem about an ideal (Gaussian) conformation of flexible chain in the melt. They ignored the chain-end effects also. Still, even with these simplifications adopted, the computational difficulties remain prohibitive to the eventual application of this approach to copolymeric systems (the more so, considering that the applicability of the Flory theorem in this case is not clearly evident). Besides, the computational accuracy for the pressure as attained in ref 4 can hardly be regarded as quite satisfactory.

An original modeling approach has been suggested by Wertheim[5] for fluid molecules which interact by forces of the chemical bonding type. Each molecule consists of a hard core with embedded attraction sites. If there are two such sites in the molecule, one may envisage the formation of a linear or a ring polymer in the system. The final expression for pressure and free energy in the Wertheim theory can be presented in the form of a series expanded according to the thermodynamic perturbation theory (TPT); the role of the unperturbed system can be assigned to any repulsive potential fluid with a known pair distribution function. The first-order TPT has been extended by Chapman, Jackson, and Gubbins[6] to a multicomponent mixture of associating molecules and to a homonuclear chain blend. The derived equation of state for chain molecules was compared to Monte Carlo computer simulations[7] for chain lengths of $N = 4$, 8, and 16; the agreement was good, especially for $N = 4$ and 8.

A somewhat different approach was used by Chiew.[8] He started from the solution of a problem on a mixture of sticky hard spheres in the Percus–Yevick approximation.[9] Further, he introduced appropriate connectivity rules postulating the formation of a given number of chains of definite length from original hard-sphere associates. This procedure has enabled the derivation of equations of state for homonuclear chains as well as heteronuclear chains of identical chemical (primary) structure. The computer-assisted testing[7] of the equation of state for a pure homopolymer has yielded an excellent result.

An important feature of both the TPT approach and the Chiew method (the name polymer–Percus–Yevick (PPY) approximation for the latter appears to be quite natural) is, along with the accuracy they provide, that the derived expressions are simple in form and permit the generalization to the copolymer case we are concerned with. This property distinguishes them advantageously from the method of deriving the equation of state directly from the partition function (so-called virial equation for pressure). A major obstacle here is that the virial equation of state for hard chain molecules is a function of both pair and triplet correlation functions.[4,10] As has been ascertained,[11,12] the three-particle contribution to the equation of state is quite significant (about 30%). An attempt was made[4] to split the triplet correlations by analogy with the Kirkwood superposition approximation; however, this has led to an appreciable error in the estimation of the three-particle term—for short chains at least.[12] Apart from this, the intermolecular correlation functions in the virial equation of state are functions of a a priori unknown intramolecular monomer–monomer correlations.

It has been our intention in this work to extend the PPY approximation and the TPT to the general case of a solution (or a melt) of heterochains differing among themselves in both the length and primary structure. Further, we shall consider, by way of example, a solution of the binary copolymer to derive an equation of state. Finally, we shall focus on certain aspects of the methods we have developed.

A point to be emphasized is that in what follows we ignore the attraction between monomers, that is, only idealized "athermal" chains to come into play.

Theory and Results

The compressibility factor Z of a polymer system in both the TPT (of the first order) and the PPY approximations is presumed to include two terms of which one accounts for the contribution due to nonbonded units and other one for the contribution from bonded units in the chain

$$Z = Z_{\mathrm{HS}} + Z_{\mathrm{bond}} \tag{1}$$

By definition, $Z \equiv \beta P/\rho$, where P is the pressure, $\beta \equiv 1/k_{\mathrm{B}}T$ is the reciprocal temperature, $\rho = N_0/V$ is the particle density, V is the volume of the system, $N_0 = \sum_k n_k N_k$ is the total number of monomers in an M-component system containing n_k molecules of the kth type, each with degree of polymerization N_k ($k = 1, 2, ..., M$).

PPY Approximation. Now we give a brief characterization of the PPY theory.[8] Suppose, we have a solution of the problem on an N_0-component mixture of hard spheres with diameters σ_i and densities ρ_i ($i = 1, 2, ..., N_0$); the interaction between the particles is effected via an attractive pair potential shaped as an infinitely deep and an infinitely narrow well. This is the well-known problem on sticky hard spheres (or hard spheres with surface adhesion) analytically solvable in the Percus–Yevick approximation.[9] One must go over from this system of associated hard spheres to an M-component mixture made up of n_k chains of the kth type of length N_k each such that $\sum_k n_k N_k = N_0$. This transition is carried out in two steps (priority not essential). First, one puts $\rho_i = 1/V$ for all i, that is, the total number of the spherical species is presumed to be equal to the total number of spheres. Second, the pair distribution function $g_{ij}(r)$ in the region $r < \sigma_{ij} = 1/2(\sigma_i + \sigma_j)$ for any particles i and j in *direct contact* to each other is taken in the form

$$g_{ij}(r) = \frac{1}{4\pi\rho_j{\sigma_{ij}}^2}\delta(r - \sigma_{ij}) = \frac{V}{4\pi{\sigma_{ij}}^2}\delta(r - \sigma_{ij})$$

where

$$j = i + 1 \begin{cases} \text{at } i = 1, 2, \ldots, N_k - 1 & \text{for first chain of } k\text{th type} \\ \text{at } i = N_k + 1, \ldots, 2N_k - 1 & \text{for second chain of } k\text{th type} \\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots & \\ \text{at } i = (n_k - 1)N_k + 1, \ \ldots, n_k N_k - 1 & \text{for } n_k\text{th chain of } k\text{th type} \end{cases}$$

$$(k = 1, 2, \ \ldots, M)$$

so that

$$\frac{1}{V}\int_0^{\sigma_{ij}} g_{ij}(r)\, \mathrm{d}r = 1$$

For the remaining pairs ij (chemically unbonded spheres), the function $g_{ij}(r) = 0$, for $r < \sigma_{ij}$. As is evident, $g_{ij}(r) = g_{ji}(r)$. (For all pairs ij in the region of $r > \sigma_{ij}$, the direct correlation function $c_{ij}(r)$ is subject to a condition of its being equal to zero, in accordance with the Percus–Yevick approximation for hard spheres[13]). We obtain, as result, a total of $\sum_k^M n_k$ chains, each composed of *various* spheres.

With the chains assorted into groups each containing n_k chains (N_k-mers) and with the chain primary structure within the group identified, we have constructed the desired M-component chain system.

Within the PPY theory, the equation of state is obtained by introducing the above constraints into the compressibility-route equation of state for a mixture of sticky hard spheres.[9] The compressibility factor takes the form of eq 1, where

$$Z_{\mathrm{HS}} = \frac{1}{1-\xi_3} + \frac{3\xi_1\xi_2}{\xi_0(1-\xi_3)^2} + \frac{3\xi_2^{\,3}}{\xi_0(1-\xi_3)^3} \qquad (2)$$

and the quantities ξ_j (j = 0–3) are defined, invoking the above-mentioned transition, as

$$\xi_j = \frac{\pi}{6}\sum_{i=1}^{N_0}\rho_i\sigma_i^{\,j} = \frac{\pi}{6}\sum_{k=1}^{M}\rho_{\mathrm{c}(k)}\sum_{s=1}^{N_k}\sigma_{sk}^{\,j} \qquad (3)$$

Here $\rho_{\mathrm{c}(k)} = n_k/V$ is the density of the chains of the kth type, and σ_{sk} is the diameter of a sphere located at the site s in the chain of type k. The chain contribution Z_{bond} is expressed as

$$Z_{\mathrm{bond}}^{\ \mathrm{PPY}} = -\sum_{k=1}^{M}\sum_{s=1}^{N_k-1}\frac{\rho_{\mathrm{c}(k)}}{\rho}\left[\frac{1}{1-\xi_3} + \frac{3\xi_2}{2(1-\xi_3)^2}\sigma_{sk}^{\,*}\right] \qquad (4)$$

Here our notations are

$$\sigma_{sk}^{\,*} \equiv \sigma_{sk}\sigma_{(s+1)k}/\sigma_{sk,(s+1)k}$$

$$\sigma_{sk,(s+1)k} = (\sigma_{sk} + \sigma_{(s+1)k})/2 \qquad (5)$$

To be noted, the term within square brackets in eq 4 is none other than the radial distribution function at contact for hard spheres with diameters σ_{sk} and $\sigma_{(s+1)k}$ in the Percus–Yevick approximation:[14]

$$g_{\mathrm{HS}}^{\ [sk,(s+1)k]}(\sigma) = \frac{1}{1-\xi_3} + \frac{3\xi_2}{2(1-\xi_3)^2}\sigma_{sk}^{\,*} \qquad (6)$$

Therefore

$$Z_{\mathrm{bond}}^{\ \mathrm{PPY}} = -\sum_{k=1}^{M}\sum_{s=1}^{N_k-1}\frac{\rho_{\mathrm{c}(k)}}{\rho}g_{\mathrm{HS}}^{\ [sk,(s+1)k]}(\sigma) \qquad (7)$$

These results as compared with eq 19 in ref 8 describe a more general case of polymer components differing among themselves not only in chain length but also in their *primary structure*. Therefore, an additional component index for the chain unit diameter has appeared; a similar index was absent in eq 19 of Chiew's paper.

TPT of Polymerization. We turn now to results ensuing from the TPT as applied to molecules capable of polymerization.[5,6] As has been mentioned in the introduction, each molecule (monomer) tractable by this theory is presumed to have a hard core with incorporated binding sites—two sites, A and B, in our particular case—which can interact with the binding sites of other molecules. In the relationships as furnished by the TPT for the difference of thermodynamic functions of an associative and a nonassociative (purely repulsive) system, each molecule of type s possesses the fractions $X_{\mathrm{A}}^{(s)}$ and $X_{\mathrm{B}}^{(s)}$ of its binding sites not engaged in interaction with other molecules. In order to form a set of chains with fixed lengths, one must pass to a limit of total binding when the $X_{\mathrm{A}}^{(s)}$ and $X_{\mathrm{B}}^{(s)}$ for all s are equal to zero. Chapman et al.[6] have obtained, at this limit, the following expression for the contribution of Z_{bond} to the compressibility factor of an M-component mixture of homopolymers:

$$Z_{\mathrm{bond}}^{\ \mathrm{TPT}} = -\sum_{k=1}^{M}\frac{\rho_{\mathrm{c}(k)}}{\rho}(N_k-1)\left[1 + \rho\frac{\partial \ln \Delta^{(kk)}}{\partial\rho}\right] \qquad (8)$$

where

$$\Delta^{(kk)} \equiv \int g_{\mathrm{R}}^{\ (kk)}(\mathbf{r})f^{(kk)}(\mathbf{r}_{\mathrm{AB}})\,\mathrm{d}\mathbf{r} \qquad (9)$$

$g_{\mathrm{R}}^{(kk)}(\mathbf{r})$ is the pair distribution function of a reference (monomer) fluid, $f_{\mathrm{AB}}^{(kk)}(\mathbf{r}_{\mathrm{AB}}) = \exp(-\beta\,\phi^{(kk)}(\mathbf{r}_{\mathrm{AB}})) - 1$ is the Mayer function, and $\phi^{(kk)}(\mathbf{r}_{\mathrm{AB}})$ is the pair interaction potential for the binding sites A and B of neighboring monomers in the chain. The integration in the right side of eq 9 is carried out over all the separations of two monomer centers and an angle average over all their orientations.

To be noted, no constraints as regards the shape of monomers and of the bonding potential type are imposed on eq 8. For a mixture of homonuclear chains made up of *tangent* hard spheres of diameter σ_k (k = 1, ..., M), considering that the function $\Delta^{(kk)}$ in this case becomes proportional to the radial distribution function at contact $g_{\mathrm{HS}}^{(kk)}(\sigma)$, eq 8 takes the form as shown:[5]

$$Z_{\mathrm{bond}}^{\ \mathrm{TPT}} = -\sum_{k=1}^{M}\frac{\rho_{\mathrm{c}(k)}}{\rho}(N_k-1)\left[1 + \rho\frac{\partial \ln g_{\mathrm{HS}}^{\ (kk)}(\sigma)}{\partial\rho}\right] \qquad (10)$$

The approach as described in ref 6 and applied by us to the system of heteronuclear chains has led to the following expression, which is a generalization of eq 10:

$$Z_{\mathrm{bond}}^{\ \mathrm{TPT}} = -\sum_{k=1}^{M}\sum_{s=1}^{N_k-1}\frac{\rho_{\mathrm{c}(k)}}{\rho}\left[1 + \rho\frac{\partial \ln g_{\mathrm{HS}}^{\ [sk,(s+1)k]}(\sigma)}{\partial\rho}\right] \qquad (11)$$

(To be noted, the partial derivative with respect to ρ in the above formulas is taken at constant values of β and n_k, k = 1, ..., M).

The TPT as distinct from the PPY theory puts no restriction on the choice of expressions for Z_{HS} and g_{HS} within the Percus–Yevick approximation. In particular, one may use more accurate formulas as suggested by Mansoori, Carnahan, Starling and Leland[15] (MCSL):

$$Z_{\mathrm{HS}}^{\ \mathrm{MCSL}} = Z_{\mathrm{HS}} - \frac{\xi_3\xi_2^{\,3}}{\xi_0(1-\xi_3)^3} \qquad (12)$$

$$g_{\mathrm{HS(MCSL)}}^{\ [sk,(s+1)k]}(\sigma) = g_{\mathrm{HS}}^{\ [sk,(s+1)k]}(\sigma) + \frac{\xi_2^{\,2}}{2(1-\xi_3)^3}\sigma_{sk}^{\,*2} \qquad (13)$$

where Z_{HS} and g_{HS} are obtained using eqs 2 and 6, respectively. The chain term within the TPT framework, invoking eq 13, takes the form

$$Z_{\mathrm{bond}}^{\ \mathrm{TPT}} = -\frac{1}{1-\xi_3}\sum_{k=1}^{M}\sum_{s=1}^{N_k-1}\frac{\rho_{\mathrm{c}(k)}}{\rho}\left[2 + \left(\frac{1}{2}\frac{\xi_2^{\,2}}{(1-\xi_3)^3}\sigma_{sk}^{\,*2} - \frac{1}{1-\xi_3}\right)\left(g_{\mathrm{HS(MCSL)}}^{\ [sk,(s+1)k]}(\sigma)\right)^{-1}\right] \qquad (14)$$

$Z_{\text{bond}}{}^{\text{TPT}}$ may be expressed through $Z_{\text{bond}}{}^{\text{PPY}}$:

$$Z_{\text{bond}}{}^{\text{TPT}} = Z_{\text{bond}}{}^{\text{PPY}} + \left(\frac{3}{2}\frac{\xi_2}{(1-\xi_3)^2}\right)^2 \sum_{k=1}^{M}\sum_{s=1}^{N_k-1}\frac{\rho_{c(k)}}{\rho}\sigma_{sk}{}^{*2}\frac{1-\frac{4}{9}\left(1-\frac{3}{4}\frac{\xi_2}{1-\xi_3}\sigma_{sk}{}^{*}\right)\delta}{g_{\text{HS}}{}^{[sk,(s+1)k]}(\sigma)} \tag{15}$$

where δ is 0 or 1. For the function g_{HS} in eq 11 taken in the PY approximation, $\delta = 0$, and taken in the form of (13), $\delta = 1$.

Certain Conclusions. It is seen in the above expressions that the chain contribution to the equation of state in the spirit of both approaches in question is dependent (providing that the component densities are given) on the contact radial distribution functions for monomer system. Noteworthy is the fact that the equations of state include neither intermolecular nor intramolecular monomer–monomer distribution functions. This is a major distinction of compressibility-route equation of state from the virial-route equation exhibiting an explicit dependence on the intermolecular correlation functions.[4,10,11] Further, one will observe that the Z_{bond} expressions include pair quantities $\sigma_{sk}{}^{*}$. An ensuing consequence is that the primary structure of heterochains will be reflected in the equation of state (and other thermodynamic functions) only through the number of the available chain unit diads. Viewed thermodynamically, the order of diad arrangement within the given type of chain plays no role.

Among other general inferences ensuing from the above equations we shall note the following. One will see in eq 15 that $Z_{\text{bond}}{}^{\text{PPY}}$ in absolute value is always greater than $Z_{\text{bond}}{}^{\text{TPT}}$, and therefore, the total compressibility factor as estimated by the PPY approximation is always smaller than the TPT compressibility factor (despite the fact that $Z_{\text{HS}}{}^{\text{PY}} > Z_{\text{HS}}{}^{\text{TPT(MCSL)}}$). One will see, with reference to eq 15, that the difference in the values of Z_{bond} as estimated by the TPT and PPY approaches tends to diminish with decreasing component density. Finally, we wish to note that, as should be expected, the monomer connectivity results in a reduced pressure relative to the pressure in a system of disconnected chain units.

Freed Approach. Freed[16] has developed an alternative version of perturbation theory in a continuum space. His theory has yielded results much similar to those by TPT. Freed has performed a cluster expansion of the partition function of homopolymer in Mayer modified functions modeling the chemical bonds between chain units. The reference system was represented by nonbonded monomers, the connectivity was defined by a Dirac δ-function type potential. Provided that only pair correlations between the monomers were retained in the cluster expansion, an expression for the configurational partition function was derived (eq 5.10 in ref 16; our notation):

$$Q = 2^{-n}Q_{\text{R}}(4\pi g_{\text{R}}(\mathbf{r})/V)^{n(N-1)}$$

where Q_{R} is the partition function, $g_{\text{R}}(\mathbf{r})$ is the pair distribution function for the reference fluid, and $|\mathbf{r}|$ is the bond length between connected monomers. Given the pressure as defined by the formula

$$\beta P = \partial \ln Q/\partial V$$

and using an ensemble of hard spheres for the reference fluid, we obtain for the compressibility factor

$$Z^{\text{Freed}} = Z_{\text{HS}} + \frac{N-1}{N}\left[1 + \rho\frac{\partial \ln g_{\text{HS}}(\sigma)}{\partial \rho}\right] \tag{16}$$

A comparison of the binding term in eq 16 with eq 10 or 11 for a pure homopolymer reveals a complete identity of the zeroth-order approximation of the Freed theory with the first-order TPT approximation.[6] This agreement is not accidental: within these two approximations for the chain term, only the contribution due to one-bond diagrams in the cluster expansions is taken into account, ignoring three-particle and higher-order correlations. However, these approaches are distinct in the respect that the Freed theory requires the use of a clearly-defined, namely, virial-route compressibility factor Z_{HS} for the nonbonded monomers.[17]

Thermodynamic Potentials. All residual thermodynamic functions (except for the ideal-gas contribution) can be represented, much as the equation of state, by the sum of contributions due to bonded and nonbonded monomers. The formulas derived for the first term (per monomer) reproduce the known relationships for a hard-sphere mixture.

The Helmholtz free energy F is found by integrating the thermodynamic relationship

$$Z = \rho((\partial \beta F/N_0)/\partial \rho)_{\beta,\{n_k\}}$$

Using eqs 1, 2, and 4, we obtain, in the PPY approximation

$$F^{\text{r}} \equiv F - F_{\text{id}} = F_{\text{HS}} + F_{\text{bond}}$$

where

$$\frac{\beta F_{\text{HS}}}{N_0} = -\ln(1-\xi_3) + \frac{3\xi_1\xi_2}{\xi_0(1-\xi_3)} + \frac{3\xi_2{}^3}{2\xi_0(1-\xi_3)^2} \tag{17}$$

$$\beta F_{\text{bond}}{}^{\text{PPY}} = -\sum_{k=1}^{M}\sum_{s=1}^{N_k-1} n_k\left[-\ln(1-\xi_3) + \frac{3\xi_2}{2(1-\xi_3)}\right] \tag{18}$$

The TPT chain term, with reference to eq 11, is

$$\beta F_{\text{bond}}{}^{\text{TPT}} = -\sum_{k=1}^{M}\sum_{s=1}^{N_k-1} n_k \ln g_{\text{HS}}{}^{[sk,(s+1)k]}(\sigma) \tag{19}$$

If eq 12 is used for Z_{HS} in the TPT method, then the nonbonded contribution into free energy is

$$\frac{\beta F_{\text{HS}}{}^{\text{MCSL}}}{N_0} = \frac{\beta F_{\text{HS}}}{N_0} + \frac{\xi_2{}^3}{\xi_0\xi_3{}^2}\left[\ln(1-\xi_3) + \frac{\xi_3}{(1-\xi_3)^2}\left(1-\frac{3}{2}\xi_3\right)\right] \tag{20}$$

Since for the system of interest the internal energy is identical with that of the ideal gas, the residual entropy S^{r} is equal to $-F^{\text{r}}/T$. The Gibbs potential can be derived from the thermodynamic relationship

$$\frac{\beta}{N_0}(G - G_{\text{id}}) \equiv \frac{\beta}{N_0}G^{\text{r}} = Z - Z_{\text{id}} + \frac{\beta F^{\text{r}}}{N_0}$$

where the ideal-gas compressibility factor (per monomer) Z_{id} is

$$Z_{\text{id}} = \sum_{k=1}^{M}\frac{\rho_{c(k)}}{\rho} \equiv \sum_{k=1}^{M}\frac{\Phi_k}{N_k} = \frac{1}{\langle N\rangle} \tag{21}$$

Here $\langle N\rangle$ is the number-average degree of polymerization, and Φ_k is the segment fraction of the k-type chains ($\Phi_k \equiv n_kN_k/N_0$).

We give also the formulas for chemical potential of a component.

We have, for chemical potential of the ith component

$$\mu_i^{\,r} = \mu_{i,\mathrm{HS}} + \mu_{i,\mathrm{bond}}$$

where within the framework of the PPY approximation

$$\frac{\beta\mu_{i,\mathrm{HS}}}{N_i} = -\ln(1-\xi_3) + Z_{\mathrm{HS}}\left(\xi_3^{(i)} + \frac{\xi_2^{(i)}}{\xi_2}(1-\xi_3)\right) - \frac{\xi_2^{(i)}}{\xi_2} + 3\frac{\xi_1^{(i)}\xi_2}{\xi_0(1-\xi_3)} + \frac{3}{2}\frac{\xi_2^{\,2}\xi_2^{(i)}}{\xi_0(1-\xi_3)^2} \qquad (22)$$

$$\frac{\beta\mu_{i,\mathrm{bond}}^{\mathrm{PPY}}}{N_i} = \left(1-\frac{1}{N_i}\right)\ln(1-\xi_3) - \frac{3}{2}\frac{\xi_2}{1-\xi_3}\sum_{s=1}^{N_i-1}\sigma_{si}^{*} + Z_{\mathrm{bond}}^{\mathrm{PPY}}\left(\xi_3^{(i)} + \frac{\xi_2^{(i)}}{\xi_2}(1-\xi_3)\right) + \frac{\xi_2^{(i)}}{\xi_2}\left(1-\frac{1}{\langle N\rangle}\right) \qquad (23)$$

and within the framework of the TPT method

$$\frac{\beta\mu_{i,\mathrm{HS}}}{N_i} = -\ln(1-\xi_3) + Z_{\mathrm{HS}}^{\mathrm{MCSL}}\left(\xi_3^{(i)} + \frac{\xi_2^{(i)}}{\xi_2}(1-\xi_3)\right) - \frac{\xi_2^{(i)}}{\xi_2} + 3\frac{\xi_1^{(i)}\xi_2}{\xi_0(1-\xi_3)} + \frac{3}{2}\frac{\xi_2^{\,2}\xi_2^{(i)}}{\xi_0(1-\xi_3)^2} + \frac{\xi_3\xi_2^{\,3}}{\xi_0(1-\xi_3)^2}\left(\frac{\xi_2^{(i)}}{\xi_2} - \frac{\xi_3^{(i)}}{\xi_3}\right) + \Delta f_{\mathrm{HS}}\left(3\frac{\xi_2^{(i)}}{\xi_2} - 2\frac{\xi_3^{(i)}}{\xi_3}\right) \qquad (24)$$

where $\Delta f_{\mathrm{HS}} \equiv \beta\,(F_{\mathrm{HS}}^{\mathrm{MCSL}} - F_{\mathrm{HS}})/N_0$ (see eq 20)

$$\frac{\beta\mu_{i,\mathrm{bond}}^{\mathrm{TPT}}}{N_i} = -\frac{1}{N_i}\sum_{s=1}^{N_i-1}\ln g_{\mathrm{HS}}^{[si,(s+1)i]}(\sigma) + Z_{\mathrm{bond}}^{\mathrm{TPT}}\left(\xi_3^{(i)} + \frac{\xi_2^{(i)}}{\xi_2}(1-\xi_3)\right) + \frac{\xi_2^{(i)}}{\xi_2}\left(1-\frac{1}{\langle N\rangle}\right) \qquad (25)$$

We have introduced for convenience the "partial" quantities

$$\xi_j^{(k)} \equiv \frac{\pi}{6}\rho\frac{1}{N_k}\sum_{s=1}^{N_k-1}\sigma_{sk}^{\,j}$$

so that

$$\sum_{k=1}^{M}\Phi_k\xi_j^{(k)} = \xi_j \qquad (26)$$

Other quantities, essential for mixture thermodynamics (partial volume of a component, isothermal compressibility) and specified by both theories, are given in the Appendix.

Binary Copolymer in a Solvent. Now we proceed to the consideration of an important application of the derived general relationships bearing upon a polymer system whose chain components are formed by units (hard spheres) of two species. We introduce a monatomic solvent (denoted by a subscript 1) into our system. Suppose each chain molecule is made up of two species of units A and B with diameters σ_A and σ_B, respectively. (For simplicity, we make no distinction between the terminal and inner unit diameters). We define the primary structure of a heterochain of the kth type in terms of a random variable t_{sk} ($s = 1, 2, ..., N_k$) such that

$$t_{sk} = \begin{cases} 1, & \text{if site } s \text{ in the } k\text{-type chain locates an A unit} \\ 0, & \text{if site } s \text{ in the } k\text{-type chain locates a B unit} \end{cases}$$

The diameter of the (sk)th sphere is

$$\sigma_{sk} = \sigma_A t_{sk} + \sigma_B(1-t_{sk})$$

It is readily seen that

$$\sigma_{sk}^{\,j} = \sigma_A^{\,j}t_{sk} + \sigma_B^{\,j}(1-t_{sk})$$

or

$$\sigma_{sk}^{\,j} = \sigma^j[1 + t_{sk}(\gamma^j - 1)] \qquad j = 0\text{–}3 \qquad (27)$$

Here we introduce the A-to-B diameter ratio

$$\gamma \equiv \sigma_A/\sigma_B = \sigma_A/\sigma$$

(for connotational simplicity, we omit the subscript in σ_B). We denote the spherical diameter ratio for solvent "atom" and chain unit B as

$$\omega \equiv \sigma_1/\sigma_B = \sigma_1/\sigma$$

Then the quantity ξ_j (see eq 3) is written as

$$\xi_j = \frac{\pi}{6}\rho\sigma^j[\Phi(1 + \overline{P\{A\}}(\gamma^j - 1)) + \Phi_1\omega^j] \qquad (28a)$$

where $\Phi = \sum_{k=2}^{M}\Phi_k$ is the total (segment) fraction of polymer, and $\Phi_1 = 1 - \Phi$ is the solvent fraction,

$$\overline{P\{A\}} = \sum_{k=2}^{M}\frac{\Phi_k}{\Phi}\frac{N_A^{(k)}}{N_k} = \sum_{k=2}^{M}\frac{\Phi_k}{\Phi}P_k\{A\}$$

is the average fraction of A units in the system, and $N_A^{(k)}$ and $P_k\{A\}$ are the number of A units and their fraction in the chain of type k, respectively.

It appears convenient to introduce a dimensionless density (the packing fraction), $\eta = \sum_{k=1}^{M}\rho_{c(k)}U_k$, where U_k is the proper volume of a molecule of the kth component. Then eq 28a is replaced by

$$\xi_j = \eta\sigma^{j-3}\frac{\Phi(1 + \overline{P\{A\}}(\gamma^j - 1)) + \Phi_1\omega^j}{\Phi(1 + \overline{\mathrm{P\{A\}}}(\gamma^3 - 1)) + \Phi_1\omega^3} \qquad (28b)$$

or, more succinctly

$$\xi_j = \eta\sigma^{j-3}\alpha_j \qquad (28c)$$

In a similar manner, we can represent the quantities $\xi_j^{(k)}$ (see eq 26) in the form

$$\xi_j^{(k)} = \eta\sigma^{j-3}\alpha_j^{(k)}$$

$$\alpha_j^{(k)} \equiv \frac{(1 + P_k\{A\}(\gamma^j - 1))}{\Phi(1 + \overline{P\{A\}}(\gamma^3 - 1)) + \Phi_1\omega^3} \qquad k \geq 2 \qquad (29)$$

$$\alpha_j^{(1)} = \alpha_j - \sum_{k=2}^{M}\Phi_k\alpha_j^{(k)}$$

We expand now the quantity σ_{sk}^{*} as defined by eq 5 for this particular case. Using eq 27, we obtain, on performing simple transformations

$$\sigma_{sk}^* = \sigma\left[1 + \frac{\gamma-1}{2}(t_{sk} + t_{(s+1)k}) - \frac{(\gamma-1)^2}{4}\frac{(t_{sk} - t_{(s+1)k})^2}{1 + \frac{\gamma-1}{2}(t_{sk} + t_{(s+1)k})}\right]$$

Further

$$\frac{1}{N_k}\sum_{s=1}^{N_k-1}\sigma_{sk}^* = \frac{\sigma}{N_k}\left[N_k - 1 + \frac{\gamma-1}{2}(2N_{AA}^{(k)} + N_{AB}^{(k)} + N_{BA}^{(k)}) - \frac{1}{2}\frac{(\gamma-1)^2}{\gamma+1}(N_{AB}^{(k)} + N_{BA}^{(k)})\right] = \sigma\left[1 - \frac{1}{N_k} + (\gamma-1)\left(P_k\{AA\} + \frac{P_k\{AB\} + P_k\{BA\}}{\gamma+1}\right)\right] \tag{30}$$

Here $N_{AA}^{(k)}$, $N_{AB}^{(k)}$, and $N_{BA}^{(k)}$ denote the number of diads AA, AB, and BA in a chain of the kth type, respectively; accordingly, $P_k\{AA\}$ and so on are the fractions of these diads.

Now we can write expressions for terms of the equation of state. We confine ourselves to the PPY approximation. Taking into account eqs 28c and 30, also eqs 2 and 4, we obtain

$$Z_{HS} = \frac{1}{1-\eta} + \frac{3\eta}{(1-\eta)^2}\frac{\alpha_1\alpha_2}{\alpha_0} + \frac{3\eta^2}{(1-\eta)^3}\frac{\alpha_2^{\,3}}{\alpha_0} \tag{31}$$

$$Z_{bond}^{PPY} = -\frac{\Phi}{1-\eta}\left[1 - \frac{1}{\langle N\rangle} + \frac{3\eta}{2(1-\eta)}\alpha_2\left(1 - \frac{1}{\langle N\rangle} + (\gamma-1)\left(\overline{P\{AA\}} + \frac{\overline{P\{AB\}} + \overline{P\{AB\}}}{\gamma+1}\right)\right)\right] \tag{32a}$$

where $\langle N\rangle$ denotes the number-average degree of polymerization of chain molecules and

$$\overline{P\{AA\}} = \sum_{k=2}^{M}\Phi_k P_k\{AA\}/\Phi$$

and so on, are the average diadic fractions in the copolymer.

For a solution containing long chains (all $N_k \gg 1$), we can neglect the effect due to terminal units and regard the diadic fraction $P_k\{XY\}$ as a probability for the occurrence of the respective pair chain units XY in a chain of the given type. In this case $P_k\{AB\} = P_k\{BA\}$ and $P_k\{AA\} = P_k\{A\} - P_k\{AB\}$, and eq 32a simplifies to

$$Z_{bond}^{PPY} \cong -\frac{\Phi}{1-\eta}\left[1 + \frac{3\eta}{2(1-\eta)}\alpha_2\left(1 + (\gamma-1)\left(\overline{P\{A\}} - \frac{\gamma-1}{\gamma+1}\overline{P\{AB\}}\right)\right)\right] \tag{32b}$$

The analysis of the equations derived has allowed us to draw a number of conclusions.

First, the equation of state of a binary copolymer in a solvent does not require the use of absolute values for hard-sphere diameters as parameters and, once the value of η is given, a major factor becomes the diameter ratio only.

Second, the structure of a copolymer is reflected in the equation of state only through the average of monadic and diadic unit fractions. It is clear, however, that the primary structure of a real chain is determined also by triadic, tetradic, etc. unit fractions. This implies that the notion of "component" in our model stands in need of redefinition in a more precise manner. So, by the term component it is to be understood an assemblage of chain molecules each in possession of the same number of various diads.

Finally, it is to be noted that the equations of state (eqs 31 and 32) differ from that of the solution of a monodisperse binary copolymer of fixed composition only in N being replaced by $\langle N\rangle$ and in the monadic and diadic fractions being replaced by their weight-averaged values. Consequently, the equation of state for a solution of polydisperse copolymer will yield the same result as the respective equation for an *equivalent* monodisperse copolymer of fixed composition with $N = \langle N\rangle$ and $P\{XY\} = \overline{P\{XY\}}$ (XY = AA, AB, BA). This property for a homopolymer system is currently known as the congruence principle.[18]

These conclusions hold for both the PPY approximation and the TPT method. They remain true for thermodynamic potentials also. One will not meet with difficulty in deriving the appropriate expressions.

Discussion

We have dwelt on two possible approaches to the thermodynamics of athermal homo- and heteronuclear chain molecules, namely, the nonperturbative PPY theory[8] and perturbative theories.[5,6,16] These approaches treat the chain molecules from an atom–atom standpoint. Indeed, in both cases we start from a reference system of atoms (hard spheres in the PPY and, generally speaking, hard, but not necessarily spherical particles in the TPT method), whose properties are known with a sufficient accuracy, and then we subject this system to a higher level refinement through introducing a constraint on atom–atom connectivity. An essential point is that the transition from the atomic to the chain fluid would not degrade the accuracy accounted for by the excluded volume of monomers. Viewed in this light, the theories under consideration are not equivalent.

In the PPY theory, as follows from the logic of its inference, the mutual impenetrability of monomers, belonging to the same chain or to different chains, has been strictly considered. The potential source of errors in this approach is the assumption that the direct atom–atom correlation functions have been taken equal to zero at distances greater than the interatomic contact separation.[13]

In the first-order TPT, the neglect of three-particle and higher-order *correlations leads to the fact that the* excluded-volume effect, in its part associated with the intrachain interactions, is unaccounted for. Otherwise stated, monomers that belong to the same chain can overlap. Apparently, this inadequacy of TPT will be more manifest in describing long flexible chains. Simultaneously, the results by this theory provide an acceptably good description of the pseudoexperimental (Monte Carlo and the molecular dynamics simulation) data,[7,11] including relatively long freely jointed hard-sphere chains (see below). This concordance is not accidental and, in part, may be attributed to the fact the three-particle contribution to the equation of state of flexible chains is insignificant (although high-order contributions should not be necessarily small).[5]

Regrettably, for lack of pseudoexperimental data, we are unable to estimate with certainty the predictive power of the above equations of state for heterochains. To illustrate the adequacy of the PPY and TPT approaches, we have compared these to the pseudoexperiment for monodisperse homochains in two extreme cases—very

Table I
Chain Compressibility Factor (=ZN) of the Homonuclear 4-mer Fluid

η	MC[a]	PPY	TPT(CS)[b]	TPT(PYv)[c]
0.1072	2.25	2.32	2.37	2.39
0.205	4.73	4.69	4.88	4.90
0.252	6.40	6.54	6.82	6.76
0.262	7.46	7.01	7.32	7.23
0.278	8.02	7.85	8.19	8.04
0.289	8.70	8.48	8.85	8.65
0.310	9.80	9.84	10.27	9.93
0.323	10.93	10.80	11.25	10.82
0.340	12.2	12.19	12.68	12.08
0.359	13.5	13.99	14.51	13.67
0.376	16.10	15.83	16.38	15.26
0.399	18.7	18.75	19.31	17.72
0.417	21.7	21.45	22.00	19.91
0.437	25.1	24.96	25.47	22.68

[a] Monte Carlo simulation data.[7] [b] The TPT method (eq 16) with the Carnahan–Starling expressions for Z_{HS} and g_{HS}. [c] The TPT method with the Percus–Yevick function g_{HS} and the virial-route factor Z_{HS}.

Table II
Chain Compressibility Factor of the Homonuclear 201-mer Fluid

η	MD[a]	PPY	TPT(CS)	TPT(PYv)
0.105	36.80	50.11	53.26	55.02
0.157	79.44	92.94	100.46	103.51
0.209	152.11	155.70	169.85	173.02
0.262	256.20	250.09	273.56	273.26
0.314	407.16	387.80	422.85	411.45
0.367	621.54	599.32	647.96	609.61
0.419	927.79	917.60	979.13	884.94
0.471	1354.76	1415.50	1484.03	1278.63

[a] The molecular dynamics simulation data.[11]

short ($N = 4$) and sufficiently long ($N = 201$) chains; the relevant data are summarized in Tables I and II.

For very short chains (Table I) the compressibility factor can be obtained with very good accuracy for each of the three methods, perhaps, with a touch of preference for the PPY approximation. Will these theories, considering their atom–atom genesis, be equally good for long chains as well? The data in Table II answer, on the whole, in the affirmative to that question. Once again, the PPY approximation seems to be somewhat more advantageous, especially at large η's.

An attempt at improving the PPY approach through the use of Carnahan–Starling expressions for functions Z_{HS} and g_{HS} has led to markedly deteriorated (lowered) results vis-à-vis the "canonical" variant. This circumstance and the fact that the TPT(PYv) method has proved to be more accurate than the TPT(CS) provide evidence that the success of the theories in question is to be sought in a felicitous compensation of the unbonded and bonded terms in the equation of state.

The chain of tangent hard spheres viewed as a molecular model is, unquestionably, an idealization (however useful it might happen to be). More realistic appears to be an alternative chain model made up of fused hard spheres, which would be a better way to account for the effect of chemical bonding. A possible and sufficiently simple route to improvement of the original model has been proposed in ref 19, where the TPT equation of state was correlated to the results of a scaled particle theory.

To briefly summarize, we have presented the equations of state and thermodynamic potentials for a multicomponent mixture of hard-sphere heterochain molecules. The derived expressions provide the description of a molecular system in a continuum space and account, with good accuracy, for short-ranged (packing) effects. Within the framework of these relationships, the chemical structure of heterochains is described at the level of the numbers of the available diad units.

Hopefully, the above approaches will lay a foundation for thermodynamic studies of real polymer liquids, copolymer liquids included. The next step in this direction is the inclusion of attractive interactions.

Appendix

In this Appendix we give expressions for the reciprocal isothermal compressibility of a mixture and the partial molecular volume of a component within the PPY and TPT methods.

In these methods, reciprocal isothermal compressibility (multiplied by β/ρ)

$$\beta\left(\frac{\partial P}{\partial \rho}\right)_{T,\{n_i\}} = \left(\frac{\rho}{\beta}K_T\right)^{-1} \equiv \tilde{K}_T^{-1}$$

is expressed in the following manner.

PPY theory

$$\tilde{K}_T^{-1}(1-\xi_3) = 2Z^{\mathrm{PPY}} - \frac{1}{1-\xi_3}\frac{1}{\langle N\rangle} + \frac{3\xi_2^{\,3}}{\xi_0(1-\xi_3)^3} \tag{A.1}$$

TPT theory

$$\tilde{K}_T^{-1}(1-\xi_3) = 2Z^{\mathrm{TPT}} - \frac{1}{1-\xi_3}\frac{1}{\langle N\rangle} + \frac{3\xi_2^{\,3}}{\xi_0(1-\xi_3)^3} - \frac{\xi_3\xi_2^{\,3}(2-\xi_3)}{\xi_0(1-\xi_3)^3} + \frac{1}{1-\xi_3}\sum_{k=1}^{M}\sum_{s=1}^{N_k-1}\frac{\Phi_k}{N_k}\left\{1 + \left(\frac{1}{2}\frac{\xi_2^{\,2}\sigma_{sk}^{*2}}{(1-\xi_3)^3} - \frac{1}{1-\xi_3}\right)^2 (g_{\mathrm{HS}}^{[sk,(s+1)k]}(\sigma))^{-2} - \frac{2}{1-\xi_3}(g_{\mathrm{HS}}^{[sk,(s+1)k]}(\sigma))^{-1}\right\} \tag{A.2}$$

The partial volume of the ith component

$$v_i = \left(\frac{\partial V}{\partial n_i}\right)_{T,P,\{n_{j\neq i}\}}$$

is expressed by somewhat cumbersome formulas. For brevity, we introduce the *component* compressibility factors:

$$Z_{\mathrm{HS}}^{(i)} = \frac{1}{1-\xi_3} + \frac{3\xi_1^{(i)}\xi_2}{\xi_0(1-\xi_3)^2} + \frac{3\xi_2^{\,2}\xi_2^{(i)}}{\xi_0(1-\xi_3)^3}$$

$$Z_{\mathrm{HS}}^{(i)\mathrm{MCSL}} = Z_{\mathrm{HS}}^{(i)} - \frac{\xi_3^{(i)}\xi_2^{\,3}}{\xi_0(1-\xi_3)^3}$$

$$Z_{\mathrm{bond}}^{(i)\mathrm{PPY}} = -\frac{1}{N_i}\sum_{s=1}^{N_i-1} g_{\mathrm{HS}}^{[si,(s+1)i]}(\sigma)$$

$$Z_{\mathrm{bond}}^{(i)\mathrm{TPT}} = -\frac{1}{1-\xi_3}\frac{1}{N_i}\sum_{s=1}^{N_i-1}\left[2 + \left(\frac{\xi_2^{\,2}}{2(1-\xi_3)^3}\sigma_{si}^{*2} - \frac{1}{1-\xi_3}\right)(g_{\mathrm{HS(MCSL)}}^{[si,(s+1)i]}(\sigma)]^{-1}\right]$$

The quantities, multiplied by Φ_i and summed over all i's, yield respectively Z_{HS}, $Z_{\mathrm{HS}}^{\mathrm{MCSL}}$, $Z_{\mathrm{bond}}^{\mathrm{PPY}}$, and $Z_{\mathrm{bond}}^{\mathrm{TPT}}$ (for a definition of $\xi_j^{(i)}$, see eq 26).

With these notations, we have

PPY theory

$$\frac{\rho_{\mathrm{c}(i)}v_i}{\Phi_i} = \xi_3^{(i)} + \frac{\xi_2^{(i)}}{\xi_2}(1-\xi_3) + \breve{K}_T\left\{-Z^{\mathrm{PPY}}\frac{\xi_2^{(i)}}{\xi_2} + Z_{\mathrm{HS}}^{(i)} + Z_{\mathrm{bond}}^{(i)\mathrm{PPY}}\right\} \quad (\mathrm{A.3})$$

where $\breve{K}_T$ is expressed by eq A.1.

TPT theory

$$\frac{\rho_{\mathrm{c}(i)}v_i}{\Phi_i} = \xi_3^{(i)} + \frac{\xi_2^{(i)}}{\xi_2}(1-\xi_3) + \breve{K}_T\left\{-Z^{\mathrm{TPT}}\frac{\xi_2^{(i)}}{\xi_2} + Z_{\mathrm{HS}}^{(i)\mathrm{MCSL}} + Z_{\mathrm{bond}}^{(i)\mathrm{TPT}} + \left(\frac{\xi_3^{(i)}}{\xi_3} - \frac{\xi_2^{(i)}}{\xi_2}\right)\left[\frac{\xi_2^{3}\xi_3^{2}}{\xi_0(1-\xi_3)^3} + \frac{\xi_2^{2}\xi_3}{(1-\xi_3)^5}\sum_{k=1}^{M}\sum_{s=1}^{N_k-1}\frac{\Phi_k}{N_k}\sigma_{sk}^{*2}(g_{\mathrm{HS}}^{[sk,(s+1)k]}(\sigma))^{-1}\right]\right\} \quad (\mathrm{A.4})$$

where $\breve{K}_T$ is expressed by eq A.2. It is readily seen in the above relations that

$$\sum_{i=1}^{M}\rho_{\mathrm{c}}(i)v_i = 1$$

which is obvious for the partial volumes.

The two other thermodynamic coefficients—the thermal expansion coefficient

$$\alpha_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,\{n_i\}}$$

and the thermal pressure coefficient

$$\gamma_V = \frac{1}{P}\left(\frac{\partial P}{\partial T}\right)_{V,\{n_i\}}$$

are expressed in quite a simple manner:

$$\alpha_P T = \breve{K}_T Z \qquad \text{or} \qquad \alpha_P = K_T P/T$$

and γ_V is the same for the purely repulsive system in question and for a mixture of ideal gases

$$\gamma_V = 1/T$$

References and Notes

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