Local Composition Model for Chainlike Molecules: A New Simplified Version of the Perturbed Hard Chain Theory

A simple analytical equation for chainlike molecules interacting with square-well potential is derived by replacing the complicated attractive term in the perturbed hard chain theory (PHCT) of Beret, Donohue, and Prausnitz with a theoretical but simple expression derived by Lee, Lombardo, and Sandler. The resulting simplified perturbed hard chain theory (SPHCT) reproduces both experimental vapor pressure and liquid density data for a number of fluids over a wide temperature and pressure range with good accuracy.

The three pure-component parameters in the SPHCT have been obtained for several *n*-alkanes and multipolar fluids. Average errors in predicted vapor pressures and liquid densities, over a wide temperature and pressure range, are about 3 and 4%, respectively. Preliminary mixture calculations indicate that the SPHCT predicts *K* factors and Henry's constants with reasonable accuracy without the use of any binary parameters.

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Introduction

The perturbed hard chain theory (PHCT) developed by Beret and Prausnitz (1975a, b) and Donohue and Prausnitz (1978) is applicable for both liquid and gas phase properties of fluids ranging in molecular complexity from methane to large hydrocarbons and polymers. The PHCT has been applied successfully to predict thermodynamic properties of numerous and varied types of systems of industrial interest.

Beret and Prausnitz (1975a), who proposed an approximation for the density-dependent rotational and vibrational motions, applied the PHCT to pure fluids including polymers. The liquid densities of polymers were well-predicted, with errors less than 1%. Donohue and Prausnitz (1978) changed the constants in the attractive terms to fit more accurately the properties of alkanes and obtained the pure-component parameters for several fluids, including high-boiling hydrocarbons. More important, they also extended the PHCT to mixtures by using mixing rules derived from the perturbation theory and showed that the mixture *K* factors and heat of mixing for several nonpolar fluid mixtures can be predicted accurately with low values of a binary interaction parameter (usually less than 0.02). Kaul et al. (1980) predicted Henry's constants using the PHCT with similar low values of binary interaction parameter. They also empirically extended the PHCT to predict the second virial coefficient of both pure fluids and mixtures. Liu and Prausnitz (1979a) showed that the PHCT also can be used to accurately predict the solubilities of gases in liquid polymers, where the light component is supercritical, whereas the usual approach using excess functions is not useful in treating such supercritical gas-polymer systems. Liu and Prausnitz (1979b, 1980) also applied the PHCT for phase equilibrium calculations in polymeric systems (polymer-solvent, polymer-polymer, polymer-polymer-solvent), taking into account the molecular weight distribution of polymeric molecules. Ohzono et al. (1984) correlated the pure-component parameters reported by Donohue and Prausnitz (1978) and Kaul et al. (1980), with group volumes of Bondi (1968). Using these correlations, they evaluated the parameters for pure polymers and showed that the Henry's constant of several solutes in polymers could accurately be predicted with a small value for the binary interaction parameter (less than 0.02).

However, the equation of state derived by Beret and Prausnitz and by Donohue and Prausnitz from the PHCT partition function is complex. This is because the attractive term in the

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original PHCT used a perturbation expansion for square-well molecules that was based on the molecular dynamic results of Alder et al. (1972) and on an accurate fit to the thermodynamic data of methane. As a result, the free energy and pressure are obtained as a series expansion in both density and inverse temperature; these expressions are lengthy and cumbersome. Consequently, computer calculations, especially for mixtures, are time-consuming and costly.

Since the PHCT has already been proved valuable in predicting properties of various types of systems, it is useful to consider modifications of the theory that simplify the equation of state and other thermodynamic properties. Such simplification would make the PHCT equation of state more useful to the engineering community. In this work, we replace the attractive portion of the PHCT partition function with the model of Lee, Lombardo, and Sandler (LLS; 1985). The simple expression for the attractive partition function obtained from the LLS model satisfies the high-density boundary condition for square-well molecules. Also, it shows fairly good agreement with the coordination number for the square-well fluid obtained from computer simulation calculations and is in very good agreement with the compressibility factor results for this fluid reported by Alder et al. (1972). As with the PHCT, the repulsive term is obtained from the hard-sphere equation of Carnahan and Starling (1972).

Unlike the original LLS equation, which is applicable only to small molecules, the new equation, the simplified perturbed hard chain theory (SPHCT), which is based on the PHCT partition function, takes into account the density dependence of the rotational and vibrational degrees of freedom. As a result, the SPHCT is valid at all densities for both small argon- and methanelike molecules and large hydrocarbons such as decane and eicosane as well as polymers. Even though the attractive term in the SPHCT is rigorously valid at high densities, it is also a good approximation at all densities, as can be seen from the accuracy of the predicted properties. The expressions from the SPHCT for the thermodynamic properties of pure fluids are much simpler than the PHCT and therefore, when extended to mixtures the SPHCT requires only relatively simple mixing rules. The mixing rules are based on segmental interactions of chainlike molecules. The preliminary calculations reported here involving nonpolar fluid mixtures indicate that the prediction of K factors and Henry's constants, without the use of a binary interaction parameter, are nearly as accurate as those of the computationally more difficult PHCT. However, accurate representation of mixture behavior, especially for systems involving polar compounds, will require a binary parameter just as in the PHCT.

Theory

In the generalized van der Waals theory, since the molecular translational motions are governed by repulsions and attractions, Donohue and Prausnitz (1978) proposed an approximation for the canonical ensemble partition function for chainlike molecules:

$$Q(N, V, T) = \frac{1}{N!}\left(\frac{V}{\Lambda^3}\right)^N \left(\frac{V_f}{V}\exp\frac{-\phi}{2ckT}\right)^{Nc} \tag{1}$$

where N is the number of molecules at temperature T and volume V, and Λ is the thermal de Broglie wavelength. The molecular repulsions can be expressed in terms of free volume V_f, which is the volume available to the center of mass of a molecule as it moves, while freezing the position of all other molecules in the system. The molecular attractions can be expressed as a ratio of the potential energy of a molecule, $\phi/2$, to its kinetic energy, kT, where k is the Boltzmann constant. Further, the rotational and vibrational partition function can be factored into external and internal contributions. The internal contribution depends only on the intramolecular forces. Therefore, it is a function only of temperature, and does not affect the equation of state and excess or residual properties.

Donohue and Prausnitz (1978) proposed an approximation, following Prigogine (1957), for the density dependence of the external rotational and vibrational motions. Nonidealities in the equation of state due to each of the density-dependent external rotational and vibrational degrees of freedom were treated as equivalent to those due to a translational degree of freedom. For this purpose, they introduced a parameter $3c$ as being the total number of density-dependent degrees of freedom (sum of three translational and external rotational and vibrational degrees of freedom). Further, since these $3c$ degrees of freedom affect the kinetic energy of a molecule, the attractive partition function in Eq. 1 should contain the ratio of the potential energy, $\phi/2$, to the kinetic energy, ckT, associated with the effective (density-dependent) degrees of freedom.

To obtain an expression for the potential field, $\phi/2$, in terms of state variables, one needs to know the position of molecules in space; this is given by the radial distribution function, $g(r; \rho, T)$. Properties of chainlike and large molecules can be evaluated more accurately by considering segmental rather than molecular interactions. For example, in the carbon dioxide and squalane binary system, the small carbon dioxide molecule sees only a part of the large squalane molecule, and as a result, if the energetic contribution to the equation of state were based on molecular interactions, it would be in error. For chainlike molecules, it is appropriate to divide a molecule into s number of segments with σ being the diameter of a segment. The segmental interactions are represented by a square-well potential function, with ϵ^* being the potential well depth. For convenience, the intermolecular interaction energy, $\epsilon^* s$, can be defined in terms of ϵq, where ϵ is a characteristic energy per unit external surface area and q is the external surface area of the molecule.

A simple expression for the attractive term in the partition function can be obtained in terms of the coordination number, N_c (see Supplementary Material for a detailed derivation):

$$\frac{-\phi}{2ckT} = \frac{1}{2}\int_{1/\tilde{T}=0}^{1/\tilde{T}} N_c(\rho, T)\, d\left(\frac{1}{\tilde{T}}\right) \tag{2}$$

where the reduced temperature, $\tilde{T}$, is given by

$$\tilde{T} = \frac{T}{T^*} = \frac{ckT}{\epsilon q} \tag{3}$$

Defining the coordination number for chainlike molecules, N_c, as the number of segments within the interaction range (σ to $R\sigma$ for the square-well potential) of a segment of a central molecule, we get

$$N_c = \frac{N}{V}\int_{\sigma}^{R\sigma} g(r; \rho, T)\, s\, 4\pi r^2\, dr \tag{4}$$

In the above expression, the term $(N/V)\, g(r;\, \rho,\, T)\, 4\pi r^2 dr$ gives the average number of molecules in a spherical shell of thickness dr (in this expression, the average number of molecules in the shell is taken as the total number of segments of different molecules/s), and at a distance r from a segment of a central molecule.

To evaluate the integral in Eq. 2 and obtain an expression for the potential ϕ in terms of state variables, we need to relate N_c to density and temperature. This is done by extending the LLS lattice model of Lee et al. (1985) to chainlike molecules. Each segment of a molecule occupies one site in a quasi-crystalline lattice, and that of neighboring segments occupy adjacent sites. The combinatorial term, which becomes important for polymeric molecules, is taken into account in the Carnahan-Starling expression, which we use to calculate the molecular repulsions.

Following Lee et al., segments of molecules in a binary mixture will be distributed on the lattice sites. The density dependence of a pure fluid can then be evaluated by emptying the sites occupied by segments of one of the species. Let us consider a segment of a central molecule 1. Based on the local composition model, the ratio of the probability of finding a segment of molecule 2 about the segment of the central molecule 1 to that for a segment of molecule 1 is assumed to be

$$\frac{N_{21}}{N_{11}} = \frac{s_2N_2}{s_1N_1}\,\frac{\exp\left(\dfrac{\epsilon_{21}^*}{2c_2kT/s_2}\right)}{\exp\left(\dfrac{\epsilon_{11}^*}{2c_1kT/s_1}\right)} \tag{5}$$

In Eq. 5, N_{ij} gives the number of segments of molecule i about a segment of molecule j, s_i is the number of segments on a molecule of component i, and N_i is the number of molecules of component i. The argument of the Boltzmann factor, which arises due to the presence of attractive forces, is given by the ratio of the characteristic potential energy of interaction between segments (ϵ_{ij}^*) and the effective kinetic energy per segment (c_ikT/s_i).

Replacing $\epsilon_{ij}^* s_i$ by $\epsilon_{ij}q_i$ and recognizing that since species 2 represents vacancies, i.e., $\epsilon_{21} = 0$, we get

$$\frac{N_{21}}{N_{11}} = \frac{s_2N_2}{s_1N_1}\exp\left(\frac{-\epsilon_{11}q_1}{2c_1kT}\right) = \frac{s_2N_2}{s_1N_1}\exp\left(\frac{-\epsilon q}{2ckT}\right) \tag{6}$$

If Z_M is the total number of lattice sites (maximum coordination number) in the interaction region, then

$$N_{11} + N_{21} = Z_M \tag{7}$$

Eliminating N_{21} from Eqs. 6 and 7 yields

$$N_{11} = \frac{s_1N_1Z_M}{s_1N_1 + s_2N_2\exp\dfrac{-\epsilon q}{2ckT}} \tag{8}$$

Since species 2 represents vacancies, we can relate s_2N_2 in Eq. 8 to fluid volume using

$$\frac{s_2N_2}{s_1N_1} = \frac{v - v^*}{v^*} \tag{9}$$

where v^* represents the close-packed molar volume given by $N_As\sigma^3/\sqrt{2}$, where N_A is Avogadro's number. Eliminating s_2N_2 from Eqs. 8 and 9, and observing that N_c (defined in Eq. 4) and N_{11} are identical, we get

$$N_c = N_{11} = \frac{Z_Mv^*(Y+1)}{v + v^*Y} \tag{10}$$

where

$$Y = \exp\left(\frac{\epsilon q}{2ckT}\right) - 1$$

Substituting Eq. 2 for the attractive contribution and Eq. 10 for N_c into Eq. 1, we can obtain simple expressions for the Helmholtz free energy and equation of state:

$$\frac{A - A^{IG}}{NkT} = cA^{\text{rep}} + cZ_M\ln\frac{v}{v + v^*Y} \tag{11}$$

and

$$z = 1 + c\left(z^{\text{rep}} - Z_M\frac{v^*Y}{v + v^*Y}\right) \tag{12}$$

In calculations reported here, the repulsive terms, A^{rep} and z^{rep}, are calculated from the hard-sphere equation of Carnahan and Starling (1972).

Equations 11 and 12 give the simplified perturbed hard chain theory (SPHCT). For monomeric molecules, where $s = q = c = 1$, Eqs. 11 and 12 reduce to the LLS equation. The attractive term in the SPHCT is much simpler than the comparable term of the PHCT of Donohue and Prausnitz (1978).

In our preliminary calculations on mixture properties, the following mixing rules are used in the SPHCT:

$$\langle v^*\rangle = \sum_i x_iv_i^* = \sum_i x_i\frac{s_i\sigma_{ii}^3}{\sqrt{2}} \tag{13}$$

$$\langle c\rangle = \sum_i x_ic_i \tag{14}$$

and

$$\langle cv^*Y\rangle = \sum_{ij} x_ix_j\,c_iv_{ji}^*\left(\exp\frac{\epsilon_{ij}q_i}{2c_ikT} - 1\right) \tag{15}$$

with the cross terms given by

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2}$$

and

$$\epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}}$$

The term in angular brackets, $\langle \cdot\cdot\cdot \rangle$, represents a mixture property. The above mixing rules, which are based on van der Waals' one-fluid theory, are derived following Donohue and Prausnitz (1978). More about these and other mixing rules will be discussed in a subsequent paper. For mixtures, the equation of state given by Eq. 12 becomes

$$z = 1 + \langle c \rangle z^{\text{rep}} - \frac{Z_M \langle cv^* Y \rangle}{v + \dfrac{\langle cv^* Y \rangle}{\langle c \rangle}} \tag{16}$$

where

$$z^{\text{rep}} = \frac{4\tau\tilde{\rho} - 2(\tau\tilde{\rho})^2}{(1 - \tau\tilde{\rho})^3}$$

with $\tilde{\rho} = \langle v^* \rangle / v$, and τ is a constant equal to 0.7405. The fugacity coefficient of component i, ϕ_i, is given by

$$\begin{aligned}\ln \phi_i = {} & c_i \frac{4\tau\tilde{\rho} - 3(\tau\tilde{\rho})^2}{(1 - \tau\tilde{\rho})^2} + \frac{\langle c \rangle v_i^*}{\langle v^* \rangle} \frac{4\tau\tilde{\rho} - 2(\tau\tilde{\rho})^2}{(1 - \tau\tilde{\rho})^3} \\ & - \langle c \rangle Z_M \left[2 - \frac{c_i}{\langle c \rangle} + \frac{c_i}{\langle c \rangle} \ln \left(1 + \frac{\langle cv^* Y \rangle}{\langle c \rangle v} \right) \right. \\ & \left. + \frac{v(c_i - 2\langle c \rangle) + \dfrac{1}{n} \dfrac{\partial}{\partial n_i} (n^2 \langle cv^* Y \rangle) - 2\langle cv^* Y \rangle}{\langle c \rangle v + \langle cv^* Y \rangle} \right] - \ln z \end{aligned} \tag{17}$$

where

$$\frac{1}{n} \frac{\partial}{\partial n_i} (n^2 \langle cv^* Y \rangle) = \sum_j x_j \left[c_i v_{ji}^* \left(\exp \frac{\epsilon_{ij} q_i}{2c_i kT} - 1 \right) + c_j v_{ij}^* \left(\exp \frac{\epsilon_{ji} q_j}{2c_j kT} - 1 \right) \right]$$

Results and Discussion

The SPHCT, Eqs. 11 and 12, can be used to predict properties of both small and large molecules, including polymers, since the effect of rotational and vibrational motions on the equation of state is taken into account through the parameter c. Note that the product of ϵ and q always appear together in calculating pure-component thermodynamic properties and thus can be treated as a single parameter. Also we have used $Z_M = 36$ since this gives a value of c close to 1 for methane on data reduction. Thus, for pure compounds, the SPHCT has three parameters, v^*, c, and ϵq (or $T^* = \epsilon q / ck$), and these parameters are evaluated by fitting simultaneously both vapor pressure and liquid density data.

The three pure-component parameters for 14 n-alkanes (from methane to eicosane) are given in Table 1. Also included are parameters for sulfur dioxide, methyl acetate, and diethyl ether (dipolar fluids), and for benzene and carbon dioxide (quadrupolar fluids).

Previously, it was shown that the correlation of parameters for a class of pure fluids leads to a fairly good estimates of these parameters useful for fluids of the same class for which no experimental data are available. A correlation of parameters, v^*, c, and cT^* ($= \epsilon q / k$, a characteristic energy) with carbon number for the n-alkanes is shown in Figure 1. The near-linear behavior of the correlation indicates that each segment of an n-alkane contributes almost an equal amount to the hard-core volume, energy, and the number of external degrees of freedom of each molecule. This smooth correlation suggests that these parameters relate to molecular properties rather than being merely adjustable constants needed to fit experimental data.

Table 1. Pure-Component Parameters for SPHCT Equation

Compound	T^* K	$10^5 v^*$ m^3/mol	c
n-Alkanes			
Methane	81.46	1.9408	1.0
Ethane	120.54	2.7595	1.2586
Propane	142.45	3.5848	1.3941
Butane	154.86	4.2559	1.6329
Pentane	164.69	5.2583	1.8393
Hexane	175.78	6.1837	1.9649
Heptane	180.38	6.9999	2.1990
Octane	187.39	7.5083	2.3697
Nonane	188.07	8.7043	2.6541
Decane	186.68	9.8067	3.0246
Tridecane	197.28	12.305	3.5703
Hexadecane	203.89	16.478	4.0036
Heptadecane	207.16	15.956	4.2466
Eicosane	209.65	18.542	4.9108
Multipolar Fluids			
Benzene	205.53	4.4483	1.6359
Carbon dioxide	105.61	1.4600	1.8866
Sulfur dioxide	150.08	1.8904	1.9019
Methyl-acetate	160.22	4.0160	2.4094
Diethyl ether	144.33	5.3287	2.4370

With the parameters given in Table 1, the vapor pressures and liquid densities can be calculated with average errors of less than 3 and 4%, respectively, over a wide range of temperature and pressure. The average (absolute) errors in vapor pressure and liquid densities for each fluid and the temperature and pressure ranges used for data reduction are given in the Supplementary Material to this paper. In evaluating the SPHCT parameters, about ten vapor pressure data points (from triple point to critical point) were used. Shown in Figure 2 is a comparison of predicted and experimentally measured vapor pressures for normal alkanes ranging from methane to eicosane. A similar comparison is made in Figure 3 for the multipolar fluids sulfur dioxide, carbon dioxide, and benzene. As seen in Figures 2 and 3, the calculated values are in good agreement with experimental data from the triple point to the critical point.

Liquid densities were fitted to an average of 20 to 30 data points distributed over a wide range of temperature and pressure. The average error for calculated liquid densities is about 3% for low molecular weight compounds (up to pentane) and about 5% for higher molecular weight compounds. While these errors are larger than the errors obtained by Donohue and Prausnitz (1977), the PHCT is significantly more complicated, especially for mixtures. The attractive portion of the PHCT has 63 terms with 27 constants and 10 different mixing rules, while the SPHCT has only one term, one constant, and three mixing rules; however, a comparison of CPU times shows that the SPHCT is only about seven times faster because it contains an exponential.

The value of the maximum coordination number, Z_M, depends upon the width of the attractive part of the square-well

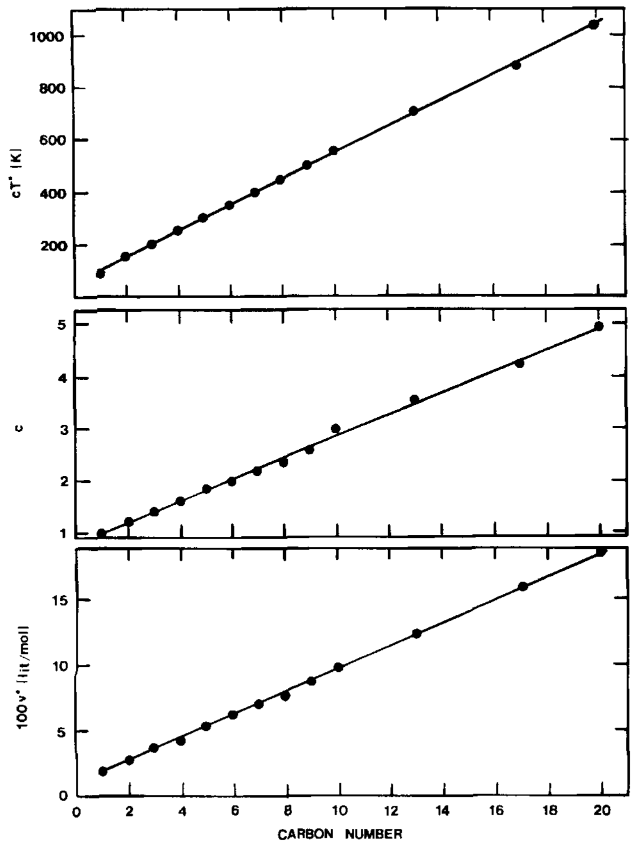

Figure 1. Pure-component parameters as a function of carbon number.

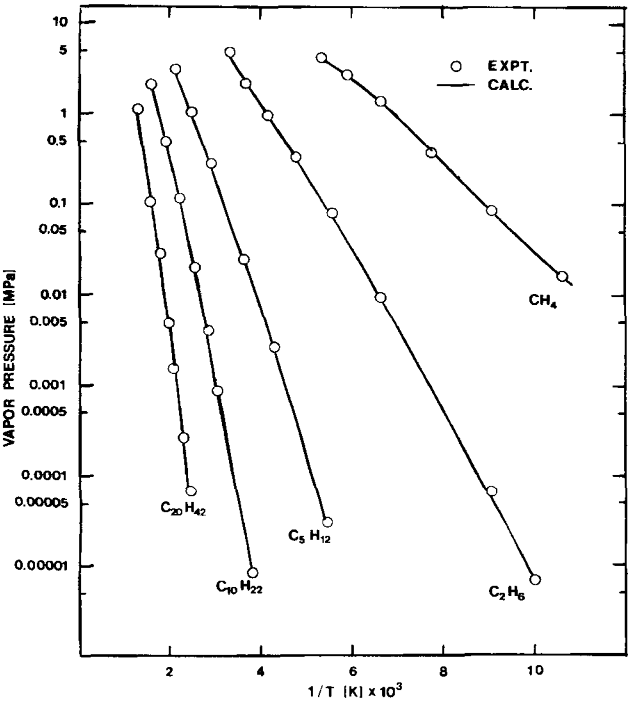

Figure 2. Experimental and SPHCT-calculated vapor pressures for *n*-alkanes.

Experimental data sources: methane, IUPAC (1976); ethane, Goodwin et al. (1976); pentane, Timmermans (1950); decane and eicosane, Vargaftik (1975).

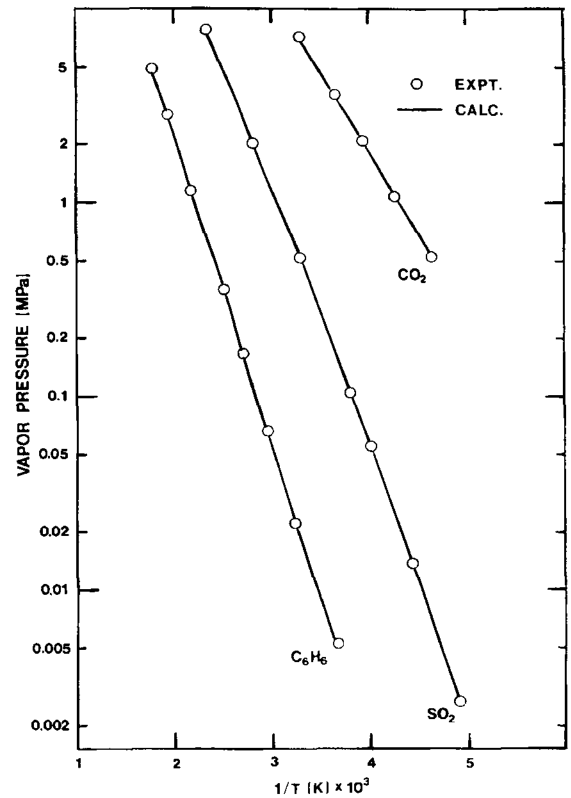

Figure 3. Experimental and SPHCT-calculated vapor pressures for multipolar fluids.

Experimental data sources: carbon dioxide, IUPAC (1976); sulfur dioxide, Kang (1961); benzene, Timmermans (1965).

potential. Lee et al. used $Z_M = 33.4$, which they obtained as the best value from data reduction of argon and methane. In Table 2, we have shown the effect of Z_M in predicting the thermodynamic properties of both low and high molecular weight compounds. It is seen from the table that for each fluid the average errors in the calculated vapor pressure and molar volumes are approximately constant. This suggests that the actual value of Z_M has little effect on the thermodynamic properties. A value of $Z_M = 18$ gives the pure-component parameters, T^*, v^*, and c, which are similar to those obtained by Donohue and Prausnitz

Table 2. Pure-Component Parameters and Average Errors in Liquid Molar Volume and Vapor Pressure for Different Z_M Values

Compound	Z_M	T^* K	$10^5 v^*$ m³/mol	c	% Abs. Avg. Dev. v_L	% Abs. Avg. Dev. P^{sat}
Ethane	18.0	232.9	2.6901	1.2020	2.5	3.3
	33.4	129.7	2.7546	1.2511	2.9	3.1
	36.0	120.5	2.7595	1.2586	2.9	3.0
Octane	18.0	362.9	7.3231	2.2517	4.2	2.8
	33.4	201.2	7.4766	2.3685	4.3	2.7
	36.0	187.4	7.5083	2.3697	4.3	3.0
Eicosane	18.0	400.1	18.031	4.8432	4.4	1.1
	33.4	223.7	18.412	4.9879	4.6	1.2
	36.0	209.6	18.541	4.9108	4.5	1.9

Table 3. Average Errors in Liquid Molar Volume and Vapor Pressure

	% Abs. Avg. Dev.							
	Molar Volume				Vapor Pressure			
Compound	SPHCT	LLS	PHCT	PR	SPHCT	LLS	PHCT	PR
n-Alkanes								
Methane	2.6	2.6	1.9	5.9	1.1	1.2	0.2	1.0
Ethane	2.9	2.2	2.5	5.1	3.0	13.8	0.8	19.3
Propane	2.5	2.2	0.8	12.3	3.7	19.0	2.4	13.5
Pentane	3.5	3.2	0.5	3.1	3.5	30.6	2.4	4.9
Hexane	4.8	3.9	2.1	2.0	3.0	46.3	2.1	12.1
Decane	2.6	5.0	1.2	5.9	1.6	61.9	2.3	9.5
Eicosane	4.5	3.6	1.5	22.1	1.9	72.6	2.4	12.5
Multipolar Fluids								
Benzene	4.1	2.8	1.5	9.5	2.7	16.6	2.4	1.7
Carbon dioxide	2.8	1.5	0.9	3.5	1.5	9.5	0.2	0.7
Sulfur dioxide	2.6	5.8	3.6	4.7	2.6	33.5	2.0	3.4

SPHCT, Simplified perturbed hard chain theory.
LLS, Lee-Lombardo-Sandler equation.
PHCT, Perturbed hard chain theory.
PR, Peng-Robinson equation.

(1978) with the PHCT equation. However, values of Z_M of 18 and 33.4 both give values of c less than unity for methane, which is physically unrealistic. Here, we use $Z_M = 36$ since this gives a value of c close to 1 for methane on reduction.

A comparison of the SPHCT equation, the LLS equation, the original PHCT equation, and the Peng-Robinson (PR) equation (Peng and Robinson, 1976) is given in Table 3. Remember that the LLS equation can be obtained from Eq. 12 by considering molecular interactions and by neglecting the rotational and vibrational contributions (i.e., $q = s = c = 1$). The errors given in Table 3 for the LLS equation are determined using parameters obtained by simultaneously fitting both liquid density and vapor pressure data with $Z_M = 33.4$. The average errors given in Table 3 for the PHCT are taken from Donohue and Prausnitz (1977).

The results in Table 3 suggest the following: The LLS equation gives molar volumes that are quite acceptable but large errors in vapor pressures for large molecules, as shown in Figure 4. However, this is to be expected since the LLS equation was derived for spherical molecules and has only two parameters whereas the other equations each have three parameters. For spherical molecules like argon and methane, the LLS equation is quite good and significantly better than most other two-parameter equations. Of the three-parameter equations, the PHCT clearly is the best, although the SPHCT is only slightly less accurate. A comparison of accuracy of the SPHCT and PR equations, both of which are of similar complexity and contain three parameters, clearly shows the value of extending equations of state developed for simple spherical molecules to more complex fluids using the perturbed hard chain ideas.

Since both the SPHCT and the LLS equations predict molar volumes with similar errors, it can be concluded that the prediction of molar volumes is insensitive to the parameter c. That is, any value of c, even $c = 1$, can be used when correlating molar volumes. On the other hand, the vapor pressure calculations are sensitive to the parameter c and therefore require, for each fluid, a characteristic value of c that is equal to or greater than one.

The advantage of including the rotational and vibrational effects (i.e., the c parameter) also can be seen in our preliminary calculations on mixture properties. For mixture calculations, the parameters σ and ϵ for n-alkanes are estimated from the slopes of v^* and cT^* vs. carbon number correlations of Figure 1, respectively. In this way, the parameter ϵ/k is found to have a value of 62.5 K and $N_A\sigma^3/\sqrt{2} = 0.008667$ L/mol.

In Figures 5 and 6, we compare the K factors for alkane mix-

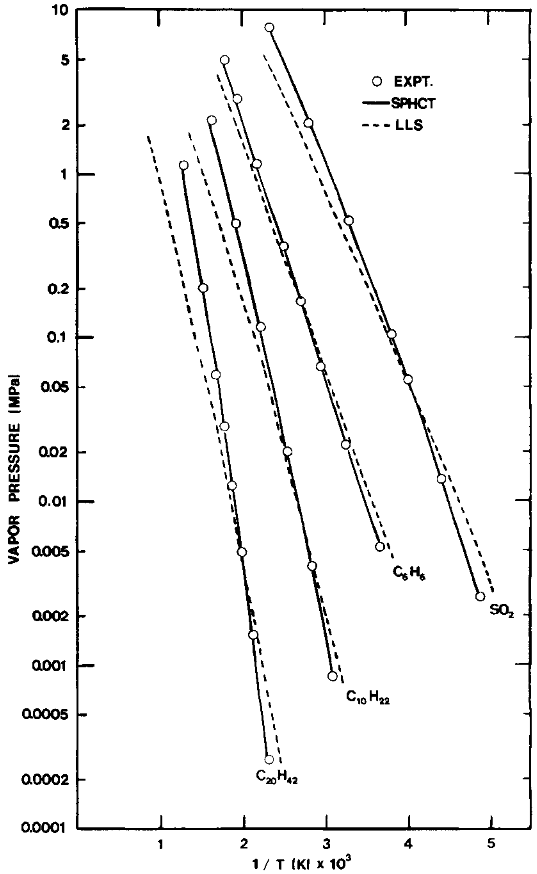

Figure 4. Experimental and SPHCT- and LLS-calculated vapor pressures for various fluids.

Experimental data sources: sulfur dioxide, Kang (1961); benzene, Timmermans (1965); decane and eicosane, Vargaftik (1975).

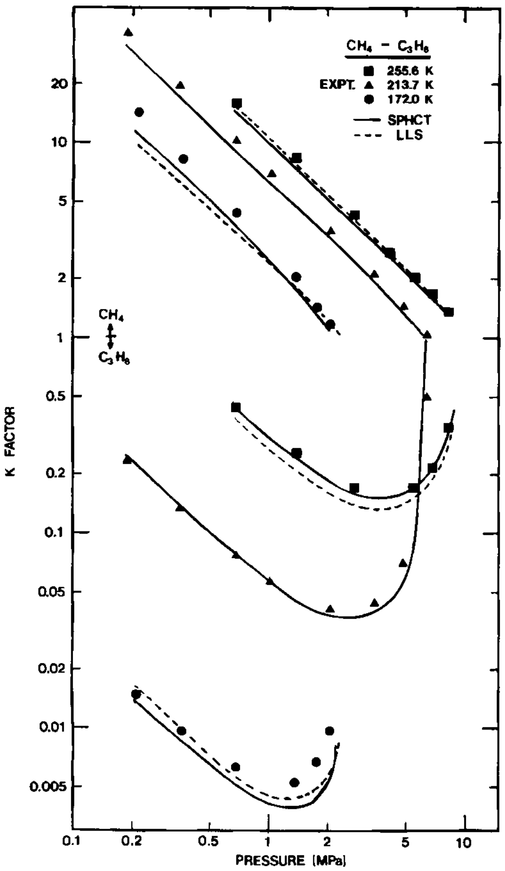

Figure 5. Experimental and calculated *K* factors for methane-propane system.

Calculations made with pure-component parameters alone; experimental data from Wichterle and Kobayashi (1972) and Akers et al. (1954).

tures calculated using Eq. 16 with experimental data. These *K* factors were calculated using only pure-component parameters—no adjustable binary interaction parameters were used. Also, for comparison we have plotted *K* factors predicted from the LLS equation, which is similar to the SPHCT equation for mixtures (Eq. 16) but neglects the segmental interactions and the effect of rotational and vibrational motions on the equation of state (i.e., $q = s = c = 1$). Again, in using the LLS equation for mixtures we have used only the pure-component parameters, v^* and E/k, obtained by fitting pure fluid liquid density and vapor pressure data with $Z_M = 33.4$, and have used no binary interaction parameters.

Shown in Figure 5 are *K* factors predicted by the SPHCT and the LLS equations along with the experimental data for the methane-propane binary system. For this system, involving low molecular weight substances, the *K* factors predicted by the LLS equation are as accurate as those predicted by the SPHCT since, in this case, the parameter c is unity for methane and is close to one for propane. However, for mixtures involving high molecular weight compounds such as the ethane-hexane mixture in Figure 6, the SPHCT equation predicts *K* factors more accurately than the unmodified LLS equation. The inaccurate prediction of *K* factors for hexane using the LLS equation is a result of the assumption that $c = 1$ for hexane, whereas in the SPHCT this parameter c has a value of 1.9649.

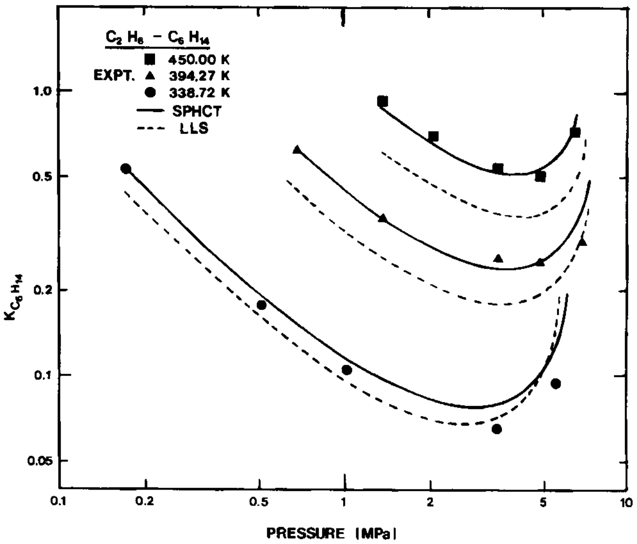

Figure 6. Experimental and calculated *K* factors for ethane-hexane system.

Calculations made with pure-component parameters alone; experimental data from Zais and Silberberg (1970).

A comparison of experimental and calculated Henry's constants of ethane in hexadecane is shown in Figure 7. Here again the Henry's constants are predicted using the SPHCT, LLS, and PHCT equations with only pure-component parameters and no binary interaction parameters. The PHCT and SPHCT equations predict Henry's constants that are much closer to the experimental data than those from the LLS equation. This is not surprising since the binary system shown in Figure 7 involves a high molecular weight hydrocarbon (hexadecane), and only the PHCT and SPHCT equations apply to such fluids.

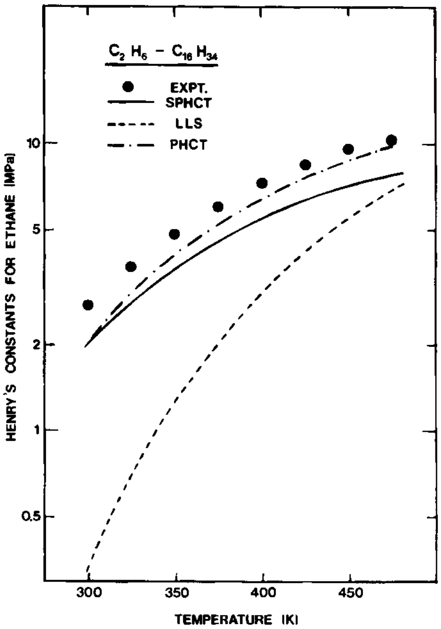

Figure 7. Experimental and calculated values of Henry's constant of ethane-hexadecane system.

Calculations made with pure-component parameters alone; experimental data from Cukor and Prausnitz (1972).

Comparisons of the predicted thermodynamic properties shown in Figure 7 and in Table 3 suggest that the simple expression for the attractive partition function derived by Lee et al., when extended to chainlike molecules, predicts properties that are only slightly less accurate than the PHCT predictions, and accurate enough for most engineering calculations. Further, this modified equation, which we have referred to as the SPHCT equation, is considerably simpler to use than the original perturbed hard chain theory equation of state. Though not presented here, mixture calculations with the PHCT and SPHCT using binary interaction parameters give similar accuracies, even for systems containing multipolar fluids. Further work on mixtures will be presented in later publications.

Conclusions

In this communication we have developed a simplified version of the perturbed hard chain theory which has a simplicity rivaling empirical cubic equations of state while still retaining all the advantages of the PHCT. Further, like the PHCT, the simplified version can be used to predict the properties, at all densities, of fluids covering the range from argon and methane to polymer molecules. The SPHCT equation predicts pure-component molar volumes and vapor pressures almost as accurately as the original PHCT. Further, the smooth correlation of the parameters in this theory with carbon number suggest that they are related to molecular properties and are not merely adjustable parameters needed to fit experimental data. These correlations allow one to determine the parameters for fluids of the same class for which no experimental data are available. Finally, preliminary calculations reported here for mixtures of alkane molecules of different sizes show that the SPHCT can be used to predict mixture properties with reasonable accuracy using only pure-component properties, and presumably with excellent accuracy if binary interaction parameters are used.

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Notation

A = Helmholtz energy
$3c$ = number of external degrees of freedom per molecule
E = characteristic interaction energy per molecule
$g(r)$ = radial distribution function
k = Boltzmann's constant
n = number of moles
N = total number of molecules
N_c = coordination number
N_{ij} = number of segments of molecule i about a segment of molecule j
N_A = Avogadro's number
P = pressure
q = molecular partition function
q = normalized surface area per molecule; $q = 4/5$ for a —CH_2— segment in alkanes
Q = canonical ensemble partition function
r = scalar distance
s = number of segments per molecule; $s = 1$ for a monomer
T = absolute temperature
T^* = characteristic temperature for intermolecular interactions
v = molar volume
v^* = characteristic volume per mole
V = system (total) volume
V_f = free volume
x = mole fraction
z = compressibility factor
Z_M = maximum coordination number

Greek letters

ϵ = characteristic energy per unit external surface area of a molecule
ϵ^* = a characteristic segmental interaction energy
Λ = thermal de Broglie wavelength
ρ = density
σ = hard-core diameter of a segment
τ = constant, =0.7405
ϕ = potential field

Superscripts

IG = ideal gas
rep = repulsions
$*$ = segmental property
$*$ = reducing parameter
$\sim$ = reduced property

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