phase. Yet the dielectric β relaxation of the copolymers preserves the feature which is characteristic of POE homopolymers. The most likely mechanism of this β relaxation might be the flip-flop transition between $tg^+t \rightleftarrows tg^-t$ conformations in the POE blocks.

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On the Statistical Thermodynamics of Multicomponent Fluids: Equation of State

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ABSTRACT: The theory previously formulated and applied to homogeneous fluids of high and low molecular weights is generalized to multicomponent systems. The configurational free energy and equation of state retain the form derived for the homogeneous liquid with the characteristic parameters now functions of composition. Hence previous conclusions regarding an effective principle of corresponding states remain valid for mixtures of varying composition. When the scaling parameters for the separate components have been derived from *PVT* studies and the experimental isobar of the mixture at atmospheric pressure has been analyzed, the isotherms of the latter can be predicted without further recourse to experiment. The first applications of the theory are made to two series of binary mixtures of low molecular weight compounds. One is the *n*-hexane + *n*-hexadecane pair. Satisfactory agreement with experiment for the components and mixtures results at atmospheric and elevated pressures ($P \lesssim 5$ kbar). The results are combined with the information for polyethylene already available to compute the increase in the thermal expansivity of the polymer upon the addition of varying amounts of n-C_{16}. The second example is the $CCl_4 + C_6H_{12}$ system, where the former component had previously been analyzed. Good agreement with experiment is obtained for the equation of state of the second member and similarly for the series of mixtures at atmospheric pressure. Finally predictions for the elevated-pressure behavior of the latter are presented.

Introduction

In recent years we have been concerned with the configurational thermodynamic properties of polymer and oligomer melts.[1,2] Most recently organic solvents have also been studied.[3] The analysis of the *PVT* properties followed a theory of the liquid state[4] based on the cell model modified by the introduction of a volume- and a temperature-dependent structure function in the form of vacancies (holes) in the quasi-lattice. This function is determined by the extremization of a configurational partition function.

The resulting equation of state has been quantitatively successful in the three types of fluids examined, i.e., amorphous high polymers, oligomers, and organic solvents, at atmospheric pressure as well as elevated pressures. The purpose of this paper is to report on a generalization of the theory to multicomponent fluids and on the first applications to mixtures of *n*-paraffins and of organic solvents. High polymer blends are not included.

Recapitulation: The Homogeneous Fluid

The characteristic parameters of the system are defined in terms of the *equivalent* *s*-mer.[1] The relation between the *s*-mer and the real chain, the *n*-mer, i.e., the definition of the segment of the former in terms of the repeat unit of the latter, is derived from the experimental equation

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of state. The molecule is characterized by s, the chain length, and $3c$, the number of effectively external, i.e., volume-dependent, degrees of freedom. The intersegmental interactions are defined by the maximum attractive energy parameter ϵ^* and a characteristic repulsion volume v^*. In terms of the latter a scaling volume and a scaling pressure are defined. The scaling temperature is determined by the balance between the thermal energy concentrated in the external degrees of freedom and the maximum intermolecular attraction. Reduced variables of state are thus defined by the scaling parameters as follows:

$$\tilde{V} = v/v^*$$
$$\tilde{P} = P/(qz\epsilon^*/sv^*) \qquad (1)$$
$$\tilde{T} = T/(qz\epsilon^*/ck)$$

with

$$qz = s(z-2) + 2$$

where z is the coordination number of the quasi-lattice. From eq 1 there follows

$$(P^*V^*/T^*)M_0 = (c/s)R \qquad (2)$$

where V^* is the repulsion volume per unit mass and M_0 is the molecular weight of the segment. The comparison of experimental and theoretical isotherms and isobars yields the scaling parameters and thence M_0, provided c/s is known. For high polymers ($s \rightarrow \infty$), the universal assignment $3c/s = 1$ has been adopted.[1] For oligomers the consistent analogue is $3c/(s+3) = 1$.[2] An effective principle of corresponding states then follows.[2]

The scaled configurational partition function for N molecules has the following form[4]

$$Z_{\text{conf}} = g(N,y)[\tilde{v}_{\text{f}}(\tilde{V},y)]^{cN} \exp[-E_0(\tilde{V},\tilde{T},y)/kT] \qquad (3)$$

where y represents the fraction of occupied sites in the lattice. The first term is the combinatory factor for (random) mixing of holes and segments. The third represents the lattice energy, with a volume dependence derived from an assumed (6–12) effective pair potential and properly modified by the vacancy factor. The second term represents a free volume. The form adopted by us is a linear superposition of solidlike and gaslike terms, weighted by y and $1-y$, respectively.[4] For the former, the cell potential has been approximated in our temperature and pressure range by a square well. Moreover, the averaging is carried out over free lengths rather than volumes. The result for the free volume per molecule or segment is

$$v_{\text{f}} = v^*\{y[(y\tilde{V})^{1/3} - 2^{-1/6}] + (1-y)(y\tilde{V})^{1/3}\}^3 \qquad (4)$$

From eq 3 and 4 there follows the scaled pressure equation:

$$\tilde{P} = -(\partial\tilde{F}/\partial\tilde{V})_{\tilde{T}} = \tilde{P}[\tilde{V},\tilde{T};\, y(\tilde{V},\tilde{T})] \qquad (5)$$

with the minimum condition

$$(\partial\tilde{F}/\partial y)_{\tilde{V},\tilde{T},c/s} = 0 \qquad (6)$$

The coupled equations (5) and (6) then yield the equation of state. We note finally that in the limit $\tilde{P} \rightarrow 0$, applicable to atmospheric pressure, eq 5 and 6 yield the simple expression

$$\ln \tilde{V} = A(s) + B(s)\tilde{T}^{3/2} \qquad (7)$$

with $A(s)$ and $B(s)$ numerics for a given s value and a specified c. Equation 7 represents an excellent approximation over the whole experimental temperature range for high polymers. Deviations have been noted at the upper range ($\tilde{T} \gtrsim 0.065$) for short chains ($s \lesssim 3$).[2a]

Multicomponent Fluid

We assume a single type of vacancies with equivalence of hole and *all* segment sizes. A modification of this simplification may subsequently be considered. With N_{h} and N_i ($1 \leq i \leq r$) the number of holes and component molecules, respectively, the fraction y of occupied sites is

$$y = \sum_i s_iN_i/(N_{\text{h}} + \sum_i s_iN_i)$$

with s_i the chain length of the respective equivalent s-mer. Furthermore the exponent cN in eq 3 is replaced by $\sum c_iN_i$.

Consider now the generalization of eq 3 term by term. Continuing with the assumption of random mixing throughout, the combinatory factor now becomes

$$\begin{aligned}\ln g(N_1,N_2,\ldots,N_r,y) = -\sum_i N_i \ln N_i + \\ \ln [(z-1)/e]\sum_i(s_i-1)N_i + (\sum_i N_i) \ln (\sum_i s_iN_i) - \\ \sum_i N_i \ln y - \sum_i s_iN_i[(1-y)/y] \ln (1-y) \quad (8)\end{aligned}$$

In respect to the free-volume factor we adopt a simplification already introduced by Prigogine et al. in their theory of mixtures based on the cell model.[5] That is, the hard core volume v^* in eq 4 is simply replaced by an average $\langle v^*\rangle$, instead of dealing explicitly with the problem of packing differently sized spheres. Finally, the lattice energy $E_0(V,T,y)$ involves ϵ^* and v^* for the homogeneous fluid, viz.

$$2E_0 = yNqz\phi$$
$$\phi = \epsilon^*\{1.011[v^*/(yv)]^4 - 2.409[v^*/(yv)]^2\} \qquad (9)$$

This now becomes

$$2E_0 = yz\{\sum_i N_iq_iX_i\phi_{ii} + \sum_{i\neq k} N_iq_iX_k\phi_{ik}\} \qquad (10)$$

where the first sum includes all self-interactions determined in the pure components with X_i representing site fractions

$$X_i = x_iq_i/\sum x_iq_i$$
$$x_i = N_i/\sum N_i$$

The ϕ_{ij} are defined in analogy to eq 9 on replacing ϵ^* by ϵ_{ij}^*, and v^* by v_{ij}^*. It will be noted that the use of the X_i or of any other purely compositional quantity again presumes random mixing.

Equation 10 may be cast in the form prescribed by eq 9 on replacing ϵ^* by an average $\langle\epsilon^*\rangle$ and qz by the mean $\langle qz\rangle = \sum x_iq_iz$ and accepting the $\langle v^*\rangle$ from the free-volume factor. A comparison of the coefficients of v^{-2} and v^{-4} in eq 10 and the extended eq 9 yields the two relations[5]

$$\langle\epsilon^*\rangle\langle v^*\rangle^m = \sum_{i,k} X_iX_k\epsilon_{ik}^*(v_{ik}^*)^m$$
$$m = 2, 4 \qquad (11)$$

Since the parameters v_{ii}^* and ϵ_{ii}^* are determined by the pure components, eq 11 provides two relations for the computation of ϵ_{12}^* and v_{12}^* in a binary system. Otherwise studies of separate pair combinations are required.

Equations 8–10 yield the configurational Helmholtz free energy:

$$\begin{aligned}F_{\text{conf}} = -kT \ln Z_{\text{conf}} = \\ NkT \ln y + kT\sum s_iN_i[(1-y)/y] \ln (1-y) - \\ 3kT\sum c_iN_i\{\ln [(y\tilde{v})^{1/3} - 2^{-1/6}y] + \tfrac{1}{3} \ln \langle v^*\rangle\} + \\ \tfrac{1}{2}\sum N_i\langle qz\rangle\langle\epsilon^*\rangle(y\tilde{v})^{-2}[1.011(y\tilde{v})^{-2} - 2.409] \quad (12)\end{aligned}$$

Here we are concerned only with volume derivatives and we have omitted certain terms in the g factor; these, of

Table I
Characteristic Parameters: $xn\text{-}C_{16} + (1 - x)n\text{-}C_6$

x	C	10^5D	$\langle s\rangle$	$-A(\langle s\rangle)$	$B(\langle s\rangle)$	$\langle V^*\rangle$, cm^3/g	$\langle T^*\rangle$, K	$\langle P^*\rangle$, bar
0	0.11993	5.8654	2.5	0.12403	21.974	1.2763	5197	7201
0.2	0.11617	4.6978	3.2	0.10768	21.264	1.2509	5895	7088
0.4	0.10675	4.1373	3.9	0.10532	21.345	1.2362	6433	6993
0.6	0.09726	3.8212	4.6	0.10337	21.422	1.2222	6799	6878
0.8	0.09093	3.5780	5.3	0.10249	21.547	1.2134	7131	6813
1.0	0.08788	3.3680	6.0	0.10188	21.650	1.2090	7448	6785

course, must be included in the computation of compositional derivatives.

The pressure equation assumes the form

$$\tilde{P}\tilde{V}/\tilde{T} = [1 - 2^{-1/6}y(y\tilde{V})^{-1/3}]^{-1} + (2y/\tilde{T})(y\tilde{V})^{-2}[1.011(y\tilde{V})^{-2} - 1.2045] \quad (13)$$

The equation of state is completed by the minimum condition on the structure function y

$$(\langle s\rangle/3\langle c\rangle)[(\langle s\rangle - 1)/\langle s\rangle + y^{-1}\ln(1 - y)] = (1 - \eta)^{-1}(\eta - \tfrac{1}{3}) + (y/6\tilde{T})(y\tilde{V})^{-2}[2.409 - 3.033(y\tilde{V})^{-2}] \quad (14)$$

where $\eta = 2^{-1/6}y(y\tilde{V})^{-1/3}$, $\langle c\rangle = \sum x_ic_i$, and $\langle s\rangle = \sum x_is_i$. The scaling parameters in eq 13 and 14 retain the definitions, eq 1, when the parameters appearing therein are replaced by the averages introduced above and hence are now functions of composition. A consideration of mass balance, moreover, indicates that eq 2 is valid with a weight-average segmental molecular weight

$$\langle M_0\rangle = \sum s_ix_iM_{0i}/\sum s_ix_i \quad (15)$$

With $\langle M_0\rangle$ thus defined by the properties of the pure components, the scaling pressure $\langle P^*\rangle$ and thence the complete equation of state for the mixture are predicted, provided $\langle V^*\rangle$ and $\langle T^*\rangle$ are known from low-pressure ($P \rightarrow 0$) studies.

With the redefinitions indicated, eq 13 and 14 have the form previously derived for the homogeneous fluid.[4] In the limit $s \rightarrow \infty$, a principle of corresponding states is satisfied when a common value for the flexibility parameter is adopted. Beyond that, superposition of curves derived with different numerical values of c/s obtains.[4] This will ensure superposition of isotherms and isobars of different mixtures with different values of $\langle c\rangle/\langle s\rangle$. In regard to finite chains, superposition of the state functions for different s values onto those for $s \rightarrow \infty$ and hence on each other was demonstrated.[2a] Significant deviations at the highest temperatures were noted only for $s = 3$. We can therefore expect a principle of corresponding states to apply at all compositions and, with some limitations, for all chain lengths.

Consider finally the validity of a principle of congruence. It implies that the equation of state of the mixture in a homologous series should be identical with that of the homogeneous system of average chain length. We note that this is not strictly a sufficient condition, since other parameters are involved in the theoretical equation of state. In a series such as the n-paraffins, however, deviations arising from the averages of these parameters in eq 13–15 may be small. A numerical example is presented later.

Application: Binary Mixtures of *n*-Paraffins

An extensively studied system is the n-C_{16} + n-C_6 pair. The primary emphasis there, as well as more generally, has been on excess functions and critical phenomena. For our first application of theory recent investigations by Dymond et al.[6] are particularly suitable, since they extend beyond 4 kbar. Moreover, a sufficient range of compositions and temperatures is explored and the absolute densities of the mixtures are explicity given.

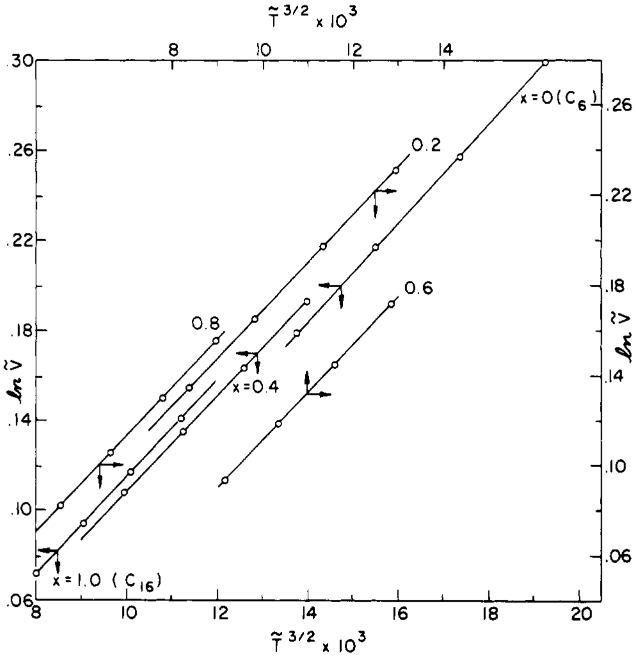

Figure 1. Reduced isobars of n-C_6, n-C_{16}, and their mixtures at atmospheric pressure: (—) eq 7; (O) experiment.

We begin with the atmospheric-pressure results. These can be cast in the form suggested by eq 7, viz.

$$\ln V = C + DT^{3/2} \quad (16)$$

In Figure 1 the appropriate plots for C_{16} ($x_1 = x = 1$) and C_6 ($x_2 = 1 - x$) are displayed over the whole experimental range, $298 \leq T \leq 373$. The construction of these graphs requires the numerical values of $A(s)$ and $B(s)$ in eq 7, and of c, in order to compute V^* and T^*. The previous assignments for C_9 and C_{17} were $s = 3.4$ and $s = 6.4$, respectively,[2] with $3c/(s + 3) = 1$, assuming an averaging of CH_3 and CH_2 units. For the present components this implies $s = 6.0$ and $s = 2.3$, if simple proportionality between s and n is accepted for $n < 9$. Actually, the best fit results from the assignment $s = 2.5$ for C_6, when elevated pressures are included (see below). With $A(s)$ and $B(s)$ determined from the theory, eq 5 and 6, by means of a least-squares procedure, we have

$$V^*(s) = \exp[C - A(s)]$$

$$T^*(s) = [B(s)/D]^{2/3} \quad (17)$$

Provided eq 16 applies to mixtures as well, eq 17 provides the scaling for each composition when $A(s)$ and $B(s)$ are determined from eq 13 and 14 with substitution of the appropriate $\langle s\rangle$ and $\langle c\rangle$ values.

The numerical values of the coefficients in eq 7 and 16 and the scaling parameters are exhibited in Table I, with the addition of the scaling pressure $\langle P^*\rangle$ (see below), where $3\langle c\rangle = \langle s\rangle + 3$.

The isobars for all compositions are plotted in Figure 1. The maximum differences between computed and

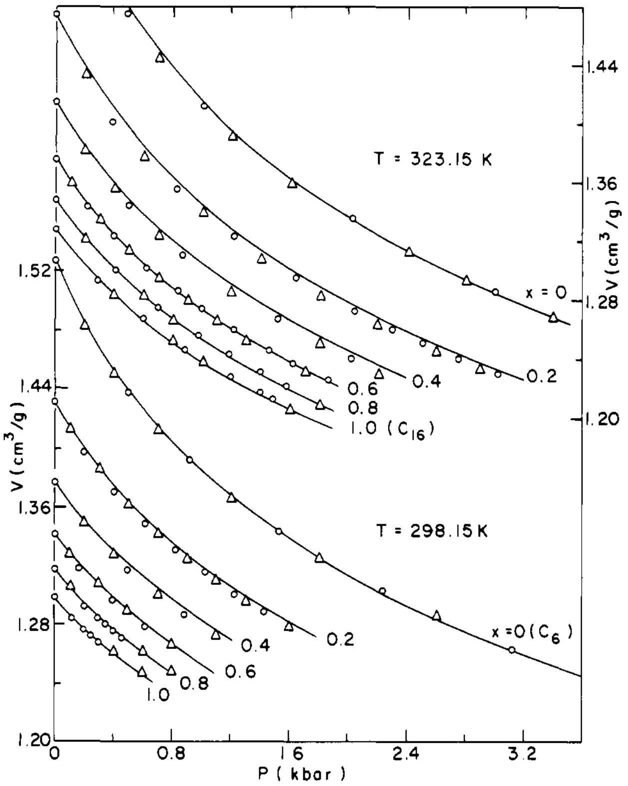

Figure 2. Isotherms of n-C_6, n-C_{16}, and their mixtures: (—) theory, eq 13 and 14; (○) experiment; (△) Tait eq 18.

measured volumes are 0.1% for C_6 and 0.02% for C_{16}. In gauging these departures, one should keep in mind, apart from experimental scatter, the accuracy of eq 16 and the approximation, eq 7. Deviations of similar magnitude as above are encountered for both relations. Larger deviations for the short chain lengths can be expected, due to the neglect of differences between CH_2 and CH_3. It is instructive to compare the characteristic values in Table I for the pure components with those derived from earlier data for C_6 and C_{16},[7] which extend over a wider temperature interval, viz., 100 and 200 K, respectively. These are $V^* = 1.2886$, 1.2080 and $T^* = 5304$, 7409, respectively. Rigorous theory yields maximum deviations of 0.06 and 0.05%, to be compared with similar experimental uncertainties quoted by the authors.[7] The approximation, eq 7, on the other hand, produces maximum deviations of 0.14 and 0.10%, respectively. This illustrates the limitations of this relation when applied to wide temperature intervals, particularly for small s values. The comparisons demonstrate the accuracy of the theory at atmospheric pressure and its sensitivity to differences between different sets of experiments. The approximation retains its usefulness by predicting thermal expansivities $\alpha = (3/2)B(s)(T/T^{*3})^{1/2}$ with maximum deviations of 3% from the empirical expressions[7] disregarding the extremes of the temperature range.

With V^* and T^* determined, the proper transformation of eq 2 (see eq 15) yields the scaling pressures P^* listed in Table I, and hence the theoretical isotherms for all compositions, without any further adjustments. The results are seen in Figures 2 and 3 together with the experimental data indicated by the circles. The largest departures, 0.8% in volume at the highest temperature, are again encountered for C_6. At 4 kbar this value has been reduced to 0.3% with a crossover similar to that observed earlier in C_9.[2a] Such a trend is also noted for C_{16}, however, with maximum deviations of only 0.14–0.3% over the entire temperature and pressure range. The influence of the larger departures in hexane persists up to $x = 0.6$. We conclude that the prediction of high-pressure isotherms for binary mixtures is quite satisfactory and should be even more so in the case of larger chain lengths.

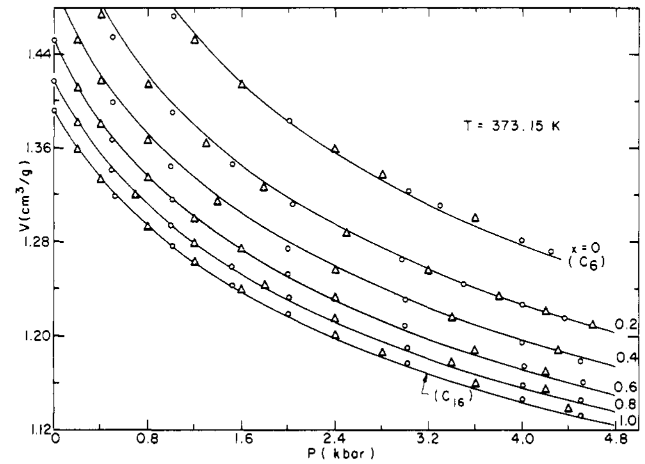

Figure 3. Isotherms of n-C_6, n-C_{16}, and their mixtures: (—) theory, eq 13 and 14; (○) experiment; (△) Tait eq 18.

Table II
Tait Parameters: xn-C_{16} + $(1 - x)n$-C_6

x	$10^{-3}B_0$	10^3B_1
0	11.708	10.324
0.2	8.608	8.468
0.4	8.738	7.900
0.6	7.037	6.860
0.8	7.214	6.640
1.0	7.088	6.380

For homogeneous fluids of low as well as high molecular weight, the empirical Tait equation has proven useful and convenient in the analysis of high-pressure isotherms. It is of interest then to examine its application to mixtures. The particular form previously adopted is

$$1 - V/V_0 = 0.0894 \ln [1 + P/B(T)] \tag{18}$$

with

$$B = B_0 \exp(-B_1T)$$

and V_0 the zero-pressure volume. When V_0 is taken from experiment, the results of eq 18 are seen as the triangles in Figures 2 and 3. The maximum overall deviation in V, including the pure components, is 0.3%, arising from fluctuations of B with P, and B_0, B_1 with T. It will be noted that in eq 18 we adhere to the "universal" value of the prelogarithmic factor, although an improvement might be obtained by treating it as an adjustable parameter. Table II displays the numerical values of B_0 and B_1 as a function of composition. Marked variations with respect to both parameters are noted between $x = 0$ and $x = 0.2$, and again between $x = 0.4$ and $x = 0.6$. Therefore fits by higher order polynomials with alternating signs would presumably be required. We have, however, found the following convenient expression to reproduce the B's in eq 18 with a maximum deviation of 2%, which amounts to less than the fluctuations of B over the entire pressure range:

$$B(x,T) = 3.91 \times 10^4 \exp(-0.01532T) + (1188 - 1.75T)x^{1/2}$$

$$0.2 \le x \le 1.0 \qquad 298 \le T \le 373 \tag{19}$$

The excess molar volumes

$$\Delta V_m = V_m - [xV_{1m} + (1 - x)V_{2m}] \tag{20}$$

Table III
Excess Volumes ($-\Delta V_m$, cm^3/mol) (P = 1 bar): xn-C$_{16}$ + $(1-x)n$-C$_6$

	T = 298.15 K			T = 323.15 K			T = 373.15 K			T = 313.15 K	
x	theory[a]	exptl	$\pm\delta(\Delta V_m)$	theory[a]	exptl	$\pm\delta(\Delta V_m)$	theory[a]	exptl	$\pm\delta(\Delta V_m)$	theory[a]	exptl[b]
0.2	0.65	0.59	0.03	0.89	0.82	0.07	1.71	1.73	0.07	0.71	0.633
0.4	0.60	0.65	0.04	0.91	0.88	0.09	1.79	1.77	0.09	0.77	0.737
0.6	0.46	0.49	0.05	0.64	0.61	0.10	1.21	1.19	0.10	0.57	0.600
0.8	0.34	0.30	0.06	0.40	0.35	0.12	0.64	0.59	0.12	0.36	0.335

[a] From solution of eq 13 and 14. Essentially identical results from eq 7. [b] From empirical relation, fitted by authors[8] to direct measurements.

Table IV
Characteristic Derived Parameters[a]

x	$\langle V_m^*\rangle$, cm^3/mol	$\langle\epsilon^*\rangle/k$, K	$\langle V_m^*\rangle_n$, cm^3/mol	$\langle\epsilon^*\rangle_n/k$ K	V_{12}^*, cm^3/mol	ϵ_{12}^*/k, K	$(V_{12}^*)_n$, cm^3/mol	$(\epsilon_{12}^*)_n/k$, K
0	44.00	352.9	18.33	147.0				
0.2	44.65	358.3	17.86	143.3	44.90	362.9	17.96	145.2
0.4	45.10	360.9	17.59	140.8	45.02	364.3	17.56	142.1
0.6	45.26	358.8	17.35	137.5	44.75	357.4	17.15	137.0
0.8	45.42	358.7	17.20	135.8	44.45	352.1	16.83	133.3
1.0	45.63	360.4	17.11	135.2				

[a] Subscript n refers to average repeat unit.

have been derived by Dymond et al.[6] from their absolute densities, rather than by direct measurement. Since the magnitudes of the ratio $\Delta V_m/V_m$ are less than 1%, deviations or inaccuracies in the individual terms in eq 20 are magnified. In Table III experimental and computed values of ΔV_m at atmospheric pressure are listed for three temperatures. Also shown are the maximum possible errors $\pm\delta(\Delta V_m)$ derived from the authors' stated error limits in their densities. Also included is a set of data obtained by direct measurement, with a stated maximum error of 0.003.[8] The gratifying agreement seen again illustrates the success of the theory.

Turning to elevated pressures, we have noted in Figures 2 and 3 enhanced departures with increasing temperature and pressure. Dymond et al. observed an inversion in sign, ΔV_m becoming positive at $x \geq 0.5$ and $P \simeq 2$ kbar. At 4 kbar, this changes to $x \gtrsim 0.35$. The change in sign is reproduced by the theory, albeit at different compositions. The theory, in accord with experiment, shows the reduction in $-\Delta V_m$ with increasing P at constant T. The authors indicated a reduced reliability of their indirectly determined excess volumes at elevated pressures. Our computed absolute volumes at elevated pressure include no further adjustment in scaling parameters, following the atmospheric-pressure analysis, but improvement in accuracy might be expected from a simultaneous determination of V^*, T^*, and P^*.

Finally, the existence of corresponding states is illustrated in Figure 4 for atmospheric pressure. The infinite s-mer is selected as the reference system for future use. The line represents eq 7 with $A(\infty) = -0.103\,35$ and $B(\infty) = 23.8345$ for $1.65 < \tilde{T} \times 10^2 < 7.03$. On application of eq 16 and 17 the points encompassing all compositions are obtained. A satisfactory superposition is seen with slight departures for hexane, x = 0. To the extent to which the theory describes the high-pressure isotherms in Figures 2 and 3, superposition will again result. An illustration of superposition at elevated pressures is seen in Figure 2 of ref 2a for a series of s values between 3 and ∞.

Characteristic Parameters

With the numerical information summarized in Table I at hand, it becomes of interest to examine the characteristic energy and volume parameters. From $\langle T^*\rangle$ for the components and the blends, the corresponding $\langle\epsilon^*\rangle$ are derived by means of eq 1. Application of eq 11 then yields v_{12}^* and ϵ_{12}^*. The results are recorded in Table IV. Two sets of quantities appear which refer to the average equivalent s-mer segment[1] and repeat unit of the average n-mer, respectively. Concerning the latter, we note the decrease of $\langle V_m^*\rangle_n = N_A\langle v^*\rangle_n$ between x = 0 and x = 1. This is to be ascribed to the difference between the v^* of CH$_3$ and CH$_2$, which in our present treatment has been averaged out.

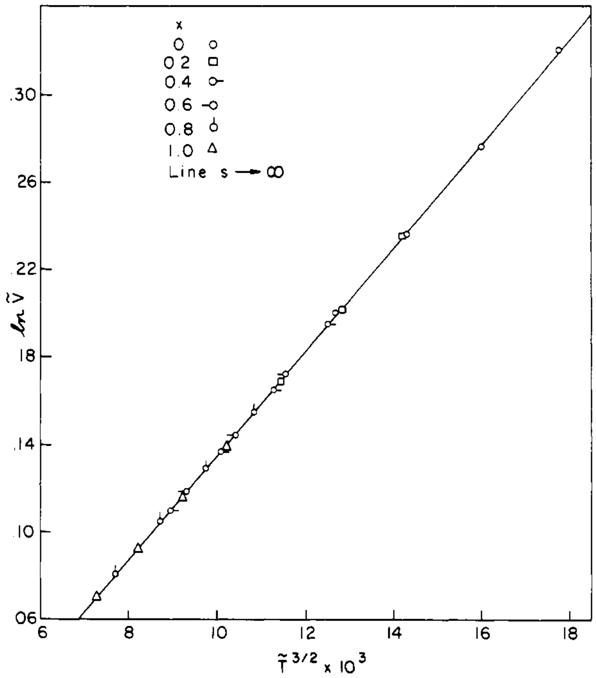

Figure 4. Reduced isobars of n-C$_6$, n-C$_{16}$, and their mixtures at atmospheric pressure, superimposed on theoretical isobar for an infinite chain.

A simple calculation will serve to determine the magnitude of the effect. For the comparison of the characteristic molar volumes V_m^*(CH$_3$) and V_m^*(CH$_2$), the averaged V_m^* for n-paraffins, n = 6,16 and n = 9,17, are available.[2] The pertinent equation is

$$\langle V_m^*\rangle_n = 2V_m^*(\mathrm{CH_3}) + (n-2)V_m^*(\mathrm{CH_2})$$

For reasons of consistency, only the pair n = 6,16 is con-

Table V
Comparison of Computed and Experimental Parameters

x	$\langle V_m{}^*\rangle_n$	$\langle V_m{}^*\rangle(x)$	$\langle T^*\rangle$	$\langle T^*\rangle(x)$
0	18.33	18.33	5197	5385
0.2	17.86	17.84	5895	5868
0.4	17.59	17.55	6433	6358
0.6	17.35	17.36	6799	6758
0.8	17.20	17.22	7131	7090
1.0	17.11	17.11	7448	7557

sidered with the result $V_m{}^*(CH_3) = 22.237$ and $V_m{}^*(CH_2) = 16.379$ cm^3/mol. Consideration of pairs 9,16 and 9,17 yields maximally differences of 0.3 and 1.5% in CH_2 and CH_3, respectively. The mean value $\langle V_m{}^*\rangle(x)$ for the blend of composition x then is

$$\langle V_m{}^*\rangle(x) = V_m{}^*(CH_2) + 2[V_m{}^*(CH_3) - V_m{}^*(CH_2)]/\langle n\rangle$$

with $\langle n\rangle$ the number-average chain length. The results are displayed in Table V and compared with $\langle V_m{}^*\rangle_n$ from Table IV. A substantial agreement between the second and third columns will be noted.

A similar argument for the composition dependence of $\langle\epsilon^*\rangle_n$ may be made, but we are not attempting a decomposition into methyl and methylene contributions which would be coupled to v^*. The primary segmental quantities $\epsilon_{12}{}^*$ and $v_{12}{}^*$ should strictly be invariant with concentration. Several factors may be responsible for the observed variations. First, there is a theoretical deficiency, due to the assumption of random mixing in eq 10. Considering the similarity of the $\epsilon^*{}_{ij}$ $(i, j = 1, 2)$ in Table IV, this should be a reasonable approximation. Another element is again the averaging of methyl and methylene interactions. Finally, eq 11 indicates the sensitivity of $\epsilon_{12}{}^*$ and $v_{12}{}^*$ to small differences between experiment and theory, which are magnified by the higher powers. No further comments are feasible in the absence of analyses on other mixtures, particularly of long-chain and/or chemically more distinct components.

The results of Table V have indicated the quantitative reasonableness of estimating scaling volumes from those of the pure components. If a similar estimate for $\langle T^*\rangle$ can be made, not only the high-pressure isotherms but the complete *PVT* function for any composition can be predicted, based on studies of the components. The average between $\epsilon_{11}{}^*$ and $\epsilon_{22}{}^*$ is 356.7, resulting in the approximations for $\langle T^*\rangle(x)$ obtained by means of eq 1 and shown in the last column of Table V. A maximum deviation of 1.5% between the last column and the exact $\langle T^*\rangle(x)$ from Table I in the preceding column ensues for $0.2 \le x \le 0.8$. The approximations in $\langle V^*\rangle(x)$ and $\langle T^*\rangle(x)$ yield a maximum error of 0.5% in V at the highest temperature and 0.2% at the lowest temperature, as derived from eq 7. Analogous simplifications can be explored for other systems and should again be most adequate for long-chain compounds. However, for accurate computations of ΔV, this approximation is not sufficient.

Finally, the approximate validity of the congruence principle, based on the theory, is illustrated by the following examples for the two compositions $x = 0.2$ and $x = 0.6$, corresponding to average chain lengths $n = 8$ and $n = 12$ and $s = 3.2$ and $s = 4.6$, respectively. The computed specific volumes at 298.15 K are 1.4305 and 1.3418, to be compared with 1.4314 and 1.3420 for n-C_8 and n-C_{12}, respectively.[9] At 333.15, the values are 1.4946 and 1.3905 vs. 1.4928 and 1.3895.

Table VI
Dependence of Thermal Expansivity on Composition: Polyethylene-n-C_{16}

x_1	w_1,[a] %	$3\langle c\rangle/\langle s\rangle$	$\langle T^*\rangle$, K	$B(\langle s\rangle)$	$\alpha(x_1)/\alpha(0)$
0	0	1.00	10812	23.83	1.00
0.900	6.8	1.03	10484	23.59	1.04
0.960	16.2	1.08	10060	23.37	1.09
0.990	44.4	1.22	8986	22.82	1.26
0.995	61.6	1.31	8441	22.53	1.37
0.998	80.1	1.40	7930	22.27	1.49
1.000	100.0	1.50	7448	21.65	1.75

[a] Weight fraction of C_{16}.

Table VII
Comparison of Computed Molar Excess Volumes for Polyethylene-n-C_{16} (A) and n-C_{16}-n-C_6 (B) Mixtures

	$T = 298.15$ K		$T = 373.15$ K	
w_1, %	$-\Delta V_m(A)$	$-\Delta V_m(B)$	$-\Delta V_m(A)$	$-\Delta V_m(B)$
44.4	4.1	0.64	5.2	1.72
61.6	2.2	0.59	2.9	1.79
80.1	1.0	0.46	1.3	1.30

Polyethylene + *n*-Hexadecane System

It is desirable to study the change in the properties of a polymer with the addition of an oligomer. In the absence, to our knowledge, of experimental *PVT* information for such a system, we may obtain reasonable estimates by using the preceding analysis and employing the results for the pure components. As a measure of the "plasticizing" effect of the low molecular weight additive, the thermal expansivity and the bulk modulus are available in the present context. Only the former is discussed here in terms of eq 7 for the polyethylene-C_{16} pair. The thermal expansivity α equals

$$\alpha = (3/2)B(\langle s\rangle)(T/\langle T^*\rangle^3)^{1/2} \qquad (21)$$

The compositional dependence of B and $\langle T^*\rangle$ involves the mean values $\langle qz\rangle$ and $\langle c\rangle$. Variations in $\langle\epsilon^*\rangle$ should be small in view of the results in Table IV and will be disregarded. The determination of $B(\langle s\rangle)$ requires the solution of the equilibrium condition, eq 14, on y for different values of $\langle c\rangle$ and $\langle s\rangle$. Numerical values in Table I indicate that only minor changes occur between the two extremes. Moreover, $B(\infty) = 23.8345$, provided the usual value of $3c/s = 1$ is maintained.[1] Hence the primary determining factor is $\langle T^*\rangle$, i.e., the ratio

$$\langle qz\rangle/\langle c\rangle = 2[5(s_1x_1 + s_2x_2) + 1]/(c_1x_1 + c_2x_2)$$

when $z = 12$. A previous evaluation yielded for the segment of polyethylene 2.26 CH_2 units,[10] compared with 2.67 for C_{16}. Variations in ϵ^*/k arise at least in part from these differences, viz., 326 vs. 360, and are reduced to 144 compared with 135 on a repeat-unit basis.

We disregard the above difference between the segments of the equivalent s-mers and assume that the segment of C_{16} represents polyethylene as well. Hence the ratio of the molecular weights M_1/M_2 equals s_1/s_2, where the index 1 refers to the short chain. With $s_1 = 6$, $c_1 = 3$, as determined for C_{16}, select $M_2 = 28054$ or $n = 2000$, $s_2 = 750$, $c_2 = 250$, and consider the ratio

$$\alpha(x_1)/\alpha(0) = [B(\langle s\rangle)/B(s_2)][T^*(0)/\langle T^*\rangle]^{3/2}$$

The substitution of the above values yields the results in Table VI, with $\langle\epsilon^*\rangle = 360.4$, the value for C_{16} in Table IV. No significant increase in the expansivity is observed below a weight fraction of 15%. At this stage, the segment ratio between the two components is 18%. A similar conclusion is reached in respect to the compressibility ratio.

Next we compare the excess volumes of this system in Table VII with the theoretical results derived from Table

Table VIII
Characteristic Parameters: $x\mathrm{CCl}_4 + (1-x)\mathrm{C}_6\mathrm{H}_{12}$

x	$-C$	10^5D	$\langle 3c \rangle$	$-A$	B	$\langle V^* \rangle$, cm³/g	$\langle T^* \rangle$, K	$\langle P^* \rangle$, bar
0	0.00957	4.7930	4.800	0.10234	18.603	1.1184	5321	7519
0.1289	0.10522	4.7957	4.761	0.10254	18.644	0.9973	5327	7566
0.2512	0.20566	4.7947	4.725	0.10273	18.683	0.9022	5335	7615
0.3720	0.29800	4.7896	4.688	0.10292	18.722	0.8228	5346	7668
0.4978	0.38865	4.7902	4.651	0.10313	18.764	0.7516	5354	7725
0.6506	0.49246	4.7978	4.605	0.10338	18.816	0.6777	5358	7792
0.7475	0.55481	4.7986	4.576	0.10354	18.849	0.6368	5363	7839
1	0.70749	4.8013	4.500	0.10399	18.940	0.5469	5379	7974

Table IX
Excess Molar Volumes ΔV_{m}:
$x\mathrm{CCl}_4 + (1-x)\mathrm{C}_6\mathrm{H}_{12}$ ($T = 303.15$ K)

x	theory	exptl[a]	exptl[b]
0.1289	0.074	0.073	0.071
0.2512	0.123	0.121	0.119
0.3720	0.162	0.147	0.148
0.4978	0.164	0.159	0.158
0.6506	0.155	0.149	0.144
0.7475	0.122	0.129	0.119

[a] Reference 11. [b] Reference 12.

III for the C_{16}–C_6 pair at the identical extreme temperatures and weight fractions. The latter correspond to mole fractions of C_{16} between 0.990 and 0.998 in the polymer mixture and only 0.23–0.61 in the other. In both systems $-\Delta V_{\mathrm{m}}$ increases with increasing temperature but remains larger for the polymer mixtures throughout. The reduced temperatures vary from 0.035 to 0.050 for the polymer mixtures and from 0.07 to 0.05 for the others at $T = 373$ K. However, even a comparison at equal $\tilde{T}$ will not change the qualitative picture.

Carbon Tetrachloride + Cyclohexane

The first component has been discussed previously,[3] with the parameters $s = 1$, $3c = 4.5$, $V^* = 0.5484$ cm³/g, $T^* = 5417$ K, and $P^* = 8009$ bar. The corresponding analysis of cyclohexane data[11] with $s = 1$ yields the following values: $3c = 4.8$, $V^* = 1.1184$ cm³/g, $T^* = 5321$ K, and $P^* = 7519$ bar. In both instances eq 7 is satisfied. We are slightly modifying the first set of parameters to $V^* = 0.5469$, $T^* = 5379$, and $P^* = 7974$, in order to be consistent with the CCl_4 data in ref 11.

Figure 5 displays the atmospheric-pressure isobars for $\mathrm{C}_6\mathrm{H}_{12}$ and its mixtures, plotted in conformity with the prescription of eq 7. Note that A and B differ for the two components, since the c's are different. Table VIII shows the quantities A, B, C, and D and the scaling parameters, with P^* obtained from eq 2 and 15. Computed and measured volumes differ maximally by 3×10^{-4} cm³/g. In Table IX experimental and theoretical molar excess volumes are compared. Two sets of data are displayed, namely, the results from ref 11 and direct measurements of ΔV_{m}, albeit at a slightly different temperature.[12] The latter authors report a temperature coefficient of 10^{-4} cm³/(mol K) for ΔV_{m} and hence our comparison is meaningful, considering the temperature difference of 5 K. A maximum deviation of 9% in two instances is accompanied by differences not exceeding 6% in all other cases.

Equations 1 and 11, combined with $\langle T^* \rangle$ and $\langle V^* \rangle$ in Table VIII yield the characteristic quantities exhibited in Table X. The interaction parameters V_{12}^* and ϵ_{12}^* are practically invariant with composition, the maximum deviations from the mean being 0.1%. We note that the smoothed value of V_{12}^* is rather close to the average $\{[(V_{11}^*)^{1/3} + (V_{22}^*)^{1/3}]/2\}^3 = 89.03$, with a difference of 0.5%.

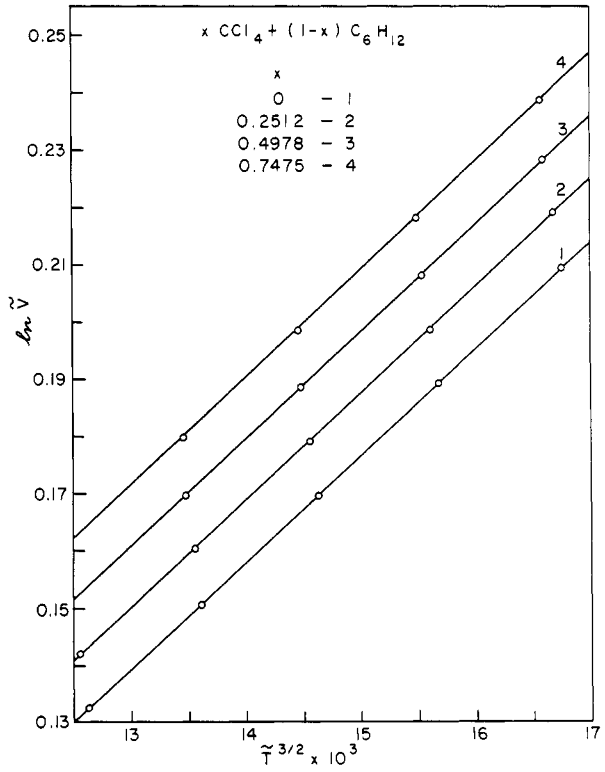

Figure 5. Reduced isobars of $\mathrm{C}_6\mathrm{H}_{12}$ and its mixtures with CCl_4 at atmospheric pressure: (—) eq 7; (O) experiment. The ordinate is shifted successively 0.01 between lines 2 and 4; T = 313–383 K.

Table X
Characteristic Derived Parameters: $x\mathrm{CCl}_4 + (1-x)\mathrm{C}_6\mathrm{H}_{12}$

x	$\langle V_{\mathrm{m}}^* \rangle$, cm³/mol	$\langle \epsilon^* \rangle / k$, K	V_{12}^*, cm³/mol	ϵ_{12}^*/k, K
0	94.13	709.5		
0.1289	92.89	704.5	88.48	699.4
0.2512	91.72	700.2	88.55	700.1
0.3720	90.57	696.2	88.64	700.9
0.4978	89.32	691.7	88.63	701.1
0.6506	87.75	685.3	88.57	699.5
0.7475	86.75	681.7	88.56	699.3
1.0	84.12	672.4		
			88.57[a]	700.1[a]

[a] Mean values.

No experimental information for the CCl_4–$\mathrm{C}_6\mathrm{H}_{12}$ pairs at elevated pressures has come to our attention. We display in Figure 6 theoretical and experimental[13] isotherms for $\mathrm{C}_6\mathrm{H}_{12}$ up to 2 kbar and 383 K, with an agreement similar to that seen in Figures 2 and 3. In the construction of the theoretical isotherms, V^* and T^* derived from ref 11 were used to predict P^*, since only two temperatures are given in ref 13. The CCl_4 component has been discussed previously.[3] Theoretical isotherms computed for a few compositions and 348 K have been included for illustration.

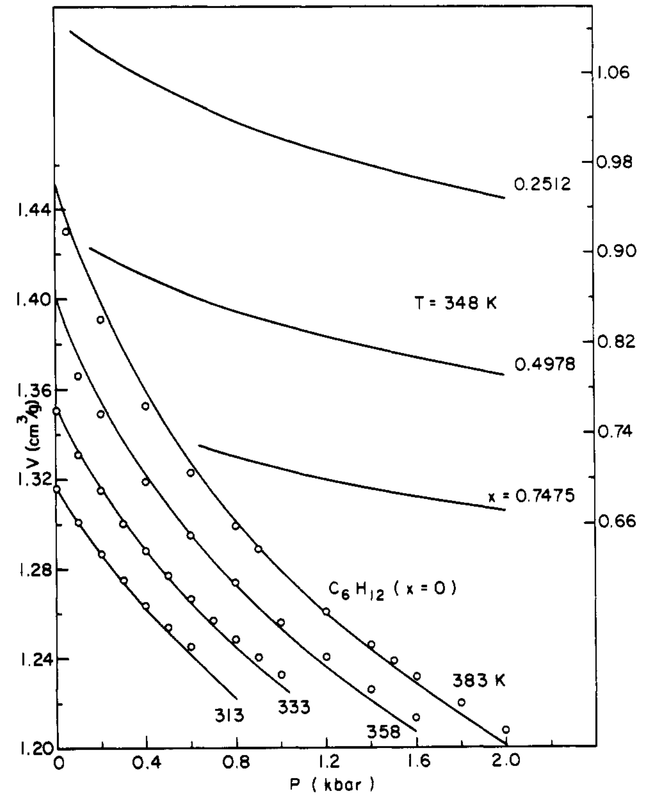

Figure 6. Theoretical and experimental isotherms of C_6H_{12} between 313 and 383 K and predictions for its mixtures with CCl_4 at 348 K. Circles from ref 13.

Conclusion

The theory is successful in accounting for the equation of state of the mixture based on information for the pure components and a minimum of data for the mixture. Specifically, predictions for elevated pressures can be derived from atmospheric isobars. However, refined numerical procedures are required for the simultaneous determination of all parameters, when atmospheric-pressure data for the liquid phase are not available. It remains to be seen what refinements must be introduced for more dissimilar pairs than those studied so far (see also earlier comments).

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Nonrandomness Binary Parameters for Polymer Solutions

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ABSTRACT: Thermodynamic functions of polymer solutions are studied with the assumption of nonrandom mixing. This nonrandomness approximation is based on the intuitive concept of local composition. Temperature dependence of local composition is studied, with the result that its quantitative influence on thermodynamic excess functions is small. An approximate expression for the combinatorial entropy is introduced in the model. Since this expression is also based on the concept of local composition, it is phenomenological. Two binary parameters are adjusted for each of the polymer solutions studied. These parameters, obtained by means of the nonrandomness approximation, represent simultaneously activity and heat-of-mixing data.

An approximation for nonrandomness in polymer-solution thermodynamics was proposed a few years ago.[1] This approximation was not rigorous but intuitive and phenomenological. It introduced very few modifications in the partition function given by Flory's one-fluid theory[2] in order to retain the theory's simplicity. The results obtained showed the interest of such an assumption and suggested new approaches treating the problem of nonrandomness. We study in this paper the influence of local site fractions and their temperature dependence on the thermodynamic excess functions. We also examine the expression for the combinatorial entropy used in ref 1 and propose an alternative expression for this function.

Following the usual notation, each of the N molecules of the system is considered to be divided into r segments with $3c$ external degrees of freedom[3] per segment. The hard-core volume of a segment, or characteristic volume, is denoted by v^*. The reduced volume is given by $\tilde{v} = v/v^*$, where v is the volume of a segment, which may be calculated from the volume of a molecule V by $v = V/r$.

Flory[2] introduced the partition function Z as

$$Z = Z_{\text{comb}}(rv^*)^{rNc}(\tilde{v}^{1/3} - 1)^{3rNc} \exp\{-E_0/kT\} \quad (1)$$

where E_0 is the intermolecular energy and Z_{comb} is the combinatorial factor which takes into account the number

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