

PVT Scaling Parameters for Polymer Melts.

II. Error in All Variables

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SYNOPSIS

An algorithm is discussed for determining best-fit scaling parameters in the *PVT* equation of state of polymer melts from experimental data. The underlying theoretical expressions are those employed in our preceding work. There it was assumed that values of pressure and temperature are known exactly and experimental uncertainty was admitted in the volume solely. This condition is now relaxed to allow for errors in *P* and *T* also. The methodology developed involves multiple small nonlinear fitting problems for two or three unknowns at a time. We employ it on the experimental data base in the earlier work, which consists of 11 polymer melts. To these is added ethylene monomer, analyzed earlier by Nies et al. by different methods. The numerical values of the scaling parameters differ by at most a fraction of a percent from those in the earlier computations and enhance the accuracy of fit but slightly. The significant improvement over the consecutive procedure (analysis of atmospheric pressure isobar, followed by isotherms at elevated pressures), seen earlier, continues therefore. The scaling parameters so obtained should represent the ultimate in computational accuracy consistent with a specified experimental accuracy. This may have a bearing ultimately on the issue of modeling molecular characteristics, expressed through the scaling parameters, versus macroscopic properties. Using the parameters determined here, it is shown that the entropy is correlated with the scaling temperature and that the flexibility parameter is related to polymer complexity.

INTRODUCTION

Simha-Somcynsky (SS) scaled *PVT* theory¹ requires superposition of a theoretical $\tilde{P}\tilde{V}\tilde{T}$ surface onto an experimental *PVT* surface, and the same procedure is required for other scaled equations of state as well. The original methodology simplified matters by employing a two-step procedure. The first step uses the atmospheric pressure isobar, yielding the scaling volume and temperature. Then, consideration of elevated pressure isotherms determines the scaling pressure *P**. This usually requires averaging over *P** values with a spread of a few percent. A detailed description is given in Ref. 2. This consecutive fit procedure, while operationally con-

venient, is inconsistent by giving undue weight to the atmospheric pressure data.

Recently, the present authors computed the scaling parameters for a series of polymer melts using a simultaneous fit procedure that considers all the data.² The new values of these parameters generally differed from the consecutive fit values by a few percent. However, there was a significant improvement in the quality of the predicted volume, often by a factor of two in $\langle |\Delta V| \rangle$, the mean of the absolute value of the difference between the calculated and experimental volume. In the simultaneous fit, as with the consecutive fit, all of the experimental uncertainty is assumed to reside solely in the volume.

This limitation is eliminated by a simultaneous inclusion of the whole *PVT* surface and the derivation of the scaling parameters by means of minimum deviation methodology given explicit knowledge of the relative accuracy in the measurements of volume, pressure, and temperature. This ap-

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proach, accounting for error in all the measured quantities, has been carried out for ethylene monomer³ and for polystyrene and other polymers.⁴

The purpose of this paper is to develop and apply a robust computational procedure that allows for stated experimental uncertainties in all three variables of state. Besides providing a definitive insight into the quantitative performance of the theory, this procedure assumes an added importance in connection with the thermodynamics of multiconstituent systems, including those with miscibility gaps, where there is high sensitivity to numerical parameter variation.⁵

In the next section, we recapitulate the basic equations of the Simha-Somcynsky (SS) theory and the Bruce-Hartmann (BH) scaled equation of state.⁶⁻⁸ Following this, our computational algorithm is described. Results for the 11 polymer melts and ethylene monomer considered in Ref. 2 are then presented. We conclude with a discussion of the findings.

THE EQUATIONS OF STATE

The SS equation is based on a lattice model, containing a fraction $1 - y$ of unoccupied sites or holes. In terms of reduced variables \tilde{P} , \tilde{V} , and \tilde{T} , it has the form

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

where $Q = 2^{-1/6}y(y\tilde{V})^{-1/3}$. The function y depends on volume and temperature in a manner determined by the principle of minimum free energy. The resulting equation is

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

Here, s is the number of segments per chain and $3c$ is the number of effective external degrees of freedom.

The scaling parameters are related by the equation

$$(P^*V^*/T^*)M_0 = (c/s)R \quad (3)$$

where M_0 is the molecular mass of the chain segment and R is the gas constant. This segment is defined by eq. (3) for a given numerical assignment to the

ratio c/s . For large chains and a homogeneous system, s tends to infinity and $3c = s$ has been conventionally assumed. For finite chain lengths, as in oligomers or monomeric-type molecules, the parameters s and c must also be specified. The preassignment of a numerical value to s is one possibility, for example, $s = 1$ in the case of ethylene.³ One may then consider c as a fourth parameter to be determined. For short chains, $3c = s + 3$ is the assignment consistent with that for the infinite chain. In any case, then, the determination of all parameters requires the inclusion of eq. (3) as an auxiliary condition to be satisfied. We note the relation $sM_0 = nM_{\text{rep}}$, where M_{rep} is the molecular mass of the repeat unit of the n -mer. For the infinite chain, M_0 is directly determined. In other instances, it is eliminated by means of this relation, and eq. (3) then becomes an auxiliary condition to be satisfied by the five parameters V^* , T^* , P^* , s , and c .

We turn next to the BH equation of state:

$$\bar{P}\bar{V}^5 = \bar{T}^{3/2} - \ln \bar{V} \quad (4)$$

involving the scaling parameters P_0 , V_0 , and T_0 . These scaling parameters have been determined with a consecutive fit method⁷ and a simultaneous fitting procedure (with error in volume only).²

ERROR IN VARIABLES ALGORITHM

We implement an error in all variables least square fit⁹⁻¹¹ for obtaining P^* , V^* , and T^* using the following procedures: Let current estimates for P^* , V^* , and T^* be given. For each of the $i = 1, \dots, N$ experimental data points (P_i, V_i, T_i) with known standard deviations for the measurement errors $\sigma_i(P)$, $\sigma_i(V)$, and $\sigma_i(T)$, we find the square of the weighted distance between (P_i, V_i, T_i) and the SS surface, defined to be D_i^2 , the minimum of the expression S_i^2 in eq. (5) below over all (P, V, T) values satisfying eqs. (1) and (2) [for "infinite chain" molecules, we set $3c = s$ and $(s-1)/s = 1$, whereas for our calculations with ethylene, we took $s = 1$ and $c = P^*V^*/(2.964T^*)$],

$$S_i^2 = (P - P_i)^2/\sigma_i(P)^2 + (V - V_i)^2/\sigma_i(V)^2 + (T - T_i)^2/\sigma_i(T)^2 \quad (5)$$

Let (P_{si}, V_{si}, T_{si}) denote the point on the SS surface where the minimum of S_i^2 is attained. Define the sum of the squares of the weighted distances D_i by

$$SSQ = SSQ(P^*, V^*, T^*) = \sum_{i=1}^N D_i^2 \quad (6)$$

The error in variables least square fit values for P^* , V^* , and T^* are, by definition, the (P^*, V^*, T^*) triple for which SSQ attains its least value. Note that if for $i = 1, \dots, N$, $\sigma_i(P)$, $\sigma_i(V)$, and $\sigma_i(T)$ are replaced by proportional values (i.e., they are all multiplied by the *same* constant), there is no effect on the (P^*, V^*, T^*) triple that minimizes SSQ , so one only needs to know relative standard deviations to obtain P^* , V^* , and T^* .

The approach described above is somewhat different from global Newton-type methods such as used by Britt and Luecke,⁹ Lybanon,¹¹ and Nies et al.³ for doing error in variables fitting. With the latter approach, P^* , V^* , T^* , and (P_{si}, V_{si}, T_{si}) , $i = 1, \dots, N$, are all iterated simultaneously, in which case one may encounter severe difficulties in finding starting values with which convergence will be obtained. Our approach, described in detail below, has the substantial advantage that it breaks up this fitting problem into multiple *small* nonlinear problems (two or three unknowns at a time) that can be solved without too much difficulty while using only moderate amounts of computer time.

Given current values for P^* , V^* , and T^* , for each of the $i = 1, \dots, N$ experimental data points, we obtained (P_{si}, V_{si}, T_{si}) as follows: First, observe that, given values for V and T , one can numerically solve the SS equations for $P = P(V, T)$ by solving eq. (2) for $y = y(V, T)$ to within 10^{-12} using the method of bisection; eq. (1) then determines P explicitly. Thus, S_i^2 in eq. (5) is reduced to a function of the two variables V and T :

$$S_i^2 = [P(V, T) - P_i]^2 / \sigma_i(P)^2 + (V - V_i)^2 / \sigma_i(V)^2 + (T - T_i)^2 / \sigma_i(T)^2 \quad (7)$$

At the minimum of S_i^2 , one has zero values of its partial derivatives, viz.

$$\frac{1}{2} \frac{\partial S_i^2}{\partial V} = \frac{[P(V, T) - P_i]}{\sigma_i(P)^2} \frac{\partial P}{\partial V} + \frac{(V - V_i)}{\sigma_i(V)^2} = 0$$

$$\frac{1}{2} \frac{\partial S_i^2}{\partial T} = \frac{[P(V, T) - P_i]}{\sigma_i(P)^2} \frac{\partial P}{\partial T} + \frac{(T - T_i)}{\sigma_i(T)^2} = 0 \quad (8)$$

where partial derivatives with respect to V or T are assumed to be evaluated holding the other variable (T or V) constant. Given values for V and T (and

values for P^* , V^* , and T^*), one has $y(V, T)$ (obtained numerically), and by differentiating both sides of eq. (2) with respect to V and with respect to T , one can (with routine algebra) find analytical expressions for $\partial y / \partial V$ and $\partial y / \partial T$, respectively, in terms of V and T [and $y = y(V, T)$]. Then, differentiating eq. (1) with respect to V and T produces analytical expressions for $\partial P / \partial V$ and $\partial P / \partial T$ in terms of V and T [and $y = y(V, T)$]. Thus, eq. (8) is effectively a system of two equations in the two unknowns V and T , which we solved for V_{si} and T_{si} using a nonlinear equation solver (ZSPOW from the International Mathematical and Statistical Libraries, Inc. [IMSL] software library with eight significant digits requested). That the solution of eq. (8) thus obtained was indeed a (local) minimum of S_i^2 was checked by comparing with the value of S_i^2 at a few nearby (V, T) points. For any given values for P^* , V^* , and T^* , the above approach provides a method for evaluating $SSQ(P^*, V^*, T^*)$. To obtain the (P^*, V^*, T^*) minimizing SSQ , we employed the nonlinear least square fit routine ZXSSQ from IMSL (with five significant digits requested, EPS = DELTA = 0, IOPT = 1). It should be emphasized that using this approach means that ZXSSQ is only searching for the three unknowns, P^* , V^* , and T^* , while each of the N "inner" nonlinear problems to find V_{si} and T_{si} [and $P_{si} = P(V_{si}, T_{si})$] minimizing S_i^2 involves only the two unknowns V_{si} and T_{si} .

The values for P^* , V^* , and T^* obtained by error in volume alone fitting² provided successful initial guesses for our error in variables fitting. The experimental values V_i and T_i generally provided adequate initial guesses for V_{si} and T_{si} for the first time S_i^2 was minimized, i.e., eq. (8) was solved. Thereafter, the most recent values of V_{si} and T_{si} were used [recall that each time ZXSSQ adjusts (P^*, V^*, T^*) , the values of V_{si} and T_{si} will change]. However, for atmospheric pressure data (P_i nominally 1 bar), this was not always sufficient. Hence, for the first time eq. (8) was solved for a data point with $P_i < 10$ bar, and whenever convergence failed in ZSPOW, S_i^2 was evaluated at each member of a 56 by 50 rectangular grid of points (V_j, T_k) centered at (V_i, T_i) with V -length $10\sigma_i(V)$ and T -length $40\sigma_i(T)$ (the lengths were rather arbitrary). The initial guess then used for the solution of eq. (8) was the (V_j, T_k) point in the grid for which S_i^2 had the least value.

For the polymer data sets corresponding to Table I, atmospheric pressure data were taken at ambient pressure rather than in a controlled pressure vessel, as was the case for the higher pressure data. We therefore took $\sigma_i(P)$ to be 0.02 bar for the atmo-

spheric pressure data points, in consideration of the effects of local height above sea level and meteorological variation [$\sigma_i(P)$ for the higher pressure data was typically $0.005 P_i$]. For example, a change in altitude of 700 feet (the approximate height above sea level of Cleveland, Ohio, where much of the data under consideration was taken) decreases the ambient pressure by roughly 0.027 bar, and a modest change in barometric pressure of 0.4 in.Hg is equivalent to a change of 0.013 bar. For the polymers where convergence of our algorithm was also obtained using, for the atmospheric pressure data, the formula for $\sigma_i(P)$ given for the higher pressure data, there was no significant change in the resulting P^* , V^* , T^* , and SSQ values (up to the number of significant digits reported in Table I). These values were also not significantly affected when $\sigma_i(P) = 0.04$ bar was used for the atmospheric pressure data in several test runs. The special considerations required for the atmospheric pressure data have not been noted before and may explain why these data are the hardest to fit to theory.¹²

One essential test that we conducted on our computer code was to fix P^* , V^* , and T^* values, take several (V_i, T_i) values, and then use the SS equations to compute the corresponding $P_i = P(V_i, T_i)$ values. Initial guesses for the V_{si} , T_{si} , and P^* , V^* , T^* were taken different from the predetermined exact values, and it was verified that our program effectively produced the exact values. We also checked that the

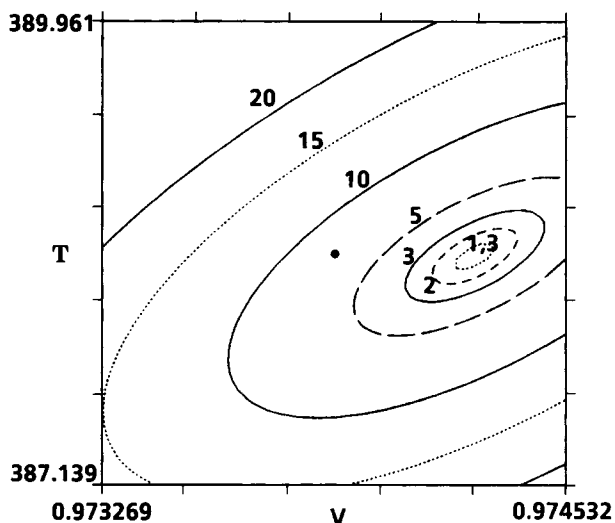


Figure 1 Contour plot of S_i for the polystyrene data point $P_i = 200$ bar, $V_i = 0.9739$ cm³/g, $T_i = 388.55$ K, with $P^* = 6985$ bar, $V^* = 0.9628$ cm³/g, $T^* = 12,788$ K, $\sigma_i(P) = 0.005P_i$, $\sigma_i(V) = 0.0004V_i$, and $\sigma_i(T) = 0.1$ K. The dot is at (V_i, T_i) .

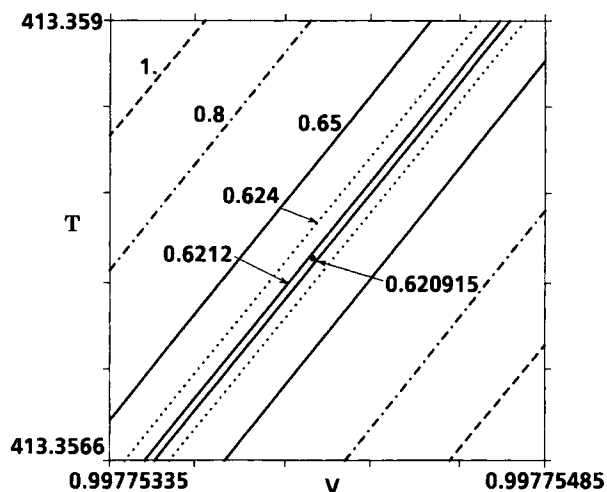


Figure 2 Contour plot of S_i for the polystyrene data point $P_i = 1$ bar, $V_i = 0.9980$ cm³/g, $T_i = 413.35$ K, with $P^* = 6985$ bar, $V^* = 0.9628$ cm³/g, $T^* = 12,788$ K, $\sigma_i(P) = 0.02$ bar, $\sigma_i(V) = 0.0004V_i$, and $\sigma_i(T) = 0.1$ K.

results in Table I were independent of the initial guess for (P^*, V^*, T^*) . These error in variables runs generally took under 1 min of CPU time on a CDC 875 main frame computer compared with a few seconds for the error in volume only runs.

If one examines contour plots of S_i [eq. (7)] as a function of V and T , one finds that relative to axis systems where $\rho \equiv$ (number of degrees K per unit distance along the T axis of the plot/number of cm³/g per unit distance along the V axis of the plot) is similar, the contour profiles of S_i are much more eccentric for atmospheric pressure data points (cf. Figs. 1 [$\rho = 2234$] and 2 [$\rho = 1600$]). It is well known that this can make the corresponding minimization problem more difficult, so the necessity of resorting to preliminary searching through a table of values to obtain an adequate initial guess for V_{si} and T_{si} for the atmospheric pressure data is not surprising.

Fitting to the BH equation of state was accomplished in a similar fashion, though the algorithm is less complicated due to the simpler form of the model.

EVALUATION OF SCALING PARAMETERS

The polymer melt experimental data selected for analysis were all available in tabulated form, rather than only graphically or as the parameters of an equation such as the Tait equation or an interpolation polynomial. There was no selection of the

data; all the experimental values reported were entered into data files. The source for three polyethylenes and three acrylate polymers are measurements of Olabisi and Simha.¹³ The former are linear (LPE), branched (BPE), and high molecular weight linear polyethylene (HMWLPE). The acrylates are poly(methyl methacrylate) (PMMA), poly(cyclohexyl methacrylate) (PCHMA), and poly(*n*-butyl methacrylate) (PnBMA). For polystyrene (PS) and poly(*o*-methyl styrene) (PoMS), data were taken from Quach and Simha,¹⁴ and for poly(vinyl acetate) (PVAc), from McKinney and Goldstein.¹⁵ For poly(dimethyl siloxane) (PDMS), we have the observations of Kubota and Ogino¹⁶ with room temperature as the reference state and those of Shih and Flory at room temperature.¹⁷ The combination of information from two sources was unavoidable in this instance, due to the lack of suitable tabulated data. Finally, there are the measurements on *cis*-1,4-polybutadiene (PBD) by Barlow.¹⁸

For the first eight polymers discussed above, we used standard deviations equal to the measurement error bounds given in the experimental papers: $\sigma_i(P) = 0.005P_i$, $\sigma_i(V) = 0.0004V_i$, and $\sigma_i(T) = 0.1$ K. [$\sigma_i(P) = 0.02$ bar for atmospheric pressure data points for all eleven polymers.] For PVAc, $\sigma_i(P) = 2$ bar, $\sigma_i(V) = 0.00001V_i$, and $\sigma_i(T) = 0.25$ K. For PDMS, $\sigma_i(P) = 0.005P_i$, $\sigma_i(V) = 0.0002V_i$, and $\sigma_i(T) = 0.01$ K, except that for atmospheric pressure data, $\sigma_i(P) = 0.02$ bar, $\sigma_i(V) = 0.0001$ cm³/g, and $\sigma_i(T) = 0.01$ K. For PBD, $\sigma_i(P) = 0.001P_i$, $\sigma_i(V) = 0.001V_i$, and $\sigma_i(T) = 0.2$ K.

Values of scaling parameters for the SS equation are listed in Table I. For each polymer, three sets of scaling parameters are given. The first set of values are the present calculations for error in all variables, the second set of values is for error in volume only, and the third set of values is for the consecutive fit algorithm. For each set of scaling parameters, a measure of the quality of the fit is also given. The measure used is the sum of the squares of the dimensionless distances from the experimental points to the Simha–Somcynsky theoretical surface divided by the number of experimental points. The quantity *SSQ* is the value being minimized by the algorithm used here. As such, it is smallest for the first set of scaling parameters. The error in volume only produces slightly worse fits. (Note that the quality-of-fit parameter used in the previous paper² was the average of the absolute value of the difference between calculated and experimental volumes.) The consecutive fit procedure is significantly poorer than either of the simultaneous fit algorithms.

Scaling parameters for the BH equation, for the same set of polymer melt data, are listed in Table II. As can be seen, the same qualitative behavior is observed here as with the SS equation. There is a small improvement in the quality of the fit using the error in all variables methodology compared with the error in volume only algorithm. The consecutive fit algorithm gives noticeably worse fits. The SS equation gives a better fit than does the BH equation in the majority of polymers, though both equations of state generally fit the data within the experimental uncertainty of the measurements.

Results for ethylene monomer are given in Table III. The data fitted were taken from Douslin and Harrison¹⁹ in the region from 10 to 150°C and in the pressure range up to about 350 bar, a total of 62 points. These data are near the critical region, where ethylene behaves more like a compressed gas than like a liquid. The standard deviations quoted by the authors for this system are $\sigma_i(P) = 0.0006$ bar, $\sigma_i(V) = 0.0008V_i$, and $\sigma_i(T) = 0.0005$ K. As compared with the Nies et al.³ results, we have a significant improvement. It is interesting that even though the SS and BH equations give almost identical results for a wide range of polymer melts, the BH equation cannot fit the ethylene data. Even though the BH equation works well for polymer melts and even for low molecular weight liquids²⁰ such as pentane, hexane, and heptane, the behavior of this gaslike material cannot be modeled by the BH equation. The SS equation, although not as accurate in this case as it is for polymer melts, still gives qualitatively acceptable results.

Having best values for scaling parameters, we now reexamine two correlations previously reported based on consecutive fit parameters. The first correlation is between the natural log of the scaling entropy factor $S^* = P^*V^*/T^*$ and the scaling temperature T^* . Although this empirically observed correlation²¹ holds only within the T^* range 9200 K < T^* < 13,000 K, the relation is of significant practical utility since one can estimate P^* from knowledge of V^* and T^* . Hence, elevated pressure behavior can be predicted from atmospheric pressure measurements. Using the scaling parameters determined here, the correlation is shown in Figure 3. The line is a least squares fit to the 10 polymer melts that fall within the T^* range of validity. PDMS is not on the line since its $T^* = 4795$ K. The line in Figure 3 is given by

$$\ln(P^*V^*/T^*) = 1.359 - 1.530 \times 10^{-4}T^* \quad (9)$$

Table I SS Scaling Parameters

	P^* (bar)	V^* (cm ³ /g)	T^* (K)	SSQ/N
Polystyrene	7157	0.9626	12,781	0.9
	7155	0.9627	12,791	0.9
	7453	0.9598	12,680	3.7
Poly(<i>o</i> -methyl styrene)	7503	0.9790	12,922	1.5
	7499	0.9793	12,940	1.5
	7458	0.9762	12,740	2.8
Poly(methyl methacrylate)	9292	0.8363	11,899	0.2
	9291	0.8363	11,900	0.2
	9147	0.8370	11,920	0.7
Poly(cyclohexyl methacrylate)	8039	0.8985	11,701	3.6
	7994	0.8993	11,740	3.6
	8382	0.8906	11,290	6.0
Poly(<i>n</i> -butyl methacrylate)	8272	0.9341	10,179	3.8
	8234	0.9346	10,200	3.9
	8456	0.9299	9,990	7.5
Polyethylene (branched)	7015	1.1626	10,234	5.1
	6979	1.1639	10,270	5.2
	6946	1.1600	10,140	7.3
Polyethylene (linear)	7773	1.1397	9,747	2.8
	7788	1.1399	9,750	3.0
	7478	1.1417	9,770	6.1
Polyethylene (high MW linear)	9027	1.1282	9,195	4.4
	9041	1.1287	9,210	4.5
	8968	1.1285	9,205	4.8
Poly(vinyl acetate)	9470	0.8129	9,359	1.2
	9467	0.8132	9,380	1.5
	9380	0.8141	9,420	1.8
Poly(dimethyl siloxane)	4795	0.9579	7,840	0.8
	4774	0.9584	7,850	1.0
	4739	0.9593	7,870	2.8
<i>cis</i> -1,4-Polybutadiene	8266	1.0749	9,155	0.1
	8256	1.0751	9,170	0.1
	7714	1.0861	9,644	0.5

For each polymer, the first line is for error in all variables fit, the second line is for error in volume only, and the third line is for consecutive fit.

with a coefficient of determination $r^2 = 0.90$. The line is in close agreement with the previous result.²¹

$$\ln(P^*V^*/T^*) = 1.319 - 1.493 \times 10^{-4}T^* \quad (10)$$

which was based on fitting to a series that included not only polymers but also oligomers, and the scaling parameters were determined using a consecutive fit

procedure. A similar correlation is observed between $\ln S_0 = \ln(P_0V_0/T_0)$ and T_0 as shown in Figure 4. As before, PDMS is an exception. The line in Figure 4 is given by

$$\ln(P_0V_0/T_0) = 4.506 - 0.001075T_0 \quad (11)$$

with $r^2 = 0.88$.

Table II BH Scaling Parameters

	P_0 (bar)	V_0 (cm ³ /g)	T_0 (K)	SSQ/N
Polystyrene	29,800	0.8724	1574	2.4
	29,600	0.8742	1591	2.5
	28,900	0.8683	1540	16.8
Poly(<i>o</i> -methyl styrene)	31,200	0.8858	1579	2.2
	31,000	0.8878	1596	2.3
	32,000	0.8788	1523	3.2
Poly(methyl methacrylate)	38,500	0.7567	1454	0.4
	38,100	0.7581	1466	0.4
	37,900	0.7539	1430	3.6
Poly(cyclohexyl methacrylate)	31,900	0.8156	1446	7.8
	30,900	0.8215	1490	9.1
	32,900	0.8038	1366	19.4
Poly(<i>n</i> -butyl methacrylate)	32,000	0.8494	1265	19
	31,300	0.8537	1291	23
	32,900	0.8390	1208	43
Polyethylene (branched)	26,100	1.0567	1265	7.1
	25,400	1.0635	1293	7.9
	27,600	1.0456	1221	11.2
Polyethylene (linear)	28,300	1.0341	1196	1.1
	28,200	1.0361	1203	1.3
	28,700	1.0294	1179	1.5
Polyethylene (high MW linear)	32,400	1.0222	1123	1.7
	32,300	1.0241	1129	1.9
	32,700	1.0189	1112	2.0
Poly(vinyl acetate)	38,200	0.7367	1150	1.3
	38,200	0.7369	1151	1.5
	38,800	0.7349	1139	2.3
Poly(dimethyl siloxane)	18,600	0.8690	965	2.9
	17,900	0.8749	989	6.6
	17,900	0.8650	950	75.3
<i>cis</i> -1,4-Polybutadiene	34,400	0.9797	1163	0.1
	34,900	0.9788	1159	0.1
	31,000	1.0003	1309	1.7

For each polymer, the first line is for error in all variables fit, the second line is for error in volume only, and the third line is for consecutive fit.

The second correlation involves the flexibility parameter s/n , which is the ratio of the number of effective segments to the number of repeat units in the chain. Effective segments are determined by the number of effective external (i.e., volume-dependent) degrees of freedom and, hence, should be related to the complexity of the repeat unit. From eq. (3) and the relations $3c = s$ and $sM_0 = nM_{\text{rep}}$ previously given, it follows that

$$s/n = 3P^*V^*M_{\text{rep}}/RT^* \quad (12)$$

$$s/n = S^*M_{\text{rep}}/27.7 \quad (13)$$

Values of M_0 and s/n for the 11 polymer melts are listed in Table IV, in order of increasing s/n ; hence, presumably, in order of increasing molecular complexity. (Note that M_{rep} here is the molecular weight of the polymer repeat unit rather than the average

Table III Simha–Somcynsky (SS) Scaling Parameters for Ethylene (High-Density Region)

	Nies et al. ³	This Work
V^* (cm ³ /g)	1.4647	1.4821
T^* (K)	3274	3369
P^* (bar)	4583	4345
c	0.692	0.645
s	1	1
SSQ/N	44	22

molecular weight per backbone carbon atom, as was previously reported.²²) We note that while the numbers are somewhat different than before, the ordering of the polymers is unchanged. Although the idea of polymer “complexity” is only qualitative, there does seem to be the expected increase from the simplest, polyethylene, to the polymers with the most complicated pendant groups: PCHMA and PNBMA.

CONCLUSIONS

Scaling parameters for 11 polymer melts and ethylene monomer have been determined using a simultaneous fit algorithm that allows for experimental error in all the experimental variables (pressure, volume, and temperature). The calculations were carried out for both the SS and BH equations of state. We conclude that

- The error in variables technique is the most accurate method of extracting scaling parameters from experimental PVT data.

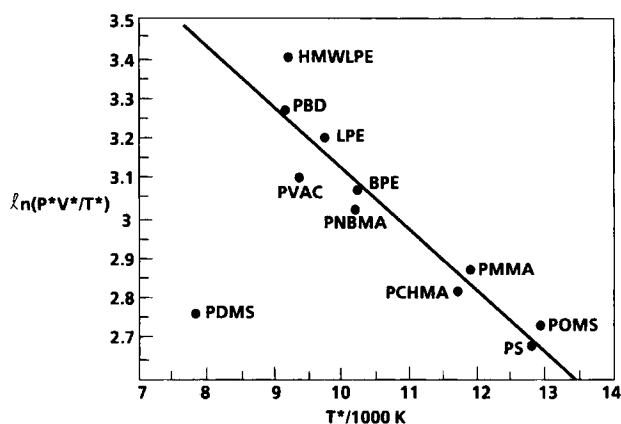


Figure 3 $\ln(P^*V^*/T^*)$ vs. T^* for polymer melts using parameters determined by the error in all variables algorithm.

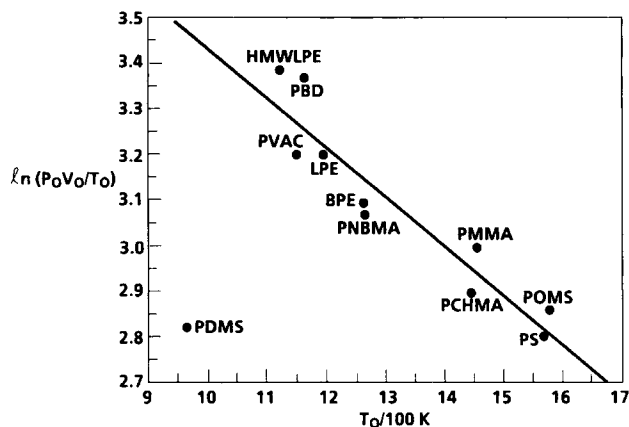


Figure 4 $\ln(P_0V_0/T_0)$ vs. T_0 for polymer melts using parameters determined by the error in all variables algorithm.

- A particularly attractive algorithm for implementing this procedure has been developed that involves multiple small nonlinear fitting problems, for two or three unknowns at a time.
- The scaling parameters found using the error in all variables algorithm differ by at most a fraction of a percent from the error in volume only algorithm. Hence, the error in volume only algorithm can be used if a difference of a fraction of a percent in scaling parameters is not significant, a simpler algorithm is desired, and/or experimental uncertainties are not known.
- The difference between 1 bar and ambient pressure can be computationally significant. This may explain some of the problems others have had in fitting atmospheric pressure data.
- The predictions of the SS and the BH equations of state are close for polymer melts and low

Table IV Flexibility Parameter

Polymer	M_{rep} (g/mol)	M_0 (g/mol)	$3c/n = s/n$
BPE	28	34.8	0.80
LPE	28	30.5	0.92
HMWLPE	28	25.0	1.12
PDMS	74	47.3	1.56
PBD	54	28.5	1.89
PS	104	51.4	2.02
PMMA	100	42.4	2.36
POMS	118	48.7	2.42
PVAC	86	33.7	2.55
PCHMA	168	44.9	3.74
PNBMA	142	36.3	3.91

molecular weight liquids but the SS equation is better in the vicinity of the critical point.

- The pressure scaling factor P^* (or P_0) can be estimated from the values of V^* and T^* (or V_0 and T_0).
- The flexibility parameter increases with increasing polymer complexity.

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