PVT Scaling Parameters for Polymer Melts

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Synopsis

Scaling parameters for two PVT equations of state are evaluated for 11 polymer melt systems using a nonlinear least square fitting algorithm that analyzes all of the experimental data simultaneously. Two different criteria are considered in this evaluation. In the first method, the fitting criterion is the difference between the calculated and experimental volume. In the second method, the criterion is the difference between the calculated and experimental pressure. In both cases, the differences between the scaling parameters obtained using the simultaneous fit procedure and those obtained using the earlier consecutive fit procedure are a few percent, which can have a significant effect in some calculations. In addition to being a more consistent method of evaluating scaling parameters, the simultaneous fit procedure leads to much better agreement between calculated and experimental values, in some cases by a factor of 2.

INTRODUCTION

Equations of state are frequently represented in scaled form. In the theory of Simha and Somcynsky (SS),[1] the pertinent parameters are the scaling pressure (P^*), the scaling volume (V^*), and scaling temperature (T^*). They are measures of the intermolecular interactions and of the external degrees of freedom of the molecule. The accurate determination of these parameters by a superposition of the experimental PVT and the theoretical reduced PVT surfaces is important for several reasons. First, it provides an accurate measure of the differences between prediction and measurement. One of the prerequisites, of course, is the validity of the theory's basic assumptions, i.e., constancy of the scaling parameters over the range of temperatures and pressures investigated. This issue is important not only for the homogeneous melt, but, moreover, for the multiconstituent system under single and multiphase conditions.[2] Secondly, it is of interest to explore possible correlations in terms of these scaling parameters, when systematically varying structures in polymer or, for that matter, in oligomer melts, such as hydrocarbons, are to be studied. This presupposes a consistent and accurate determination of the scaling parameters.

A large number of polymer melts and several oligomers have been examined in the past by comparing experimental and theoretical (SS) PVT surfaces. The results have been satisfactory indeed. These comparisons, however, made use of certain approximations in the evaluation of the scaling parameters (see below), which can affect their accuracy.

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Another scaled equation of state has recently been developed by one of us[3] and applied to polymer melts,[4] polymer solids,[5] and n-alkane liquids.[6] The scaling parameters are denoted by P_0, V_0, and T_0. The equation is semiempirical in nature and has a simple analytical form. Agreement between calculated and experimental volumes is quite good for numerous crystalline and amorphous polymers. In determining the best values to use for the scaling parameters, it was found[4] that different methods used in their determination could lead to significant differences in the quality of the agreement with experiment.

The purpose of this paper is twofold. First, we wish to reexamine experimental equation of state data, which were previously analyzed in relation to the two equations of state, that is, we redetermine the scaling parameters using a convenient mathematical algorithm. Secondly, we compare the predictions of SS and BH and examine correlations between the two sets of scaling parameters.

In the next section we recapitulate the basic relationships involved and the previous procedures used in evaluating the scaling parameters. The following section outlines our computational algorithm employed for the determination of the parameters in the respective equations of state. In the fourth section, results are displayed for 11 polymer melts for which tabulated data are readily available. The fifth section presents comparisons between SS and BH equations. In the sixth section, we comment on a reported pressure dependence of the pressure scaling parameters at low pressures. The last section summarizes the conclusions reached on the basis of the computations.

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

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

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

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

$$+[Q - 1/3][1 - Q]^{-1} \quad (2)$$

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

The earlier procedure for testing the theory and thus obtaining the scaling parameters consists of two consecutive steps. In the first step, only the isobar at atmospheric pressure is involved. Since P^* is of the order of several kilobar, $\tilde{P}$ and hence the left-hand side of eq. (1) are practically zero. This permits the elimination of $\tilde{T}$ in eq. (1) and thus in eq. (2). Finally, eq. (2) can be solved for y and ultimately the $\tilde{V}$–$\tilde{T}$ function is obtained. Superposition of double

logarithmic plots yields V^* and T^*. Consideration of the elevated pressure isotherms produces a series of P^* values, which are then averaged to generate a final value for the scaling pressure. This is the procedure applied by Quach and Simha[7] to their measurements on polystyrene and poly(o-methyl styrene). Subsequent authors[8] have facilitated the first step by noting that a very good approximation to the theoretical isobar for $\tilde{P} \to 0$ is represented by the following interpolation expression:

$$\ln \tilde{V} = S_0 + S_1 \tilde{T}^{3/2} \tag{3}$$

The numerical values of S_0 and S_1 vary only slightly with the temperature range. The results obtained by means of eq. (3) have been compared in detail with those derived by the evaluation of the coupled eqs. (1) and (2) for large and small s values.[9,10] A very satisfactory agreement with respect to the volumes $\tilde{V}$ ensues. As one might expect, the accuracy of the thermal expansivities derived from eq. (3) is not as good as for the volumes. An exact evaluation of the expansivity over a range of $\tilde{P}$ values has recently been carried out by Jain.[11] An interpolation expression for his results at $\tilde{P} = 0$ adds a small correction term proportional to $\tilde{T}$ to eq. (3) with a modification of the numerical values of S_0 and S_1. We do not concern ourselves further with these refinements in the present context. The use of eq. (3) yields a considerable simplification in the determination of V^* and T^*, and provides, moreover, an immediate test of the theory when the experimental $V-T$ measurements are plotted in the form suggested by eq. (3). A comparison of experimental and theoretical slopes and intercepts yields V^* and T^*.

The procedure of consecutive evaluation of the scaling parameters, while computationally convenient, suffers from two deficiencies. First, it gives more emphasis to low than to the more numerous elevated pressure data points. Second, frequently all measurements are carried out in the pressure cell, rather than dealing separately with atmospheric pressure. This appears to reduce the accuracy of the latter data. For these reasons, a simultaneous fit of the three scaling parameters is indicated and procedures are described in the next section.

The scaling parameters are related by the equation

$$(P^*V^*/T^*)M_0 = (c/s)R \tag{4}$$

with M_0 the molecular mass of the chain segment. This segment is defined by eq. (4) 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, we have the additional parameters s and c. The preassignment of a numerical value to s is one possibility, for example, $s = 1$ in the case of ethylene.[12] 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. (4) as an auxiliary condition to be satisfied. We note the relation $sM_0 = nM_{rep}$, 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. (4) then becomes an auxiliary condition, to be satisfied by the five parameters V^*, T^*, P^*, s, and c.

We turn next to the recently proposed BH equation of state:

$$\bar{P}\bar{V}^5 = \bar{T}^{3/2} - \ln \bar{V} \tag{5}$$

involving the scaling parameters P_0, V_0, and T_0. One procedure used[4] for determining the scaling parameters was to follow the consecutive fit method used for the SS equation. Thus, the zero pressure data were fitted to eq. (5) by the method of least squares in order to find V_0 and T_0. Then P_0 was found by trial and error fitting to the elevated pressure data, using as a criterion the mean of the absolute value of the difference between experimental and calculated volume, $\langle |\Delta V| \rangle$. Note that, for these calculations, the difference between zero pressure and atmospheric pressure was found to be insignificant.

Recognizing the desirability of treating all of the measurements in the same manner by simultaneously fitting all of the data to determine the scaling parameters, the above values were used as initial guesses and a trial and error search was made to find the scaling parameters that minimized $\langle |\Delta V| \rangle$. This procedure was used by Hartmann and Haque for polymer melts[4] and polymer solids.[5] Using this method, $\langle |\Delta V| \rangle$ is reduced on the order of 50%, compared to the consecutive fit method. While this procedure has the advantage of fitting the data simultaneously, the trial and error search is tedious.

In order to facilitate the fitting procedure, an algorithm was developed that uses a nonlinear least squares method.[6] This method not only is more convenient but also finds the minimum in a more reliable manner. One difference between this procedure and the trial and error method is that the criterion of fit is the sum of the squares of the differences between the experimental and calculated volumes rather than the absolute value of the difference. The resulting scaling parameters are almost unchanged. In this paper, we will use an improved version of the fitting algorithm for polymer melts with the two equations of state.

SIMULTANEOUS FIT ALGORITHM

Scaling parameters were determined in this work using a nonlinear least squares fitting procedure. Given a triple of initial guesses for the scaling parameters in the SS equation (P^*, V^*, T^*), for each experimental data point (P, V, T) a residual is defined as follows. Taking P^*, V^*, T^*, P, and T as fixed, numerical solution values y_n and V_n are obtained for eqs. (1) and (2), where the subscript n refers to the numerical solution. The residual is then defined to be $V - V_n$. The triple of values P^*, V^*, T^* for which the sum of the squares of the residuals for all of the experimental data points attains its minimum is considered to be the best set of reducing parameters for the experimental data.

The least squares fit program used was ZXSSQ from the International Mathematical and Statistical Libraries, Inc. (IMSL) software library. The stopping criterion was attainment of at least five significant digits of accuracy in P^*, V^*, T^*. For each experimental data point, eqs. (1) and (2) were first solved for y_n and V_n using the IMSL nonlinear equation solver routine

ZSPOW with the stopping criterion being six significant digits of accuracy in y_n and V_n. The initial guess in ZSPOW for V_n was taken to be the experimental value V. For y_n, the initial guess was the solution y of eq. (2), taking P^*, V^*, T^*, P, T, and V as given. Equation (2) was solved numerically for this initial value of y to within 10^{-4} using a standard bisection method. Note that ZSPOW is based on Newton's method, which in general doubles the number of significant digits in the solution with each iterative step within its region of convergence. Hence, by the time ZSPOW verifies six significant digits in y_n and V_n, much higher accuracy can be expected.

The only input needed for the program in addition to the experimental data are initial guesses for P^*, V^*, T^*. We have found that, for this problem, the simultaneous fit method does not require close initial guesses. Almost any reasonable set of values will suffice. The same final values are obtained for a wide variety of initial guesses that are far from the final values. The program is written in FORTRAN5 and runs, on a main frame computer (CDC875), in a few seconds for the largest data set investigated here.

The above analysis assumes that all of the experimental uncertainty is in the measurement of the volume, with pressure and temperature known exactly. A different approach was taken by Dee and Walsh.[13] They assumed that all of the uncertainty is in the pressure, with volume and temperature known exactly. Our algorithm is easily modified to make this type of calculation. In this case, the residuals are the differences between the experimental and numerically calculated pressures, $P - P_n$. Since pressure appears only in eq. (1), the two SS eqs. are not coupled as they were when volume was the error corrupted variable. The numerical solution is then simpler when P carries all of the uncertainty. The values of the scaling parameters that minimize the sum of the squares of these residuals are found as before. Note, in this case, that if a standard bisection method is used to solve eq. (2) for y_n [with eq. (1) then determining P_n], y_n should be determined to within around 12 significant digits to prevent loss of accuracy in the scaling parameters obtained using ZXSSQ.

In a like manner, one could assume that all of the uncertainty is in the temperature, with volume and pressure known exactly. However, since experimental errors in temperature measurements are generally smaller than errors in the other two variables, this type of calculation would not appear to be justified. Thus, while the mathematical formalism could be developed, we did not pursue this avenue.

Having considered the possibilities for experimental error in any one of the state variables, it is natural to combine the options and allow for error in all three of the variables. This type of extension of the usual method of least squares has been examined and is sometimes referred to as the error-in-variables method. This approach has been applied by Nies et al.[12] to ethylene. These authors obtained the four parameters c, P^*, T^*, and V^* with the preassigned value $s = 1$. For a complete description of the nonlinear least square fitting procedure used, see Refs. 14 and 15. We intend to give results for polymer melts obtained by means of this procedure in the future. In this paper, we compare their results for ethylene with ours.

For the BH equation, a similar algorithm is followed to determine the scaling parameters: P_0, V_0, T_0. The calculation is simpler because there is only

one equation to solve rather than two coupled equations. Thus, the evaluation of the residuals is simpler than for the SS eq. The minimization procedure is the same. Only the results obtained assuming that all the error is in the volume will be presented.

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. The source for three polyethylenes and three acrylate polymers are measurements of Olabisi and Simha.[16] 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[7] and for poly(vinyl acetate) (PVAc) from McKinney and Goldstein.[17] For poly(dimethyl siloxane) (PDMS), we have the observations of Kubota and Ogino[18] with room temperature as the reference state and those of Shih and Flory at room temperature.[19] 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.[20]

P^*, V^*, T^* scaling parameters and mean absolute differences $\langle |\Delta V| \rangle$ for the above 11 sets of experimental data determined assuming volume errors only, are listed in Table I.[21] For comparison, consecutive fit results are given in parentheses. The scaling parameters change maximally by a few percent. The influence on $\langle |\Delta V| \rangle$ is more significant. Averaged over the 11 systems, the change is about 30%, being reduced from 7 to 5×10^{-4} cm^3/g. Some of the changes are considerably larger. Included in those with larger changes are polymers with a comparatively large temperature range available for observation. In this connection it would be of interest to reevaluate the n-paraffin series, since a large temperature range is available.

In addition to the average difference between calculated and experimental volume for each polymer, we have also examined the maximum difference. Typically, the maximum is three times the average, though in the worst case, PMMA, the maximum is eight times the average. Whereas this ratio gives some feel for the characteristics of the fit, the ratio is based on a single data point rather than the total ensemble of points. Another characteristic of the fit is the number of times V(experimental) $- V$(calculated) changes sign along the isotherms. For most polymers, the sign changes every three or four data points, in data ensembles that vary from 41 (PMMA) to 168 (PnBMA) points, with no systematic pattern evident.

In some cases, changes in scaling parameters of a few percent, as found above, can be significant. We attach particular significance to the changes seen in connection with the equation of state and the scaling parameters of a mixture, and the prediction of free energies ΔG and enthalpies ΔH of mixing.[2,22] The theory allows for a prediction of the scaling pressure of the mixture $\langle P^* \rangle$, based on the complete equations of state of the constituents

TABLE I
SS Scaling Parameters Using Simultaneous Fit with Error in Volume Only[a]

	P^* (bar)	V^* (cm^3/g)	T^* (K)	$\langle |\Delta V| \rangle$ (10^{-4} cm^3/g)
Polystyrene	7155	0.9627	12,791	3
	(7453)	(0.9598)	(12,680)	(7)
Poly(o-methyl styrene)	7499	0.9793	12,940	4
	(7458)	(0.9762)	(12,740)	(5)
Poly(methyl methacrylate)	9291	0.8363	11,900	1
	(9147)	(0.8370)	(11,920)	(3)
Poly(cyclohexyl methacrylate)	7994	0.8993	11,740	6
	(8382)	(0.8906)	(11,290)	(8)
Poly(n-butyl methacrylate)	8234	0.9346	10,200	7
	(8456)	(0.9299)	(9990)	(9)
Polyethylene (branched)	6979	1.1639	10,270	9
	(6946)	(1.1600)	(10,140)	(11)
Polyethylene (linear)	7788	1.1399	9750	8
	(7478)	(1.1417)	(9770)	(11)
Polyethylene (high MW linear)	9041	1.1287	9210	10
	(8968)	(1.1285)	(9205)	(10)
Poly(vinyl acetate)	9467	0.8132	9380	1
	(9380)	(0.8141)	(9420)	(2)
Poly(dimethyl siloxane)	4774	0.9584	7850	2
	(4739)	(0.9593)	(7870)	(2)
Cis-1,4-polybutadiene	8256	1.0751	9170	3
	(7714)	(1.0861)	(9644)	(6)

[a] Consecutive fit values in parentheses.

and the equation of state of the mixture at a single, e.g., atmospheric pressure. Moreover, ΔG and ΔH are computed as small differences between large numbers and involve scaling factors P^* and V^* for constituents and mixtures. As has been shown,[2,22] slight variations in the P^* and $\langle P^* \rangle$ values which leave the equation of state and the volume changes of mixing practically intact, have a profound effect on the numerical values of ΔG and ΔH. Therefore, a consistent exploration of the performance of the theory in predicting these latter functions is predicated upon a consistent determination of all scaling parameters for constituents and mixture.

Simultaneous fit P_0, V_0, T_0 scaling parameters for the same sets of experimental data, assuming error in volume only, are listed in Table II,[21] with consecutive fit values in parentheses. The scaling parameters likewise change by no more than a percent or two. In this case, the simultaneous fit accuracy is 6×10^{-4} cm^3/g compared with 9×10^{-4} cm^3/g for the consecutive fit. Thus, not only is the simultaneous fit a more consistent manner of analyzing the data, but it also leads to a significant improvement in accuracy.

In comparing the simultaneous fit results for the two equations, eq. (1) is somewhat better than eq. (5), but both equations give quite good fits to measured values. In most cases, the experimental accuracy of the measurements is given as 10×10^{-4} cm^3/g, so that the predictions of both equations are within the accuracy of the measurements. Since the predictions of the two equations are so close, one can view the BH equation as an interpolation

TABLE II
BH Scaling Parameters Using Simultaneous Fit with Error in Volume Only[a]

	P_0 (bar)	V_0 (cm^3/g)	T_0 (K)	$\langle |\Delta V| \rangle$ (10^{-4} cm^3/g)
Polystyrene	29,600	0.8742	1591	5
	(28,900)	(0.8683)	(1540)	(7)
Poly(o-methyl styrene)	31,000	0.8878	1596	5
	(32,000)	(0.8788)	(1523)	(6)
Poly(methyl methacrylate)	38,100	0.7581	1466	2
	(37,900)	(0.7539)	(1430)	(5)
Poly(cyclohexyl methacrylate)	30,900	0.8215	1490	9
	(32,900)	(0.8038)	(1366)	(13)
Poly(n-butyl methacrylate)	31,300	0.8537	1291	16
	(32,900)	(0.8390)	(1208)	(23)
Polyethylene (branched)	25,400	1.0635	1293	11
	(27,600)	(1.0456)	(1221)	(14)
Polyethylene (linear)	28,200	1.0361	1203	5
	(28,700)	(1.0294)	(1179)	(6)
Polyethylene (high MW linear)	32,300	1.0241	1129	6
	(32,700)	(1.0189)	(1112)	(6)
Poly(vinyl acetate)	38,200	0.7369	1151	1
	(38,800)	(0.7349)	(1139)	(2)
Poly(dimethyl siloxane)	17,900	0.8749	989	3
	(17,900)	(0.8650)	(950)	(13)
Cis-1,4-polybutadiene	34,900	0.9788	1159	3
	(31,000)	(1.0003)	(1309)	(4)

[a] Consecutive fit values in parentheses.

formula, valid at any pressure, for the SS equation, just as eq. (3) is a useful interpolation formula at zero pressure.

Assuming that all of the experimental error is in the pressure measurement, scaling parameters were calculated for the same 11 data sets. P^*, V^*, T^* values are given in Table III along with the mean of the absolute value of the difference between experimental and calculated pressure, $\langle |\Delta P| \rangle$. The scaling parameters are very close to those in Table I, differing by 1% or less. $\langle |\Delta P| \rangle$ is

TABLE III
SS Scaling Parameters Using Simultaneous Fit with Error in Pressure Only

	P^* (bar)	V^* (cm^3/g)	T^* (K)	$\langle |\Delta P| \rangle$ (bar)
Polystyrene	7152	0.9638	12,870	8
Poly(o-methyl styrene)	7461	0.9814	13,080	9
Poly(methyl methacrylate)	9263	0.8369	11,940	3
Poly(cyclohexyl methacrylate)	7773	0.9039	11,990	15
Poly(n-butyl methacrylate)	8257	0.9359	10,280	15
Polyethylene (branched)	6923	1.1674	10,390	12
Polyethylene (linear)	7864	1.1406	9790	11
Polyethylene (high MW linear)	9179	1.1285	9221	13
Poly(vinyl acetate)	9476	0.8114	9283	2
Poly(dimethyl siloxane)	4800	0.9575	7825	2
Cis-1,4-polybutadiene	8348	1.0728	9067	6

TABLE IV
Simha–Somcynsky Scaling Parameters for Ethylene (High Density Region)

	Nies et al.	This work
V^* (cm^3/g)	1.4647	1.4875
T^* (K)	3274	3394
P^* (bar)	4583	4286
c	0.692	0.634
s	1	1
$\langle |\Delta V| \rangle$ (cm^3/g)	0.015	0.010

on the order of 10 bar, a reasonable average over all pressures. While an uncertainty of 10 bar is a small percent error when the experimental pressure is 2000 bar, it is very large at 1 bar. In fact, this method leads to the unphysical prediction of negative pressure when the experimental pressure is 1 bar. This problem arises because only the residual P(experimental) − P(calculated) is minimized, with no concern with the magnitude of P. This difficulty does not occur when volume is used since all the volumes are of the same order of magnitude.

Finally, in comparing our error in volume only calculation with the error in all variables calculations of Nies et al.[12] for ethylene, Douslin and Harrison's data[23] from 10 to 150°C, and in the pressure range up to about 350 bar were used, i.e., a total of 62 data points, as did Nies et al. As a measure of agreement between theory and experiment, we use $\langle |\Delta V| \rangle$. Results are given in Table IV. The results are qualitatively not unexpected, that is we observe a variation of a few percent in the calculated parameters and a somewhat larger average value of $\langle |\Delta V| \rangle$ when uncertainty is allowed in pressure and temperature as well as volume.

COMPARISON OF SCALING PARAMETERS

Because of the close agreement of the predictions of the two equations of state, one would expect that the scaling parameters for the two equations should be related. For the volume and temperature scaling parameters, the relation follows directly from eq. (3) in comparison with eq. (5), whence

$$V^*/V_0 = \exp(-S_0) \tag{6}$$

$$T^*/T_0 = S_1^{2/3} \tag{7}$$

where S_0 and S_1 are considered to be constants. There is no equivalent relation for the scaling pressures, so that it will be assumed that they are directly proportional, as the other two parameters are. Plots of the scaling parameters for the two equations against each other for the 11 polymer melts should then have the same slope. The results are shown in Figures 1, 2, and 3. As can be seen, the predicted correlation of the parameters is observed.

An immediate consequence of Figures 1, 2, and 3 is that one can make rather reliable estimates of one set of scaling parameters from the other. All of the data in the literature for the two equations can then be interchanged
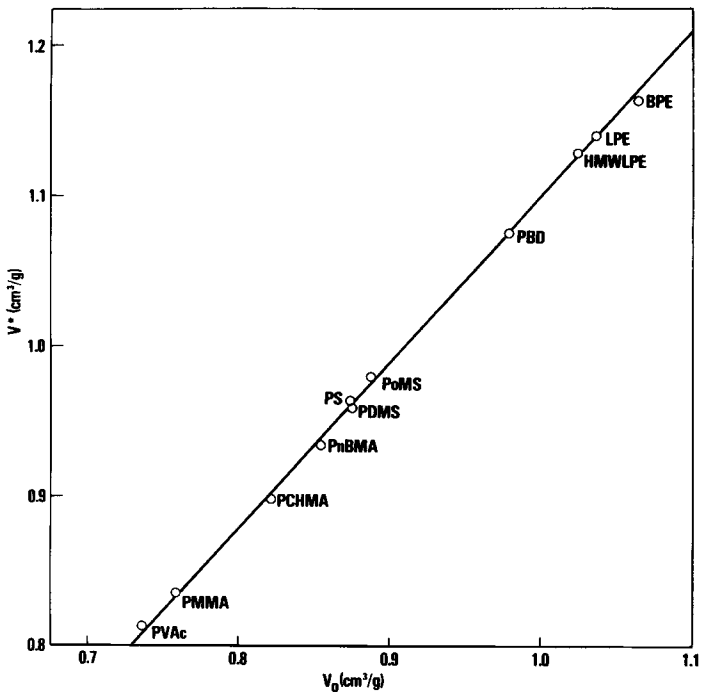
Fig. 1.   Simultaneous fit scaling volumes, eqs. (1) and (5), for various polymers. For explanation of abbreviations, see the text.
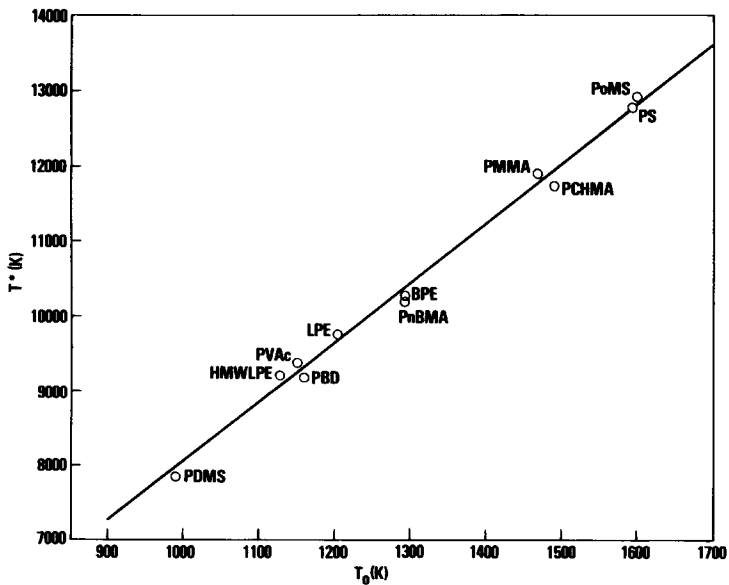

Fig. 2.   Simultaneous fit scaling temperatures, eqs. (1) and (5), for various polymers. For explanation of abbreviations, see the text.
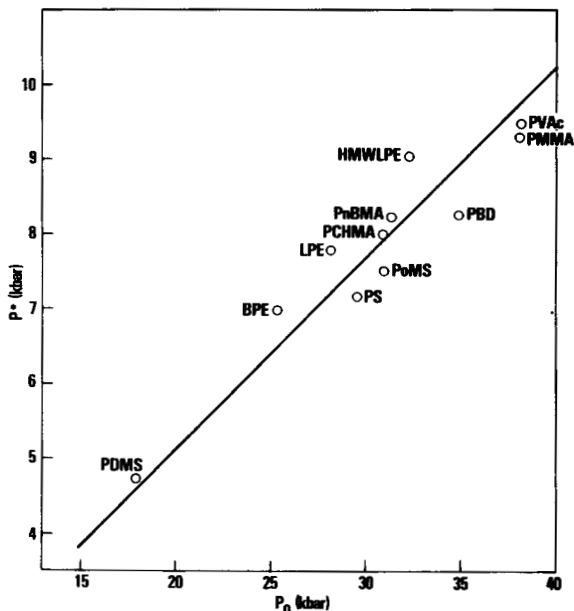
Fig. 3. Simultaneous fit scaling pressures, eqs. (1) and (5), for various polymers. For explanation of abbreviations, see the text.

without having to analyze experimental PVT data, unless highly accurate values are desired.

From Figure 1, we find $V^*/V_0 = 1.092$, based on the experimental data for the 11 polymer systems. This value implies $S_0 = -0.0880$, which is in reasonable agreement with the value of -0.1033 reported by Utracki,[24] based on a fit directly to the SS equation without consideration of experimental data. From Figure 2, we find $T^*/T_0 = 8.069$. This value implies $S_1 = 22.92$, in good agreement with the value of 23.83 based on the mathematical form of the equation alone. From Figure 3, we find $P^*/P_0 = 0.254$. In this case, there is no prior mathematical comparison to be made.

PRESSURE DEPENDENCE OF SCALING PRESSURE

It has been pointed out by Utracki[24] that if one calculates a best value for P^* at each pressure and temperature, the deviations of P^* from the average value are not random but show more significant deviations at low pressure. In some cases, there are large positive deviations at low temperature and large negative deviations at high temperature. In other cases, this temperature dependence is reversed, with high temperature giving positive deviations. Similar behavior has been observed[25] with P_0. An example of these observations is shown in Figure 4, for PnBMA, using the algorithm presented in this paper. Since this systematic behavior of the scaling pressure was unexplained, it seemed worthwhile to examine the basis for these results more closely.

The pressure dependence can be rationalized in the following manner: Using the relation $\tilde{P} = P/P^*$, the reduced pressure derivative of reduced volume at
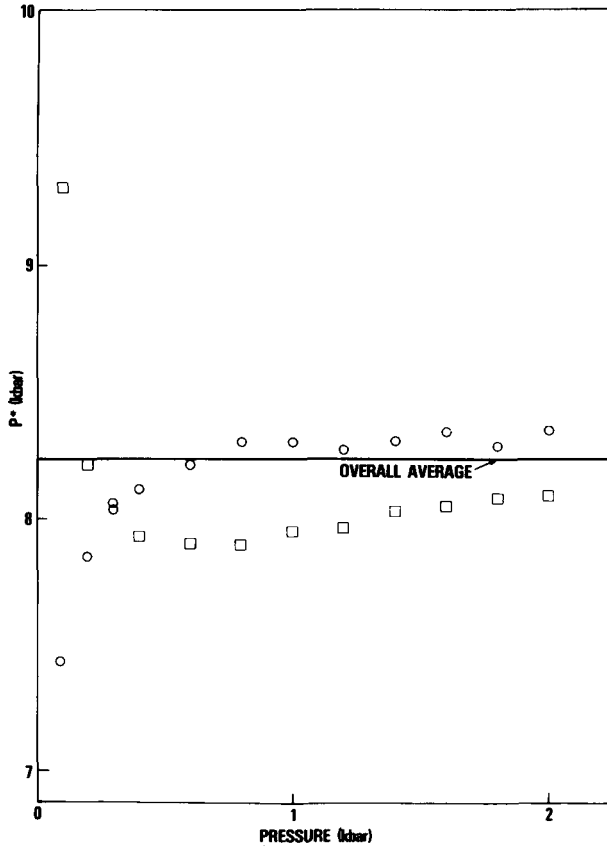
Fig. 4.   Apparent pressure dependence of scaling pressure for PnBMA. For discussion of these results, see the text: (○) 355 K; (□) 473 K.

constant reduced temperature and unreduced pressure can be written as

$$\left(\frac{\partial \tilde{V}}{\partial \tilde{P}}\right)_{\tilde{T}, P} = -\frac{P^*}{\tilde{P}}\left(\frac{\partial \tilde{V}}{\partial P^*}\right)_{\tilde{T}, P} \tag{8}$$

Approximating the derivative of $\tilde{V}$ with respect to P^* with finite differences, we find

$$\left(\frac{\partial \tilde{V}}{\partial \tilde{P}}\right)_{\tilde{T}, P} \approx -\frac{P^*}{\tilde{P}}\frac{\Delta \tilde{V}}{\Delta P^*} \tag{9}$$

Defining a reduced compressibility as

$$\tilde{k} = -\frac{1}{\tilde{V}}\left(\frac{\partial \tilde{V}}{\partial \tilde{P}}\right)_{\tilde{T}, P} \tag{10}$$

it follows that

$$\frac{\Delta V}{V} = \tilde{k}\tilde{P}\frac{\Delta P^*}{P^*} \tag{11}$$

which is the desired result. From eq. (11), we see that for a constant percent difference in V (viz., $\Delta V/V$), it is the product of $\tilde{P}$ and the difference in P^* that is constant (neglecting changes in $\tilde{k}$). Thus, at low pressure, large changes in P^* have the same effect on V as small changes do at high pressure. Since our method focuses on volume difference, the minimization procedure tends to find fits for which the volume deviations are about the same everywhere. Therefore, we see larger changes in P^* at low pressure than at high pressure because these changes represent the same volume differences.

Assuming that differences between theory and experiment are random, we can now understand why for some polymers at low pressure there are large negative deviations from the average at low temperature and large positive deviations at high temperature, as shown in Figure 4, whereas for other polymers the reverse is true. This is just a result of chance whether the experimental value is greater or lesser than the theoretical.

For any given isotherm, one would expect for a least squares fit of data that the differences between the fitted theoretical line and the experimental data would alternate, roughly, between above and below the line, leading to oscillations in the difference (positive to negative). This is the behavior observed in Figure 4.

The observations in Figure 4 are thus understandable in terms of the characteristics of the equation of state (they both behave in the same manner), namely that volume becomes insensitive to the scaling pressure at low pressure and that at all pressures the differences between theory and experiment are approximately random. Note that at zero pressure, the scaling pressure is undetermined and that the insensitivity of P^* extends up to about 200 bar.

CONCLUSIONS

Scaling parameters for 11 polymer melts have been determined using two different types of simultaneous fit of all the experimental data for two scaled PVT equations of state. The polymer melts chosen cover a wide range of molecular properties and were taken from a variety of sources for which published tabulated data were available. Based on the analysis presented here, a number of conclusions have been reached:

1. Using the more consistent procedure of fitting all the data simultaneously rather than consecutively, the scaling parameters change maximally by a few percent. These changes can be significant in some applications such as energy of mixing calculations.

2. A significant improvement in the agreement between predicted and experimental volumes is obtained by using the simultaneous rather than a consecutive fit. The improvement varies from polymer to polymer and from one equation to the other but is often a factor of 2. The improvement seems to

be more pronounced in those systems for which experimental data are available over the widest temperature range.

3. The two equations of state both make predictions of volume that are within the experimental accuracy of the measurements.

4. The scaling parameters for the two equations of state are not independent but are linearly related with a high degree of correlation. Thus, if values are known for one equation, reliable estimates for the other can be made.

5. The two equations of state are very similar to one another, and the predictions of one can be substituted for the other with little effect on the predicted volume. Thus, the BH equation is a useful interpolation formula for the SS equation.

6. PVT equations of state are insensitive to the pressure scaling parameter at low pressure.

7. The most consistent assumption for error in only one variable is to use volume as the criterion of fit, though in principle it would be desirable to allow all three variables to have experimental uncertainty.

References

1. R. Simha and T. Somcynsky, *Macromolecules*, **2**, 342 (1969).

2. R. K. Jain and R. Simha, *Macromolecules*, **13**, 1501 (1980); **17**, 2663 (1984).

3. B. Hartmann, in *Proceedings of the 22nd Canadian High Polymer Forum*, University of Waterloo, Waterloo, ON, Canada, 1983, p. 20.

4. B. Hartmann and M. A. Haque, *J. Appl. Polym. Sci.*, **30**, 1553 (1985).

5. B. Hartmann and M. A. Haque, *J. Appl. Phys.*, **58**, 2831 (1985).

6. B. Hartmann and E. Balizer, *J. Acoust. Soc. Am.*, **82**, 614 (1987).

7. A. Quach and R. Simha, *J. Appl. Phys.*, **42**, 4592 (1971).

8. R. Simha and P. S. Wilson, *Macromolecules*, **6**, 908 (1973).

9. J. E. McKinney and R. Simha, *Macromolecules*, **7**, 894 (1974).

10. R. K. Jain and R. Simha, *J. Chem. Phys.*, **72**, 4909 (1980).

11. R. K. Jain, private communication, February 1987.

12. E. Nies, L. A. Kleintjens, R. Koningsveld, R. Simha, and R. K. Jain, *Fluid Phase Equilibria*, **12**, 11 (1983).

13. G. T. Dee and D. J. Walsh, *Macromolecules*, **21**, 811 (1988).

14. H. I. Britt and R. H. Luecke, *Technometrics*, **15**, 233 (1973).

15. T. A. Duever, K. F. O'Driscoll, and P. M. Reilly, *J. Polym. Sci., Polym. Chem. Ed.*, **21**, 2003 (1983).

16. O. Olabisi and R. Simha, *Macromolecules*, **8**, 206 (1975).

17. J. E. McKinney and M. Goldstein, *J. Res. Natl. Bur. Std.*, **78A**, 331 (1974).

18. K. Kubota and K. Ogino, *Macromolecules*, **11**, 514 (1978).

19. H. Shih and P. J. Flory, *Macromolecules*, **5**, 758 (1972).

20. J. W. Barlow, *Polym. Eng. Sci.*, **18**, 238 (1978).

21. B. Hartmann, R. Simha, and A. E. Berger, *Bull. Am. Phys. Soc.*, **32**, 666 (1987).

22. R. K. Jain, R. Simha, and C. M. Balik, *Indian J. Pure Appl. Phys.*, **22**, 651 (1984).

23. D. R. Douslin and R. H. Harrison, *J. Chem. Thermodyn.*, **8**, 301 (1976).

24. L. A. Utracki, *Polym. Eng. Sci.*, **25**, 655 (1985).

25. B. Hartmann and M. A. Haque, *Bull. Am. Phys. Soc.*, **31**, 463 (1986).