Numerical evaluation of the thermodynamic equation for the state of polymer melts from pressure-volume-temperature (pVT) data

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ABSTRACT
A refinement of the numerical calculation of reducing PVT parameters has been given by using the Marquardt-Levenberg nonlinear least-squares algorithm. Three different polymers were analyzed and evaluated by the proposed method. The precision of the PVT measurement makes sense for an improvement of the evaluation by applying the Marquardt algorithm.

INTRODUCTION
The thermodynamic state of amorphous, thermoplastic polymers can be described by the statistical theory of Prigogine [1] which was modified for polymers by Simha and Somcynsky [2]. This theory treats the polymeric system as a quasi-lattice, including vacant sites which account for structural disorder. The lattice points of the quasi-lattice are either occupied by polymer segments (with volume fraction of y) or are vacant (holes with volume fraction of (1-y)) where y is a function of pressure and temperature. The obtained equation of state has the following form:

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

where the reduced variables $\tilde{P}$, $\tilde{V}$ and $\tilde{T}$ are defined in terms of the scaling parameters P*, V* and T*, as follows:

$$\tilde{P} = P/P^*; \quad \tilde{V} = V/V^*; \quad \tilde{T} = T/T^* \qquad (2)$$

The P*, V* and T* parameters describe a "reference state" which is not a corresponding state in the sense of the thermodynamic theory of real gases. This "reference state" corresponds to the hypothetical thermodynamic state where the thermal kinetic energy of the segments compensates for the potential energy of their mutual interaction. For this state holds:

$$P^*V^* = (1/3)fkT^* \qquad (3)$$

where f is the total number of volume dependent (external) degrees of freedom of the involved segments and k is the Boltzmann constant. In one respect the equation of state, written in this form, satisfies a principle of corresponding states: that is, it holds for all the compounds encompassed by the theory, independently of their molecular characteristics.
For the determination of y(P,T) in equation (1) an additional condition must be found. A possibility is to make use of the minimum condition for the Helmholtz' free energy F at thermodynamic equilibrium:

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$$(\partial F/\partial y)_{P,T} = 0 \qquad (4)$$

One obtains with this condition the following equation [2]:

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

$$+ [2^{-1/6}y(y\tilde{V}^{-1/3})-(1/3)][1 - 2^{-1/6}y(y\tilde{V})^{-1/3}]^{-1} \qquad (5)$$

Numerical evaluation of the parameters of the equation of state.

The system of coupled equations (1) and (5) requires a numerical solution. This can be provided by the algorithm of Marquardt-Levenberg [3,4,5], a method for the least-squares estimation of nonlinear parameters. The model to be fitted is described by a nonlinear equation of the type:

$$E(z) = f(x_1,\ldots,x_n; \vartheta_1,\ldots,\vartheta_n) \qquad (6)$$

where $E(z)$ is the expectation value of the observed quantity z; $x_1,\ldots, x_n$ are the independent variables, and $\vartheta_1,\ldots, \vartheta_K$ are estimates for the parameters. M values of z_i $(i = 1,\ldots, M)$ are obtained from M measurements.

The values of the parameter vector can be estimated through a nonlinear least-squares regression analysis. The minimum of $S(\underline{\vartheta})$ (the error sum of squares) is written as:

$$S(\vartheta_1,\ldots,\vartheta_K) = \sum_{u=1}^{n} \{Z_u - f(x_1,\ldots,x_n; \vartheta_1,\ldots, \vartheta_K)\}^2 \qquad (7)$$

We applied the Marquardt least-squares estimation algorithm for the nonlinear parameters $\vartheta_1,\ldots \vartheta_K$ from the IBM share software library [5]. We chose this procedure because it represents the best compromise between the linearization method and the steepest-descent algorithm [6], in that it avoids the most serious limitations of both, while combining their advantages. The computer output contains the sought P^*, V^* and T^* parameters, the observed and predicted pressure (the fit was performed for the pressure) with the corresponding temperature, volume and y function values. Detailed statistical characterization of the fit (total root mean squares error, standard error, conventional one parameter and support plane confidence intervals and parameter correlation matrix) is also given.

In our particular case, the pressure P plays the role of function $E(z)$ in the functional (6), while the volume V and the temperature T correspond to the independent variables in the same functional. A numerical solution of the transcendental equation (5) yields y $(\tilde{V},\tilde{T})$, which is inserted into equation (1). The values of the three scaling parameters and y are then adjusted by an iteration procedure of the Marquardt algorithm.

The algorithm of Marquardt requires a trial solution for the parameters to be improved by the subsequent iteration procedure. An initial set of parameters is provided by a numerical code (from Gnomix Research), which makes use of an approximate solution of the coupled equations (1) and (5) (see e.g. [7]):

$$\ln\tilde{V}_0 = A + BT^{3/2} \qquad (8)$$

This relationship is valid at atmospheric pressure, with $A = - 0.1034$ and $B = 23.835$ in the range $0.95 \leq V_0 \leq 1.40$ [7]. An analogous expression holds for the unreduced variables:

$$\ln V_0 = C + DT^{3/2} \qquad (9)$$

The constants C and D can be determined by least-squares fits of volume data (at atmospheric pressure) versus temperature. The scaling parameters V* and T* are then given by:

$$V^* = \exp(C - A); \qquad T^* = (B/D)^{2/3} \qquad (10)$$

As far as P* is concerned, a preliminary value P_j^* is calculated by solving equations (1) and (5) for each isotherm, to obtain $\tilde{P}\tilde{V}/\tilde{T}$ and a set of $\tilde{V}$ values. This is done through the relationship:

$$P_j^* = (P_j V_j/T_j)(T^*/V^*)(\tilde{P}\tilde{V}/\tilde{T})^{-1} \qquad (11)$$

where (P_j, V_j, T_j) represents an experimental point. The average over P_j^* is assumed as the final value of P*.

Calculation of thermodynamic parameters.
By evaluating the reducing PVT parameters and the y function useful thermodynamic information can directly be obtained. Some examples are given below:

- the cohesion energy density ΔE [2]:

$$\frac{\Delta E}{V} = P^*(y/2\tilde{V})[2{,}409(y\tilde{V})^{-2} - 1.011(y\tilde{V})^{-4}] \qquad (12)$$

- the thermal expansion coefficient α_0 [8]:

$$\alpha_0 = [d(\ln V(0,T))/dT] = (3/2) \cdot 23.835 \cdot T^{*(-3/2)} \qquad (13)$$

- the isothermal compressibility κ [9]:

$$\kappa = -(1/V)(\partial V/\partial P) = C\{[1 - C \cdot \ln(1 + \tilde{P}/\tilde{B})][(\tilde{P} + \tilde{B})^{-1}\} \qquad (14)$$

where the constant C has a value of 0.0894 [10] and $\tilde{B}=0.9549 \cdot \exp(-49.22\tilde{T})$ (see [9]);

- the effective segment mass M_0 [8] with one volume dependent degree of freedom of the segments and with the R gas constant:

$$M_0 = (1/3)RT^*/P^*V^* \qquad (15)$$

EXPERIMENTAL
Three polymers with different segment polarizability have been tested. PVT measurements on melts of a low density polyethylene (product of BASF Ag., sample B in IUPAC Working Party on Structure and Properties of Commercial Polymers [11]), a polyvinyl alcohol (product of Fluka) and a polyamide-6 (Grilon A 28, product of Ems Chemie) are reported. The test materials were previously dried at 120°C under vacuum (P < 1 torr) for 15 hours.
The experimental apparatus was the PVT Gnomix of the Gnomix Research [12], which allows a direct, static measurement of specific-volume changes, as a function of temperature or pressure, with an accuracy of 0.0002 cm^3/g. A piezometer test cell has to be filled with a small amount of granulate sample (ca. 1-2 g) and with mercury, which serves as a confining fluid. The lower end of the cell is closed by a flexible metal bellows. The deflection

of the latter is measured by a linear variable differential transducer (LVDT). This deflection is proportional to the change in the specific volume.

The PVT machine was operated in the isothermal mode, i.e. increasing pressures were applied at a constant temperature. The starting conditions were T = 30°C and P = 10MPa (gauge pressure) in every case. The specific volume changes are measured with reference to the starting V_r value:

$$\Delta V = V(P,T) - V_r \qquad (16)$$

RESULTS

The experimental isotherms were measured in the pressure range between 0 and 200 MPa:
- for low density polyethylene (LDPE) at the temperatures 127.1 °C; 144.3 °C; 160.4 °C; 177.3 °C and 192.3 °C (Figures 1a and 1b);
- for polyamide-6 (PA-6) at the temperatures 218.4 °C; 249.3 °C; 269.5 °C; 294.5 °C and 316.8 °C (Figures 2a and 2b);
- for polyvinylalcohol (PVA) at the temperatures 157.9 °C; 169.7 °C; 179.5 °C; 190.2 °C and 195.8 °C (Figures 3a and 3b).

The measured data were evaluated by the Gnomix numerical code and by the Marquardt fit. Solid lines in Figures 1a, 2a and 3a were calculated with P^*, V^* and T^* obtained by the numerical code and solid lines in Figures 1b, 2b and 3b with those P^*, V^* and T^* values which were obtained in the Marquardt fit. Since the parameters obtained by the Marquardt fit were calculated with starting values, which were results of the numerical code, they fit better to the measured data. Some characteristics of the results are summarized in Table 1.

Table 1
Results of numerical fits for PVT data measured on different polymer melts using the Simha-Somcynsky theory.
/G/: numerical code of Gnomix;
/M/: Marquardt nonlinear least-squares estimation.
Standard errors (St. error) were calculated
from measured and fitted pressure values.

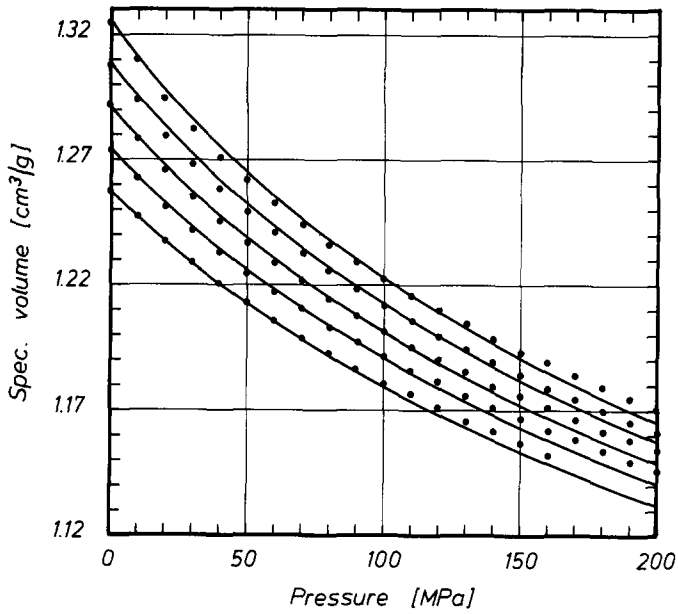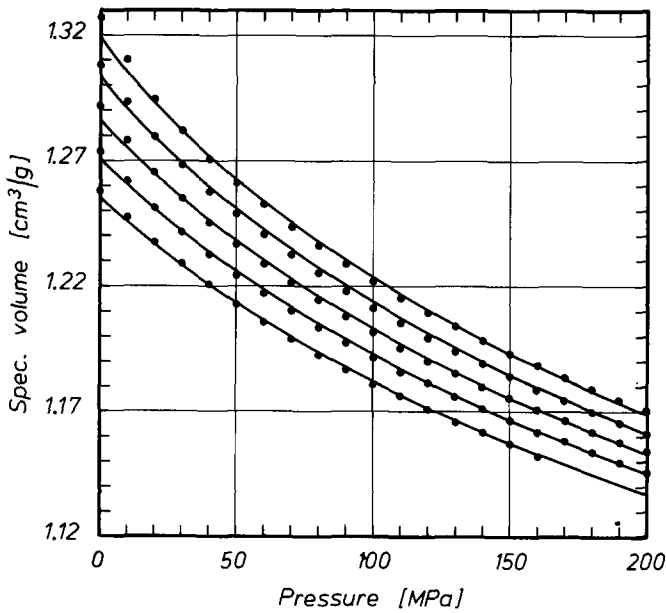|	LDPE	PA-6	PVA
P^* [MPa] /G/	829	1266	2435
P^* [MPa] /M/	837	1265	2360
St. error /G/	0.60 %	0.30 %	0.22 %
St. error /M/	0.24 %	0.23 %	0.20 %
V^* [cm^3/g] /G/	1.1290	0.9138	0.7722
V^* [cm^3/g] /M/	1.1414	0.9195	0.7812
T^* [°K] /G/	9359	11231	9226
T^* [°K] /M/	9767	11456	9531

Figure 1a

Figure 1b

Figure 1a and 1b

Comparison of experimental and theoretical isotherms for LDPE measured at 127.1 °C; 144.3 °C; 160.4 °C; 177.3 °C and 192.3 °C.
Figure 1a   Solid line - result of the numerical code.
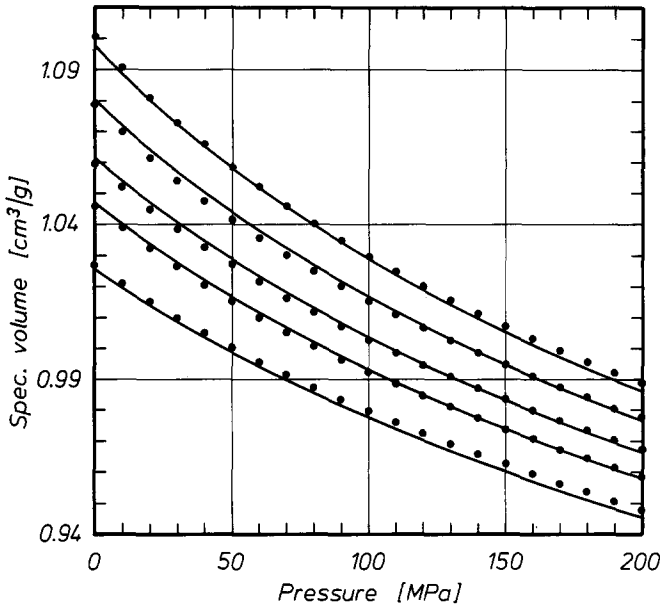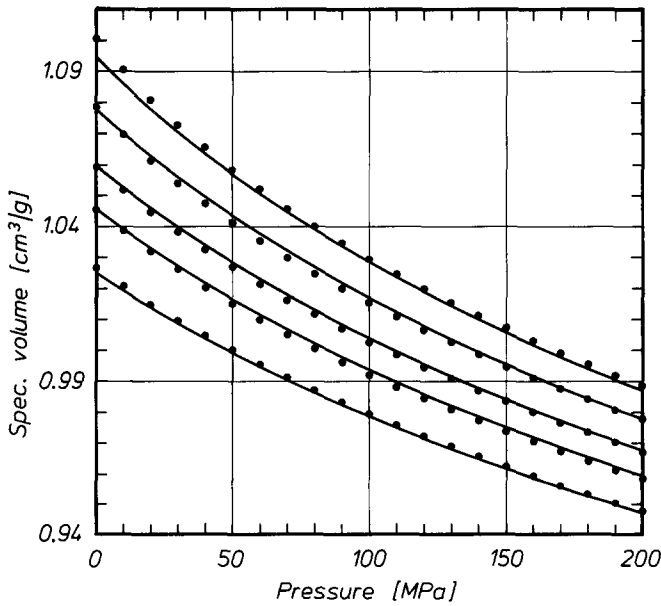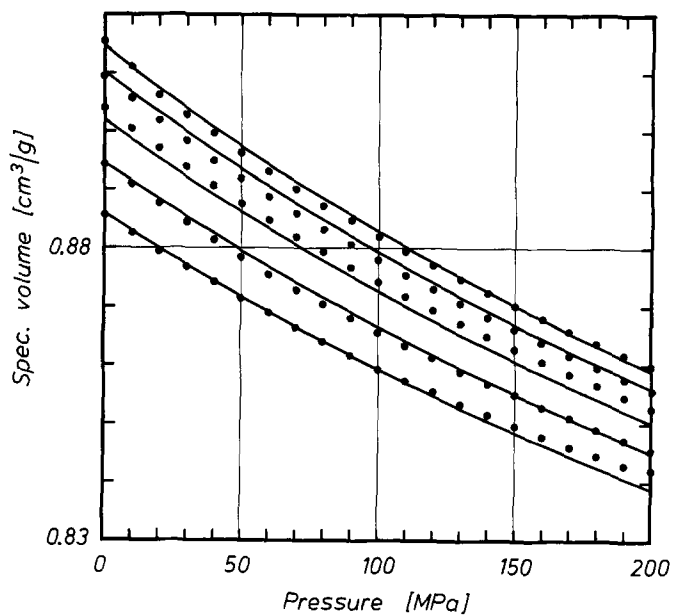Figure 1b   Solid line - result of the Marquardt fit.

Figure 2a

Figure 2b

Figure 2a and 2b

Comparison of experimental and theoretical isotherms for PA-6 measured at
218.4 ^oC; 249.3 ^oC; 269.5 ^oC; 294.5 ^oC and 316.8 ^oC.
Figure 2a Solid line - result of the numerical code.
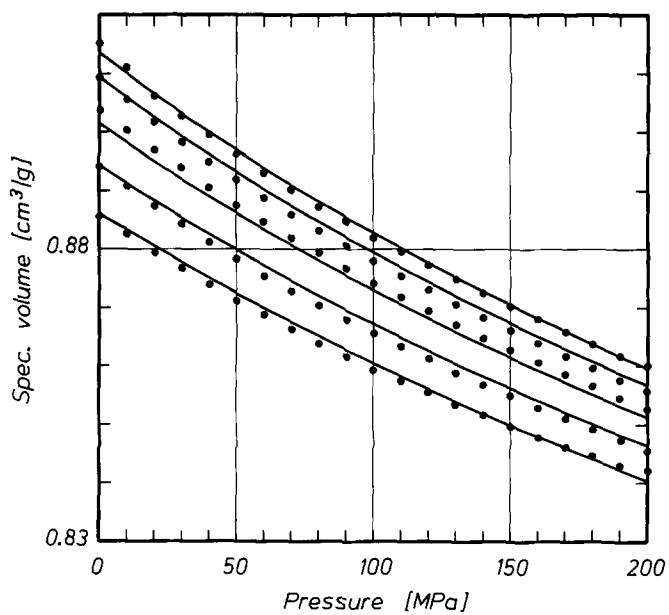Figure 2b Solid line - result of the Marquardt fit.

Figure 3a

Figure 3b

Figure 3a and 3b
Comparison of experimental and theoretical isotherms for PVA measured at
157.9 °C; 169.7 °C; 179.5 °C; 190.2 °C and 195.8 °C.
Figure 3a   Solid line - result of the numerical code.
Figure 3b   Solid line - result of the Marquardt fit.

In Table 1 standard errors in the pressure correspond to the measurement accuracy. On the other hand, the differences in V^* and T^* values obtained by the different fits exceed the accuracy of the measurement. The errors in a typical measurement are for the pressure ca. ± 0.2 MPa, for the specific voulme is ca. ± 0.0002 cm^3/g and for the temperature is ca. ± 0.3 $^\circ$C. This means that the precision of the measurement makes sense for an improvement of the evaluation e.g. by applying the Marquardt algorithm.

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