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Statistical thermodynamics predictions of the solubility parameter

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Abstract: The Simha and Somcynsky (S-S) lattice-hole theory has been shown to represent accurately the pressure–volume–temperature (*PVT*) surface of chain molecular melts and their mixtures. The characteristic scaling parameters, P^* , T^* and V^* , extracted from equation of state (eos) measurements, are known for a large number of polymers. On this basis it is possible to compute the configurational internal energy density and thus the solubility parameter δ as a function of temperature and pressure, $\delta = \delta(T, P)$. In the first part of this paper it is shown that the theory leads to an energy approximately proportional to the first power of density, that is of the van der Waals type, as found for low molar mass fluids by Hildebrand. We continue with a computation of δ for a series of polymer melts at two levels of temperature, namely $T = 25^\circ\text{C}$ and $T = T_g + 300\text{ K}$. Next, the results are compared with those listed in reference publications, all at ambient pressure. The theoretical values extrapolated from the melt to 25°C were systematically higher than those listed. However, good correlation is obtained with the high-temperature calculations for a large variety of polymers. Arguments for this low–high temperature correlation are presented in terms of corresponding levels of molecular mobility and packing in solution and in bulk.

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Keywords: cohesive energy; solubility parameter; free volume; equation of state; corresponding states; lattice-hole; Simha-Somcynsky theory

INTRODUCTION

Hildebrand¹ introduced the concept of the cohesive energy density, *CED*, and solubility in a series of articles starting in 1916. The solubility parameter, δ , introduced later, is related to *CED*:

$$\delta^2 = CED = U/V \quad (1)$$

Thus, *CED* is the internal energy of a given liquid per unit volume. The internal energy, U , binds the molecules. It may be envisaged as the amount of energy necessary to separate individual molecules of the liquid by infinite distance, and hence it's the energy of vapourization that is required to expand the created vapours to infinite volume. Thus, knowing the heat of vapourization of a liquid of interest, one may calculate U , *CED* and δ (see eg Barton²). The internal pressure, p_i , is given by:

$$\begin{aligned} p_i &\equiv (\partial U / \partial V)_T = T(\partial p / \partial T)_V \\ -p &\cong T(\partial p / \partial T)_V = T\beta - T\alpha/\kappa \\ \text{where: } \beta &\equiv (\partial p / \partial T)_V; \quad \alpha \equiv (\partial \ln V / \partial T)_T; \\ \kappa &\equiv (\partial \ln V / \partial P)_T \end{aligned} \quad (2)$$

where α , β and κ are, respectively, the isobaric thermal expansion coefficient, the isochoric thermal pressure coefficient and the isothermal compressibility.

Equations (1) and (2) provide the basis for direct measurements of *CED*, and thus of the Hildebrand (or total) solubility parameter δ at any reference pressure and temperature. It is customary to quote values of δ at ambient conditions: $P = 0.10132\text{ MPa}$ and $T = 298.15\text{ K}$. For solvents, Barton's Handbook² lists single values of the Hildebrand solubility parameter.

However, solubility is pertinent in the case of mixing at least two substances. The simplest case is represented by regular solutions at constant volume. For such systems Scatchard³ wrote the free energy of mixing as:

$$\Delta U_m = (x_i V_i + x_j V_j)(\delta_i - \delta_j)^2 \phi_i \phi_j \quad (3)$$

where x , V and ϕ are mole fraction, molar volume and volume fraction of substances i or j (see subscript). In the derivation Berthelot's geometrical mean rule $U_{ij} = (U_i U_j)^{1/2}$ was used. The author made three assumptions that in Hildebrand's words are 'not exactly true': the total energy is a sum of molecular pairs interactions, the molecules are randomly placed,

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and there is no change of volume on mixing. The concept worked quite well for mixtures of solvents interacting mainly through dispersion forces, but some problems emerged for solutions of polar or hydrogen-bonding substances.

According to Hildebrand, the solubility parameter should be inversely related to the specific volume, or: $\delta \cdot V^n \approx \text{constant}$, where the exponent n is empirical and allowed to vary. The experimental values of n for solvents range from about 0.89 to 1.09 (SiCl_4 or $\text{n-C}_7\text{H}_{16}$). Notably, the value for a van der Waals fluid is $n = 1$. The variation of n was considered to result from the fact that, besides the van der Waals dispersion forces, the polar and hydrogen-bonding interactions contribute to the internal energy.

Hansen⁴ extended Hildebrand's approach by considering two additional types of interactions, namely polar and hydrogen-bonding:

$$\Delta U_m / (V \phi_i \phi_j) = \Theta (\delta_i - \delta_j)_d^2 + (\delta_i - \delta_j)_p^2 + (\delta_i - \delta_j)_h^2 \quad (4)$$

where subscripts d , p , h refer to dispersive, polar and hydrogen-bonding forces, with $\Theta \cong 4$ being an empirical factor. Accordingly, the Hildebrand quantity is now replaced by:

$$\delta = \sqrt{\delta_d^2 + \delta_p^2 + \delta_h^2} \quad (5)$$

Note that it is customary to omit Θ .

For polymers the situation is much more complex. It is hardly possible to measure their heat of vapourization, so that the experimental value of δ under ambient conditions may only be estimated from the polymer behaviour in solutions with solvents of known solubility-parameter values. Grulke⁵ lists several methods for the determination of the polymer solubility parameter. These include solvency test, measurements of turbidity, swelling (for lightly crosslinked polymers), osmotic pressure, intrinsic viscosity, specific volume, refractive index and inverse-phase gas chromatography. Depending on the type of solvent used, as well as on the type of test, the determined δ values vary widely. For example, depending on the hydrogen-bonding strength of the solvent, δ for poly(ethyl methacrylate) is listed² as 17 to 23 (poor hydrogen-bonding capability), 16 to 27 (moderate bonding) and 19 to 23 (strong bonding). Similarly for poly(vinyl ethyl ether): $\delta = 16$ to 22 (poor), 15 to 20 (moderate) and 19 to 23 (strong). The range of values is narrower for less polar polymers, viz for PE $\delta = 16$ to 17 or for PIB $\delta = 15$ to 17, for PS $\delta = 17$ to 22, and for PC $\delta = 19$ to 22. However, there is a fundamental question: why should the internal energy of a substance depend on the method of testing?

For polymers, there is also a question regarding the meaning of δ at $T = 298$ K. Excepting elastomers, most polymers at this temperature are either in a glassy or crystalline state, viz PS with the glass transition at $T_g = 373$ K, PC at $T_g = 418$ K; or PE ($T_g = 145$ K, $T_m = 415$ K); PA-6 ($T_g = 323$ K, $T_m = 492$ K). For

many semi-crystalline polymers it is impossible to have true solutions at temperatures even only 50 °C below their melting point (eg PP solutions).

There is no doubt that the solubility-parameter concept has been useful in industrial applications, especially those involving solutions. Attempts to adopt it to mixtures of polymers met with less success. At best, ΔU_m (see eqns (3) and (4)) is considered an antagonistic contribution to miscibility (related to the heat of mixing), which has to be minimized (eg see Coleman *et al*⁶).

The aim of this work is to calculate values of the solubility parameter from the statistical thermodynamic theory of Simha and Somcynsky⁷ (S-S) and to compare these singular values (the intensive thermodynamic quantity!) with the values cited in the standard tables. It is hoped that such a comparison will provide better understanding of the energies involved and ultimately may lead to a new method for calculating experimentally valid values of δ .

SIMHA AND SOMCYNKY EQUATION OF STATE AND CONFIGURATIONAL INTERNAL ENERGY

The lattice-hole theory of polymer and oligomer melts in the original formulation by S-S has proven quantitatively successful in its applications to the configurational thermodynamics of single- and multi-constituent melts. This may be judged by the performance of the theoretical equation of state (eos), summarized for 56 polymers by Rodgers.⁸ An important contribution of the theory is the incorporation of the volume and the temperature-dependent hole fraction, $h = h(V, T)$, related to the free volume. In addition to entering into the thermodynamic functions, h also serves as a link to other quantities. For example, it correlates bulk properties with surface tension.^{9,10} The interpretation of h as a particular type of free volume fraction has resulted in correlation of equilibrium with transport properties, specifically with the constant stress viscosity of melts, their mixtures¹¹ and filled systems,¹² as well as with viscoelastic functions.¹³ The h -function has moreover been significant in the formulations of the kinetics of volume relaxation.^{14,15} Its extension into the glassy state has led to a theory of elastic moduli.¹⁶ The connection of h with the results of positronium annihilation spectroscopy has also been demonstrated.^{17,18}

The most frequently used function of the S-S theory is the equation of state (eos). The theory represents it in scaled form, with scaling parameters defined by the intersegmental potential and a flexibility factor, in two coupled equations. The scaled variables of state are: $\tilde{P} = P/P^*$; $\tilde{T} = T/T^*$; $\tilde{V} = V/V^*$, where the scaling parameters are expressed as:⁷

$$P^* = zq\varepsilon^*/sv^*; \quad T^* = zq\varepsilon^*/Rc; \quad V^* = v^*/M_0$$

$$\therefore P^*V^*/RT^* = (1/M_0)(c/s) \quad (6)$$

The eos is given in form of the coupled equations:

$$\tilde{P}\tilde{V}/\tilde{T} = (1 - \eta)^{-1} + 2yQ^2(AQ^2 - B)/\tilde{T} \quad (7)$$

with

$$3c[(\eta - 1/3)/(1 - \eta) - yQ^2(3AQ^2 - 2B)/6\tilde{T}] + (1 - s) - s \ln[(1 - y)/y] = 0 \quad (8)$$

In the above relationships: $y = 1 - h$ is the fraction of occupied lattice sites, s is the number of segments per chain of molar mass M , c is the number of external degrees of freedom per chain, M_0 is the segmental molar mass M/s , v^* is the molar repulsion volume between a segment pair, ε^* is the molar attraction energy between a segment pair, $qz = s(z - 2) + 2$ is the number of intermolecular contacts, the constants A , B and z equal, respectively, 1.011, 1.2045 and 12, $Q = 1/(y\tilde{V})$ and $\eta = 2^{-1/6}yQ^{1/3}$ are dimensionless quantities. The coupled eqns (7) and (8) can be solved for $\tilde{V} = \tilde{V}(\tilde{T}, \tilde{P})$ as well as $h = h(\tilde{T}, \tilde{V})$. Note that the eos expressed in reduced variables defines the common eos surface for all liquids, differentiated by their characteristic reducing parameters: P^* , T^* , V^* . For polymeric liquids ($s \gg 1$) the computation is simplified by the customary assumption $3c/S \rightarrow 1$, thus only the first three characteristic reducing parameters are required.

The S-S theory also provides a direct expression for the cohesive energy density:

$$\begin{aligned} \tilde{U} &\equiv U/P^*V^* \\ &= -(1/2)y(y\tilde{V})^{-2}[2.409 - 1.011(y\tilde{V})^{-2}] \\ CED &= \tilde{U}/\tilde{V}; \quad \text{and} \quad \delta^2 = CED = \tilde{U}/\tilde{V} \times P^* \quad (9) \end{aligned}$$

Equations (7) and (8) are used to determine the numerical values of the reducing parameters. For this purpose the experimental PVT data are fitted to the coupled eos relations using MicroMath *Scientist*™ commercial software, which minimizes the differences between the experimental data and the theory by the non-linear least-squares algorithm. To calculate CED or δ from the P^* , T^* and V^* values of a specific polymer, the situation is reversed: eqns (7) – (9) directly provide the values of $\tilde{V}$, $\tilde{U}$, CED and δ for any desired T and P values.

CALCULATIONS

General case: reduced variables of state

The general S-S predictions for $\tilde{U}(\tilde{P}, \tilde{T})$ and $\delta(\tilde{P}, \tilde{T})$ are shown in Figs 1–4 within the full range of reduced variables:¹⁹

$$1.6 < 100 \times \tilde{T} < 7.1 \quad \text{and} \quad 0 < 100 \times \tilde{P} < 35 \quad (10)$$

The range of variables in the inequalities (10) is much wider than that experienced by a single resin. For example, the upper limit of $\tilde{P}$ depends on the

lowest value of P^* computed for polyolefins, but these degrade at lower temperature than the assumed maximum $T_d = 500^\circ\text{C}$, hence for high values of $\tilde{P}$ the upper limit of $\tilde{T}$ is too high. Similarly, the lower limit of $\tilde{T}$ originates in T_g of PE, $T_g \cong 148\text{ K}$. However, since PE melts at least 250 K above T_g , this limit is too low.

Under isobaric conditions (Fig 1) $\tilde{U}$ decreases with increasing $\tilde{T}$. Figure 2 presents the dependence as $\tilde{U}$ versus $1/\tilde{V}$ at ambient pressure. The least-squares fit (within full range of $\tilde{T}$) to the linear and power-law

Figure 1. Reduced internal energy, $\tilde{U} = U/P^*V^*$, versus reduced temperature, $\tilde{T} = T/T^*$, within the full range of reduced pressure, $\tilde{P} = P/P^*$.

Figure 2. $\tilde{U} = U/P^*V^*$ versus $1/\tilde{V} = V^*/V$ at ambient pressure. The shown range of $1/\tilde{V}$ is equivalent to variation of, eg $T = 100$ to 350°C for molten PS. The lines are least squares fit to data points computed from eos, eqns (7)–(9), viz:

$$\begin{aligned} \tilde{U}\tilde{V} &= 0.6601 + 0.019538\tilde{V}; \quad r^2 = 0.99992 \\ \tilde{U}\tilde{V} &= 0.6796 \times \tilde{V}^{0.03223}; \quad r^2 = 0.99994 \end{aligned}$$

dependence is shown. From the latter the value of the exponent, $n = 0.9855$ is calculated close to the van der Waals value of $n = 1.0$. The dependence of Fig 2 is generalized in Fig 3 where the product $\tilde{U}\tilde{V}$ is plotted *versus* $\tilde{V}$ for the full range of independent variables. Furthermore, n increases linearly with $\tilde{P}$: $n = 0.9856 + 0.1099\tilde{P}$; $r^2 = 0.9999$. Thus the van der Waals condition ($n = 1$, $\tilde{U}\tilde{V} = \text{constant}$) is followed exactly at $\tilde{P} \cong 0.1309$, ie at pressures of about $P = 65$ to 140 MPa, depending on the polymer. The approximate van der Waals form of eqn (9) has been recognized earlier by Simha and Wilson,²⁰ based on the approximate constancy of the product $y\tilde{V}$ at $\tilde{P} = 0$.

To close this general discussion, Fig 4 displays the predicted variation of the solubility parameter with temperature and pressure. It is noteworthy that the strongest decrease of the reduced solubility parameter with increasing reduced temperature is at the lowest (ie ambient) pressure¹⁹ with:

$$\partial\tilde{\delta}/\partial\tilde{T}|_{\tilde{P}\rightarrow 0} = 0.95788 - 0.000848\tilde{T} \quad (11)$$

Computation of δ from S-S eos data

To compute the solubility parameter values for the S-S eos, the reducing parameters, P^* , T^* and V^* , must be known and the value of the independent variables must be selected. As far as the first objective is concerned, data published by Rodgers,⁸ Zoller and Walsh²¹ as well as those determined by the authors, were used.

Of the two independent variables the ambient pressure, $P = 0.10132$ MPa is an easy choice. Selection of the temperature is more complex. On the one hand, it is traditional to list the solubility parameters at $T = 25^\circ\text{C}$. When dealing with solvents to use the ambient temperature makes perfect sense. However, what is the molecular environment of 'supercooled'

Figure 3. The product $\tilde{U}\tilde{V}$ versus $\tilde{V}$ for the indicated values of $P_r \equiv \tilde{P}$. The computed isobaric values for the exponent n of eqn (9') are also shown.

Figure 4. The predicted temperature dependence of the solubility parameter in reduced variables, $\tilde{\delta} = \tilde{\delta}(\tilde{T}, \tilde{P})$ versus $\tilde{T}$ at reduced pressures, $\tilde{P}$, indicated on the right hand side of the Figure.

PE, PA or PET macromolecules at a temperature so far below T_g and T_m ? By contrast, other polymers, such as elastomers like PDMS or PIB, are liquid under the ambient conditions. There seems to be a dichotomy.

An alternative approach is to compute δ for polymers at a characteristic internal temperature, eg at constant distance from the glass transition, viz at $T = T_g + \Delta$. Consequently, δ values were computed at several temperatures. In Table 1 the values of the reducing parameters, T_g , and δ values at $T = 25^\circ\text{C}$, 300°C , T_g , and $T_g + 300^\circ\text{C}$ are shown. In the last column, the solubility parameter values listed by Grulke⁵ are displayed as δ_{list} .

Comparison of theoretical predictions of δ with listed values

A quick glance on data listed in Table 1 shows that the assumption of constant absolute temperature for the computations results in poor correlation with the listed values—the agreement is worse for 25 than for 300°C . Better agreement is obtained using the internal temperature approach, but again the values computed for T_g are significantly higher than those listed.

The data in Fig 5 indicate that $\delta_{\text{list}} \approx \delta_{25} - 4$ with the random scatter of $\pm 4 \text{ MPa}^{1/2}$. By contrast, the results presented in Fig 6 suggest that $\delta_{\text{list}} \approx \delta_{T_g+300}$ with about half as large a scatter as before. The thin straight lines in Fig 6 connect points belonging to the same type of polymer. It is important to note that there is good agreement between trends observed experimentally and those predicted by eos, eg see the low δ value observed for PTFE and the high value for PA-66. The largest difference is observed for LDPE and PIB, but, since HDPE and PB are well predicted, the deviation cannot be assigned to their non-polar character. Furthermore, the reduction

Table 1. Computed and listed values of the solubility parameter, δ (MPa^{1/2})

Polymer	P^* (bar)	T^* (K)	V^* (mL g ⁻¹)	T_g (K)	δ_{25}	δ_{300}	δ_{T_g}	δ_{T_g+300}	δ_{list}
EVA25	6669	10 430	1.1046	365	21.048	17.436	20.209	16.157	17
EVA40	7380	10 330	1.0441	377	22.104	18.262	21.048	16.721	18.6
HDPE	5368	11 560	1.201	241	19.199	16.330	19.719	16.681	16.2
LDPE	6365	10 640	1.1745	148	20.632	17.186	20.222	18.801	17
LDPE(Z)	7220.9	10 484	1.1728	148	22.138	18.378	21.608	19.935	17
PA-6	6435	15 290	0.8146	323	21.728	19.523	21.560	19.088	21.5
PA-6 (U)	12 574	11 134	0.89193	323	29.760	25.322	28.826	23.742	21.5
PA-66 (Z)	13 730	11 573	0.89849	323	31.821	26.740	31.315	25.247	24.74
PB	5758	10 940	1.1684	237	19.714	16.543	20.339	16.978	16.98
PB (Z)	6085	10 808	1.1635	237	20.226	16.918	20.88	17.372	16.98
PBD	8031	9532	1.0833	258	22.715	18.312	23.308	18.566	17.06
PC	9844	11 810	0.8156	418	26.080	22.293	24.488	20.155	19.7
PC (Z)	9926	11 802	0.8158	418	26.186	22.380	24.586	20.232	19.7
PCHMA	8128	11 300	0.8952	356	23.543	19.915	22.820	18.755	
PDMS	4973	7825	0.9583	152	17.091	12.736	19.107	14.708	15.6
PEA	7390	9929	0.8764	249	21.961	17.934	22.618	18.303	19.2
PEMA	9534	9910	0.8653	338	24.935	20.350	24.304	19.208	18.31
PEO	9076	10 170	0.8818	210	24.444	20.104	25.665	21.139	20.2
PET	11 330	11 740	0.7419	342	27.955	23.863	27.342	22.775	21.54
PIB	6814	11 400	1.0947	200	21.585	18.299	22.535	19.208	16.47
PMA	8438	10 360	0.8427	283	23.647	19.552	23.856	19.398	20.7
PMMA	9235	11 880	0.836	378	25.282	21.640	24.276	20.158	19.98
PnBMA	8256	10 680	0.9317	293	23.513	19.605	23.581	19.308	17.9
PoMS	7298	12 800	0.9772	409	22.701	19.745	21.562	18.174	
PP(Z)	6042.7	10 535	1.1827	273	20.355	16.720	17.951	16.674	18.8
PPE (U)	8461	10 865	0.8765	480	23.871	19.994	21.353	16.856	
PPG	8254	10 690	0.865	480	23.514	19.610	20.979	16.452	
PS	7133	12 680	0.9611	373	22.416	19.459	21.657	18.310	18.7
PS (U&S)	7941	12 133	0.9573	373	23.513	20.221	22.664	18.945	19.33
PS (U)	6995	12 684	0.9623	373	22.199	19.272	21.448	18.135	18.62
PS1301 (U)	7435	11 723	0.95259	373	22.641	19.321	21.782	18.037	18.62
PSF	10 740	12 740	0.7904	520	27.523	23.915	24.646	20.389	20.26
PSF (Z)	10 873	12 560	0.788	520	27.642	23.947	24.696	20.341	20.26
PTFE	6581	8126	0.4339	390	19.850	15.054	18.303	12.882	12.7
PVAc	9427	9389	0.8135	305	24.536	19.681	24.423	19.090	17
PVAc (Z)	9566	9419	0.8141	305	24.732	19.859	24.618	19.266	19
PVC	7917	12 160	0.7214	354	23.485	20.206	22.859	19.180	21.42
PVME	8005	10 420	0.9653	243	23.056	19.094	23.772	19.548	18.5

International acronyms for polymers were used (see Appendix).

The scaling parameters marked Z were taken from a book by Zoller and Walsh,²¹ those marked by U were measured in the authors' laboratories; U&S data were recently recomputed; the other data were taken from Rodgers.⁸

of scatter is noteworthy. The δ values computed for the $T_g + 300$ reference temperature correlate better with the solution measurements for high temperature polymers as well as for elastomers.

DISCUSSION

Since the work of Prigogine *et al.*,²² the importance of eos contributions to the free energy of mixing has been recognized. The S-S theory has been employed in this context also. However, its application to the calculation of internal energies and related functions is relatively new.

Table 1 and Fig 5 display systematic differences between computed and tabulated data. Before considering the reasons for such differences, it is appropriate to reflect on certain aspects of the underlying theory.

To begin with, the eos is quantitatively accurate and yields correspondingly accurate values of the scaling parameters for a given polymer system. Discrepancies found for different resins, nominally belonging to the same family, originate from the presence of additives in some commercial products (eg up to 10 wt% of an oil in PS); they may also arise from differences in experimental data or in the numerical evaluation procedures. Most importantly, there is eqn (9) for the internal energy, U , and the solubility parameter, δ , and the numerical representation by an exponential expression in the density seen in Figs 2 and 3. The isothermal change, ΔU , with pressure can be extracted from PVT data by means of Tait equation fits^{23,24} and compares satisfactorily with theoretical predictions. However, the internal pressure, p_i , and the derivative $(\partial U/\partial V)_T$ show deviations, but these amount to less than 10% in PS²³ and similar in PVAc.²⁴

Figure 5. Comparison of listed and computed at 25°C solubility parameters (in $\text{MPa}^{1/2}$). Solid line indicates equality; dotted line is the equality shifted to higher values by 8 units.

Figure 6. Comparison of listed and computed (at $T_g + 300$ K) solubility parameters. Solid line indicates equality. International polymer acronym (see Appendix) identifies each data point.

What can be said about the theoretical dependence of U on density:

$$\tilde{U} = A/\tilde{V}^n \quad (9')$$

seen in Figs 2 and 3? The close approach of $n = 0.97$ at atmospheric pressure to values quoted by Hildebrand for low-molecular-mass fluids of diverse structures is noteworthy. We recall in this connection a quantitative success of the theoretical eos in dealing with such systems.^{25,26} One might expect failures of the theory and systematic distinctions in strongly polar and hydrogen-bonding fluids, but neither the eos⁷ nor current results (see Fig 6) indicate such distinctions.

The different energetic contributions are embodied by the parameters ε^* and v^* in eqn (6), which define the scaling parameters.

Finally we turn to the predicted temperature dependence of the solubility parameter, $\delta = (U/\tilde{V})^{1/2}$. Equation (9), with the power dependence of $\tilde{U}$ seen in Figs 2 and 3 (and eqn (9')), yields:

$$\delta = \delta_0 \exp\{-\alpha T(n+1)/2\}; \quad \text{with} \quad \alpha T = \tilde{\alpha} \tilde{T} \quad (12)$$

The performance of the theory in respect to the thermal expansions is illustrated in Fig 2 of reference 20 for atmospheric pressure in reduced coordinates. Although only a series of methacrylates was included, we will assume a general validity of the pattern seen. A maximum of 6% for $\tilde{\alpha}$ in the temperature-dependent spectrum of deviations from experiment appears. For the polymers in Figs 5 and 6 this should translate with eqn (12) to errors of less than 10% over the range of 100 K and of corresponding reduced temperatures. However, the shift from $\delta(\text{calc})$ to the listed values by $ca\ 4\ \text{MPa}^{1/2}$ in Fig 5 is nearly independent of temperature and it amounts to 4/23 to 4/15, ie is considerable.

It appears that we must look for rationalizations for the discrepancies observed other than theoretical deficiencies. In a general way, our results are in concordance with the well-known view that there is no thermodynamic equivalence between macromolecules in a non- Θ -solvent and in their melts, in a supercooled or equilibrium state. This view was established in terms of radii of gyration, obtained by means of small-angle neutron scattering (SANS).

Another possible rationalization for the high δ values computed for 25°C may be related to the volumetric expansion upon heating. Consider that the product $\delta V \propto (\tilde{U}\tilde{V})^{1/2}$ is approximately constant according to eqn (9') with n approximately unity. For the polymers listed in Table 1, the numerical value of the product δV equals 22.3 ± 1.1 . This quantifies the expected result that an enlarged volume (and thus a higher temperature) is required to reduce the computed δ to the listed values. This is readily translated into a statement in terms of free volume, ie in the frame of the lattice-hole model the hole fraction $h = 1 - y$. At atmospheric pressure the product yV is practically temperature-independent,²⁰ and therefore $y = 1 - h = \text{constant} \times \delta$.

A detailed examination would be required to establish the numerical relationship between the thermodynamic properties of the (extrapolated) high-temperature melt and the solution. However, as a simple test of the hypothesis, the values of the free volume parameter h were computed for 29 types of polymers discussed in this paper. The computations were carried out for $T = 25^\circ\text{C}$ (hence far below the conditions used to determine the scaling parameters) and at $T_g + 300^\circ\text{C}$. The data are shown in form of the

Figure 7. Computed values of the free volume parameter h at 25 °C (solid) and at $T_g + 300$ °C (cross-hatched) for 29 polymers. International polymer acronym (see Appendix) identifies each set of data.

bar graph in Figure 7—the average value of difference: $\Delta h = h_{T_g+300} - h_{25} = 0.18$.

The free volume fraction of solvents that were used to determine the polymers' solubility parameters depends on their nature. At 25 °C the values of h for *n*-dodecane and *n*-hexadecane are about 0.17 and 0.19, respectively.¹¹ The h values at 25 °C for more volatile solvents, used in extrusion foaming, CO₂, HFC-142 and HFC-134, range from 0.24 to 0.54.²⁷ Evidently, the polymer values of h_{T_g+300} correlate better with solvent h values at 25 °C than those of h_{25} .

CONCLUSIONS

The emphasis here has been on the CED and, derived from it, the solubility parameter. These functions can be computed from the S-S eos, using the characteristic reducing parameters. The aim of this paper was to investigate correlations between the solubility parameters calculated for polymers from the Simha and Somcynsky theory with the values listed in the standard tables, determined in solutions under ambient conditions. The values computed for 25 °C are about 4 MPa^{1/2} higher than the 'preferred' experimental values. Alternatively, taking the glass transition temperature as reference, good correlation between the listed and computed values at $T_g + 300$ was found. One possible explanation for the need to go to such a high temperature is to provide an equivalent state as reflected in the volume or free volume.

It has been shown that the free volume at $T_g + 300$ is similar to that dissolution of polymer would introduce. Thus, one of the results of this analysis is a more quantitative corroboration of a lack of thermodynamic

equivalence between macromolecules in solution and in the melt, as measured by the solubility parameter. However, since there is a great variety of solvents that are used for determining the solubility parameter for a given polymer, and each solvent is characterized by a different free volume fraction at ambient conditions, an exact comparison between free volume in melt and in solution is not feasible. Furthermore, the selected temperature of $T_g + 300$ is arbitrary—possibly better correlation between the two sets of data could be found at some other $T_g + \Delta$ temperature, but in view of the wide range of the listed δ values this does not seem necessary. Thus, another outcome of this analysis is a need for a more precise definition of the solubility parameter, not only in terms of the interactions (poor moderate and strong or dispersive, polar and hydrogen-bonding), but also as far as the free volume is concerned.

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Appendix

EVA25, EVA40	Poly(ethylene- <i>co</i> -vinyl acetate) with 25 and 40 wt% vinyl acetate
HDPE	High density polyethylene (<i>ca</i> 960 kg m ³)
LDPE	Low density polyethylene (<i>ca</i> 918 kg m ³)
PA-6	Poly- ϵ -caprolactam
PA-66	Poly(hexamethylene diamine–adipic acid), poly-hexamethylene–adipamide
PB	Poly-1-butene, polybutylene
PBD	Polybutadiene
PC	Bisphenol-A polycarbonate
PCHMA	Poly(cyclohexyl methacrylate)

PDMS	Polydimethylsiloxane
PEA	Polyethylacrylate
PEMA	Polyethylmethacrylate
PEO	Polyethylene glycol, usually PEG
PET	Poly(ethylene terephthalate)
PIB	Polyisobutene
PMA	Poly(methyl acrylate)
PMMA	Polymethylmethacrylate
PnBMA	Poly(n-butyl methacrylate)
PoMS	Poly(<i>o</i> -methylstyrene)
PP	Polypropylene
PPE	Poly(2,6-dimethyl 1,4-phenylene ether)
PPG	Polypropylene glycol
PS	Polystyrene (PS1301 = from Nova Chem)
PSF	Polysulfone
PTFE	Polytetrafluoroethylene
PVAc	Poly(vinyl acetate)
PVC	Poly(vinyl chloride)
PVME	Poly(vinyl methyl ether)