

## A Semiempirical Equation of State for Polymer Melts

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### Synopsis

An explicit reduced equation of state is developed by combining results of the hole theory with a semitheoretical expression for the temperature dependence of the reduced Tait parameter  $\bar{B}$  which is found to be in good agreement with experiment. This approach circumvents the implicit character of the theoretical equations.

Two procedures are explored to derive for a given system the PVT surface and the compressional energy and entropy changes from the corresponding reduced functions. One rests on the usual superposition of experimental and analytical isotherms and isobars. The other, and more approximate method, utilizes a correlation between the scaling temperatures, pressures, and volumes obtained previously, and requires only experimental data at atmospheric pressure and a single temperature above the glass transition ( $T_g$ ) or the melting temperature ( $T_m$ ). The good agreement between experiment and theory noted previously is shown to extend to the semiempirical relationships. Finally, internal pressure data for oligomers and polymers at atmospheric pressure and encompassing a wide range of reduced temperatures are examined. The ensemble of data can be described by simple power relationships between the internal energy and the density. The exponents, however, depart significantly from the van der Waal's value of unity.

### INTRODUCTION

From the practical point of view, studies of the pressure-volume-temperature (PVT) behavior of thermoplastic materials are motivated by the need for (a) knowledge of material properties at fabricating conditions; (b) knowledge of material properties at use conditions.

On the other hand, such investigations represent a chapter in the continuing story of relating macroscopic properties to molecular characteristics. However, a recent review<sup>1</sup> illustrates the need for accurate, generalized, yet simple equations of state which would provide design engineers with the required data. A multitude of empirical isothermal equations of state have been presented.<sup>2,3</sup> Although they contain no explicit temperature dependence, these relations have been of substantial value for smoothing, interpolation, and extrapolation of isotherms and for the computation of compressibilities and compressional thermodynamic functions.<sup>1-4</sup> van der Waals-type relations<sup>5,6</sup> developed for polymers have included corrections for molecular contractability.<sup>7,8</sup> Another, corresponding states approach utilizes the glass temperature as a scaling factor.<sup>9</sup> Most of these equations have been only moderately successful. However, the

Tait equation, an isothermal relationship, has proven particularly useful in the analysis of organic polymers<sup>10-15</sup> following the work of Cutler on hydrocarbons.<sup>16</sup> Most recently, it has been applied to selenium melt.<sup>17</sup>

In spite of their quantitative success, the Tait equation and similar relations share the disadvantages inherent in empirical equations, which render molecular interpretations difficult. An acceptable equation of state, apart from yielding quantitative predictions, should provide some insight into the molecular architecture of the system in terms of a minimum possible set of parameter. Statistical mechanical theory provides in principle such a rational basis. An evaluation of experiment in the frame of such a theory then yields a set of characteristic scaling parameters. These, in turn, should give an insight into the interplay of intra- and intermolecular forces in determining the conformational and configurational states of the system. However, in practice, such a program, particularly for chain-molecular systems, remains at best incomplete. An obvious alternative is to combine the simplicity of empirical equations of state with the advantages of statistical mechanical theory in developing tractable, yet general, relations viable for the discussion of PVT and configurational thermodynamic functions.

### THE EQUATION OF STATE

In reduced co-ordinates, the Tait relation is<sup>10-15</sup>

$$1 - \tilde{V}(\tilde{P}, \tilde{T})/\tilde{V}(0, \tilde{T}) = C \ln [1 + \tilde{P}/\tilde{B}(\tilde{T})] \quad (1)$$

with  $C = 0.0894$ , being a satisfactorily "universal" constant for organic polymers. A rationalization of eq. (1) was given by Nanda and Simha<sup>18</sup> based on the expressions

$$\tilde{V}_0 C = -(\partial \tilde{P}/\partial \tilde{V})_{\tilde{T}}/(\partial^2 \tilde{P}/\partial \tilde{V}^2)_{\tilde{T}} \quad (2)$$

$$\tilde{B} = -\tilde{V}_0 C (\partial \tilde{P}/\partial \tilde{V})_{\tilde{T}} - \tilde{P} \quad (3)$$

where the tildes identify the reduced variables  $\tilde{P} = P/P^*$ ,  $\tilde{V} = V/V^*$ ,  $\tilde{T} = T/T^*$ ,  $\tilde{B} = B/P^*$ ; and the starred quantities are the scaling parameters characteristic of the particular theory employed, provided such a theory does indeed lead to a principle of corresponding states. In eqs. (2), (3), and others to follow,  $\tilde{V}_0$  stands for  $\tilde{V}(0, \tilde{T})$  of eq. (1).

A computation of the derivatives in eq. (2) from the Prigogine<sup>19-21</sup> cell theory equation of state indeed indicates<sup>18,22</sup>  $C$  to be but a slowly varying function of volume or temperature in contrast to the behavior of  $\tilde{B}$ . The point of the calculation was to establish the Tait equation as a reduced equation of state. The quantitative inadequacies of the cell theory have been discussed for oligomers<sup>23</sup> and polymers.<sup>24,25</sup> A hole theory<sup>26</sup> has been shown to largely remove these inadequacies.<sup>4,13,14,27</sup> The equation of state derived in the hole theory is

$$\frac{\tilde{P}\tilde{V}}{\tilde{T}} = [1 - 2^{-1/6}y(y\tilde{V})^{-1/3}]^{-1} + (2y/\tilde{T})(y\tilde{V})^{-2}[1.011(y\tilde{V})^{-2} - 1.2045] \quad (4)$$

with the following condition on the hole fraction  $(1 - y)$ :

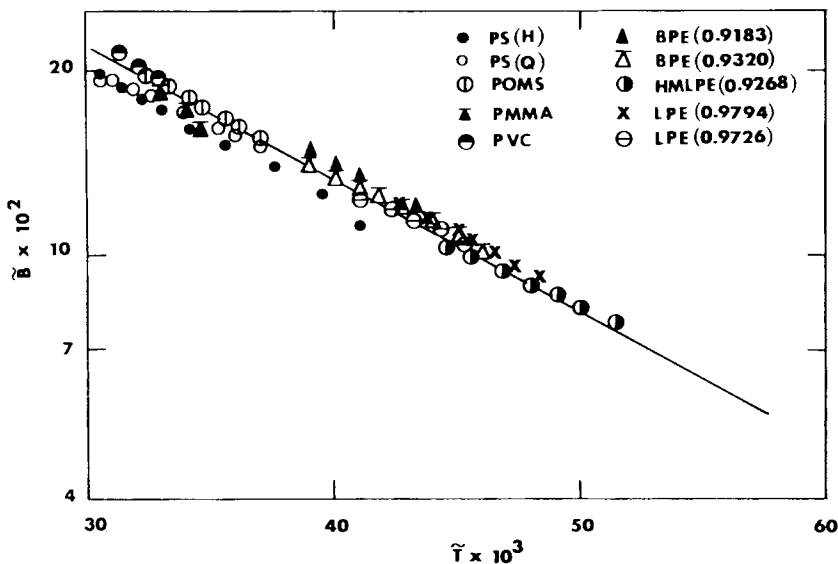


Fig. 1. Reduced Tait parameter  $\bar{B}$  as a function of reduced temperature.

$$(s/3c)[1 + y^{-1} \ln(1 - y)] = (y/6\bar{T})(y\bar{V})^{-2}[2.409 - 3.033(y\bar{V})^{-2}] \\ + [2^{-1/6}y(y\bar{V})^{-1/3} - 1/3][1 - 2^{-1/6}y(y\bar{V})^{-1/3}]^{-1} \quad (5)$$

where  $3c/s$  represents the number of external degrees of freedom per chain segment. Due to the transcendental form of eq. (5), the equation of state is not explicit and a numerical solution is required. This inconvenience is avoided at atmospheric pressure by noting that the theoretical result desired from eq. (4) with  $\bar{P} \rightarrow 0$  and eq. (5) can be represented for  $3c/s = 1$  by the interpolation formula<sup>14</sup>

$$\ln \bar{V}_0 = -0.10335 + (23.8345 \times \bar{T}^{3/2}) \quad (6a)$$

or

$$\ln \bar{V}_0 = -0.10335 + \frac{2}{3}\alpha T \quad 1.65 < \bar{T} \times 10^2 < 7.03 \quad (6b)$$

with a standard deviation of 0.16%, where  $\alpha$  represents the thermal expansivity  $1/V(\partial V/\partial T)_P$ . These equations have been extensively compared with experimental data.<sup>28</sup> In view of the quantitative success of the theoretical equation of state, it would be desirable to have a simple interpolation formula available at elevated pressures as well.

The purpose of this paper is to develop and test the consequences of such an equation. We proceed through the reduced Tait parameter  $\bar{B}$  as derived by eqs. (2) and (3). Previously, we have used<sup>14</sup> a simplification by assigning the "universal" value to  $C$  rather than the value following from eq. (2). A combination of eqs. (1), (4), and (5) yields  $\bar{B}$  as a function of the reduced temperature  $\bar{T}$ , and the result is shown in Figure 1. This extends an earlier computation to higher temperature (see Fig. 6 of ref. 14). It is seen that over the whole range,  $\bar{B}$  is an exponential function of temperature. This has indeed been found experimentally in several polymer systems.<sup>13,15,27</sup> Also displayed in Figure 1 are results

TABLE I  
 Characteristic Parameters and Related Properties

	Material	$\rho_{20^\circ\text{C}}$ , cc/g	$T^*$ , °K	$V^*$ , cc/g	$P^*$ , bar	$T_g$ , °K	$P^*V^*/T^*$ , bar-cc/ g-°K
1	C <sub>7</sub>	—	5888	1.2365	7648	—	1.6061
2	C <sub>9</sub>	—	6500	1.2235	7600	—	1.4306
3	C <sub>11</sub>	—	6910	1.2131	7580	—	1.3310
4	C <sub>13</sub>	—	7277	1.2059	7552	—	1.2515
5	C <sub>17</sub>	—	7797	1.1955	7520	—	1.1530
6	C <sub>20</sub>	—	7979	1.1900	7490	—	1.1171
7	C <sub>30</sub>	—	8700	1.1800	7460	—	1.0118
8	C <sub>40</sub>	—	9068	1.1738	7433	—	0.9622
9	HMWLPE	0.9268	9205	1.1285	8968	(191)	1.0994
10	PVAc	1.1896	9412	0.8140	9408	304	0.8137
11	LPE	0.9794	9772	1.1417	7478	(203)	0.8737
12	H. Rubber	0.9109	9831	1.0774	7465	204	0.8181
13	HR-6% S	0.9596	9877	1.0286	8690	226	0.9050
14	HR-11.5% S	1.0090	9925	0.9743	10269	252	1.0080
15	PnBMA	1.0571	9988	0.9299	8456	293	0.7873
16	LPE <sup>a</sup>	0.9726	10046	1.1548	7160	(208)	0.8231
17	BPE	0.9320	10139	1.1601	6946	(210)	0.7948
18	BPE <sup>a</sup>	0.9183	10328	1.1641	6765	(214)	0.7625
19	i-PMMA	1.2190	11170	0.8160	10088	320	0.7370
20	PCHMA	1.1011	11290	0.8906	8382	380	0.6612
21	PVC <sup>a</sup>	1.3928	11320	0.7105	10345	349	0.6493
22	PMMA <sup>a</sup>	1.1876	11890	0.8350	9303	378	0.6533
23	PMMA	1.1834	11920	0.8370	9147	378	0.6423
24	PS	1.0466	12680	0.9598	7453	365	0.5641
25	PS <sup>a</sup>	1.0471	12700	0.9625	7638	362	0.5789
26	PoMS	1.0217	12740	0.9762	7458	404	0.5715

<sup>a</sup> Experimental data from ref. 38.

for several amorphous polymers in the liquid state. Here, the original data have been reduced by the appropriate pressure and temperature scaling parameters listed in Table I. These have been derived earlier by the superposition of experimental and theoretical isobars and isotherms.<sup>4,13,27,28</sup> The extent of agreement illustrated by Figure 1 allows us to proceed. The equation of the straight line is

$$\bar{B} = 0.9549 \exp(-49.22\bar{T}) \quad (7)$$

Equations (1), (6), and (7) then yield the reduced equation of state:

$$\bar{V}(\bar{P}, \bar{T}) = 0.9018 \exp(23.8345\bar{T}^{3/2}) \times [1.0 - 0.0894 \ln\{1.0 + 1.0472\bar{P} \exp(49.22\bar{T})\}] \quad (8)$$

Therefore, the reduced thermal expansivity is

$$\bar{\alpha} = 35.7518\bar{T}^{1/2} - 49.22\bar{\kappa}\bar{P} \quad (9)$$

where the isothermal compressibility  $\bar{\kappa}$  is given by

$$\bar{\kappa} = C \left\{ \left( 1 - C \ln \left( 1 + \frac{\bar{P}}{\bar{B}} \right) \right) (\bar{P} + \bar{B})^{-1} \right\} \quad (10)$$

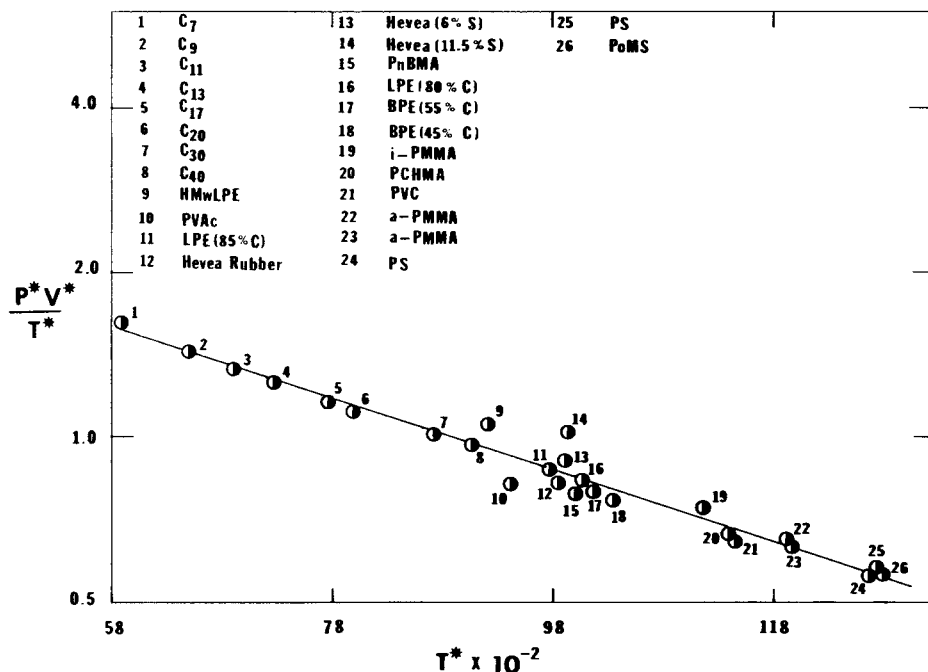


Fig. 2. Correlation between characteristic compressibility factor and characteristic temperature for polymers and oligomers appearing in Table I. Solid line, eq. (12).

The configurational contribution to the Grüneisen parameter can also be calculated following the recent development by Warfield:<sup>29</sup>

$$\tilde{\gamma}_L = \frac{1}{2} \left( \frac{\partial(1/\bar{\kappa})}{\partial \bar{P}} \right)_{\bar{T}} = \frac{1}{2} [(1/C - 1) - \ln(1 + \bar{P}/\bar{B})] \quad (11)$$

According to eq. (11),  $\gamma_L$  should assume a universal maximum value of 5.093 for organic polymers. With increasing pressure,  $\gamma_L$  decreases at a higher rate for the more compressible material. Note also that slight variations in  $C$  will produce somewhat larger fractional changes in  $\gamma_L$  since  $d\gamma_L/\gamma_L = -(1 - C)^{-1} dC/C$ .

Of paramount practical importance is the accuracy in the PVT description of thermoplastic materials. The very satisfactory performance<sup>4,13,27,28</sup> of the theoretical eqs. (4) and (5) does not necessarily imply a similar success of the semiempirical eq. (8). Moreover, we now have two ways of evaluating PVT relations from eq. (8). The first utilizes the scaling parameters in Table I to convert from the reduced to the actual variables of state (calculation A). The second, and more approximate one, makes use of an empirical correlation<sup>4</sup> between the scaling parameters (calculation B). The correlation relation is

$$\ln \left( \frac{P^*V^*}{T^*} \right) = 1.3191 - \left( \frac{3}{2.01} \right) (T^* \times 10^{-4}) \quad (12)$$

The adequacy of eq. (12) may be judged from Figure 2. Then, for a new polymer, only a knowledge of  $\alpha$  and  $V_0$  at a single  $T \geq T_g$  or  $T \geq T_m$  is needed. Substitution into eq. (6b) provides  $V^*$ . From the known  $\bar{V}_0$  and  $T$ ,  $T^*$  is obtained by means of eq. (6a). Alternatively,  $V^*$  and  $T^*$  can be derived more accurately by



118.7	Exp.	1.0097	.9960	.9839	.9735	.9639	.9554	.9476	.9407	.9341	.9280	.9220
	Calc. A	1.0092	.9950	.9827	.9719	.9622	.9535	.9456	.9383	.9315	.9252	.9193
	Calc. B	1.0092	.9959	.9842	.9739	.9647	.9563	.9486	.9415	.9350	.9288	.9231
133.1	Exp.	1.0200	1.0051	.9920	.9807	.9707	.9617	.9531	.9457	.9390	.9323	.9264
	Calc. A	1.0197	1.0043	.9912	.9797	.9695	.9603	.9520	.9444	.9373	.9308	.9247
	Calc. B	1.0197	1.0052	.9928	.9818	.9721	.9632	.9552	.9478	.9410	.9346	.9286
146.4	Exp.	1.0300	1.0140	.9999	.9884	.9778	.9681	.9596	.9517	.9447	.9375	.9312
	Calc. A	1.0296	1.0131	.9992	.9871	.9763	.9668	.9581	.9501	.9428	.9361	.9298
	Calc. B	1.0296	1.0141	1.0009	.9893	.9790	.9698	.9614	.9537	.9466	.9400	.9338
160.2	Exp.	1.0404	1.0229	1.0081	.9956	.9841	.9741	.9653	.9568	.9496	.9432	.9365
	Calc. A	1.0402	1.0225	1.0076	.9948	.9835	.9735	.9644	.9562	.9486	.9416	.9351
	Calc. B	1.0402	1.0235	1.0094	.9972	.9863	.9767	.9679	.9599	.9525	.9456	.9393
174.3	Exp.	1.0513	1.0321	1.0161	1.0024	.9906	.9799	.9707	.9627	.9545	.9479	.9412
	Calc. A	1.0512	1.0322	1.0164	1.0028	.9910	.9805	.9710	.9624	.9546	.9473	.9406
	Calc. B	1.0512	1.0333	1.0183	1.0053	.9939	.9838	.9746	.9663	.9586	.9515	.9449
187.5	Exp.	1.0614	1.0403	1.0237	1.0098	.9974	.9864	.9770	.9683	.9590	.9515	.9448
	Calc. A	1.0619	1.0415	1.0247	1.0104	.9980	.9871	.9772	.9683	.9602	.9527	.9458
	Calc. B	1.0619	1.0427	1.0267	1.0131	1.0011	.9905	.9810	.9723	.9644	.9570	.9502
199.5	Exp.	1.0713	1.0493	1.0314	1.0163	1.0032	.9919	.9817	.9727	.9641	.9565	.9492
	Calc. A	1.0718	1.0501	1.0324	1.0174	1.0045	.9932	.9830	.9738	.9654	.9577	.9506
	Calc. B	1.0718	1.0513	1.0345	1.0202	1.0077	.9967	.9868	.9779	.9697	.9621	.9551

<sup>a</sup> Exp. = Experiment; Calc. A = calculated with the  $P^*$ ,  $V^*$ ,  $T^*$  obtained via the usual superposition ( $P^* = 8456$  bar,  $V^* = 0.9229$ ,  $T^* = 9988^\circ\text{K}$ );  
 Calc. B = calculated with the  $V^*$ ,  $T^*$  obtained via superposition,  $P^*$  from eq. (12) ( $P^* = 9046$  bar).  
<sup>b</sup>  $P$  = Pressure.

TABLE III  
Specific Volume of Linear Polyethylene<sup>a</sup>

t, °C		Specific volume, cc/g																				
		P <sup>b</sup> = 1 bar	200 bar	400 bar	600 bar	800 bar	1000 bar	1200 bar	1400 bar	1600 bar	1800 bar	2000 bar										
142.1	Exp.	1.2692	1.2467																			
	Calc. A	1.2686	1.2455																			
152.9	Calc. B	1.2686	1.2454																			
	Exp.	1.2787	1.2549	1.2352	1.2185																	
165.4	Calc. A	1.2791	1.2545	1.2343	1.2172																	
	Calc. B	1.2791	1.2544	1.2342	1.2170																	
171.1	Exp.	1.2915	1.2664	1.2458	1.2284	1.2131	1.1995															
	Calc. A	1.2914	1.2652	1.2439	1.2258	1.2103	1.1965															
180.9	Calc. B	1.2914	1.2651	1.2437	1.2256	1.2100	1.1962															
	Exp.	1.2970	1.2710	1.2498	1.2320	1.2163	1.2026	1.1903	1.1793													
189.6	Calc. A	1.2972	1.2702	1.2482	1.2298	1.2139	1.2000	1.1875	1.1762													
	Calc. B	1.2972	1.2700	1.2481	1.2296	1.2137	1.1997	1.1872	1.1759													
199.7	Exp.	1.3075	1.2802	1.2582	1.2395	1.2235	1.2093	1.1968	1.1855	1.1753	1.1660											
	Calc. A	1.3072	1.2787	1.2559	1.2367	1.2203	1.2059	1.1931	1.1815	1.1710	1.1614											
189.6	Calc. B	1.3072	1.2786	1.2557	1.2365	1.2200	1.2056	1.1928	1.1812	1.1707	1.1610											
	Exp.	1.3165	1.2879	1.2648	1.2455	1.2290	1.2147	1.2015	1.1900	1.1794	1.1694											
199.7	Calc. A	1.3162	1.2864	1.2627	1.2429	1.2260	1.2112	1.1981	1.1860	1.1756	1.1657											
	Calc. B	1.3162	1.2863	1.2625	1.2427	1.2257	1.2109	1.1978	1.1860	1.1752	1.1654											
199.7	Exp.	1.3271	1.2971	1.2734	1.2534	1.2362	1.2213	1.2081	1.1966	1.1857	1.1756											
	Calc. A	1.3269	1.2955	1.2707	1.2502	1.2327	1.2175	1.2040	1.1919	1.1809	1.1708											
199.7	Calc. B	1.3269	1.2954	1.2705	1.2499	1.2324	1.2172	1.2036	1.1915	1.1805	1.1704											

<sup>a</sup> Exp. = Experiment; Calc. A = calculated with the  $P^*$ ,  $V^*$ ,  $T^*$  obtained via the usual superposition ( $P^* = 7478$  bar,  $V^* = 1.1417$ ,  $T^* = 9772^\circ\text{K}$ );

Calc. B = calculated with the  $V^*$ ,  $T^*$  obtained via superposition,  $P^*$  from eq. (12) ( $P^* = 7445$  bar).

<sup>b</sup>  $P$  = Pressure.



the usual superposition procedure.<sup>4,13,27,28</sup> In either case, the unknown parameter is  $P^*$  which is readily computed from eq. (12). The goodness of fit of procedures A and B with experiment is illustrated in Table II for poly(*n*-butyl methacrylate) above its  $T_g$  and in Table III for polyethylene above its  $T_m$ . The former allows for a wide range of temperatures above  $T_g$ , whereas the latter represents an example of crystallizable polymer. For both systems, the discrepancies, which are much less than 1% in all cases, increase with increasing pressure. For poly(*n*-butyl methacrylate), the deviations at 2000 bar in calculation A range from -0.3% to +0.15% as temperature increases from 73.5° to 199.5°C. At similar conditions, the range is +0.7% to +0.62% for calculation B. The more positive tendencies in the error reflect the overestimation of  $P^*$  (7% higher than case A).

For polyethylene, the average discrepancy between calculations A, B, and experiment at 2000 bar is -0.42% and -0.45%, respectively. In this instance, the slightly more negative tendencies for calculation B reflect the underestimation of  $P^*$  (4.4% lower than case A). Nonetheless, the agreement between experiment and the semiempirical procedure is excellent.

Being able to generate PVT data for any polymer from a minimum knowledge of volume and thermal expansivity at atmospheric pressure and a single  $T \geq T_g$  and  $T \geq T_m$  represents one of the significant achievements of this work. It must be cautioned, however, that eq. (12) may be in error for polymers with very low reduced glass transition temperatures and/or high values of  $T^*$ . Then, procedure B may be unreliable.

## THERMODYNAMIC FUNCTIONS

Here, we consider the compressional energy  $\Delta\tilde{U} = \tilde{U}(\tilde{P}, \tilde{T}) - \tilde{U}(0, \tilde{T})$ , the corresponding entropy  $\Delta\tilde{S}$ , and the internal pressure  $(\partial\tilde{U}/\partial\tilde{V})_{\tilde{T}} = \tilde{P}_i$ . The Tait relation and eq. (7) yield the following expressions:

$$\Delta\tilde{U} = -(\tilde{T}\tilde{\alpha}_0/C - 49.22\tilde{T} + \tilde{T}\tilde{\alpha}_0 - 1)\tilde{P}\tilde{V}_0C + (\tilde{T}\tilde{\alpha}_0\tilde{B} + \tilde{T}\tilde{\alpha}_0\tilde{P} - 49.22\tilde{T}\tilde{B} - \tilde{B})(\tilde{V}_0 - \tilde{V}) \quad (13)$$

$$\Delta\tilde{S} = [\Delta\tilde{U} - C\tilde{V}_0\tilde{P} + \tilde{B}(\tilde{V}_0 - \tilde{V})]/\tilde{T} \quad (14)$$

$$\tilde{P}_i = \tilde{T}\tilde{\alpha}_0(\tilde{P} + \tilde{B})\tilde{V}/C\tilde{V}_0 - \tilde{P}(49.22\tilde{T} + 1) \quad (15)$$

where  $\tilde{\alpha}_0$  is the reduced thermal expansivity at zero pressure. In Figures 3-7, we compare the semiempirical calculations with the hole theory and the experimental data. For the compressional energy and entropy, Figures 3-5, a principle of corresponding states is satisfied, at least for the high polymers, but the differences between the theoretical and the semiempirical relations increase at higher temperatures and pressures. As anticipated, therefore, the difference in the internal pressure under compression, Figure 6, is more pronounced.

Much larger deviations are observed between the experimental data and the semiempirical result on one hand and the hole theory on the other in respect to the internal pressure at atmospheric pressure, see Figure 7. Since  $P_i = (\partial U/\partial V)_T$ , the appearance of a maximum in the  $P_i-V_0$  or  $P_i-T$  function is readily understood from the familiar shape of the potential energy curve and the fact that the system starts out from the bottom of the well at low temperature, to pass to the right with increasing temperature. The theory, however, locates the maximum at too

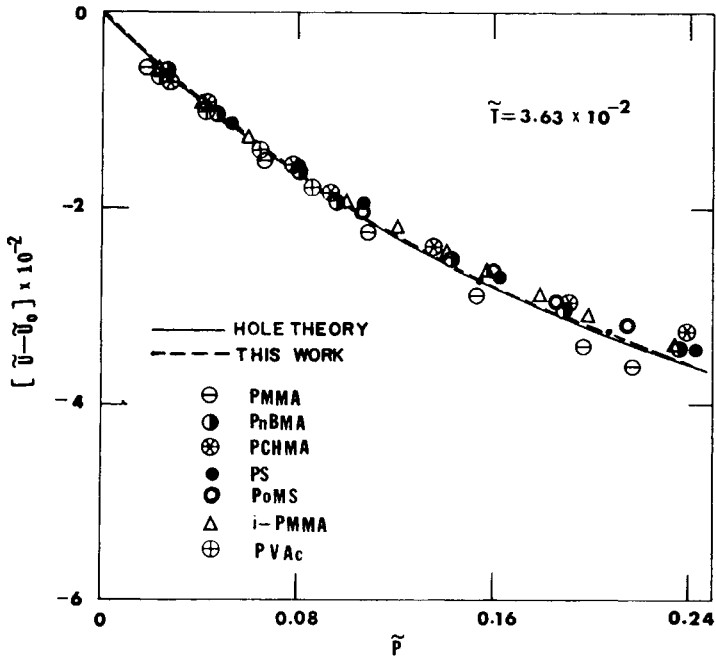


Fig. 3. Change of reduced configurational internal energy as a function of reduced pressure at constant temperature.

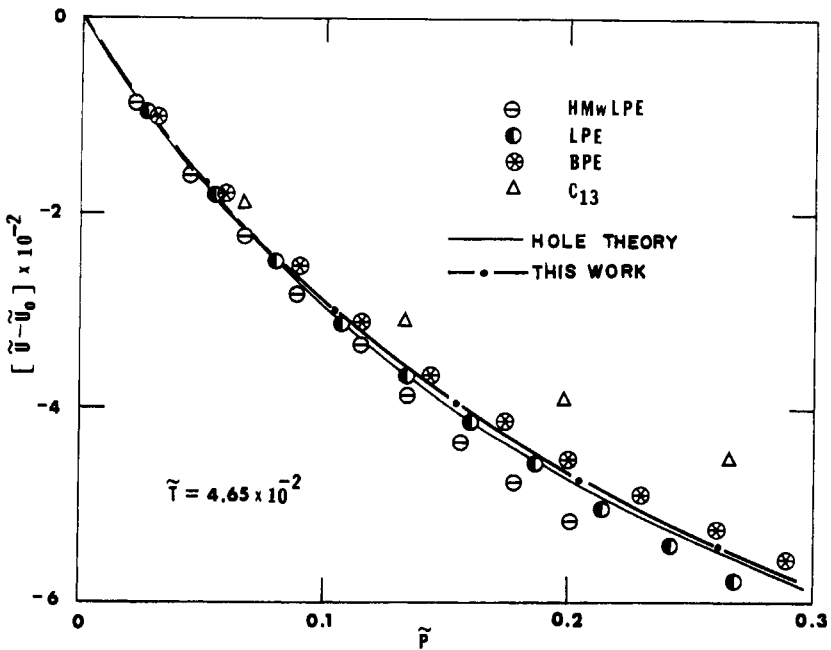


Fig. 4. Change of reduced configurational internal energy as a function of reduced pressure at constant temperature for polyethylenes and  $n$ -C<sub>13</sub>.

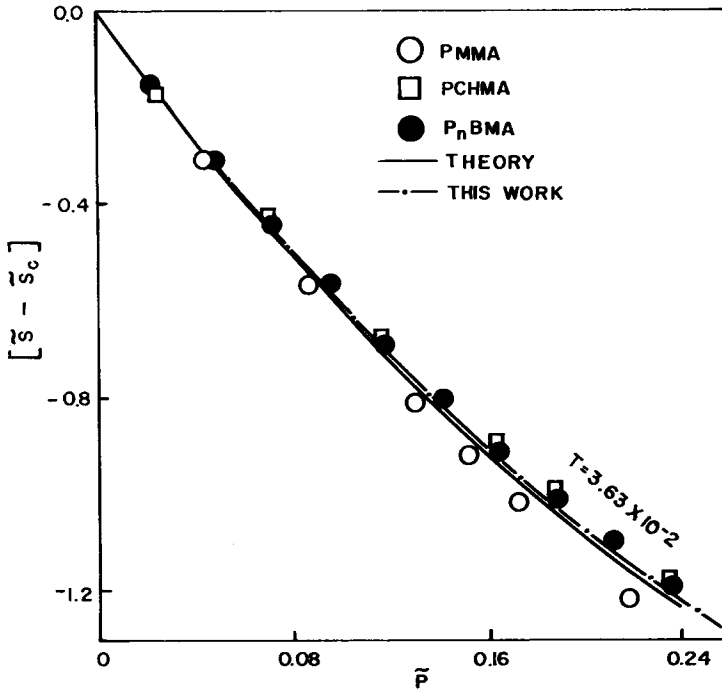


Fig. 5. Change of reduced configurational entropy as a function of reduced pressure at a constant temperature.

high a temperature, whereas experimentally it is hardly seen in the range under consideration, except possibly for poly(*n*-butyl methacrylate), see no. 15 in Figure 7. This deficiency, pronounced at elevated temperatures, which we have pointed out in previous<sup>4,13,27</sup> discussions, is not exhibited to the same extent by the semiempirical relation. The reader may also judge the approximate validity of a principle of corresponding states in respect to the internal pressure by means of Figure 7 and consider the element of experimental error. For convenience, three additional empirically derived curves (A, B, and C) are drawn to encompass the multitude of data exhibited in Figure 7. They can all be represented by exponential relations, viz.,

A:

$$\bar{P}_i = \frac{0.6012}{\bar{V}^{2.993}} \tag{16a}$$

B:

$$\bar{P}_i = \frac{0.5332}{\bar{V}^{2.869}} \tag{16b}$$

C:

$$\bar{P}_i = \frac{0.4659}{\bar{V}^{2.665}} \tag{16c}$$

These should be compared with the expression obtained by Nanda et al.,<sup>30,31</sup> with proper allowance made for the different coordinates of the cell and the hole

theories, namely,

$$\tilde{P}_i = \frac{0.982}{\tilde{V}^{2.850}} \quad (17)$$

Equations (16b) and (17) can be made almost identical by dividing the latter by a constant factor of 1.845. Now, eq. (17) was obtained from cohesive energy data, and so this result implies a relation between the scaling factor  $P^*$  as obtained by two different methods.

The internal energy  $\tilde{U}$  is obtained by integration of eq. (16). Thus,

$$\tilde{U} = - \frac{a}{(m-1)\tilde{V}^{(m-1)}} \quad (18)$$

with  $(m-1)$  equal to 1.993, 1.869, and 1.665, respectively. Hence, the single exponent, suggested by Hildebrand and Scott<sup>32</sup> and Frank,<sup>33</sup> remains, but it is closer to 2 than 1, a fact which expresses the well-known inadequacy of a van der Waal's expression for the internal energy. Another method of arriving at the exponent in eq. (18) has been extensively used by Allen et al.<sup>34</sup> and by Bagley<sup>35</sup> who employ the relation

$$P_i = (m-1)(\text{c.e.d.}) \quad (19)$$

where c.e.d. represents the cohesive energy density obtained for polymers from swelling measurements, a procedure of limited accuracy. It is not possible to

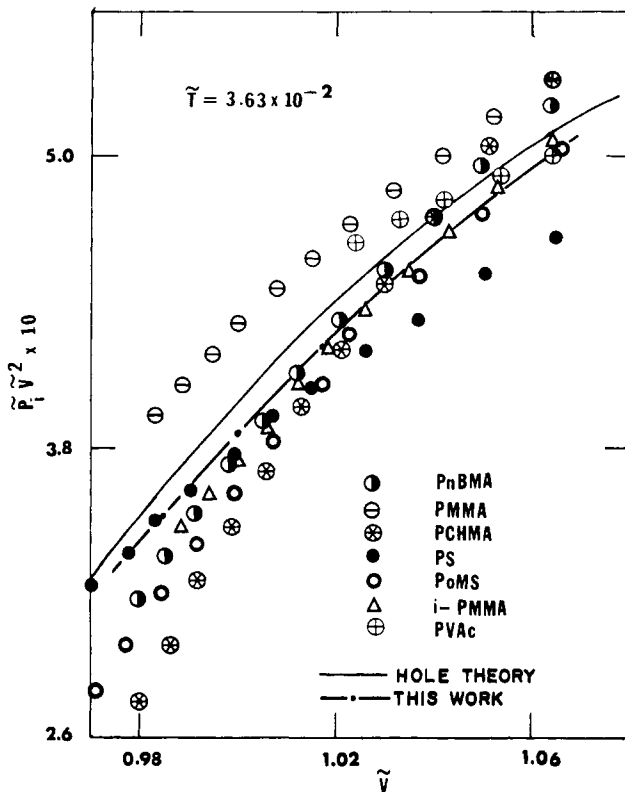


Fig. 6. Reduced internal pressure as a function of reduced volume at constant temperature.

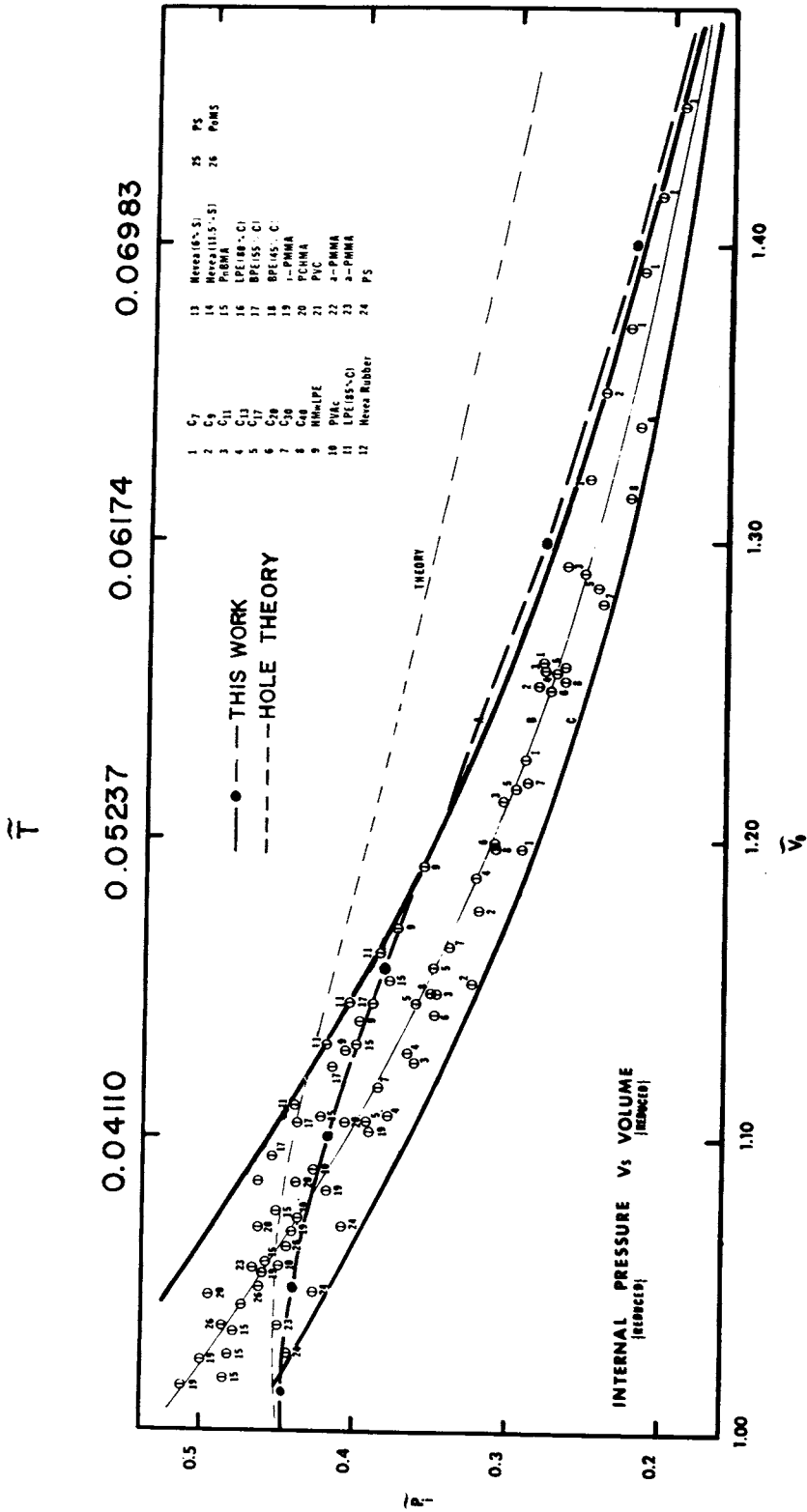


Fig. 7. Reduced internal pressure as a function of reduced volume and/or reduced temperature at atmospheric pressure.

calculate c.e.d. directly from PVT measurements except via eq. (19). However, it is possible to use the theory to compute  $\tilde{P}_i$  as well as c.e.d. and inspect the ratio  $\tilde{P}_i/c.e.d.$  One finds that for a reduced temperature range of 0.0373–0.0573, the ratio decreases monotonically from  $\sim 0.80$  to  $\sim 0.74$ . That is, c.e.d.  $> P_i$ , contrary to observation.<sup>34–36</sup>

Finally, the corresponding states behavior illustrated in Figure 7 can be utilized to develop a relation for the isothermal compressibility as  $\tilde{P} \rightarrow 0$ :

$$\tilde{P}_i = \tilde{T} \tilde{\alpha}_0 / \tilde{\kappa} \quad (20)$$

Equations (6) and (16) are substituted for  $\tilde{\alpha}_0$  and  $\tilde{P}_i$  to give

$$\kappa = 1.5 \left( \frac{\tilde{V}^m}{a} \right) (\ln \tilde{V}_0 + 0.10335) \quad (21)$$

where  $a$  and  $m$  are the parameters of eqs. (16).

So far, the discussion has centered on the properties of amorphous high polymers above the glass transition temperature and on semicrystalline polymers above the melting point. We note, however, in Figure 7 a series of data points for oligomers derived from Doolittle's measurements.<sup>37</sup> No particular pattern is discernible, except for the wider range of temperatures covered. However, a detailed examination<sup>1</sup> of  $\Delta U$  and of the characteristic product  $P_i V^2$  as a function of pressure shows significant departures from the pattern defined by the high polymers, and thus the theory as well as the semiempirical results. This is primarily the result of the higher temperatures in question. Although this is not apparent in the  $\tilde{V}-\tilde{T}$  function at atmospheric pressure,<sup>1,28</sup> the theory remains most appropriate at lower temperatures, the introduction of holes notwithstanding. This carries over to the semiempirical expressions employed here.

## CONCLUSIONS

A complete reduced equation of state has been developed, based on the reduced form of the Tait equation, by inserting the temperature dependence of the Tait parameter  $\tilde{B}$  and the reduced volume at atmospheric pressure,  $\tilde{V}_0$ . Both quantities are derived from theory, but the semiempirical character of the analysis arises from the acceptance of the experimental constancy of the Tait parameter,  $C$ .

Two procedures are explored to derive for a given system the PVT surface, the internal pressure, and the compressional energy and entropy changes from the corresponding reduced functions. Agreement with experiment is satisfactory.

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