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A universal equation of state for polymer liquids

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Recently it has been shown that the compression response of polymer liquids, glasses and solutions satisfies a strong temperature–pressure superposition principle. Using a phenomenological argument, a new isothermal equation of state was developed to describe this new principle quantitatively. In this paper we extend the range of applicability of this new equation of sate, enabling it to describe quantitatively polymer liquids at any temperature. This is achieved by taking advantage of the empirical observation that for polymers both the density and the logarithm of the bulk modulus are linear functions of temperature. This allows the development of a corresponding states equation of state where each polymer is distinguished by a characteristic temperature T^*, pressure P^* and mass density ρ^*. These parameters have been tabulated for 61 polymer liquids. The accuracy of the new equation of state approaches the accuracy of experimental *PVT* data. The equation of state parameters (T^*, P^*, ρ^*) also have simple physical interpretations. One in particular is significant: the reduced temperature, T/T^*, is shown to be equal to the free volume fraction at temperature T. This may prove to be useful for the interpretation of gas permeability through polymers. It is also shown that $1/\rho^*$ is related to the calculated van der Waals' volume and that P^* is a measure of the cohesive energy density. The new equation of state will be useful for extrapolating equation of state properties and estimating bounds for negative pressures.

(Keywords: polymer liquids; compression response; equation of state)

INTRODUCTION

Numerous equations of state have been developed to describe the pressure–volume–temperature (*PVT*) behaviour of polymer liquids and glasses[1–18]. These equations of state, in general, suggest corresponding states behaviour for polymer *PVT* properties and require three scaling parameters: a temperature T^*, a pressure P^* and a mass density ρ^* (or specific volume). Recently, Rodgers[19] tabulated these parameters for six different equations of state and 56 polymers. In addition, there are phenomenological isothermal or adiabatic compressibility equations[20]. These latter equations are usually expressed in pressure–volume form. They are used for smoothing *PVT* data, interpolation and extrapolation. Among these, the original Tait equation[21], and its modification[22] have been used for many kinds of liquids and glasses. In geophysics where very high pressures are encountered, the most frequently used equation is the Murnaghan equation[23]. Both the original Tait and Murnaghan equations are based on the linearity of the bulk modulus with pressure. The modified version of the Tait equation, which was criticized by Hayward[24], has been used almost exclusively for non-polar organics since the work of Cutler *et al.*[25] in 1958. The modified Tait equation suffers from the defect that it leads to a negative volume at sufficiently high pressure[26,27]. The Murnaghan equation ignores the experimental observation that the bulk modulus exhibits negative curvature at high pressures[28,29].

Recently, the present authors demonstrated on general thermodynamic grounds that the compression response of polymers and organic liquids satisfies a strong temperature–pressure superposition principle[28,29]. Using this superposition principle and a Padé analysis of the bulk modulus, the following equation of state was developed[28,29]:

$$\ln(V/V_0) = \frac{\omega}{(1-\omega)B_1}\left[1 - \left(1 + \frac{B_1 P}{\omega B_0}\right)^{1-\omega}\right] \tag{1}$$

where V is the volume at T and P, and V_0 is the volume at T and a reference pressure P_0 that is normally taken to be atmospheric (zero) pressure. The remaining constants in equation (1) are defined by the series expansion of the bulk modulus B in pressure:

$$B = B_0 + B_1 P + \tfrac{1}{2} B_2 P^2 + \cdots \tag{2}$$

and ω is a measure of the negative curvature in the bulk modulus (if $B_2 = 0$, $\omega = 1$ and if $B_2 < 0$, $\omega < 1$). As $\omega \rightarrow 1$, equation (1) reduces to the linear modulus approximation[29] or the Murnaghan equation[23].

$$\ln(V/V_0) = -\frac{1}{B_1}\ln(1 + B_1 P/B_0) \tag{3}$$

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The first pressure coefficient B_1 of the bulk modulus, which is dimensionless, has been shown to be closely related to the asymmetry of the free energy around its minimum[28,29]. For polymers, B_1 has an almost universal value of 10 that is temperature-independent. If this universal value of B_1 is adopted, a single universal compression curve can be constructed for all organic polymers[29].

In the above equations, the low pressure volume V_0 and modulus B_0 are unknown functions of temperature. Equation (1) is very useful for predicting the compression at high pressures from a knowledge of these low pressure quantities V_0 and B_0. It would be more useful and complete if the temperature dependences of V_0 and B_0 were known. To achieve this goal, we make use of two empirical observations: (1) the zero pressure density is to an excellent approximation a linear function of temperature, and (2) the logarithm of the bulk modulus is a linear function of temperature. These two observations can be combined with equation (1) to obtain a corresponding states equation of state where each polymer is distinguished by a characteristic temperature T^*, pressure P^* and mass density ρ^*.

TEMPERATURE–PRESSURE SUPERPOSITION

The concept of temperature–pressure superposition is discussed in detail in our previous communications[28,29]. Below we briefly describe it enough to support subsequent discussions. The compression strain ϵ, defined as $\ln(V/V_0)$, can be obtained by integrating the inverse of the bulk modulus B:

$$\begin{aligned}\epsilon &= -\int_{P_0}^{P}\frac{\mathrm{d}P}{B}\\ &= -\int_{P_0}^{P}\frac{\mathrm{d}P}{B_0+B_1(P-P_0)+\frac{1}{2}B_2(P-P_0)^2+\cdots}\\ &= -\Delta p+\frac{1}{2!}B_1(\Delta p)^2-\frac{1}{3!}(2B_1^2-B_0B_2)(\Delta p)^3+\cdots\end{aligned} \tag{4}$$

where

$$\Delta p \equiv (P-P_0)/B_0 \tag{5}$$

Equation (4) is a general and rigorous expression for the compression. It suggests that the compression is only a function of the reduced pressure P/B_0 or, more generally, Δp. Examples of compression satisfying temperature–pressure superposition are shown in *Figures 1* and *2* for linear polyethylene[30] (LPE) and polystyrene[31] (PS), respectively. The reference pressure P_0 used here is atmospheric pressure (0.1 MPa), which is usually called zero pressure. The dominant temperature dependence of the compression is absorbed into the reference bulk modulus B_0. The empirical moduli for LPE and PS are listed in *Table 1*.

The observed temperature–pressure superposition implies that the first few coefficients, B_1 and B_0B_2 in equation (4), are relatively temperature-insensitive. The first pressure coefficient B_1 of the bulk modulus is the governing parameter for compression. Our investigation shows that the average value of B_1 is 10.7 for a large group of polymers that vary widely in backbone structure and composition. Cutler *et al.*[25] performed an extensive analysis of *PVT* properties of organic and polymer liquids with the modified Tait equation. They found a temperature-independent and universal value of the Tait constant C of 0.0894. Formally, this is the same as $B_1 = 10.2$ because for the Tait equation, $B_1 = 1/C - 1$. Given that the uncertainty in experimental B_1 values is about ±1, Cutler's analysis and our own ($B_1 = 10.7$) are very consistent.

There is some history for B_1 that is relevant. Early in this century, Mie[32] proposed a semi-empirical expression

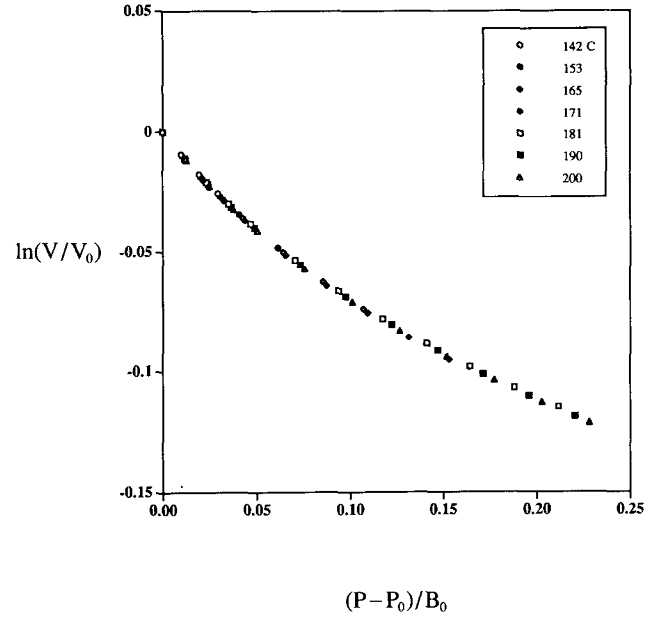

Figure 1 Compression strain of LPE as a function of dimensionless pressure $(P - P_0)/B_0$. The zero pressure bulk moduli are tabulated in *Table 1*. *PVT* data for LPE are from ref. 30

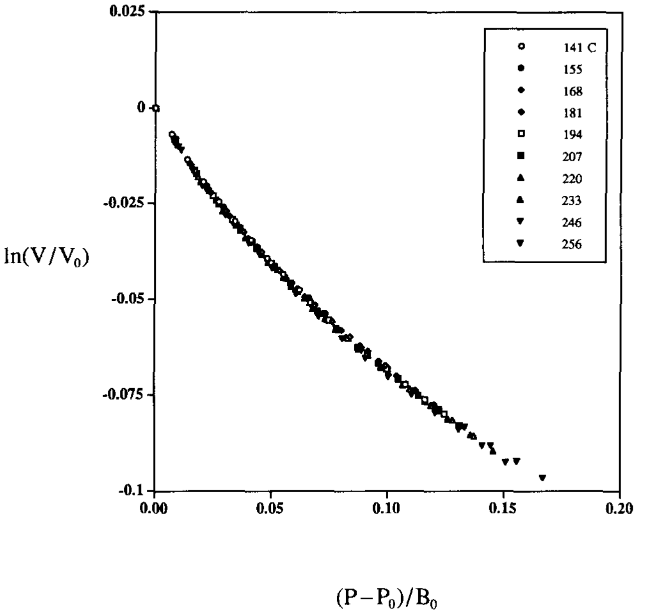

Figure 2 Compression strain of PS as a function of dimensionless pressure $(P - P_0)/B_0$. The zero pressure bulk moduli are tabulated in *Table 1*. *PVT* data for PS are from ref. 31

Table 1 Zero pressure bulk moduli B_0 for LPE and PS at the indicated temperatures

LPE		PS	
Temp. (°C)	B_0 (MPa)	Temp. (°C)	B_0 (MPa)
142	1010.4	141	1451.5
153	975.3	155	1362.8
165	931.6	168	1309.8
171	912.7	181	1246.8
181	850.8	194	1203.7
190	816.7	207	1145.1
200	789.0	220	1092.4
		233	1030.4
		246	994.0
		256	899.6

for the intermolecular potential $\phi = R/r^n - A/r^m$, where R and A are positive constants, and n and m are integers. Moelwyn-Hughes[33] suggested that near the triple point, the compressibility of simple liquids can provide information on the potential indices n and m. In our notation, he derived $B_1 = (n+m+6)/3$ and $-B_0B_2 = (n+3)(m+3)/9$. Later, Barker[34] also came to a similar conclusion with his bundle of cylinders model for polymers. The argument leading to this conclusion is based on equating the external pressure to the internal pressure $\partial U/\partial V|_T$, where U is the internal energy (see also ref. 18). Although this is a serious approximation, it is still very suggestive that B_1 might be temperature-independent and universal. Note that for $m = 6$ and $n = 18$, $B_1 = 10$.

As mentioned previously, both the Tait and the Murnaghan equations are based on the linearity of the bulk modulus with pressure. This near-linearity of the bulk modulus is known to be a common property of condensed matter including metals, salts and organic liquids[35–38]. Truncating the modulus series after the linear term in equation (4) and integrating yields the linear modulus approximation or Murnaghan equation, equation (3). Meanwhile, the original Tait equation can be obtained from the assumed linearity of the secant modulus[24]:

$$-V_0\frac{P-P_0}{V-V_0} = B_0 + \frac{1}{C}(P-P_0) \tag{6}$$

Tammann[22] modified the above equation by treating the left-hand side of the equation as $-V_0\partial P/\partial V$ and integrating to obtain the so-called modified Tait equation below:

$$\epsilon = \ln\left[1 - C\ln\left(1+\frac{1}{C}\Delta p\right)\right] \tag{7a}$$

or the more familiar form

$$\frac{V}{V_0} = 1 - C\ln\left(1+\frac{P}{CB_0}\right) \tag{7b}$$

Hayward[24] criticized this modified version as a misinterpretation of Tait's original work. Nevertheless, the 'modified' Tait equation has been widely used for polymers for many years with good success. In the literature it is simply known as the Tait equation and hereafter we shall also refer to equation (7) as the Tait equation. As can be seen by inspection, the Tait equation leads to negative volumes at sufficiently high pressures. In this regard, the linear modulus approximation, equation (3), is superior to the Tait equation in that the volume smoothly goes to zero at infinite pressure.

In deriving equation (1), which we will refer to as the Padé equation of state, we considered the asymptote of the bulk modulus at infinite pressure to be given by

$$\lim_{P\to\infty}\frac{\partial\ln B}{\partial\ln P} = \omega \tag{8}$$

which means that the modulus diverges as P^{ω}. Values of $\omega < 1$ imply a negative curvature to the modulus which is consistent with experiments[29]. Using a Padé analysis, ω can be estimated as $\omega = B_1^2/(B_1^2 - B_0B_2)$. Since negative curvature implies $B_2 < 0$, this implies $\omega < 1$. The governing parameter for compression is B_1 because of the near-linearity of the bulk modulus. The curvature parameter ω plays a subsidiary role, but is still very important. It will be discussed more later.

UNIVERSAL PADÉ EQUATION OF STATE FOR POLYMER LIQUIDS

As mentioned earlier, the Padé equation of state, equation (1), is an isothermal equation of state. The low (zero) pressure volume V_0 and modulus B_0 are unknown functions of temperature for a given polymer. If one believes that polymer PVT properties satisfy a corresponding states principle, as theoretical models have suggested, then both V_0 and B_0 should satisfy a corresponding states principle. This has been our assumption and guide. What we are looking for is a characteristic mass density ρ^* and pressure P^* such that the dimensionless variables ρ^*V_0 and B_0/P^* are functions of the reduced temperature T/T^* only. Our

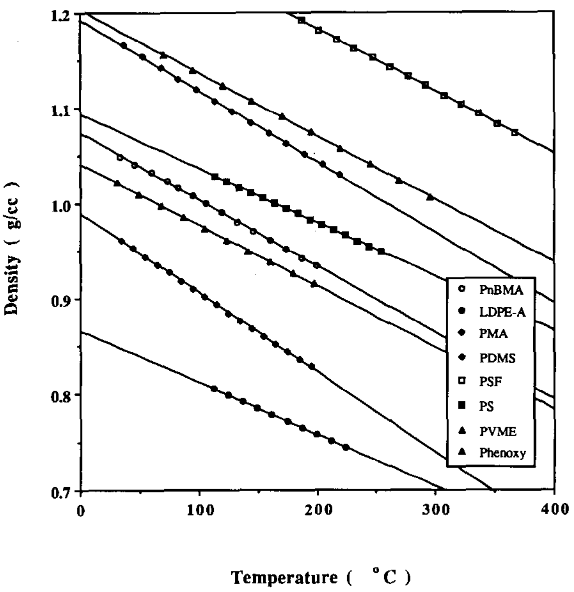

Figure 3 Zero pressure densities for eight polymers over a large temperature region. The straight lines are least-squares lines through the data. *Table 3* shows the polymer names and references for the *PVT* data

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* Most of the polymers tested here showed linear zero pressure density. A few polymers such as ethylene–propylene 50/50 rubber and poly(4-methyl-1-pentene) (PMP) are exceptions. According to Zoller[53], PMP may have suffered thermal degradation. Ethylene–propylene rubber is not included in this study.

Table 2 Regression equations of zero pressure isobar and bulk modulus for eight selected polymers in the liquid state

Polymer[a]	Zero pressure isobar (v in $cm^3 g^{-1}$, ρ in $g gm^{-3}$)[b]	Bulk modulus, B_0 (MPA)[b]
PnBMA	$v = 0.9352 + 4.9988 \times 10^{-4} t + 1.268 \times 10^{-7} t^2 - 1.8023 \times 10^{-9} t^3$	$10915.90 \exp(-5.344 \times 10^{-3} T)$
LDPE-A	$v = 1.1484 \exp(6.950 \times 10^{-4} t)$	$7792.25 \exp(-5.344 \times 10^{-3} T)$
PMA	$v = 0.8356 \exp(6.795 \times 10^{-4} t)$	$8999.12 \exp(-4.493 \times 10^{-3} T)$
PDMS	$\rho = 0.9919 - 8.925 \times 10^{-4} t + 2.65 \times 10^{-7} t^2 - 3.0 \times 10^{-11} t^3$	$5099.92 \exp(-5.851 \times 10^{-3} T)$
PSF	$v = 0.7644 + 3.419 \times 10^{-4} t + 3.126 \times 10^{-7} t^2$	$11421.12 \exp(-3.757 \times 10^{-3} T)$
PS[c]	$v = 0.9190 + 3.228 \times 10^{-4} t + 4.332 \times 10^{-7} t^2$	$7141.39 \exp(-3.841 \times 10^{-3} T)$
PVME	$v = 0.9585 \exp(6.653 \times 10^{-4} t)$	$8452.34 \exp(-4.588 \times 10^{-3} T)$
Phenoxy	$v = 0.76644 \exp(1.921 \times 10^{-5} T^{3/2})$	$13310.54 \exp(-4.378 \times 10^{-3} T)$

[a] *Table 3* shows the polymer names with the experimental temperature regions for these regression equations
[b] Units are °C for t and K for T
[c] Data for PS are from ref. 31

approach to discovering these relations is strictly empirical. Using the empirical data listed in *Table 2* (see *Table 3* for names of polymers and experimental temperature regions for regression equations), the zero pressure density of eight polymers is plotted in *Figure 3*. These eight polymers were selected because they are representative of a broad class of polymers that exhibit linear density as a function of temperature*. The solid straight lines shown in *Figure 3* are least-squares lines. It is easy to establish the desired corresponding states relation from the slopes and intercepts of the various lines. If the linear equation of a polymer in density is

$$\rho_0 = a - mT = a[1 - T/(a/m)] = 1/V_0 \qquad (9)$$

then the desired scaling parameters are

$$\rho^* = a \quad \text{and} \quad T^* = a/m \qquad (10)$$

Thus, we have a deceptively simple relation for the reduced density, $\tilde{\rho}_0 \equiv \rho_0/\rho^*$:

$$\tilde{\rho}_0 = 1 - \tilde{T} = 1/(\rho^* V_0) \qquad (11)$$

where $\tilde{T} \equiv T/T^*$ is the reduced temperature. Figure 4 shows superposition of the zero pressure densities of the eight polymers shown in *Figure 3*. This observation of linear density has not been generally recognized, probably because the volume is well known not to be linear in temperature (Bondi[58] pointed out long ago that $d\rho/dT$ for liquids was a constant over a wide temperature range, but his observation has been largely overlooked). The reduced volume is plotted in *Figure 5*, note the small positive curvature.

Typically, the bulk modulus B_0 at zero pressure decreases exponentially with temperature, $B_0 \sim e^{-bT}$. This exponential behaviour of the bulk modulus with temperature has long been recognised as characteristic of a broad class of materials including liquid mercury

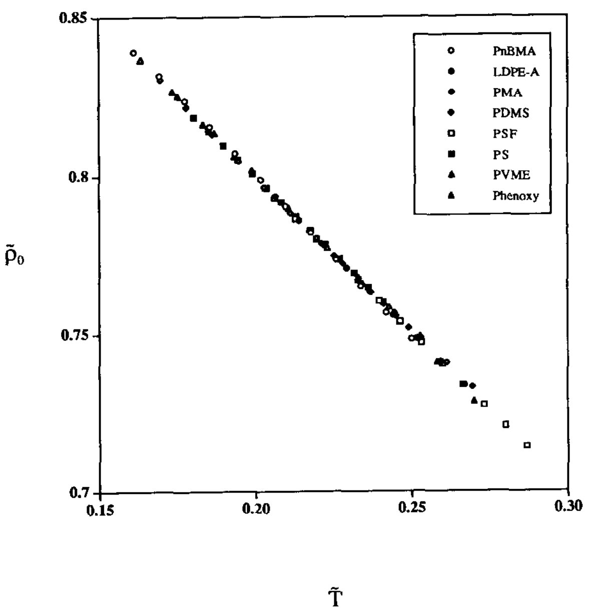

Figure 4 Reduced zero pressure density plotted as a function of reduced temperature for the eight polymers shown in *Figure 3*

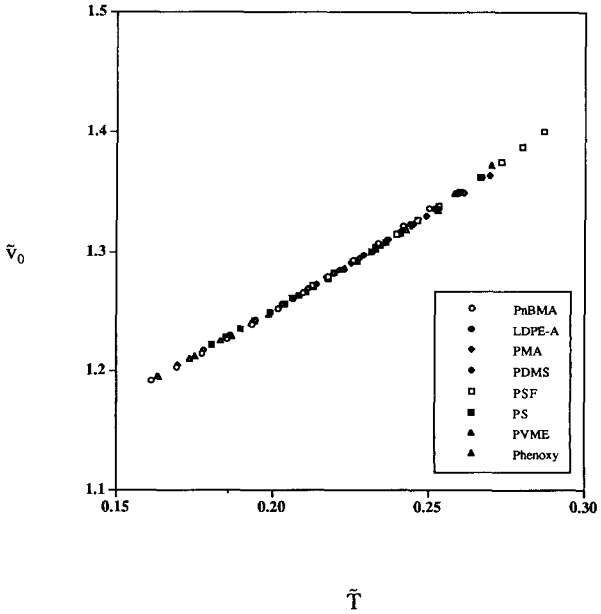

Figure 5 Reduced zero pressure volume plotted as a function of reduced temperature for the eight polymers shown in *Figure 3*. Note the slight upward curvature

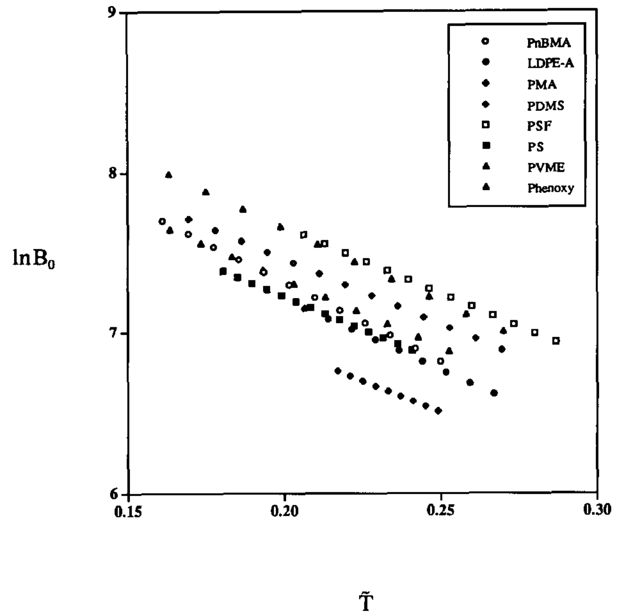

Figure 6 Semi-log plot of the zero pressure bulk moduli for the eight polymers shown in *Figure 3*

(see ref. 35 and refs therein. Certainly this functional form for the modulus is unsuitable for water because it exhibits a maximum at ~45°C). In *Figure 6* the logarithm of B_0 is plotted against the reduced temperature for the same eight polymers featured in *Figures 3–5*. Although some curvature is noted, the linearity of $\ln B_0$ with temperature is really quite good. Also note that the slopes of these curves are nearly identical; this implies that $B_0 \sim e^{-\tilde{b}\tilde{T}}$ where $\tilde{b} = bT^*$ is a dimensionless, universal slope. If these data are plotted against temperature instead of reduced temperature, the slopes would all be different. This strongly supports the notion that a corresponding states principle is operative. As $T \to 0$, $\ln B_0 \to \ln P^*$ where P^* is a characteristic pressure. Thus, the curves in *Figure 6* can be superposed by shifting along the y-axis by $-\ln P^*$. This superposition is illustrated in *Figure 7*. For the 61 polymers that we have studied, $\tilde{b} = 9 \pm 1$. Thus, for polymer liquids, we have a universal modulus equation

$$B_0 = P^* \exp[-9\tilde{T}] \tag{12}$$

To summarize, the three requisite equation of state parameters T^*, P^* and ρ^* are all determined from zero (atmospheric) pressure density and modulus data. The physical meaning of these parameters will be discussed in detail later. Using these equation of state parameters for our eight featured polymers (see *Table 4*), the experimental *PVT* data are replotted in reduced form in *Figure 8*. This figure demonstrates beautifully a corresponding states principle in polymer liquids. It is remarkable that the zero pressure behaviour completely determines the compression response over a wide pressure range (up to 2000 bar in *Figure 8*).

Equations (11) and (12) combined with equation (1) completely define the *PVT* behaviour of a polymer liquid:

$$\frac{V}{V_0} \equiv \frac{\tilde{\rho}_0}{\tilde{\rho}} = \tilde{v}(1-\tilde{T}) = \exp\left\{\frac{\omega}{(1-\omega)B_1}\left[1-\left(1+\frac{B_1\tilde{P}e^{9\tilde{T}}}{\omega}\right)^{1-\omega}\right]\right\} \tag{13}$$

where $\tilde{P} \equiv P/P^*$ and $\tilde{v}(T,P) = 1/\tilde{\rho}$. We now test the performance of this equation using universal values of ω and B_1. From the Tait equation, we have

$$\omega = \frac{C(1/C-1)^2}{1+C(1/C-1)^2} = \frac{B_1^2}{B_1^2+B_1+1} \tag{14}$$

so that, for Cutler's constant $C = 0.0894$, $\omega = 0.9$ and $B_1 = 10.2$. We begin with this pair of values because

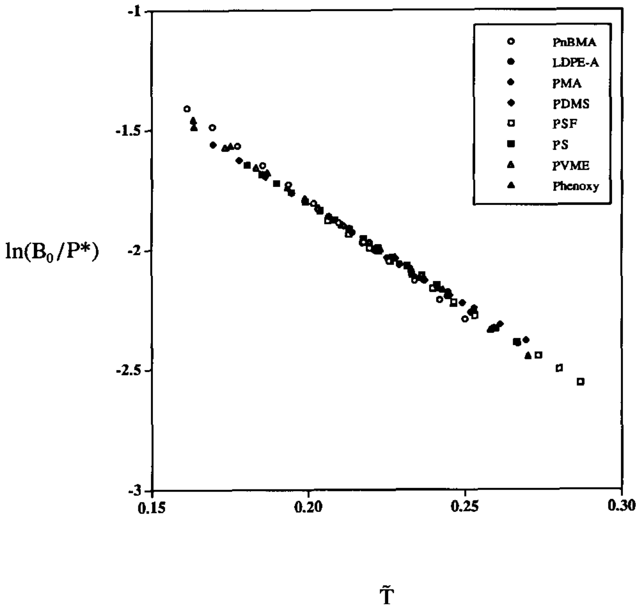

Figure 7 Reduced zero pressure bulk modulus *versus* reduced temperature. The average slope is 9 which is chosen as $\tilde{b}$. See equation (12)

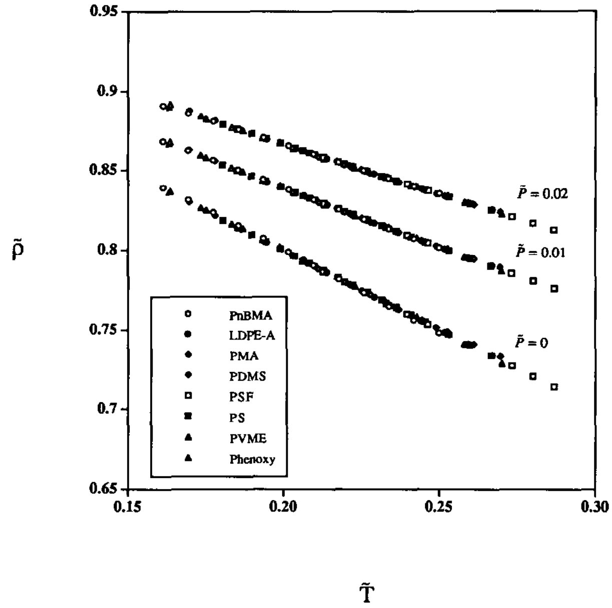

Figure 8 Reduced density of polymer liquids as a function of reduced pressure and temperature. Highest absolute pressures are 2000 bar. Scaling parameters are tabulated in *Table 4*

Table 3 Polymer names and the experimental temperature–pressure range for polymer liquids

Polymer	Name	T (°C)	P (MPa)	Ref.
PDMS[a]	Poly(dimethyl siloxane)	25–70	0–100	39, 40[b]
PS	Polystyrene	115–196	0–200	41[b]
PoMS	Poly(*o*-methyl styrene)	139–198	0–180	41[b]
PMMA	Poly(methyl methacrylate)	114–159	0–200	30[b]
PnBMA	Poly(n-butyl methacrylate)	34–200	0–200	30[b]
PCHMA	Poly(cyclohexyl methacrylate)	123–198	0–200	30[b]
PEA	Poly(ethyl acrylate)	37–210	0–196	19[b,c]
PEMA	Poly(ethyl methacrylate)	113–161	0–196	19[b,c]
PMA	Poly(methyl acrylate)	37–220	0–196	19[b,c]
PVAc	Poly(vinyl acetate)	35–100	0–80	19, 42[b]
LPE	Linear polyethylene (PE)	142–200	0–200	30[b]
BPE	Branched PE	125–198	0–200	30[b]
LDPE-A	Low density PE-A	112–225	0–196	43
LDPE-B	Low density PE-B	112–225	0–196	43
LDPE-C	Low density PE-C	112–225	0–196	43
PBD	Poly(butadiene)	4–55	0–283.5	19, 44[b]
PBD8	Poly(butadiene) with 8% 1,2-content	25–200	0–200	45
PBD24	Poly(butadiene) with 24% 1,2-content	25–200	0–200	45
PBD40	Poly(butadiene) with 40% 1,2-content	25–200	0–200	45
PBD50	Poly(butadiene) with 50% 1,2-content	25–200	0–200	45
PBD87	Poly(butadiene) with 87% 1,2-content	25–200	0–200	45
i-PB	Poly(1-butene)	133–246	0–196	46
PAr	Polyarylate	177–310	0–176.5	47
PCL	Poly(caprolactone)	100–148	0–200	19[b]
PC	Polycarbonate (PC)	151–340	0–176.5	47
BCPC	Bisphenol chloral PC	220–280	0–50	48[b]
HFPC	Hexafluoro bisphenol-A PC	220–280	0–50	48[b]
TMPC	Tetramethyl bisphenol-A PC	210–290	0–50	48[b]
PET	Poly(ethylene terephthalate)	274–342	0–196	49
PIB	Poly(isobutylene)	53–110	0–100	19, 40, 50[b]
PIB8	Poly(isobutylene) with 8% 3,4-content	25–200	0–200	45
PIB14	Poly(isobutylene) with 14% 3,4-content	25–200	0–200	45
PIB41	Poly(isobutylene) with 41% 3,4-content	25–200	0–200	45
PIB56	Poly(isobutylene) with 56% 3,4-content	25–200	0–200	45
i-PP	Istoactic polypropylene	170–297	0–196	46
a-PP	Atactic polypropylene	80–120	0–100	19[b]
Phenoxy	Poly(phenoxy)	68–300	0–176.5	47
Psulfone	Polysulfone	202–371	0–196	47
PEO	Poly(ethylene oxide)	88–224	0–68.5	19[b]
PVME	Poly(vinyl methyl ether)	30–198	0–200	19[b]
PEEK	Poly(ether ether ketone)	346–398	0–200	51
PTFE	Poly(tetrafluoroethylene)	330–372	0–39	52[b]
PTHF	Poly(tetrahydrofuran)	62–166	0–78.5	19[b]
PMP	Poly(4-methyl-1-pentene)	241–319	0–196	53
PA6	Polyamide-6	236–296	0–196	54
PA66	Polyamide-66	246–298	0–196	54
PECH	Poly(epichlorohydrin)	60–140	0–200	19[b]
PVC	Poly(vinyl chloride)	100–150	0–200	19[b]
EVA18	Poly(ethylene–vinyl acetate) 18%	112–219	0–176.5	19, 55
EVA25	Poly(ethylene-vinyl acetate) 25%	94–223	0–176.5	19, 55
EVA28	Poly(ethylene-vinyl acetate) 28%	94–235	0–176.5	19, 55
EVA40	Poly(ethylene-vinyl acetate) 40%	75–235	0–176.5	19, 55
SAN3	Poly(styrene-acrylonitrile) 2.7%	105–266	0–200	48[b]
SAN6	Poly(styrene-acrylonitrile) 5.7%	96–267	0–200	19, 48[b]
SAN15	Poly(styrene-acrylonitrile) 15.3%	132–262	0–196	48[b]
SAN18	Poly(styrene-acrylonitrile) 18.0%	104–255	0–196	48[b]

Table 3 Continued

Polymer	Name	T (°C)	P (MPa)	Ref.
SAN40	Poly(styrene-acrylonitrile) 40%	100–270	0–196	48[b]
SAN70	Poly(styrene-acrylonitrile) 70%	100–271	0–196	56
SMMA20	Poly(styrene-methyl methacrylate) 20%	110–270	0–196	56
SMMA60	Poly(styrene-methyl methacrylate) 60%	110–270	0–200	56
PPO	Poly(phenylene oxide)	203–320	0–176.5	57

[a] For PDMS, the zero pressure density was measured for $t = 20$–207°C by Shih and Flory[39]

[b] References cited here have tablulated experimental *PVT* data for given polymers

[c] *PVT* data for PMA, PEA and PEMA were kindly provided by D. J. Walsh of Du Pont

almost half of previously reported polymer *PVT* data have been 'smoothed' using the Tait equation. Instead of raw tabular data, much of the *PVT* data is reported in the form of regression equations such as those shown in *Table 2*. Employing a non-linear least-squares routine, all the characteristic parameters T^*, P^* and ρ^* for 61 polymer liquids were obtained and are listed in *Table 4*. The average deviation between equation (13) and regenerated empirical data is also reported in *Table 4*. The final average value of the mean deviation for 61 polymers is 0.00034 $\mathrm{cm}^3\,\mathrm{g}^{-1}$. This result is statistically superior to six other equations of state recently reviewed by Rodgers[19].

The universal value of B_1 lies between 10 and 11, and $\omega = 0.9$ indicates a slight negative curvature of the modulus. As mentioned in our previous communication[29], the linear modulus approximation, equation (3), with $\omega = 1$ is still very accurate. Therefore, we compare the performance of equation (13) for various pairs of B_1 and ω. To do this comparison in an unbiased way, we only use tabulated *PVT* data. These data have not been regressed with the Tait or any other equation. *Table 5* shows the average deviation between tabulated *PVT* data for 30 polymers and for various B_1/ω pairs. The overall average deviation (0.0005) for these 30 polymers is slightly higher than before for the Cutler pair 10.2/0.9 because we are dealing with unsmoothed data. From this table, it is clear that the Cutler's pair is adequate, even though the best choice appears to be 10.5/0.9. It is also seen that the linear modulus approximation with $B_1 = 10$ gives as good a fit as the Cutler pair. For most polymers used in this table, the dimensionless pressure does not exceed 0.2 and the non-linearity in the modulus is still not prominent enough to be statistically vivid. The linear modulus approximation works because the slight negative curvature in the modulus is compensated by a smaller B_1. However, we believe that the non-linearity in the bulk modulus becomes important for extrapolation of volume data to high pressures where the Padé equation with $\omega < 1$ should prove superior to the linear approximation.

A non-linear modulus also has important implications in the region of negative pressures. The universal Padé equation moves smoothly from positive to negative pressures. At a well-defined negative pressure, the modulus goes to zero. This is the mechanical stability limit or pseudo spinodal point. This situation is schematically shown in *Figure 9*. The spinodal pressure is given by $P_s = -\omega B_0/B_1$. At the spinodal pressure the spinodal volume becomes

$$V_s = V_0 \exp\left(\frac{\omega}{(1-\omega)B_1}\right) \qquad (15)$$

Note that the spinodal volume approaches infinity as $\omega \to 1$! This divergence is aphysical and strongly supports a value for ω of less than unity. For the 10.2/0.9 pair it can be seen that polymers would rupture at a negative pressure of $-0.088B_0$ and at a volume of 2.414 V_0 universally. Summarizing the above discussion, the curvature parameter ω is physically important even though its statistical improvement in describing existing polymer *PVT* data is not always apparent.

INTERNAL PRESSURE AND HEAT CAPACITY DIFFERENCE

Various thermodynamic functions can be derived from the universal Padé equation using standard thermodynamic relations. We consider here the internal pressure P_i, defined as the volume derivative of the internal energy $\partial U/\partial V|_T$. This quantity is known to be closely related to the strength of the intermolecular interaction or cohesive properties of polymers[59,60]. It is given by the standard formula:

$$P_i = T\alpha B - P \qquad (16)$$

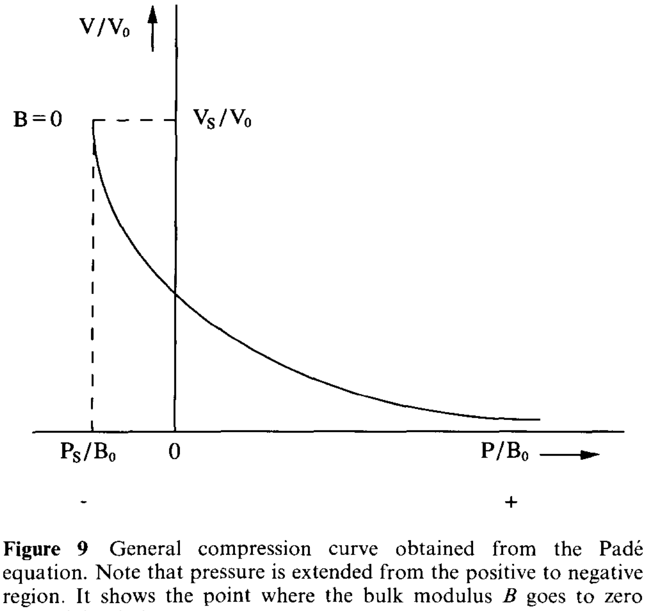

Figure 9 General compression curve obtained from the Padé equation. Note that pressure is extended from the positive to negative region. It shows the point where the bulk modulus B goes to zero (spinodal point)

Table 4 Optimized characteristic parameters and the average deviation $\langle|\Delta V|\rangle$ for 61 polymer liquids

Polymer	ρ^* (g cm^{-3})	T^* (K)	P^* (MPa)	Avg $\lvert\Delta V\rvert \times 10^4$ (cm^3 g^{-1})	Max. $\lvert\Delta V\rvert \times 10^4$ (cm^3 g^{-1})
PDMS	1.2390	1375.1	6212.9	1.8	11.0
PS	1.2247	2277.2	7867.6	2.4	14.2
PoMS	1.1950	2380.6	7772.1	1.1	5.0
PMMA	1.4007	2184.2	9873.0	0.7	1.8
PnBMA	1.2558	1855.9	9025.3	5.0	27.6
PCHMA	1.2971	2195.1	8515.1	4.4	23.9
PEA	1.3518	1747.4	9131.8	6.0	36.2
PEMA	1.3639	1771.2	11257.0	0.8	3.6
PMA	1.4043	1829.0	10623.9	5.6	36.3
PVAc	1.4455	1696.0	10399.9	1.4	7.1
LPE	1.0536	1655.0	9943.5	3.2	21.8
PBE	1.0285	1751.9	8630.7	2.5	17.1
LDPE-A	1.0150	1865.4	8214.5	2.8	13.7
LDPE-B	1.0063	1923.8	7983.8	2.5	10.8
LDPE-C	1.0133	1880.5	8225.3	3.8	26.0
PBD	1.0971	1633.8	9443.2	5.2	29.8
PBD8	1.0743	1798.6	9136.3	5.0	20.5
PBD24	1.0685	1819.0	8708.0	6.2	21.7
PBD40	1.0687	1842.9	8352.0	5.1	26.5
PBD50	1.0629	1892.0	7757.3	7.4	22.9
PBD87	1.0529	1905.6	7241.8	2.1	16.7
i-PB	1.0148	1924.1	6891.1	2.7	15.3
PAr	1.4621	2243.9	11557.3	3.8	14.9
PCL	1.3036	1849.0	9530.1	0.5	2.3
PC	1.4554	2070.3	12106.1	3.6	12.0
BCPC	1.6747	2249.1	9931.3	4.5	22.4
HFPC	1.8996	1788.2	10173.1	2.7	8.2
TMPC	1.3772	1908.0	10573.0	1.7	11.3
PET	1.6132	2022.2	15278.8	1.5	8.4
PIB	1.0659	2130.2	7045.3	0.5	1.7
PIB 8	1.0579	1921.0	7669.6	1.7	8.8
PIB 14	1.0677	1911.3	8219.9	2.7	7.0
PIB 41	1.0672	1912.7	8112.3	3.6	9.6
PIB 56	1.0718	1854.5	8600.1	2.4	11.8
i-PP	0.9885	1991.5	6118.1	3.5	12.7
a-PP	1.0320	1776.2	6202.8	5.8	26.8
Phenoxy	1.3808	2103.4	12728.1	5.3	21.1
Psulfone	1.5026	2232.2	13286.4	2.0	11.6
PEO	1.3439	1789.1	10805.4	4.9	30.1
PVME	1.2215	1861.3	9270.5	4.7	26.4
PEEK	1.5636	2126.5	14335.5	0.5	2.8
PTFE	2.7490	1400.7	9757.5	5.0	25.0
PTHF	1.1681	1843.0	8160.2	2.8	16.3
PMP	0.9912	1885.0	6452.5	5.7	39.2
PA6	1.4025	3140.3	5718.4	4.5	22.6
PA66	1.4521	2195.2	8391.9	2.5	13.0
PECH	1.5952	2068.9	8899.3	0.7	3.9
PVC	1.5996	2395.4	7551.2	3.2	17.2
EVA18	1.0433	1878.9	8107.5	2.5	9.9
EVA25	1.0709	1848.3	7957.5	2.9	9.4
EVA28	1.0821	1812.5	8622.1	5.7	22.0
EVA40	1.1282	1856.1	8441.9	3.5	17.3
SAN3	1.2453	2185.7	7878.5	4.2	22.8
SAN6	1.2665	2010.7	8896.8	4.1	12.8
SAN15	1.2723	2170.4	8602.0	1.7	6.8
SAN18	1.2732	2208.4	8495.6	2.5	9.2

Table 4 Continued

Polymer	ρ^* (g cm^{-3})	T^* (K)	P^* (MPa)	Avg $\lvert\Delta V\rvert \times 10^4$ (cm^3 g^{-1})	Max. $\lvert\Delta V\rvert \times 10^4$ (cm^3 g^{-1})
SAN40	1.2734	2435.2	7772.6	6.6	43.3
SAN70	1.3130	2546.6	9177.0	2.6	15.6
SMMA20	1.2839	2105.6	8531.3	5.2	14.0
SMMA60	1.3499	2099.5	8858.9	6.0	30.1
PPO	1.3926	1810.4	11776.9	4.5	27.1
Average				3.4	

where α is the thermal expansion coefficient. From the universal Padé equation P_i is given by:

$$\tilde{P}_i = P_i/P^* = \frac{\tilde{T}e^{-\tilde{b}\tilde{T}}}{1-\tilde{T}}\left(1+\frac{B_1}{\omega}\tilde{P}e^{\tilde{b}\tilde{T}}\right)^{\omega} - (1+\tilde{b}\tilde{T})\tilde{P} \tag{17a}$$

At zero pressure, the internal pressure is simply

$$\tilde{P}_i = \tilde{T}e^{-\tilde{b}\tilde{T}}/(1-\tilde{T}) \tag{17b}$$

Using the universal value $\tilde{b} = 9$, we find that the reduced internal pressure has a universal maximum at $\tilde{T} = 0.13$. Most polymer liquid data fall in the range $0.15 < \tilde{T} < 0.3$ so it is difficult to observe this predicted maximum. In this normal temperature range, the internal pressure decreases with temperature. This situation is shown in *Figure 10*. However, there is indirect evidence that the maximum exists. The difference in the constant pressure C_p and constant volume C_v heat capacities is related to the internal pressure by $C_p - C_v = V\alpha P_i$. If we rescale the heat capacities by $P^*/\rho^* T^*$ to render them dimensionless, then we have from the Padé equation

$$\tilde{C}_p - \tilde{C}_v = \tilde{T}e^{-\tilde{b}\tilde{T}}/(1-\tilde{T})^3 \tag{18}$$

which is valid at low pressures. The heat capacity difference has a predicted maximum at $\tilde{T} = 0.19$ which is in the normal experimental range. Experimental errors in α are magnified in calculating the heat capacity difference (over those in P_i) since α appears as a square. The experimental and calculated values are illustrated in *Figure 10* where a hint of the predicted maximum is observed.

Table 5 Comparison of the fitting performance of the universal Padé equation for various cases of B_1 and ω

	Average deviation, $\lvert\Delta V\rvert \times 10^4$ (cm^3 g^{-1})]	
B_1	$\omega = 0.9$	$\omega = 1$
9.5[a]	5.7	5.2
10	5.1	4.9
10.2	4.9	5.0
10.5	4.8	5.2
11	4.9	6.0

[a] This case is included to show that the overall average deviation has a minimum around $B_1 = 10$ under the linear modulus approximation ($\omega = 1$)

PHYSICAL INTERPRETATION OF THE CHARACTERISTIC PARAMETERS

The universal Padé equation is a corresponding states equation of state with three characteristic parameters. These parameters not only scale the temperature, pressure and mass density, but also have sound physical interpretations. The characteristic mass density ρ^* is obtained by extrapolating zero pressure densities to absolute zero. The reciprocal of this quantity, $1/\rho^*$, is the specific volume v^* at absolute zero temperature. According to Bondi[58] and van Krevlan[60], $v^* = 1.3v_w$ where v_w is the van der Waal's volume. This implies that the packing fraction of disordered polymers is $1/1.3 = 0.77$ universally at zero temperature. This number probably originates in the extrapolated packing fraction at absolute zero of poly(methylene), based on Biltz's data[58]. *Table 6* shows the calculated values for the van der Waals' density and ρ^* density for several polymers. The van der Waals' density is the ratio of the molecular weight of the polymer repeat unit to the van der Waals' volume. It is notable that the average value of the ratios of these two quantities is 1.288 ± 0.052, which is very close to the Bondi constant of 1.3. The

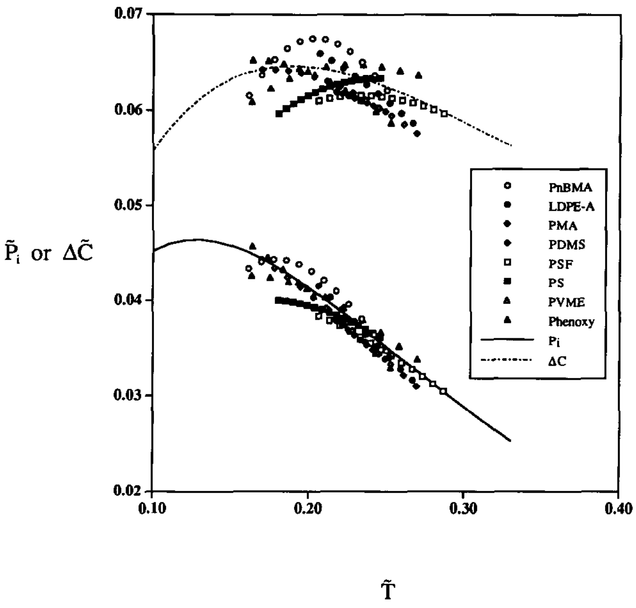

Figure 10 Reduced zero pressure internal pressure and heat capacity difference as functions of reduced temperature. Upper part of this figure represents the heat capacity difference of polymer liquids. Lines are calculated from equations (17b) and (18)

Table 6 Comparison of the van der Waals' density ρ_w and characteristic density ρ^*

Polymer	v_w[a] ($cm^3 mol^{-1}$)	MW_r[b] ($g mol^{-1}$)	ρ_w[c] ($g cm^{-3}$)	ρ^* ($g cm^{-3}$)	ρ_w/ρ^*
PDMS	47.6	74.1	1.557	1.239	1.257
PS	62.9	104.0	1.653	1.225	1.350
PoMS	74.0	118.0	1.595	1.195	1.334
PMMA	56.1	100.0	1.783	1.401	1.273
PnBMA	86.8	142.2	1.638	1.256	1.305
PCHMA	99.2	168.0	1.694	1.297	1.306
PEA	56.1	100.1	1.784	1.352	1.319
PEMA	66.3	114.1	1.720	1.364	1.261
PMA	45.9	86.0	1.875	1.404	1.335
PVAc	45.9	86.0	1.874	1.446	1.296
PBD	37.5	54.0	1.440	1.097	1.313
i-PB	40.9	56.0	1.369	1.015	1.349
PAR	191.0	358.4	1.876	1.462	1.283
PCL	66.4	114.0	1.718	1.304	1.318
PC	136.2	254.2	1.866	1.455	1.282
HFPC	151.4	362.2	2.392	1.900	1.259
TMPC	180.8	310.2	1.716	1.377	1.246
PET	94.2	192.0	2.038	1.613	1.264
PIB	40.9	56.0	1.369	1.066	1.285
i-PP	30.7	42.0	1.368	0.989	1.384
Phenoxy	163.6	284.4	1.739	1.381	.1259
Psulfone	235.2	442.5	1.881	1.503	1.252
PEO	24.2	44.0	1.819	1.344	1.354
PVME	35.7	58.0	1.624	1.222	1.330
PTFE	32.0	100.0	3.126	2.749	1.137
PA6	64.2	113.1	1.761	1.402	1.256
PA66	128.3	226.1	1.763	1.452	1.214
PVC	29.2	62.5	2.140	1.600	1.338
PPO	71.3	120.1	1.684	1.393	1.210
				Average:	1.288
				Standard deviation:	0.052

[a] van der Waals' volume

[b] Molecular weight of repeating unit

[c] van der Waals' density, obtained from MW_r/v_w

deviations from 1.3 describe the individual packing efficiency of polymers according to structure.

A common definition of fractional free volume (*FFV*) is

$$FFV = (v - v^*)/v \qquad (19a)$$

Usually, v^* is determined from tabulated van der Waals' volumes and the Bondi recipe $v^* = 1.3v_w$. However, the above discussion suggests that a better measure of v^* is $1/\rho^*$. Using this in equation (19a) yields the remarkable result that the fractional free volume equals the reduced temperature:

$$FFV = 1 - \tilde{\rho}_0 = \tilde{T} \qquad (19b)$$

This result is valid only at low (atmospheric) pressure; at elevated pressures the Padé equation of state, equation (13), must be used to calculate the reduced density $\tilde{\rho}$. The interpretation here is that the characteristic temperature T^* is a scaling parameter that converts the absolute temperature into a free volume fraction. Using the T^* values given in *Table 4*, the *FFV* can be calculated at the glass transition temperature (T_g) for many common polymers. A broad spectrum of *FFV* values is obtained, with most falling in the range 0.1 to 0.2. There is no suggestion that T_g is an iso-free volume state.

The characteristic pressure P^* is obtained by extrapolating the low pressure bulk modulus to absolute zero. Thus, one interpretation of P^* is that it is the bulk modulus at absolute zero temperature and zero pressure. We can also make another identification. As $T \to 0$, the Helmholtz energy $\to$ the configurational energy U which we approximate by

$$U = \frac{R}{r^n} - \frac{A}{r^m} = \frac{R}{V^{n/3}} - \frac{A}{V^{m/3}} \qquad (20a)$$

where r is the equilibrium distance between monomers and we have made the substitution $r = V^{1/3}$. Thus, at zero temperature, we have $P = -\partial U/\partial V|_{T=0}$ and $B = V\partial^2 U/\partial V^2|_{T=0}$. Setting $P = 0$ then yields

$$U = \frac{9B_0V_0}{n(n-m)}\left[\left(\frac{V_0}{V}\right)^{n/3} - \frac{n}{m}\left(\frac{V_0}{V}\right)^{m/3}\right] \qquad (20b)$$

where the subscript 0 indicates, as before, the zero pressure state. Thus, at $T = 0$, the cohesive energy density (CED), $-U_0/V_0$, is given by

$$CED = -U_0/V_0 = 9B_0/nm = 9P^*/nm \qquad (21)$$

since $B_0 \rightarrow P^*$ as $T \rightarrow 0$. For the 6–12 Lennard–Jones potential, $CED = P^*/8$. Thus, in addition to the identification of P^* with the zero temperature bulk modulus, we see that P^* is also related to the CED at zero temperature.

In summary, the three characteristic parameters ρ^*, T^* and P^* are related to the van der Waals' density, free volume fraction and cohesive energy density, respectively.

SUMMARY

We have shown that the Padé equation of state, equation (13), with $B_1 = 10.2$ and $\omega = 0.9$

$$\frac{V}{V_0} \equiv \frac{\tilde{\rho}_0}{\tilde{\rho}} = \tilde{v}(1 - \tilde{T}) = \exp\{0.882[1 - (1 + 11.3\tilde{P}e^{9\tilde{T}})^{0.1}]\}$$

is superior in correlating polymer PVT data than any other known three-parameter equation of state. The accuracy of the Padé equation of state approaches the accuracy of experimental PVT data. The requisite three equation of state parameters, a characteristic temperature T^*, pressure P^* and mass density ρ^*, have been tabulated for 61 polymers in *Table 4*. Procedures for determining these parameters for other polymers have been outlined. It is remarkable that these three parameters, determined from low (zero) pressure PVT behaviour, completely define the high pressure compression response. They also have simple physical interpretations. The reduced temperture T/T^* is shown to be equal to the free volume fraction at temperature T. This may prove to be useful for the interpretation of gas permeability and diffusion through polymers. It is also shown that $1/\rho^*$ is related to the calculated van der Waals' volume and that P^* is a measure of the cohesive energy density at absolute zero temperature. It is predicted that the internal pressure and the heat capacity difference should pass through a maximum as a function of temperature at universal values of the reduced temperature. Some experimental support for this prediction is found. Finally, this new equation of state should be useful for extrapolating PVT properties beyond normal experimental ranges and estimating bounds for negative pressures.

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