Pressure–Volume–Temperature Relationships for Polymeric Liquids: A Review of Equations of State and Their Characteristic Parameters for 56 Polymers

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SYNOPSIS

A review of theoretical equations of state for polymer liquids is presented. Characteristic parameters for six equations of state, as well as parameters for the empirical Tait equation, are given for 56 polymers where pressure–volume–temperature (PVT) data over a wide range of conditions could be found in the literature. New PVT data are presented for four polymers: poly(epichlorohydrin), poly(ε-caprolactone), poly(vinyl chloride), and atactic polypropylene. All six equations of state provide adequate fits of the experimental specific volume data for the 56 polymers in the low pressure range (up to 500 bar). The modified cell model of Dee and Walsh, the Simha–Somcynsky hole theory, the Prigogine cell model, and the semiempirical model of Hartmann and Haque, were all found to provide good fits of polymer liquid PVT data over the full range of experimental pressures. The Flory–Orwoll–Vrij and the Sanchez–Lacombe lattice-fluid equations of state were both significantly less accurate over the wider pressure range. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Pressure–volume–temperature (PVT) relationships for polymeric materials is a subject of importance to polymer scientists and engineers, particularly from a process design standpoint. Equally important is the need for equations of state that adequately described this behavior over a wide range of temperature and pressure. This article presents a review of several equations of state for polymers in the liquid state (i.e., above the melting point for crystalline polymers or above the glass transition for amorphous polymers). A summary of available PVT data for polymer liquids from the literature is also presented. In addition, previously unpublished PVT data for poly(epichlorohydrin), poly(ε-caprolactone), poly(vinyl chloride), and atactic polypropylene, are also made available. Finally, a useful compendium of the characteristic parameters for 6 different equations of state, as well as parameters for the em-

pirical Tait equation, are given for 43 homopolymers and 13 copolymers. This should serve as a valuable reference for those concerned with the pressure-volume–temperature relationships of polymer liquids.

Numerous theoretical equations of state for polymer liquids have been developed.[1-16] These, at the minimum, provide accurate fitting functions with which to analyze PVT data. The equations also provide valuable thermodynamic information and can be used to predict the properties of polymer blends and solutions. It seems that nearly all equations of state for polymer liquids provide a reasonably good fit to PVT data, especially at low pressures. However, there is a major difference between the various equations in their abilities to fit PVT data over a wide range of pressure and to predict thermodynamic properties of polymer blends and solutions, particularly phase separation behavior. Most equations require an empirical interaction parameter, determined from at least one experimental data point, in order to describe accurately the phase behavior. This review is concerned only with the equations' PVT fitting capabilities for polymer liquids

**Table I   Summary of PVT Data for 43 Homopolymer Liquids Over an Extensive Range
of Temperature and Pressure**

| Polymer | Symbol | Range of Data | | Presentation | | Ref. |
		(T, °C)	(P, bar)	Table	Eqs.	
High-density polyethylene	HDPE	140–203	0–1960	Y	N	19
Low-density polyethylene	LDPE	121–175	0–1960	Y	N	19, 20
Polystyrene	PS	115–196	0–2000	Y	Tait	19, 22, 39
Poly(o-methylstyrene)	PoMS	139–198	0–1800	Y	Tait	22
Poly(vinyl acetate)	PVAc	35–100	0–800	Y	Polynomial	23, 20
Poly(methyl methacrylate)	PMMA ·	114–159	0–2000	Y	Tait	24, 19
Poly(cyclohexyl methacrylate)	PcHMA	123–198	0–2000	Y	Tait	24
Poly(n-butyl methacrylate)	PnBMA	34–200	0–2000	Y	Tait	24
Branched polyethylene	BPE	125–198	0–2000	Y	Tait	24
Linear polyethylene	LPE	142–200	0–2000	Y	Tait	24
High MW linear polyethylene	HMLPE	137–200	0–2000	Y	Tait	24
Polyisobutylene	PIB	53–110	0–1000	Y	Tait	20, 25
Poly(dimethylsiloxane)	PDMS	25–70	0–1000	Y	Tait	20, 26, 27
Poly(4-methyl-1-pentene)	PMP	241–319	0–1960	Y	Tait	28
Poly(tetrafluoroethylene)	PTFE	330–372	0–390	Y	Tait	29
Polysulfone	PSF	202–371	0–1960	N	Tait	30
cis-1,4-polybutadiene	PBD	4–55	0–2835	Y	N	31
Poly(ethylene oxide)	PEO	88–224	0–685	N	Figure	32
Poly(tetrahydrofuran)	PTHF	62–166	0–785	N	Figure	32
Low-density polyethylene "A"	LDPE-A	112–225	0–1960	N	Tait	33
Low-density polyethylene "B"	LDPE-B	112–225	0–1960	N	Tait	33
Low-density polyethylene "C"	LDPE-C	112–225	0–1960	N	Tait	33
i-Polypropylene	i-PP	170–297	0–1960	N	Tait	34–36
i-Poly(1-butene)	i-PB	133–246	0–1960	N	Tait	34, 37
Poly(ethylene terephthalate)	PET	274–342	0–1960	N	Tait	38
Poly(2,6-dimethylphenylene oxide)	PPO	203–320	0–1765	N	Tait	39
Bisphenol-A Polycarbonate	PC	151–340	0–1765	N	Tait	40, 48
Polyarylate (Ardel)	PAr	177–310	0–1765	N	Tait	40
Phenoxy	PH	68–300	0–1765	N	Tait	40
Poly(ether ether ketone)	PEEK	346–398	0–2000	N	Tait	42
Poly(vinyl methyl ether)	PVME	30–198	0–2000	N	Figure	43, 44
Polyamide 6	PA6	236–296	0–1960	N	Tait	45
Polyamide 6,6	PA66	246–298	0–1960	N	Tait	45, 46
Poly(methyl acrylate)	PMA	37–220	0–1960	N	Figure	47
Poly(ethyl acrylate)	PEA	37–217	0–1960	N	Figure	47
Poly(ethyl methacrylate)	PEMA	113–161	0–1960	Y	N	47
Tetramethyl bisphenol-A polycarbonate	TMPC	218–290	0–1600	Y	Tait	48
Hexafluoro bisphenol-A polycarbonate	HFPC	159–280	0–2000	Y	Tait	48
Bisphenol chloral polycarbonate	BCPC	155–284	0–2000	Y	Tait	48
Poly(epichlorohydrin)	PECH	60–140	0–2000	Y	N	49
Poly(ε-caprolactone)	PCL	100–148	0–2000	Y	N	49
Poly(vinyl chloride)	PVC	100–150	0–2000	Y	N	49, 19
a-Polypropylene	a-PP	80–120	0–1000	Y	N	49, 50

and with presenting a complete summary of their characteristic parameters. The subject of how well the various theories predict the thermodynamic properties of polymer blends and solutions may be addressed in a separate, forthcoming article.

Equation-of-state theories for polymer liquids can be roughly classified into three categories: cell models, lattice–fluid models, and hole models. The criteria for these classifications is the mathematical formalism that is used in accounting for the com-

Table II   Summary of PVT Data for 13 Random Copolymer Liquids Over an Extensive Range of Temperature and Pressure

| Polymer | Symbol | Range of Data | | Presentation | | Ref. |
		(T, °C)	(P, bar)	Table	Eqs.	
Ethylene/propylene 50 wt %	EP50	140–250	0–625	Y	N	21
Ethylene/vinyl acetate 18 wt %	EVA18	112–219	0–1765	N	Empirical	41
Ethylene/vinyl acetate 25 wt %	EVA25	94–233	0–1765	N	Empirical	41
Ethylene/vinyl acetate 28 wt %	EVA28	94–235	0–1765	N	Empirical	41
Ethylene/vinyl acetate 40 wt %	EVA40	75–235	0–1765	N	Empirical	41
Styrene/acrylonitrile 2.7 wt %	SAN3	105–266	0–2000	Y	Tait	48
Styrene/acrylonitrile 5.7 wt %	SAN6	96–267	0–2000	Y	N	48
Styrene/acrylonitrile 15.3 wt %	SAN15	132–262	0–2000	Y	Tait	48
Sytrene/acrylonitrile 18.0 wt %	SAN18	104–255	0–2000	Y	Tait	48
Styrene/acrylonitrile 40 wt %	SAN40	100–270	0–2000	Y	Tait	48
Styrene/acrylonitrile 70 wt %	SAN70	100–271	0–2000	N	Tait	51
Styrene/methyl methacrylate 20 wt %	SMMA20	110–270	0–2000	N	Tait	51
Styrene/methyl methacrylate 60 wt %	SMMA60	110–270	0–2000	N	Tait	51

pressibility and thermal expansion of the system. Cell models restrict volumetric changes in the system to changes in cell volume, that is, the space surrounding a polymer segment placed on a lattice framework. In contrast, lattice–fluid models allow empty sites or lattice vacancies while the cell volume is assumed constant. Hole models make allowances for both cell expansion and lattice vacancies. These three classes of models are based on different assumptions about the physics of the polymer liquid state, for example, in the form of the intersegmental potential (hard-sphere, square-well, Lennard–Jones 6–12, etc.) and the local geometry (simple cubic, hexagonal close packaging, etc.) of segmental contacts.

In 1974, Curro[17] presented a review of polymeric equations of state, covering the crystalline and glassy states (not included in the present review) as well as polymer liquids. Since then, several new equations of state have been developed,[10–16] and some of these

for polymer liquids have been included in this review. No attempt has been made to address all of the equations of state that have been developed for polymer liquids; rather, six of the most commonly used theories will be discussed. Furthermore, complete derivations of the various equations of state are not presented. Readers are referred to the original publications for a more detailed theoretical development.

PRESENTATION OF POLYMER LIQUID PVT DATA

Compilation of Polymer Liquid PVT Data from the Literature

It has only been within the last two decades that high quality data on the specific volume behavior of polymers, as a function of temperature and pressure, have become readily available. This availability has

Table III   Summary of Additional PVT Data Not Used In This Study

| Polymer | Range of Data | | Comments | Ref. |
	(T, °C)	(P, bar)		
i-Poly(1-pentene)	104–172	1	Table, atmospheric pressure only	52
Poly(vinylidene fluoride)	175–240	1	Polynomial, atmospheric pressure only	53
Polyoxymethylene	155–185	183–1509	Figure only, not enough detail	35
Poly(butylene terephthalate)	215–280	207–1034	Figure only, not enough detail	46
Qiana nylon	270–320	207–1034	Figure only, not enough detail	46
Natural rubber sulfur vulcanizates	10–82	0–10130	10, 13, 16, 18, 20, 22, 25, and 28% S	18
PS/PPO blends	30–350	0–1765	20, 40, 50, 60, and 80 % PPO	39
PS/PVME blends	30–198	0–2000	50 % PVME (figure only)	43
Liquid crystalline polymers	105–356	0–1960	Figures only	54

been partially in response to the need for such data to evaluate the various theoretical models describing the PVT properties of polymers that have been published. But, this has also been coincidental with advances in the experimental equipment necessary to obtain accurate and reproducible PVT data. Now, as new polymers are developed, their PVT properties are routinely determined, although, unfortunately, these are not always made available in the open literature. Given the vast number of polymers being manufactured, there is not an enormous amount of PVT data available for polymer liquids. In fact, there are some items that are notably absent from the list (or at best, limited data is available), including such common commercial products as nylons 11 and 12, poly(vinylidene chloride), poly(vinylidene fluoride), and poly(butylene terephthalate).

Tables I through III summarize PVT data for polymer liquids, which can be found in the literature.[18-54] Table I lists 43 homopolymers, while Table II gives 13 copolymers, for which substantial data exists, either in tabular form or reported with coefficients for an empirical representation of the data, such as the Tait equation (see later discussion). Also included are a few polymers where figures of sufficient detail were presented from which numerical values could be extracted. The experimental ranges of temperature and pressure covering the liquid region are also given. For those polymers where multiple data sets have been found, the one with the most extensive data range is reflected in the "Data Range" and "Presentation" columns in Tables I and II and is listed first in the "References" column. In most cases, the absolute values of specific volume are accurate to at least ± 0.001 cm^3/g, whereas modern dilatometric instrumentation has permitted relative volume changes to be measured to ± 0.0001 cm^3/g. These data will be used in fitting the characteristic parameters for the various theoretical equations of state reviewed in this article. Table III lists additional PVT data that have not been used in this study. These include a few polymers for which limited data exists (e.g., atmospheric pressure only) and where figures of insufficient detail were given without tabular data. References for some PVT data of polymer blends are also given, as well as references for a few liquid crystalline polymers.

New PVT Data for Four Polymers

Recently, PVT data for four polymers were obtained[48] in order to determine their characteristic parameters for use in predicting equilibrium gas sol-

ubilities with the Sanchez–Lacombe lattice–fluid equation of state.[55,56] The polymers used in this work were poly(epichlorohydrin) (PECH) (M_w = 700,000), poly(ε-caprolactone) (PCL) (M_w = 32,000), poly(vinyl chloride) (PVC) (M_w = 63,000), and atactic polypropylene (a-PP) (M_w > 30,000). All polymers except PVC were purchased from Scientific Polymer Products, Inc; poly(vinyl chloride) was donated by Vista Chemical. These previously unpublished data are made available at this time and their characteristic parameters for the various equations of state are included in this study.

The densities of the polymers at 20°C and atmospheric pressure were determined using a density gradient column. The changes in specific volume as a function of temperature and pressure were measured by using a PVT apparatus, which has been fully described elsewhere.[57] The apparatus consists of a sample cell containing about 1–1.5 g of sample and mercury as a confining fluid. A flexible bellows closes off one end of the cell. The movement of the bellows upon changing temperature or pressure is used to calculate the volume change of the sample cell. In the isothermal mode, volume readings are obtained at fixed-pressure intervals (usually 10 MPa

Table IV   Specific Volume of Poly(epichlorohydrin) in the Liquid State as a Function of Temperature and Pressure

Pressure Bar	Specific Volume, cm^3/g (Temperature, °C)				
	60.0	80.0	100.0	120.0	140.0
0	0.7472	0.7559	0.7650	0.7738	0.7828
100	0.7437	0.7521	0.7606	0.7691	0.7777
200	0.7401	0.7482	0.7562	0.7643	0.7726
300	0.7370	0.7449	0.7525	0.7606	0.7684
400	0.7341	0.7417	0.7491	0.7569	0.7645
500	0.7313	0.7388	0.7459	0.7535	0.7607
600	0.7288	0.7360	0.7430	0.7503	0.7573
700	0.7261	0.7334	0.7400	0.7471	0.7539
800	0.7238	0.7308	0.7372	0.7440	0.7506
900	0.7216	0.7284	0.7346	0.7413	0.7478
1000	0.7192	0.7261	0.7321	0.7387	0.7449
1100	0.7170	0.7239	0.7298	0.7361	0.7421
1200	0.7153	0.7216	0.7275	0.7336	0.7396
1300	0.7133	0.7195	0.7253	0.7311	0.7371
1400	0.7114	0.7174	0.7232	0.7289	0.7344
1500	0.7094	0.7153	0.7211	0.7266	0.7321
1600	0.7077	0.7135	0.7190	0.7245	0.7298
1700	0.7060	0.7117	0.7169	0.7224	0.7276
1800	0.7043	0.7100	0.7151	0.7203	0.7254
1900	0.7027	0.7082	0.7133	0.7183	0.7233
2000	0.7012	0.7065	0.7114	0.7163	0.7211

increments) at a constant temperature. Following measurements along an isotherm, the temperature is changed by 8–10°C, and the process is repeated. The absolute accuracy of the device is $(1-2) \times 10^{-3}$ cm^3/g; however, volume changes as small as $(1-2) \times 10^{-4}$ cm^3/g can be resolved. A version of this PVT apparatus is available as a complete instrument from Gnomix Research, Boulder, Colorado. Tables IV through VII present the PVT data covering the liquid region for the four polymers mentioned above.

Empirical Representations: The Tait Equation

Perhaps the most common empirical representation of polymeric PVT data is that of the Tait equation.[58] It is, in fact, not a true equation of state, but rather an isothermal compressibility model (i.e., a volume–pressure relationship). The general form of the Tait equation is:

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

where the coefficient C is usually taken to be a universal constant equal to 0.0894.[59] The zero-pressure isotherm $V(0, T)$ is usually given by:

$$V(0, T) = V_0 \exp(\alpha T) \quad (2)$$

where α is the thermal expansion coefficient. The Tait parameter $B(T)$ is usually given by:

$$B(T) = B_0 \exp(-B_1 T) \quad (3)$$

Thus, the Tait equation is normally a four-parameter (V_0, α, B_0, B_1) representation of the experimental PVT data. In some cases, eqs. (2) and (3) do not fit the data accurately, and polynomial expressions are used:

$$V(0, T) = a_0 + a_1 T + a_2 T^2 \quad (4)$$

$$B(T) = b_0 + b_1 T + b_2 T^2 \quad (5)$$

Table VIII summarizes the Tait equation parameters for the 56 polymers listed in Tables I and II. These parameters have either been reported by the investigating authors or determined for this work from tabular data given in the various references.

Recently, a new isothermal equation of state for solid and liquid polymers was introduced by Sun, Song, and Yan.[60] This empirical volume–pressure relationship is given by:

Table V   Specific Volume of Poly(ε-caprolactone) in the Liquid State as a Function of Temperature and Pressure

Pressure Bar	Specific Volume, cm^3/g (Temperature, °C)					
	100.6	110.9	120.2	130.1	139.4	148.2
0	0.9647	0.9719	0.9773	0.9833	0.9890	0.9950
100	0.9584	0.9651	0.9702	0.9760	0.9814	0.9871
200	0.9522	0.9571	0.9628	0.9687	0.9737	0.9789
300	0.9467	0.9520	0.9566	0.9622	0.9678	0.9728
400	0.9415	0.9465	0.9512	0.9566	0.9618	0.9665
500	0.9369	0.9418	0.9461	0.9514	0.9563	0.9607
600	0.9324	0.9369	0.9413	0.9463	0.9507	0.9553
700	0.9280	0.9326	0.9367	0.9417	0.9452	0.9504
800	0.9240	0.9284	0.9323	0.9369	0.9409	0.9455
900	0.9202	0.9243	0.9284	0.9326	0.9367	0.9410
1000	0.9164	0.9206	0.9248	0.9287	0.9326	0.9371
1100	0.9130	0.9171	0.9212	0.9247	0.9285	0.9329
1200	0.9095	0.9138	0.9170	0.9210	0.9247	0.9289
1300	0.9064	0.9104	0.9135	0.9176	0.9212	0.9253
1400	0.9033	0.9072	0.9103	0.9142	0.9174	0.9216
1500	0.9005	0.9041	0.9069	0.9107	0.9138	0.9181
1600	0.8974	0.9010	0.9040	0.9075	0.9106	0.9145
1700	0.8948	0.8981	0.9012	0.9044	0.9081	0.9111
1800	0.8922	0.8953	0.8985	0.9013	0.9046	0.9078
1900	0.8894	0.8925	0.8955	0.8986	0.9021	0.9044
2000	0.8870	0.8898	0.8928	0.8961	0.8987	0.9013

Table VI Specific Volume of Poly(vinyl chloride) in the Liquid State as a Function of Temperature and Pressure

Pressure Bar	Specific Volume, cm³/g (Temperature, °C)					
	100.2	110.1	120.1	130.1	140.0	150.0
0	0.7401	0.7432	0.7476	0.7519	0.7561	0.7610
100	0.7363	0.7394	0.7436	0.7474	0.7512	0.7561
200	0.7322	0.7358	0.7397	0.7425	0.7456	0.7509
300	0.7289	0.7321	0.7361	0.7391	0.7421	0.7470
400	0.7260	0.7291	0.7329	0.7355	0.7385	0.7431
500		0.7263	0.7296	0.7322	0.7351	0.7396
600		0.7234	0.7266	0.7291	0.7320	0.7362
700		0.7207	0.7238	0.7263	0.7287	0.7330
800		0.7182	0.7211	0.7235	0.7259	0.7301
900			0.7188	0.7208	0.7232	0.7273
1000			0.7162	0.7184	0.7208	0.7244
1100			0.7139	0.7158	0.7184	0.7219
1200			0.7114	0.7136	0.7158	0.7194
1300				0.7114	0.7136	0.7171
1400				0.7092	0.7113	0.7145
1500				0.7071	0.7092	0.7122
1600				0.7052	0.7071	0.7099
1700				0.7033	0.7048	0.7080
1800					0.7030	0.7058
1900					0.7008	0.7039
2000					0.6990	0.7019

$$P = \frac{B(T,0)}{(n-m)} \left\{ \left[\frac{V(T,0)}{V(T,P)} \right]^{n+1} - \left[\frac{V(T,0)}{V(T,P)} \right]^{m+1} \right\} \quad (6)$$

where $n = 6.14$ and $m = 1.16$ are general constants for polymer systems. The zero-pressure isotherm $V(T,0)$ and the parameter $B(T,0)$ must be determined from experimental data and are expressed similarly as in eqs. (2)–(5) above. The authors showed that the Tait equation can be derived as an approximate solution in their formalism in developing eq. (6). It remains to be seen if this alternative to the longstanding Tait equation will be accepted by polymer scientists and researchers.

Theoretical Equations of State

An alternative to empirical representations of PVT behavior is to develop a theoretical model, starting from an understanding of the forces that exist between molecules. In principle, these forces could be calculated from quantum mechanics; however, since the "true" potential energy function is not known

exactly, one usually assumes that these forces obey an empirical potential "law," such as the "hard-sphere" or Lennard–Jones "6–12" potential. The use of statistical mechanics bridges the gap between quantum and continuum mechanics, allowing one

Table VII Specific Volume of Atactic Polypropylene in the Liquid State as a Function of Temperature and Pressure

Pressure Bar	Specific Volume, cm³/g (Temperature, °C)				
	80.0	90.0	100.0	110.0	120.0
0	1.2095	1.2164	1.2261	1.2366	1.2468
100	1.1979	1.2048	1.2137	1.2233	1.2326
200	1.1863	1.1939	1.2015	1.2102	1.2187
300	1.1773	1.1844	1.1922	1.1997	1.2081
400	1.1693	1.1761	1.1832	1.1903	1.1983
500	1.1620	1.1685	1.1752	1.1820	1.1897
600	1.1550	1.1615	1.1675	1.1740	1.1815
700	1.1486	1.1548	1.1604	1.1669	1.1736
800	1.1424	1.1481	1.1539	1.1601	1.1666
900	1.1367	1.1428	1.1478	1.1539	1.1599
1000	1.1312	1.1369	1.1419	1.1479	1.1536

to take statistical averages using molecular variables to obtain macroscopically observable quantities. The normal procedure involves the formulation of the canonical partition function, a summation of the Boltzmann's distribution of energies over all possible states of the system. Various simplifying assumptions are introduced in formulating the partition function. However, once given an expression for the partition function, all thermodynamic quantities can be determined by appropriate differentiation. For example, the thermodynamic pressure P is given by:

$$P \equiv kT \frac{\partial \ln Q}{\partial V} \qquad (7)$$

where Q is the partition function and k is Boltzmann's constant. The resulting expression for P as a function of temperature and volume is the equation of state.

In the sections to follow, several theoretical equations of state will be described. These equations of state have been grouped into three classifications based on their formalism in developing the models; these are cell theories, lattice–fluid theories, and hole theories. All of these theories can represent PVT data for polymer liquids, usually in "reduced" or dimensionless variables. The thermodynamic variables P, v, and T are made dimensionless by forming a ratio with a corresponding characteristic parameter of the same dimensional units, thus the following dimensionless variables are defined:

$$\tilde{P} \equiv P/P^*, \quad \tilde{v} \equiv v/v^*, \quad \tilde{T} \equiv T/T^* \qquad (8)$$

where P^*, v^*, and T^* are the "reducing" or characteristic parameters. Most satisfy the principle of corresponding states; that is, the equations of state in reduced variables are considered as universal functions for all polymer liquids. The PVT behavior in terms of the real thermodynamic variables for individual materials are obtained from the relations in eq. (8) and their three characteristic parameters.

One of the main purposes of this article is to present a compendium of the characteristic parameters (for the six featured equations of state) for as many polymers as there are sufficient data. Therefore, tables of the characteristic parameters for all of the homopolymers and copolymers listed in Tables I and II will be given for each of the equations of state discussed in the following sections. A standard, nonlinear, least-squares regression method is used to simultaneously fit the three characteristic parameters to the actual experimental PVT data, where it has been given in numerical form in the

various references. In those cases where tabular data have not been presented, the Tait equation will be used to generate data over evenly spaced increments covering the experimental ranges of temperature and pressure. The minimization function, used in the least-squares regression, is $\Sigma(P_{exp} - P_{calc})^2$. The fitted characteristic parameters are then used to calculate the average deviation from the experimental specific volume of $\Sigma|(v_{exp} - v_{calc})|/N$, where N is the number of data points. Since the accuracy of the fits are better over a restricted data range, and since often only data and thermodynamic functions at low pressures are needed for engineering work, the characteristic parameters are fit over a pressure range of 0 to 500 bar, as well as over the full available range, typically 0 to 2000 bar.

CELL THEORIES

In cell theories, the polymer molecules are modeled as having two distinct sets of modes contributing to the partition function, namely internal and external modes (associated with internal motions of the molecules and intermolecular interactions, respectively). This conceptual separation of modes was first proposed by Prigogine et al.[3,4] Only the external modes will affect the PVT properties of the system. In this formalism, a polymer molecule is divided into segments, or r-mers, with each mer having $3c$ degrees of freedom, where $c(< 1)$ is a constant, accounting for the intermolecular constraints on the segments. The compressibility and thermal expansion of the system are explained solely by changes in the cell volume. The various theories that have developed differ in the form of the intermolecular potential used and the local geometry of segmental contacts. Prigogine et al.[3,4] took the Lennard–Jones and Devonshire cell model for liquids[1] and applied it to polymer fluids. Two forms of the resulting cell model (CM) were developed; the first uses the harmonic oscillator approximation for the potential[3] and the second applies the "square-well" approximation to the Lennard–Jones "6–12" potential.[4] Both forms use hexagonal close packing for the cell geometry. The "square-well" approximation is the more common of the two Prigogine cell models. Di Benedetto[5,6] developed a cell model that assumes the chain segments interact with a cylindrically symmetric (rather than spherically symmetric) "square-well" potential. Di Benedetto's model was followed shortly thereafter by the Flory, Orwoll, and Vrij (FOV) model,[7] which uses a hard-sphere type repulsive potential and soft attraction of unspecified character, together with a simple cubic cell geometry.

Table VIII **Tait Equation Parameters for 56 Polymer Liquids**[a]

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

Polymer	$V(0, T)$, cm^3/g[b]	$B(T)$, bar	Source
HDPE	$1.1595 + 8.0394 \times 10^{-4}\, t$	$1799 \exp(-4.739 \times 10^{-3}\, t)$	19, This work
LDPE	$1.1944 + 2.841 \times 10^{-4}\, t + 1.872 \times 10^{-6}\, t^2$	$2022 \exp(-5.243 \times 10^{-3}\, t)$	19, This work
PS	$0.9287 \exp(5.131 \times 10^{-4}\, t)$	$2169 \exp(-3.319 \times 10^{-3}\, t)$	22
PoMS	$0.9396 \exp(5.306 \times 10^{-4}\, t)$	$2619 \exp(-4.114 \times 10^{-3}\, t)$	22
PVAc	$0.82496 + 5.820 \times 10^{-4}\, t + 2.940 \times 10^{-7}\, t^2$	$2049 \exp(-4.346 \times 10^{-3}\, t)$	23, This work
PMMA	$0.8254 + 2.8383 \times 10^{-4}\, t + 7.792 \times 10^{-7}\, t^2$	$2875 \exp(-4.146 \times 10^{-3}\, t)$	24
PcHMA	$0.8793 + 4.0504 \times 10^{-4}\, t + 7.774 \times 10^{-7}\, t^2$ $- 7.7534 \times 10^{-10}\, t^3$	$2952 \exp(-5.220 \times 10^{-3}\, t)$	24
PnBMA	$0.9341 + 5.5254 \times 10^{-4}\, t + 6.5803 \times 10^{-6}\, t^2$ $+ 1.5691 \times 10^{-10}\, t^3$	$2267 \exp(-5.344 \times 10^{-3}\, t)$	24
BPE	$0.9399 \exp(7.341 \times 10^{-4}\, t)$	$1771 \exp(-4.699 \times 10^{-3}\, t)$	24
LPE	$0.9172 \exp(7.806 \times 10^{-4}\, t)$	$1767 \exp(-4.661 \times 10^{-3}\, t)$	24
HMLPE	$0.8992 \exp(8.502 \times 10^{-4}\, t)$	$1683 \exp(-4.292 \times 10^{-3}\, t)$	24
PIB[c]	$(0.9297 - 5.123 \times 10^{-4}\, t + 6.15 \times 10^{-8}\, t^2)^{-1}$	$1907 \exp(-4.146 \times 10^{-3}\, t)$	20, 25
PIB	$1.0750 \exp(5.651 \times 10^{-4}\, t)$	$2003 \exp(-4.329 \times 10^{-3}\, t)$	This work
PDMS[d]	$(0.9919 - 8.925 \times 10^{-4}\, t + 2.65 \times 10^{-7}\, t^2$ $- 3.0 \times 10^{-11}\, t^3)^{-1}$	$1041 \exp(-5.851 \times 10^{-3}\, t)$	20, 26
PDMS	$1.0079 \exp(9.121 \times 10^{-4}\, t)$	$894 \exp(-5.701 \times 10^{-3}\, t)$	This work
PMP	$1.4075 - 9.095 \times 10^{-4}\, t + 3.497 \times 10^{-6}\, t^2$	$376.7 + 2.134\, t - 7.0445 \times 10^{-3}\, t^2$	28
PTFE	$0.3200 - 9.5862 \times 10^{-4}\, t$	$4252 \exp(-9.380 \times 10^{-3}\, t)$	29
PSF	$0.7644 + 3.419 \times 10^{-4}\, t + 3.126 \times 10^{-7}\, t^2$	$3659 \exp(-3.757 \times 10^{-3}\, t)$	30
PBD	$1.0970 \exp(6.600 \times 10^{-4}\, t)$	$1777 \exp(-3.593 \times 10^{-3}\, t)$	31, This work
PEO	$0.8766 \exp(7.087 \times 10^{-4}\, t)$	$2077 \exp(-3.947 \times 10^{-3}\, t)$	32, This work
PTHF	$1.0043 \exp(6.691 \times 10^{-4}\, t)$	$1786 \exp(-4.223 \times 10^{-3}\, t)$	32, This work
LDPE-A	$1.1484 \exp(6.950 \times 10^{-4}\, t)$	$1929 \exp(-4.701 \times 10^{-3}\, t)$	33
LDPE-B	$1.1524 \exp(6.700 \times 10^{-4}\, t)$	$1966 \exp(-4.601 \times 10^{-3}\, t)$	33
LDPE-C	$1.1516 \exp(6.730 \times 10^{-4}\, t)$	$1867 \exp(-4.391 \times 10^{-3}\, t)$	33
i-PP	$1.1606 \exp(6.700 \times 10^{-4}\, t)$	$1491 \exp(-4.177 \times 10^{-3}\, t)$	34
i-PB	$1.1417 \exp(6.751 \times 10^{-4}\, t)$	$1675 \exp(-4.533 \times 10^{-3}\, t)$	34
PET	$0.6883 + 5.90 \times 10^{-4}\, t$	$3697 \exp(-4.150 \times 10^{-3}\, t)$	38
PPO	$0.78075 \exp(2.151 \times 10^{-5}\, T^{3/2})$, T in K	$2278 \exp(-4.290 \times 10^{-3}\, t)$	39
PC	$0.73565 \exp(1.859 \times 10^{-5}\, T^{3/2})$, T in K	$3100 \exp(-4.078 \times 10^{-3}\, t)$	40
PAr	$0.73381 \exp(1.626 \times 10^{-5}\, T^{3/2})$, T in K	$2969 \exp(-3.375 \times 10^{-3}\, t)$	40
PH	$0.76644 \exp(1.921 \times 10^{-5}\, T^{3/2})$, T in K	$3599 \exp(-4.378 \times 10^{-3}\, t)$	40
PEEK	$0.7158 \exp(6.690 \times 10^{-4}\, t)$	$3880 \exp(-4.124 \times 10^{-3}\, t)$	42
PVME	$0.9585 \exp(6.653 \times 10^{-4}\, t)$	$2158 \exp(-4.588 \times 10^{-3}\, t)$	43, This work
PA6	$0.7597 \exp(4.701 \times 10^{-4}\, t)$	$3767 \exp(-4.660 \times 10^{-3}\, t)$	45
PA66	$0.7657 \exp(6.600 \times 10^{-4}\, t)$	$3164 \exp(-5.040 \times 10^{-3}\, t)$	45
PMA	$0.8365 \exp(6.795 \times 10^{-4}\, t)$	$2358 \exp(-4.493 \times 10^{-3}\, t)$	47, This work
PEA	$0.8756 \exp(7.241 \times 10^{-4}\, t)$	$1932 \exp(-4.839 \times 10^{-3}\, t)$	47, This work
PEMA	$0.8614 \exp(7.468 \times 10^{-4}\, t)$	$2609 \exp(-5.356 \times 10^{-3}\, t)$	47, This work
TMPC	$0.8497 + 5.073 \times 10^{-4}\, t + 3.832 \times 10^{-7}\, t^2$	$2314 \exp(-4.242 \times 10^{-3}\, t)$	48
HFPC	$0.6111 + 4.898 \times 10^{-4}\, t + 1.730 \times 10^{-7}\, t^2$	$2366 \exp[(-5.156 \times 10^{-3}\, t)$	48
BCPC	$0.6737 + 3.634 \times 10^{-4}\, t + 2.370 \times 10^{-7}\, t^2$	$3634 \exp[(-4.921 \times 10^{-3}\, t)$	48
PECH	$0.7216 \exp(5.825 \times 10^{-4}\, t)$	$2383 \exp(-4.171 \times 10^{-3}\, t)$	49, This work
PCL	$0.9049 \exp(6.392 \times 10^{-4}\, t)$	$1890 \exp(-3.931 \times 10^{-3}\, t)$	49, This work
PVC	$0.7196 + 5.581 \times 10^{-5}\, t + 1.468 \times 10^{-6}\, t^2$	$2942 \exp(-5.321 \times 10^{-3}\, t)$	49, This work
a-PP	$1.1841 - 1.091 \times 10^{-4}\, t + 5.286 \times 10^{-6}\, t^2$	$1621 \exp(-6.604 \times 10^{-3}\, t)$	49, This work
EP50	$1.2291 + 5.799 \times 10^{-5}\, t + 1.964 \times 10^{-6}\, t^2$	$4870 \exp(-8.103 \times 10^{-3}\, t)$	21, This work
EVA18	$1.02391 \exp(2.173 \times 10^{-5}\, T^{3/2})$, T in K	$1882 \exp(-4.537 \times 10^{-3}\, t)$	41, This work
EVA25	$1.00416 \exp(2.244 \times 10^{-5}\, T^{3/2})$, T in K	$1844 \exp(-4.734 \times 10^{-3}\, t)$	41, This work
EVA28	$1.00832 \exp(2.241 \times 10^{-5}\, T^{3/2})$, T in K	$1835 \exp(-4.457 \times 10^{-3}\, t)$	41, This work
EVA40	$1.06332 \exp(2.288 \times 10^{-5}\, T^{3/2})$, T in K	$2051 \exp(-4.989 \times 10^{-3}\, t)$	41, This work

Table VIII *(Continued)*

| Polymer | $V(P, T) = V(0, T)\{1 - C \ln[1 + P/B(T)]\}$ | | |
	$V(0, T)$, cm^3/g^b	$B(T)$, bar	Source
SAN3	$0.9233 + 3.936 \times 10^{-4}\, t + 5.685 \times 10^{-7}\, t^2$	$2398 \exp(-4.376 \times 10^{-3}\, t)$	48
SAN6	$0.9211 + 4.370 \times 10^{-4}\, t + 5.846 \times 10^{-7}\, t^2$	$2269 \exp(-4.286 \times 10^{-3}\, t)$	48, This work
SAN15	$0.9044 + 4.207 \times 10^{-4}\, t + 4.077 \times 10^{-7}\, t^2$	$2384 \exp(-3.943 \times 10^{-3}\, t)$	48
SAN18	$0.9016 + 4.036 \times 10^{-4}\, t + 4.206 \times 10^{-7}\, t^2$	$2404 \exp(-3.858 \times 10^{-3}\, t)$	48
SAN40	$0.8871 + 3.406 \times 10^{-4}\, t + 4.938 \times 10^{-7}\, t^2$	$2893 \exp(-4.431 \times 10^{-3}\, t)$	48
SAN70	$0.8528 + 3.616 \times 10^{-4}\, t + 2.634 \times 10^{-7}\, t^2$	$3354 \exp(-3.923 \times 10^{-3}\, t)$	51
SMMA20	$0.9063 + 3.570 \times 10^{-4}\, t + 6.532 \times 10^{-7}\, t^2$	$2320 \exp(-4.143 \times 10^{-3}\, t)$	51
SMMA60	$0.8610 + 3.350 \times 10^{-4}\, t + 6.980 \times 10^{-7}\, t^2$	$2610 \exp(-4.611 \times 10^{-3}\, t)$	51

^{a} The ranges of validity for the temperature and pressure are the same as given in Tables I and II. Unless otherwise noted, the parameter C is taken as a universal constant for all polymers equal to 0.0894.

^{b} Unless otherwise noted, the temperature t is in °C.

^{c} The parameter C for PIB, given in Ref. 20, is equal to 0.087132. For convenience, the Tait equation parameters have been redetermined for this work with $C = 0.0894$.

^{d} The parameter C for PDMS, given in Ref. 20, is equal to 0.100916. For convenience, the Tait equation parameters have been redetermined for this work with $C = 0.0894$.

Of all the theoretical equations of state (including lattice–fluid and hole theories), the FOV model is the one most extensively applied. Finally, Dee and Walsh[14,15] modified the Prigogine "square-well" CM theory by introducing a numerical factor to decouple the potential from the choice of cell geometry. The additional factor q was found to be a universal constant for several polymers and thus the modified cell model (MCM) remains a three-parameter theory, as are the other equations of state reviewed in this article. In the subsections below, only the FOV model, the Prigogine "square-well" CM, and the MCM will be discussed.

Flory, Orwoll, Vrij (FOV) Model

Flory, Orwoll, and Vrij[7] derived their equation of state in dimensionless variables as:

$$\frac{\tilde{P}\tilde{v}}{\tilde{T}} = \frac{\tilde{v}^{1/3}}{(\tilde{v}^{1/3} - 1)} - \frac{1}{\tilde{T}\tilde{v}} \qquad (9)$$

where $\tilde{v} \equiv v/v^*$ with $v^* = \sigma^3$, $\tilde{T} \equiv T/T^*$ with $T^* = s\eta/(ck)$, and $\tilde{P} \equiv P/P^*$ with $P^* = ckT^*/v^*$. The s is the number of contacts per segment, η is the segment–segment interaction energy, and k is Boltzmann's constant. The σ is the "hard-sphere" radius, and thus v^* is identified as the hard-core cell volume.

FOV model characteristic parameters (P^*, T^*, and v^*), for the polymers listed in Tables I and II, are given in Table IX.

Prigogine "Square-well" Cell Model (CM)

The dimensionless equation of state, derived from the Prigogine cell model,[4] using the "square-well" approximation to the Lennard–Jones "6–12" potential, is:

$$\frac{\tilde{P}\tilde{v}}{\tilde{T}} = \frac{\tilde{v}^{1/3}}{(\tilde{v}^{1/3} - 0.8909)} - \frac{2}{\tilde{T}}\left(\frac{1.2045}{\tilde{v}^2} - \frac{1.011}{\tilde{v}^4}\right) \qquad (10)$$

where the reduced variables and characteristic parameters have the same definitions as in the FOV model. The first term on the right side of eq. (10) is similar to the FOV model, except for the factor $0.8909 \,(= 2^{-1/6})$, arising from the choice of hexagonal close packing as the cell geometry; this term is equal to 1 in the FOV model, which, as stated earlier, uses a simple cubic geometry. The second term on the right side of eq. (10) reflects the Lennard–Jones "6–12" potential. The constants 1.2045 and 1.011 are explicit for the L–J potential given hexagonal close packing.

Table X gives CM characteristic parameters (P^*, T^*, and v^*) for the polymers listed in Tables I and II.

Dee and Walsh Modified Cell Model (MCM)

Dee and Walsh[14,15] modified the above formalism for the cell model by first noting that the potential and the nard-core cell volume were coupled by the

Table IX   Characteristic Parameters for the FOV Equation of State

Polymer[b]	For P = 0 to 500 bar				For Full Range of Experimental P[a]			
	P^* bar	T^* K	v^* cm³/g	Avg Δv 10⁴ cm³/g	P^* bar	T^* K	v^* cm³/g	Avg Δv 10⁴ cm³/g
HDPE	3461	8082	1.0506	9.9	3767	7002	1.0129	43.7
LDPE	4188	7433	1.0270	10.4	5292	6356	0.9794	36.9
PS	4411	8728	0.8385	3.9	4052	8118	0.8277	19.2
PoMS	4564	8886	0.8540	2.2	4415	8463	0.8457	11.1
PVAc	6056	6540	0.7113	2.7	5997	6449	0.7090	4.2
PMMA	5848	8264	0.7309	1.2	5688	7717	0.7204	10.1
PcHMA	5318	8072	0.7835	2.8	4614	7700	0.7772	18.5
PnBMA	5404	7082	0.8158	6.4	5096	6794	0.8087	18.0
BPE	4642	7205	1.0183	11.9	4531	6710	0.9992	30.7
LPE	5067	7053	1.0065	4.2	5376	6548	0.9818	23.6
HMLPE	5853	6756	1.0012	6.5	6043	6458	0.9855	17.9
PIB	4045	7708	0.9524	3.8	3960	7396	0.9455	8.1
PDMS	3327	5414	0.8354	10.1	3269	5184	0.8264	15.0
PMP	3234	7984	1.0689	14.8	3950	7079	1.0203	43.6
PTFE	4049	7088	0.4215	6.5	4049	7088	0.4215	6.5
PSF	7283	9171	0.6962	5.8	7382	8664	0.6847	17.4
PBD	4885	6494	0.9435	5.4	4544	5522	0.9173	29.8
PEO	6014	7229	0.7743	8.8	6016	7147	0.7719	10.3
PTHF	4724	7145	0.8811	6.4	4598	7006	0.8774	10.3
LDPE-A	4612	7441	1.0218	8.9	4695	6774	0.9963	41.6
LDPE-B	4530	7593	1.0276	8.4	4564	6896	1.0025	41.9
LDPE-C	4533	7540	1.0252	9.0	4710	6809	0.9974	41.8
i-PP	3498	7966	1.0494	13.9	3974	7011	1.0072	67.7
i-PB	3835	7680	1.0222	9.5	4039	6838	0.9897	54.3
PET	7865	8701	0.6597	2.9	8510	8215	0.6452	11.5
PPO	5856	7882	0.7676	7.4	6509	7360	0.7472	24.6
PC	6659	8481	0.7179	6.8	6710	8039	0.7070	20.2
PAr	6357	9063	0.7120	4.0	6512	8470	0.6991	16.0
PH	7442	8195	0.7456	6.5	7132	7869	0.7389	16.9
PEEK	7266	9272	0.6842	1.9	8329	8667	0.6642	12.8
PVME	5186	7264	0.8436	10.4	5128	6607	0.8266	30.8
PA6	4052	10480	0.7098	2.7	4110	9182	0.6896	27.5
PA66	5105	8621	0.7099	2.5	5583	7865	0.6885	22.5
PMA	5537	7297	0.7382	8.4	5992	6894	0.7277	17.6
PEA	4903	7020	0.7683	8.1	5115	6599	0.7563	24.9
PEMA	6367	7050	0.7602	8.9	6413	6703	0.7503	11.0
TMPC	5155	8286	0.7755	6.9	5142	8156	0.7720	8.3
HFPC	5488	7614	0.5575	4.7	5427	7360	0.5521	11.9
BCPC	6438	8576	0.6110	3.7	6110	8287	0.6065	10.9
PECH	5231	7719	0.6396	2.9	5246	7192	0.6312	8.9
PCL	4828	7377	0.7982	2.9	4862	6754	0.7830	13.1
PVC	4903	8354	0.6292	3.4	5018	7752	0.6201	8.8
a-PP	3975	6521	0.9824	4.0	4059	6351	0.9755	7.3
EP50	3512	8469	1.0682	17.8	3602	8377	1.0650	17.8
EVA18	4500	7440	0.9923	11.8	4536	6870	0.9724	32.1
EVA25	4506	7451	0.9709	7.0	4448	6770	0.9475	36.2
EVA28	4721	7420	0.9654	9.8	4805	6759	0.9416	34.3
EVA40	4988	7379	0.9177	6.0	4755	6766	0.8985	33.0
SAN3	4529	8393	0.8240	6.3	4533	7897	0.8129	18.8
SAN6	5102	8041	0.8188	7.4	5031	7622	0.8087	19.5
SAN15	4826	8516	0.8114	4.6	4650	8053	0.8020	16.4
SAN18	4808	8558	0.8082	5.0	4610	7999	0.7974	19.4
SAN40	4881	8870	0.7960	5.0	4747	8369	0.7869	17.4
SAN70	5574	9326	0.7740	3.7	5009	8701	0.7648	20.9
SMMA20	4863	8250	0.8037	5.3	4758	7521	0.7865	32.0
SMMA60	5232	8133	0.7618	3.7	4913	7558	0.7494	26.9

[a] The ranges of experimental temperature (the same for both sets of parameters) and pressure are given in Tables I and II. Note also that the full range of pressure for PTFE is only 0 to 390 bar.

[b] Characteristic parameters for PSF, LDPE-A, LDPE-B, LDPE-C, i-PP, i-PB, PET, PPO, PC, PAr, PH, PEEK, PA6, PA66, SAN70, SMMA20, and SMMA60 were fit to data generated by the Tait equation with parameters from Table VIII.

Table X   Characteristic Parameters for the CM Equation of State

Polymer[b]	For P = 0 to 500 bar				For Full Range of Experimental P[a]			
	P^* bar	T^* K	v^* cm³/g	Avg Δv 10⁴ cm³/g	P^* bar	T^* K	v^* cm³/g	Avg Δv 10⁴ cm³/g
HDPE	4206	4709	1.1450	10.9	4177	5007	1.1606	16.8
LDPE	4927	4374	1.1193	33.0	5917	4047	1.0958	22.7
PS	5848	5063	0.9114	2.3	5990	5167	0.9148	5.7
PoMS	5926	5113	0.9270	2.8	6227	5214	0.9302	6.3
PVAc	7524	3786	0.7734	1.8	7559	3781	0.7731	1.7
PMMA	7491	4743	0.7929	0.6	7650	4783	0.7941	1.9
PcHMA	6412	4671	0.8521	3.9	6301	4873	0.8606	8.4
PnBMA	6458	4119	0.8883	9.2	6830	4237	0.8931	16.4
BPE	5181	4218	1.1123	12.0	5352	4309	1.1179	11.9
LPE	5466	4133	1.1003	3.1	5881	4124	1.0978	8.9
HMLPE	6053	3984	1.0978	6.4	6646	3962	1.0935	10.4
PIB	5738	4539	1.0373	2.1	5800	4593	1.0393	3.3
PDMS	3887	3227	0.9163	4.0	3880	3254	0.9180	5.2
PMP	3354	4808	1.1807	8.4	4000	4721	1.1652	16.6
PTFE	3239	4488	0.4829	8.8	3239	4488	0.4829	8.8
PSF	8033	5365	0.7602	6.9	8445	5358	0.7593	5.4
PBD	6694	3793	1.0265	3.3	6815	3811	1.0269	3.7
PEO	6886	4234	0.8453	8.8	6968	4226	0.8447	8.0
PTHF	5783	4183	0.9608	5.7	5768	4185	0.9609	5.4
LDPE-A	5279	4380	1.1173	8.5	5498	4430	1.1195	9.8
LDPE-B	5269	4466	1.1231	7.8	5446	4537	1.1267	9.9
LDPE-C	5247	4439	1.1208	7.8	5523	4461	1.1210	9.0
i-PP	3860	4757	1.1534	10.4	4258	4712	1.1470	14.9
i-PB	4384	4550	1.1200	7.8	4606	4600	1.1216	11.5
PET	8057	5133	0.7235	3.0	8688	5070	0.7193	4.6
PPO	6019	4681	0.8437	6.9	6685	4585	0.8355	10.9
PC	7389	4972	0.7843	8.2	7747	4969	0.7835	5.8
PAr	7416	5279	0.7759	2.2	7760	5257	0.7745	3.3
PH	8807	4768	0.8118	9.2	9032	4837	0.8145	7.4
PEEK	7240	5507	0.7528	1.7	7970	5418	0.7465	5.0
PVME	6356	4230	0.9187	9.8	6770	4298	0.9210	9.2
PA6	5198	6138	0.7736	2.6	4654	7048	0.7956	8.0
PA66	5534	5075	0.7773	1.7	5509	5231	0.7841	6.9
PMA	6666	4241	0.8036	5.0	7683	4318	0.8054	10.7
PEA	5769	4097	0.8374	7.1	6527	4167	0.8394	10.8
PEMA	7306	4094	0.8281	8.6	7728	4190	0.8321	8.1
TMPC	5543	4877	0.8492	7.7	6094	4875	0.8473	9.0
HFPC	5811	4488	0.6108	6.7	6207	4525	0.6116	5.9
BCPC	7361	4981	0.6656	5.1	7621	5046	0.6676	5.0
PECH	6941	4497	0.6958	2.7	7577	4662	0.6997	5.1
PCL	5981	4331	0.8707	3.1	6320	4478	0.8758	4.9
PVC	6586	4833	0.6835	4.0	7192	4938	0.6855	4.9
a-PP	4698	3834	1.0733	6.6	4934	3884	1.0758	8.5
EP50	4398	4978	1.1656	14.9	4535	4982	1.1653	15.0
EVA18	5221	4414	1.0872	4.1	5445	4434	1.0874	6.0
EVA25	5106	4338	1.0584	6.5	5376	4368	1.0592	6.2
EVA28	5333	4324	1.0527	7.0	5729	4319	1.0509	7.1
EVA40	5680	4288	0.9996	8.3	5849	4326	1.0012	6.0
SAN3	5456	4897	0.8980	7.9	6032	4969	0.8995	8.6
SAN6	5969	4694	0.8928	7.8	6408	4761	0.8950	8.0
SAN15	5845	4970	0.8843	5.5	6188	5069	0.8875	6.5
SAN18	6004	4987	0.8799	4.7	6304	5070	0.8826	5.8
SAN40	6079	5158	0.8663	6.5	6536	5273	0.8696	6.9
SAN70	7307	5426	0.8418	4.3	7231	5676	0.8493	8.8
SMMA20	5842	4831	0.8767	2.0	6007	4908	0.8795	6.5
SMMA60	6187	4754	0.8308	2.7	6229	4884	0.8362	8.2

[a] The ranges of experimental temperature (the same for both sets of parameters) and pressure are given in Tables I and II. Note also that the full range of pressure for PTFE is only 0 to 390 bar.

[b] Characteristic parameters for PSF, LDPE-A, LDPE-B, LDPE-C, i-PP, i-PB, PET, PPO, PC, PAr, PH, PEEK, PA6, PA66, SAN70, SMMA20, and SMMA60 were fit to data generated by the Tait equation with parameters from Table VIII.

Table XI Characteristic Parameters for the MCM Equation of State

Polymer[b]	For P = 0 to 500 bar				For Full Range of Experimental P^a			
	P^* bar	T^* K	v^* cm³/g	Avg Δv 10⁴ cm³/g	P^* bar	T^* K	v^* cm³/g	Avg Δv 10⁴ cm³/g
HDPE	4059	6227	1.0826	10.1	3681	6573	1.0984	15.7
LDPE	4801	5744	1.0594	6.7	5642	5239	1.0310	21.8
PS	5508	6804	0.8654	1.8	5303	6947	0.8694	3.5
PoMS	5615	6850	0.8795	2.5	5614	7019	0.8840	4.0
PVAc	7216	5034	0.7325	1.3	7199	5018	0.7320	1.4
PMMA	7126	6353	0.7522	0.7	6991	6390	0.7534	1.4
PcHMA	6203	6190	0.8063	3.6	5684	6477	0.8159	7.4
PnBMA	6301	5447	0.8403	5.9	6278	5586	0.8451	13.0
BPE	5147	5509	1.0481	11.2	4986	5605	1.0538	8.8
LPE	5494	5372	1.0352	2.9	5629	5338	1.0326	3.6
HMLPE	6174	5156	1.0309	5.8	6482	5118	1.0274	7.1
PIB	5278	6178	0.9875	2.0	5211	6247	0.9896	2.7
PDMS	3775	4228	0.8644	5.0	3665	4249	0.8660	5.5
PMP	3392	6194	1.1073	8.7	3821	5977	1.0899	9.9
PTFE	3540	5696	0.4486	8.2	3540	5696	0.4486	8.2
PSF	8036	7000	0.7162	4.9	8150	6955	0.7148	3.4
PBD	6221	5143	0.9765	2.9	5798	5140	0.9778	5.1
PEO	6814	5543	0.7973	6.8	6847	5526	0.7966	6.3
PTHF	5561	5543	0.9093	4.3	5488	5539	0.9093	4.3
LDPE-A	5187	5736	1.0539	6.6	5109	5748	1.0549	5.0
LDPE-B	5148	5863	1.0601	6.0	5017	5904	1.0626	4.8
LDPE-C	5135	5822	1.0577	5.9	5128	5791	1.0564	4.7
i-PP	3826	6180	1.0853	8.5	4001	6015	1.0758	10.3
i-PB	4299	5949	1.0559	6.1	4242	5934	1.0558	5.2
PET	8250	6635	0.6792	2.7	8654	6522	0.6744	3.2
PPO	6149	6043	0.7917	5.8	6664	5874	0.7824	10.2
PC	7382	6488	0.7390	5.1	7470	6452	0.7377	3.5
PAr	7263	6942	0.7328	1.1	7368	6872	0.7307	2.0
PH	8664	6297	0.7679	4.3	8479	6376	0.7704	4.6
PEEK	7479	7095	0.7056	1.5	7965	6950	0.6992	2.7
PVME	6129	5623	0.8702	6.6	6155	5670	0.8720	5.1
PA6	4914	8199	0.7335	2.4	3911	9449	0.7568	7.0
PA66	5541	6598	0.7313	1.4	5140	6784	0.7385	2.7
PMA	6465	5604	0.7602	2.5	7137	5678	0.7615	7.1
PEA	5637	5391	0.7913	4.5	6055	5454	0.7928	6.1
PEMA	7196	5370	0.7813	9.0	7256	5487	0.7856	7.7
TMPC	5564	6335	0.7987	7.3	5895	6343	0.7980	6.9
HFPC	5875	5812	0.5739	5.5	6035	5829	0.5743	4.8
BCPC	7252	6533	0.6281	4.4	7230	6586	0.6297	4.7
PECH	6511	6062	0.6612	2.0	6714	6282	0.6654	3.2
PCL	5723	5741	0.8241	2.9	5666	5909	0.8295	3.2
PVC	6158	6527	0.6496	4.0	6378	6684	0.6524	4.2
a-PP	4559	5044	1.0137	5.9	4665	5110	1.0165	5.9
EP50	4202	6580	1.1026	16.0	4313	6579	1.1022	15.5
EVA18	5147	5795	1.0263	2.4	5076	5764	1.0251	3.1
EVA25	5050	5686	0.9987	3.4	5017	5670	0.9983	3.8
EVA28	5286	5662	0.9930	3.9	5394	5603	0.9900	4.8
EVA40	5614	5628	0.9437	4.7	5460	5631	0.9443	4.2
SAN3	5260	6462	0.8490	7.6	5545	6512	0.8500	6.9
SAN6	5819	6166	0.8430	6.0	5990	6201	0.8441	6.3
SAN15	5649	6563	0.8361	4.1	5692	6658	0.8390	4.7
SAN18	5736	6622	0.8333	3.5	5747	6671	0.8349	4.7
SAN40	5799	6854	0.8206	5.3	5948	6956	0.8232	5.6
SAN70	6884	7299	0.7996	2.9	6383	7647	0.8077	7.3
SMMA20	5654	6372	0.8288	2.0	5496	6425	0.8309	4.3
SMMA60	6019	6256	0.7850	2.7	5709	6401	0.7902	6.5

ᵃ The ranges of experimental temperature (the same for both sets of parameters) and pressure are given in Tables I and II. Note also that the full range of pressure for PTFE is only 0 to 390 bar.

ᵇ Characteristic parameters for PSF, LDPE-A, LDPE-B, LDPE-C, i-PP, i-PB, PET, PPO, PC, PAr, PH, PEEK, PA6, PA66, SAN70, SMMA20, and SMMA60 were fit to data generated by the Tait equation with parameters from Table VIII.

choice of cell geometry. To decouple the model from a specific geometry, they introduced a numerical factor that scales the hard-core cell volume in the free volume term. This factor, q, was found to be nearly constant for several polymers and equal to about 1.07. They derived the MCM equation of state in dimensionless variables as:

$$\frac{\tilde{P}\tilde{v}}{\tilde{T}} = \frac{\tilde{v}^{1/3}}{(\tilde{v}^{1/3} - 0.8909q)} - \frac{2}{\tilde{T}}\left(\frac{1.2045}{\tilde{v}^2} - \frac{1.011}{\tilde{v}^4}\right) \quad (11)$$

where the reduced variables and characteristic parameters have the same definitions as in the FOV and CM models. Equation (11) is formally identical with the CM equation of state, except for the additional constant parameter q, which can also be viewed as a correction to the hard-core cell volume. The value of $q = 1.07$ corresponds approximately to a 25% increase in the hard-core volume of the Prigogine cell model.

MCM characterstic parameters (P^*, T^*, and v^*), for the polymers listed in Tables I and II, are given in Table XI.

LATTICE–FLUID THEORIES

To improve on the cell model for the liquid state, two other classes of models were developed, namely lattice–fluid and hole theories. The proposition that most of the volume change takes place by the presence of holes on a lattice has led to the development of lattice–fluid models. In these theories, vacant cells, or holes, are introduced in the lattice to describe the extra entropy change in the system as a function of volume and temperature. The lattice size (or cell volume) is fixed so that the changes in volume can only occur by the appearance of new holes, or vacant sites, on the lattice. With the symmetrical lattice construction, the powerful tools of statistical mechanics can be used to evaluate the partition function for a system of N polymer molecules, which share the lattice with a population of empty sites. Sanchez and Lacombe[10,11] performed a steepest descent calculation to evaluate the partition function. The segmental parameter c is set equal to 1, thus no recourse is necessary to the idea of a separation of internal and external modes. Panayiotou and Vera[12] followed an alternative formalism in calculating the number of mer–mer contacts and they incorporated a temperature dependent segmental interaction energy. This does not offer a significant improvement, while at the same time makes the theory less amenable to interpretation. Therefore, only the SL lattice–fluid model is discussed below.

Sanchez and Lacombe (SL) Lattice–Fluid Model

Sanchez and Lacombe[10,11] derived a dimensionless equation of state for classical fluids based on the Ising (lattice) fluid model:

$$\frac{\tilde{P}\tilde{v}}{\tilde{T}} = -\tilde{v}[\ln(1 - 1/\tilde{v}) + (1 - 1/r)/\tilde{v}] - \frac{1}{\tilde{T}\tilde{v}} \quad (12)$$

or equivalently

$$\tilde{\rho} = 1 - \exp[-(\tilde{\rho}^2 + \tilde{P})/\tilde{T} - (1 - 1/r)\tilde{\rho}] \quad (13)$$

where $\tilde{\rho}$ ($\equiv \rho/\rho^*$), $\tilde{P}$ ($\equiv P/P^*$), and $\tilde{T}$ ($\equiv T/T^*$) are the dimensionless mass density, pressure, and temperature, respectively, and r is the number of lattice sites occupied by the r-mer. (Note that $\tilde{\rho} = 1/\tilde{v}$.) The characteristic equation-of-state parameters are related to the mol wt M by

$$RT^*\rho^*/P^* = M/r \quad (14)$$

where R is the gas low constant.

Since r remains explicit in the reduced equation of state, a simple corresponding-states principle is not, in general, satisfied. However, for a polymer liquid, $r \rightarrow \infty$, and the equation of state can be simplified to

$$\tilde{\rho} = 1 - \exp[-(\tilde{\rho}^2 + \tilde{P})/\tilde{T} - \tilde{\rho}] \quad (15)$$

Thus, all polymer liquids of sufficiently high mol wt should satisfy a corresponding-states principle. The characteristic "pressure" P^* is identified as the hypothetical cohesive energy density of the liquid at absolute zero temperature and ρ^* is identified as the corresponding mass density. The characteristic temperature T^* is related to the segmental interaction energy by $T^* = \varepsilon^*/k$.

Characteristic parameters (P^*, T^*, and ρ^*) for the SL equation of state are given in Table XII for the polymers listed in Tables I and II.

HOLE THEORIES

As mentioned in the preceding section, hole theories are another class of models meant to improve on the cell model for the liquid state. As in the lattice–fluid theories, vacant cells, or holes, are introduced in the lattice, which describe the major part of the thermal expansion; but changes in cell volume, which have a nonnegligible influence on the thermodynamic properties, are also allowed. In the Simha–Somcynsky (SS) hole model,[8,9] the "square-well" approximation to the cell potential is used and nonnearest neighbor contributions to the lattice en-

Table XII   Characteristic Parameters for the SL Equation of State

Polymer[b]	For P = 0 to 500 bar				For Full Range of Experimental P[a]			
	P^* bar	T^* K	ρ^* g/cm^3	Avg Δv 10^4 cm^3/g	P^* bar	T^* K	ρ^* g/cm^3	Avg Δv 10^4 cm^3/g
HDPE	2887	736	0.8670	11.1	3662	615	0.9137	55.2
LDPE	3494	679	0.8861	13.1	4679	577	0.9340	44.7
PS	3669	773	1.0928	7.7	3715	688	1.1199	31.3
PoMS	3810	796	1.0703	3.3	4057	725	1.0938	18.9
PVAc	5042	592	1.2822	4.5	5013	582	1.2874	6.4
PMMA	4883	742	1.2498	1.8	5169	668	1.2812	15.7
PcHMA	4429	735	1.1624	4.1	4101	675	1.1843	26.4
PnBMA	4359	641	1.1185	16.3	4421	596	1.1378	36.5
BPE	3819	669	0.8898	13.7	4113	601	0.9193	41.6
LPE	4152	660	0.8983	5.1	4798	596	0.9316	30.3
HMLPE	4785	634	0.9020	7.0	5235	594	0.9244	22.7
PIB	3428	663	0.9675	7.1	3504	623	0.9791	15.0
PDMS	2744	501	1.0857	11.5	2885	466	1.1084	20.5
PMP	2672	746	0.8465	16.4	3557	650	0.8966	49.8
PTFE	3572	630	2.2150	9.9	3572	630	2.2150	9.9
PSF	5948	852	1.3017	8.9	6353	787	1.3340	26.5
PBD	4135	565	0.9747	8.7	4402	462	1.0151	43.9
PEO	4895	666	1.1727	13.6	4922	656	1.1776	15.5
PTHF	3931	645	1.0361	12.3	3856	626	1.0431	19.2
LDPE-A	3821	685	0.8893	14.1	4299	603	0.9236	58.7
LDPE-B	3762	696	0.8851	13.9	4214	610	0.9193	59.8
LDPE-C	3762	692	0.8869	14.7	4318	606	0.9229	59.5
i-PP	2908	737	0.8649	19.7	3664	633	0.9126	83.2
i-PB	3913	706	0.8892	15.2	3775	609	0.9312	71.5
PET	6421	818	1.3684	3.0	7261	761	1.4081	13.1
PPO	4788	739	1.1771	8.0	5541	681	1.2166	28.0
PC	5425	785	1.2635	11.5	5744	728	1.2925	31.9
PAr	5240	833	1.2766	7.0	5687	760	1.3102	24.5
PH	5844	740	1.2244	19.4	6074	690	1.2450	39.9
PEEK	5930	872	1.3191	1.8	7137	804	1.3679	12.5
PVME	4254	650	1.0848	24.3	4630	567	1.1198	61.5
PA6	3438	935	1.2892	4.0	4225	785	1.3502	34.3
PA66	4204	805	1.2746	3.1	5173	713	1.3329	25.2
PMA	4581	664	1.2349	16.9	5219	606	1.2645	36.4
PEA	4014	640	1.1857	16.9	4506	581	1.2171	49.1
PEMA	5241	653	1.1927	8.7	5675	602	1.2212	14.7
TMPC	4239	774	1.1664	7.2	4324	752	1.1774	11.3
HFPC	4487	714	1.6207	5.1	4554	680	1.6455	14.7
BCPC	5311	794	1.4845	4.7	5136	753	1.5035	14.5
PECH	4397	679	1.4349	6.3	4824	606	1.4699	17.8
PCL	4035	668	1.1427	3.9	4534	589	1.1796	19.4
PVC	4147	736	1.4577	3.4	4690	656	1.4956	14.0
a-PP	3324	597	0.9262	5.2	3542	570	0.9383	12.4
EP50	2911	766	0.8543	21.8	3014	753	0.8582	24.9
EVA18	3774	701	0.9097	9.3	4077	612	0.9452	47.9
EVA25	3711	687	0.9353	13.4	3970	602	0.9702	56.2
EVA28	3877	685	0.9404	15.9	4241	604	0.9748	53.1
EVA40	4093	679	0.9905	13.6	4198	600	1.0233	54.8
SAN3	3790	765	1.1056	8.7	3916	701	1.1287	29.5
SAN6	4237	738	1.1104	12.0	4297	686	1.1311	29.6
SAN15	3998	776	1.1224	8.0	4041	712	1.1451	25.6
SAN18	4002	772	1.1299	10.0	4001	703	1.1532	30.3
SAN40	4087	799	1.1475	10.3	4121	734	1.1688	28.8
SAN70	4608	819	1.1864	11.9	4664	726	1.2162	40.8
SMMA20	4025	750	1.1341	11.1	4347	658	1.1737	51.4
SMMA60	4324	743	1.1950	8.4	4460	662	1.2308	44.0

[a] The ranges of experimental temperature (the same for both sets of parameters) and pressure are given in Tables I and II. Note also that the full range of pressure for PTFE is only 0 to 390 bar.
[b] Characteristic parameters for PSF, LDPE-A, LDPE-B, LDPE-C, i-PP, i-PB, PET, PPO, PC, PAr, PH, PEEK, PA6, PA66, SAN70, SMMA20, and SMMA60 were fit to data generated by the Tait equation with parameters from Table VIII.

ergy are included. The resulting equation of state must be solved simultaneously with an expression that minimizes the partition function with respect to the fraction of occupied sites. At atmospheric pressure, empirical relationships have been found that avoid this mathematical encumbrance. Recently, Nies and Stroeks[16] presented a modified hole theory whereby the conformational entropy term is approximated by an expression credited to Huggins,[61] instead of the more common expression of Flory[62] used by Simha and Somcynsky. In addition, contact fractions replace site fractions in expressions for the internal energy and for the segmental free length. These modifications produce relatively minor effects on the equation of state of a pure polymer fluid, but reportedly lead to improved correlations of miscibility behavior.[63] Only the SS model will be discussed in the subsection that follows.

Simha and Somcynsky (SS) Model

The Simha–Somcynsky[8,9] (SS) hole model equation of state in dimensionless variables is derived as:

$$\frac{\tilde{P}\tilde{v}}{\tilde{T}} = \frac{(y\tilde{v})^{1/3}}{[(y\tilde{v})^{1/3} - 0.8909y]}$$
$$- \frac{2y}{\tilde{T}}\left(\frac{1.2045}{(y\tilde{v})^2} - \frac{1.011}{(y\tilde{v})^4}\right) \quad (16)$$

with

$$(s/3c)[1 + y^{-1}\ln(1-y)]$$
$$= -\frac{[\frac{1}{3}(y\tilde{v})^{1/3} - 0.8909y]}{[(y\tilde{v})^{1/3} - 0.8909y]}$$
$$- \frac{y}{6\tilde{T}}\left(\frac{2.409}{(y\tilde{v})^2} - \frac{3.033}{(y\tilde{v})^4}\right) \quad (17)$$

where y is the fraction of occupied sites. The reduced variables and characteristic parameters have the same definition as in the FOV model. Equation (17) results from the fact that the fraction of occupied sites is not an independent parameter; rather, it must satisfy the condition $\partial \ln Q/\partial y = 0$. The term $s/3c$, or the so-called "flexibility ratio," is usually taken to be equal to 1. Note that one recovers the Prigogine cell model when $y = 1$, that is, when there are no holes or vacant cells on the lattice. The factor 0.8909 in the first term on the right-hand side of eq. (16) arises from the choice of hexagonal close packing as the cell geometry. The second term on the right-hand side of eq. (16) reflects the Lennard–Jones "6–12" potential. The constants 1.2045 and

1.011 are explicit for the L–J potential given hexagonal close packing.

At atmospheric pressure, Simha et al.[64] found an empirical volume–temperature relationship:

$$\ln \tilde{v} = A + B\tilde{T}^{3/2} \quad (18)$$

valid over the range $0.95 \le \tilde{v} \le 1.40$, thereby avoiding the necessity of solving eqs. (16) and (17) simultaneously for the fraction of occupied sites. The values of the constants A and B in eq. (18) are given as -0.10335 and 23.8345, respectively.

SS model characteristic parameters (P^*, T^*, and v^*) for the polymers listed in Tables I and II are given in Table XIII.

OTHER THEORIES

There are other equations of state that incorporate various ideas from the cell, lattice–fluid, and hole theories, as well as empirical notions. One of the more interesting of these semiempirical theories is the model of Hartmann and Haque (HH).[13] In this theory, the zero-pressure isobar of the Simha–Somcynsky model, and an empirical volume dependence of thermal pressure, is combined with the theoretical temperature dependence of thermal pressure presented by Pastine and Warfield.[65] The resulting equation of state is mathematically simpler and has been found to represent PVT data as well or better than the SS model. It is interesting to note also that Hartmann and Haque have found their model to be applicable in the same form to polymer solids as well, with different values of the characteristic parameters.[66]

Another empirical equation of state that is occasionally cited is that of Spencer and Gilmore.[2] They found that the PVT behavior of polymer melts could be represented reasonably well by a modified Van der Waals equation of state. Their equation relates the total pressure (applied pressure p plus internal pressure π) to the mol wt of an interacting unit, usually taken to be that of the structural repeat unit, $(p + \pi)(v - \omega) = RT/M_u$. The ω is defined as the specific volume at zero temperature and pressure. Characteristic parameters for the Spencer-Gilmore equation of state have not been determined for this review.

Hartmann and Haque (HH) Model

The Hartmann and Haque[13] (HH) equation of state in dimensionless variables is derived as:

$$\tilde{P}\tilde{v}^5 = \tilde{T}^{3/2} - \ln \tilde{v} \quad (19)$$

Table XIII   Characteristic Parameters for the SS Equation of State

	For P = 0 to 500 bar				For Full Range of Experimental P^a			
Polymer[b]	P^* bar	T^* K	v^* cm³/g	Avg Δv 10⁴ cm³/g	P^* bar	T^* K	v^* cm³/g	Avg Δv 10⁴ cm³/g
HDPE	5368	11560	1.2010	9.8	5063	12290	1.2190	14.3
LDPE	6365	10640	1.1745	6.7	7936	9595	1.1380	22.6
PS	7133	12680	0.9611	1.9	7159	12840	0.9634	3.5
PoMS	7298	12800	0.9772	2.3	7461	13080	0.9814	4.6
PVAc	9427	9389	0.8135	1.2	9474	9348	0.8126	1.4
PMMA	9235	11880	0.8360	0.7	9264	11940	0.8369	1.0
PcHMA	8128	11530	0.8952	3.6	7722	12030	0.9047	6.6
PnBMA	8256	10080	0.9317	4.7	8560	10310	0.9358	13.1
BPE	6905	10080	1.1578	10.2	6923	10390	1.1674	9.9
LPE	7422	9712	1.1392	2.8	7864	9793	1.1406	9.0
HMLPE	8458	9172	1.1284	4.1	9213	9207	1.1278	11.0
PIB	6814	11400	1.0947	1.3	6866	11360	1.0940	2.0
PDMS	4973	7825	0.9583	4.4	5014	7864	0.9592	4.8
PMP	4686	11060	1.2139	9.0	5453	11030	1.2050	17.9
PTFE	6581	8126	0.4339	13.6	6581	8126	0.4339	13.6
PSF	10740	12740	0.7904	1.9	11160	12770	0.7903	3.6
PBD	8031	9532	1.0833	3.4	8150	9225	1.0766	3.6
PEO	9076	10170	0.8818	4.3	9145	10150	0.8812	4.1
PTHF	7308	10300	1.0090	3.8	7255	10280	1.0087	4.0
LDPE-A	6919	10560	1.1664	5.0	7162	10580	1.1664	6.5
LDPE-B	6845	10830	1.1743	4.7	7036	10860	1.1734	5.9
LDPE-C	6837	10740	1.1713	4.3	7188	10660	1.1679	6.1
i-PP	5179	11260	1.1977	5.6	5730	11060	1.1884	12.6
i-PB	5758	10940	1.1684	4.8	6037	10920	1.1666	7.5
PET	11330	11740	0.7419	1.8	11940	11800	0.7426	5.7
PPO	8254	10690	0.8650	1.9	9294	10580	0.8602	9.1
PC	9844	11810	0.8156	1.5	10200	11830	0.8156	3.7
PAr	9591	12830	0.8120	0.4	10030	12390	0.8091	2.6
PH	11330	11610	0.8508	2.4	11390	11730	0.8529	3.5
PEEK	10410	12360	0.7663	1.6	10860	12580	0.7705	8.5
PVME	8005	10420	0.9653	5.4	8481	10360	0.9632	6.8
PA6	6435	15290	0.8146	2.1	5499	16870	0.8327	4.4
PA66	7486	11980	0.8060	2.1	7069	12640	0.8195	5.2
PMA	8438	10360	0.8427	3.4	9691	10460	0.8431	9.3
PEA	7390	9929	0.8764	4.7	8308	10040	0.8773	8.8
PEMA	9534	9910	0.8653	9.4	9870	10190	0.8710	8.1
TMPC	7502	11480	0.8796	8.0	8192	11540	0.8794	9.6
HFPC	7953	10370	0.6291	5.7	8510	10550	0.6317	6.6
BCPC	9596	12020	0.6952	4.4	9878	12190	0.6975	4.7
PECH	8441	11270	0.7339	2.1	9131	11370	0.7343	3.1
PCL	7536	10700	0.9199	3.0	7845	10870	0.9173	3.0
PVC	7977	12160	0.7214	3.9	8495	12350	0.7230	4.2
a-PP	6048	9360	1.1243	6.7	6277	9494	1.1274	7.4
EP50	5545	12230	1.2235	15.9	5720	12220	1.2227	15.8
EVA18	6798	10670	1.1362	3.2	7056	10630	1.1341	4.7
EVA25	6669	10430	1.1046	3.6	6978	10440	1.1040	5.6
EVA28	6994	10370	1.0979	1.7	7472	10310	1.0949	6.7
EVA40	7380	10330	1.0441	5.1	7539	10360	1.0446	5.4
SAN3	6914	11980	0.9417	8.5	7642	12070	0.9416	8.1
SAN6	7669	11360	0.9337	5.9	8238	11490	0.9352	7.0
SAN15	7441	12180	0.9275	3.9	7792	12360	0.9299	5.0
SAN18	7509	12320	0.9250	3.4	7853	12380	0.9255	4.2
SAN40	7582	12750	0.9109	5.5	8118	12900	0.9124	5.6
SAN70	8937	13560	0.8874	2.4	8747	13790	0.8906	3.6
SMMA20	7440	11800	0.9190	3.3	7640	11800	0.9186	4.2
SMMA60	7942	11570	0.8700	4.2	7911	11780	0.8739	5.5

[a] The ranges of experimental temperature (the same for both sets of parameters) and pressure are given in Tables I and II. Note also that the full range of pressure for PTFE is only 0 to 390 bar.

[b] Characteristic parameters for PSF, LDPE-A, LDPE-B, LDPE-C, i-PP, i-PB, PET, PPO, PC, PAr, PH, PEEK, PA6, PA66, SAN70, SMMA20, and SMMA60 were fit to data generated by the Tait equation with parameters from Table VIII.

Table XIV   Characteristic Parameters for the HH Equation of State

Polymer[b]	For P = 0 to 500 bar				For Full Range of Experimental P^a			
	B_0 bar	T_0 K	v_0 cm³/g	Avg Δv 10⁴ cm³/g	B_0 bar	T_0 K	v_0 cm³/g	Avg Δv 10⁴ cm³/g
HDPE	21200	1426	1.0898	11.4	19680	1582	1.1163	18.4
LDPE	25020	1312	1.0658	6.8	28160	1212	1.0418	19.7
PS	30210	1548	0.8693	2.4	29560	1603	0.8754	5.8
PoMS	30430	1560	0.8837	3.1	30960	1608	0.8891	5.6
PVAc	38440	1149	0.7365	1.5	38170	1151	0.7368	1.4
PMMA	38660	1445	0.7557	0.9	38190	1467	0.7582	1.7
PcHMA	32570	1412	0.8109	4.7	30380	1517	0.8249	10.1
PnBMA	32840	1235	0.8439	7.5	32680	1309	0.8552	19.7
BPE	26260	1241	1.0510	10.4	25100	1313	1.0677	12.2
LPE	27780	1193	1.0336	2.8	28040	1211	1.0381	5.4
HMLPE	31360	1124	1.0232	3.8	32120	1135	1.0261	6.6
PIB	29910	1395	0.9902	2.7	29760	1422	0.9935	3.7
PDMS	19220	973	0.8717	5.0	18370	1006	0.8795	6.8
PMP	16550	1371	1.1059	9.0	16710	1449	1.1228	15.5
PTFE	32510	900	0.3683	7.1	32510	900	0.3683	7.1
PSF	40940	1564	0.7168	3.3	39720	1623	0.7246	7.1
PBD	34890	1163	0.9794	3.2	33330	1199	0.9855	4.0
PEO	35120	1250	0.7998	4.4	35040	1254	0.8005	4.0
PTHF	29230	1268	0.9150	5.6	28940	1276	0.9165	5.9
LDPE-A	26380	1305	1.0597	7.1	25160	1387	1.0769	13.3
LDPE-B	26340	1338	1.0667	7.0	25090	1426	1.0842	13.3
LDPE-C	26240	1327	1.0640	6.2	25380	1396	1.0781	11.3
i-PP	18980	1400	1.0909	7.6	18520	1475	1.1066	14.5
i-PB	21700	1358	1.0629	7.4	20660	1452	1.0818	14.2
PET	41990	1436	0.6724	1.9	40710	1484	0.6802	3.8
PPO	30940	1310	0.7848	2.2	30790	1339	0.7906	5.6
PC	37480	1450	0.7398	3.8	36440	1502	0.7474	8.6
PAr	37560	1577	0.7362	1.5	37090	1614	0.7408	3.8
PH	44980	1420	0.7703	5.2	43570	1481	0.7784	12.6
PEEK	38260	1508	0.6939	1.2	36680	1568	0.7044	4.3
PVME	32330	1278	0.8742	9.3	32450	1342	0.8836	12.1
PA6	26350	1884	0.7386	3.1	22640	2255	0.7654	7.8
PA66	27790	1478	0.7323	2.7	24530	1643	0.7559	7.0
PMA	33740	1268	0.7631	5.5	36800	1334	0.7712	12.4
PEA	29030	1218	0.7942	6.2	30760	1284	0.8038	15.4
PEMA	36940	1217	0.7846	9.3	36540	1298	0.7976	8.7
TMPC	27760	1414	0.7990	8.0	29070	1430	0.8010	8.1
HFPC	29270	1271	0.5707	6.1	29200	1306	0.5758	6.3
BCPC	37130	1475	0.6302	5.2	36410	1520	0.5356	5.9
PECH	35850	1378	0.6639	2.8	37750	1456	0.6734	5.4
PCL	30150	1320	0.8301	3.1	30130	1411	0.8418	5.2
PVC	34000	1484	0.6524	4.1	35950	1532	0.6559	4.4
a-PP	23440	1158	1.0214	6.8	23830	1197	1.0292	7.8
EP50	21890	1510	1.1104	18.0	22470	1516	1.1112	17.3
EVA18	26460	1310	1.0299	6.4	25210	1380	1.0443	9.5
EVA25	25800	1280	1.0014	7.6	24740	1356	1.0171	12.3
EVA28	27080	1272	0.9951	4.8	26460	1333	1.0077	10.5
EVA40	28720	1265	0.9459	8.9	27160	1339	0.9604	13.1
SAN3	27190	1473	0.8539	9.7	28400	1534	0.8615	9.9
SAN6	29740	1396	0.8466	7.4	30100	1448	0.8545	9.7
SAN15	29530	1498	0.8410	5.3	29570	1564	0.8495	7.4
SAN18	30370	1512	0.8380	5.2	30240	1566	0.8448	7.8
SAN40	30650	1563	0.8250	7.5	31380	1630	0.8326	8.6
SAN70	37540	1657	0.8027	4.9	35780	1776	0.8140	11.7
SMMA20	29280	1454	0.8336	5.2	28120	1539	0.8453	11.5
SMMA60	30940	1423	0.7892	6.3	29120	1530	0.8037	13.9

[a] The ranges of experimental temperature (the same for both sets of parameters) and pressure are given in Tables I and II. Note also that the full range of pressure for PTFE is only 0 to 390 bar.

[b] Characteristic parameters for PSF, LDPE-A, LDPE-B, LDPE-C, i-PP, i-PB, PET, PPO, PC, PAr, PH, PEEK, PA6, PA66, SAN70, SMMA20, and SMMA60 were fit to data generated by the Tait equation with parameters from Table VIII.

Table XV   Comparison of 6 Equation-of-State Theories for Fitting PVT Data of Polymer Liquids

Equation of State	Overall Average Δv (cm^3/g) for 56 Polymer Liquids[a]	
	P = 0 to 500 bar	P = Full Data Range
Flory, Orwoll, Vrij (FOV) model	±0.0007	±0.0022
Prigogine cell model (CM)	±0.0006	±0.0008
Dee and Walsh modified cell model (MCM)	±0.0005	±0.0006
Sanchez–Lacombe (SL) lattice-fluid model	±0.0010	±0.0033
Simha–Somcynsky (SS) hole model	±0.0004	±0.0007
Hartmann and Haque (HH) model	±0.0006	±0.0009

[a] The overall average Δv is calculated as Σ (avg Δv for the individual homo- and copolymers)/56.

where the reduced variables are defined as $\tilde{P} \equiv P/B_0$, $\tilde{v} \equiv v/v_0$, and $\tilde{T} \equiv T/T_0$. The characteristic "pressure" B_0 is formally identified as the isothermal bulk modulus extrapolated to zero temperature and pressure. As noted above, at zero pressure, one obtains the same proportionality between ln $\tilde{v}$ and $\tilde{T}^{3/2}$ as in the Simha–Somcynsky hole theory.

HH model characteristic parameters (B_0, v_0, and T_0) for the polymers listed in Tables I and II are given in Table XIV.

COMPARISONS AND CONCLUSIONS

Six theoretical equations of state for polymer liquids have been reviewed and their characteristic parameters have been determined for 56 homo- and copolymers, for which experimental specific volume data over a wide range of temperatures and pressures were available from the literature. Two sets of characteristic parameters were given in Tables IX to XIV; the first covers a pressure range of 0 to 500 bar (sufficient for most engineering work), while the second covers the full range of experimental pressure (typically 0 to 2000 bar). Average deviations between experimental and calculated specific volumes were also determined and an overall average deviation was calculated for the 56 polymers for all six equations of state using both sets of characteristic parameters. Table XV compares the performance of the various theories. At low pressures (0 to 500 bar), the overall average deviation for the 56 polymers varies in the range of ±0.0004 to 0.0010 cm^3/g. These values are near the accuracy limits of the experimental measurements, with all six equations of state performing adequately. However, as expected, the overall average deviation over the wider pressure range increases for all equations, and large differences between the theories become ap-

parent. Four theories, the Simha–Somcynsky hole theory, the Dee and Walsh modified cell model, the Prigogine cell model, and the Hartmann and Haque model, were found to maintain excellent fitting capabilities with overall average deviations in the range of ±0.0006 to 0.0009 cm^3/g. The Flory–Orwoll-Vrij and Sanchez–Lacombe lattice–fluid theories were found to suffer a significant loss in performance over the wider pressure range, with overall average deviations in the range of ±0.0022 to 0.0033 cm^3/g.

Of the six equations of state reviewed in this work, the Dee and Walsh modified cell model and the Simha–Somcynsky hole model give the best fit of polymer liquid PVT data over a wide range of temperature and pressure, with the Sanchez–Lacombe lattice–fluid theory being consistently less accurate. The semiempirical Hartmann and Haque model also appears to offer good performance while being mathematically simpler than either the MCM or SS model. That is not to say that these theories are the best overall equations of state when it comes to predicting thermodynamic properties of polymer blends and solutions. Indeed, the Sanchez–Lacombe lattice–fluid theory, shown here to be the worst of the six equations of state for fitting polymer liquid PVT data, has proven to be good at predicting gas and organic vapor solubilities in polymer liquids[55,56] as well as in semicrystalline polymer solids above the glass transition[67] without any experimentally determined adjustable parameters. Phase separation behavior (LCST and UCST) in polymer solutions and miscible blends is also an area where the various equations of state differ widely in their performance. This may be the subject of another review.

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