

# On the equation of state of crystalline polyvinylidene fluoride

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The crystalline state theory based on the cell model and discussed previously, is employed to describe the equation state of polyvinylidene fluoride (PVF<sub>2</sub>). The recent experimental results on the compression ratios for PVF<sub>2</sub> (phases I and II) up to  $14 \times 10^3$  kg cm<sup>-2</sup> are well represented by a Tait relation. The comparison of theory and experiment for phase II shows satisfactory agreement for the isobar at atmospheric pressure and the isotherm at room temperature up to about  $5 \times 10^3$  kg cm<sup>-2</sup>. For phase I such an agreement is observed only up to about  $3 \times 10^3$  kg cm<sup>-2</sup>. Above these values, the theory predicts too large a compression. An empirical adjustment of the scaling pressure would be required to achieve agreement over the entire pressure range. This is in contrast to the earlier success for crystalline polyethylene over a much wider range. The difference between the two polymers in respect to the theory may arise from the asymmetry in the repeat unit of PVF<sub>2</sub>. Finally we illustrate theoretical isotherms for low compressibility conditions and their excellent approximation by a Tait relation. The theory corresponds to high *B*-values for low compressibilities, whereas PVF<sub>2</sub> in both phases is characterized not only by a low compressibility, but also by its comparatively high isothermal volume derivative, particularly in phase I.

## 1. Introduction

In recent years *P-V-T* studies of crystalline polymers have evoked considerable interest, as is illustrated by the extensive X-ray measurements on linear polyethylene (LPE) over a range of temperatures and pressures [1-5]. We have recently analysed these results in terms of the theoretical equation of state developed earlier for crystalline polymers [6-8]. Satisfactory agreement ensued below the melting range for the atmospheric pressure isobar and for a room temperature isotherm of LPE [9] up to ~45 kbar. Such extensive X-ray data are not yet available for other crystalline polymers. However, the volumetric data for the crystalline phase were indirectly derived from the dilatometric measurements on polypropylene, polyethylene glycol and polytetrahydrofuran in the semicrystalline state [10]. For this purpose the melt theory [11] was employed by extrapol-

ation into the solid range, to compute the contributions of the amorphous fraction. Once again the theoretical equation of state was found satisfactory in respect to the compression and the thermal expansion of polymer crystals. Small deviations in the thermal expansion observed in the melting range were ascribed partly to the approximate treatment of the anharmonic contributions in the theory and partly to the presence of a pre-melt relaxation process. Finally, for computational convenience, a Tait-type equation was developed which accurately represents the theory [9].

The purpose of this paper is to analyse the recent X-ray measurements of Newman *et al.* [12] on polyvinylidene fluoride (PVF<sub>2</sub>) in phases I and II up to  $14 \times 10^3$  kg cm<sup>-2</sup> in terms of the crystalline state theory and to provide additionally some empirical relationships. In an earlier publication

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[8] we compared the thermal expansion of PVF<sub>2</sub> (II) at atmospheric pressure with experiment [13], resulting in a satisfactory agreement.

## 2. Empirical Tait equation

The experimental results [12] for the room temperature isotherms of phases I and II (see Fig. 8 [12]) can be fitted by the empirical Tait equation;

$$\Delta V/V_0 = C \ln(1 + P/B) \quad (1)$$

where  $C = 0.056$ ,  $B = 4222 \text{ kg cm}^{-2}$  for phase II;  $C = 0.034$ ,  $B = 4072 \text{ kg cm}^{-2}$  for phase I; and  $\Delta V/V_0$  represents the compression ratio. The bulk compressibility  $\beta$  is given by:

$$\beta = -(1/V_0)(\partial V/\partial P)_T = C/(P + B) \quad (2)$$

The results from Equations 1 and 2 are displayed in Fig. 1, where the points represent the experimental data (see Fig. 8, [12]). With the exception of  $\beta$  for phase II, the agreement with Equations 1 and 2 is quite satisfactory. A better fit for phase II in respect to  $\beta$  could not be obtained without impairing the agreement in  $\Delta V/V_0$ . The reasons for the discrepancy between the extent of agreement for  $\Delta V/V_0$  and its derivative for phase II, and the differences between the fits for I and II remain unclear.

## 3. Theory

The theoretical equation of state for a polymer crystal has the form [6–8]:

$$\tilde{P} = \tilde{P}(\tilde{V}, \tilde{T}, c/s, \tilde{\theta}_0) \quad (3)$$

where  $\tilde{P}$ ,  $\tilde{V}$  and  $\tilde{T}$  are the reduced pressure, volume, and temperature respectively. This equation is derived on the basis of a cell model. The real polymer chain, an  $n$ -mer, is replaced by an equivalent  $s$ -mer with each segment which surrounds a central segment, occupying a lattice site. The scaling pressure  $P^*$ , volume  $V^*$ , and temperature  $T^*$  are defined in terms of an intersegmental attractive and repulsive potential. The ratio  $3c/s$  represents the effective number of external degrees of freedom per segment of the  $s$ -mer, and explicitly enters the anharmonic terms in Equation 3. The parameter  $\tilde{\theta}_0 = h\nu_0/kT^*$  represents a reduced quantum temperature, with  $\nu_0$  a characteristic frequency. It is explicitly defined by the following relation [8]:

$$M_0^{5/6} \tilde{\theta}_0 = 13.189(c/s)^{1/2} \tilde{V}_0^{-4/3} \times (11.053 \tilde{V}_0^{-2} - 5.2797)^{1/2} (T^{*1/2} V^{*1/3})^{-1} \quad (4)$$

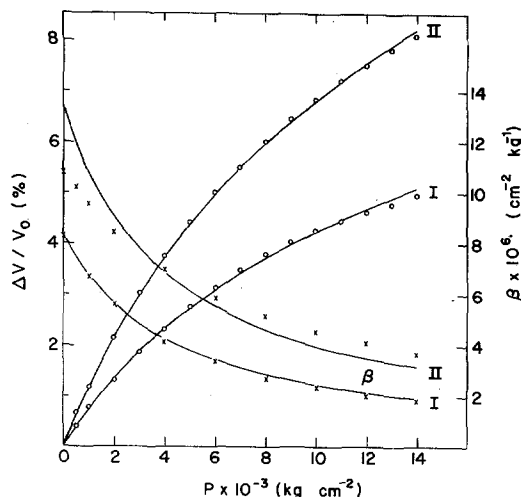


Figure 1 Compression ratios  $\Delta V/V_0$  and compressibilities  $\beta$  for phases I and II as functions of pressure. Lines, Equations 1 and 2; circles and crosses, experiment [12].

where  $M_0$  is the molecular weight of the segment in the equivalent  $s$ -mer, and  $\tilde{V}_0$  denotes the reduced volume at  $T = 0$  and  $P = 0$ . The scaling parameters  $V^*$ ,  $P^*$  and  $T^*$  obey the relation [9]:

$$(P^* V^* / T^*) M_0 = (c/s) R \quad (5)$$

where  $R$  is the gas constant. The ratio  $c/s$ , which enters into the expansion of the cell potential underlying Equation 3, has been previously [6–9] set equal to unity, as yielding the best agreement with experiment. Using the same assignment,  $\tilde{V}_0$  is computed from the limiting form of Equation 3. Then there remain three independent parameters. The scaling factors are obtained by a self-consistent procedure which satisfies Equations 3 to 5. For this purpose, a first pair of  $V^*$ ,  $T^*$  values is arrived at by a suitable choice of  $\tilde{\theta}_0$ , and by superposition of theoretical and experimental isobars at atmospheric pressure ( $\tilde{P} = 0$ ). Equations 4 and 5 then yield a first value of  $P^*$ . The comparison of Equation 3 with experiment at elevated pressures then indicates whether a revised value of  $\tilde{\theta}_0$  is to be obtained from Equations 4 and 5. If it does not differ significantly from the previous value,  $V^*$  and  $T^*$  also remain nearly constant. Ultimately, a self-consistent set  $P^*$ ,  $V^*$ ,  $T^*$ ,  $\tilde{\theta}_0$ , is derived, yielding the best representation of experimental isotherms and isobars.

## 4. Results

Scaling parameters for PVF<sub>2</sub> (II) have been obtained by the above procedure using the thermal

TABLE I Parameter sets for Figs. 2 and 3

Set	$\tilde{\theta}_0 \times 10^3$	$V^*$ ( $\text{cm}^3 \text{g}^{-1}$ )	$T^*$ (K)	$P^*$ ( $\text{kg cm}^{-2}$ )	$V_0(25^\circ \text{C})$ ( $\text{cm}^3 \text{g}^{-1}$ )
Phase II					
1	21.1	0.5420	7798	24 444	0.5335
2	22.3	0.5420	7798	26 024	0.5330
3	24.0	0.5424	7870	29 292	0.5333
Phase I					
4	27.5	0.5155	7798	35 362	0.5075
5	35.1	0.5155	7798	48 818	0.5084
6	39.3	0.5140	7798	56 788	0.5078
7	19.3	0.5245	9940	32 822	0.5076
8	24.0	0.5245	9940	43 427	0.5081
9	26.9	0.5235	9940	50 287	0.5075

expansion data of Nakagawa and Ishida [13] at atmospheric pressure and the measurements of Newman *et al.* [12] at elevated pressures. We have employed several sets of these parameters in order to explore agreement with experiment over the widest range of pressures, and these are displayed in Table I. For phase II only slight variations in  $\tilde{\theta}_0$  have been admitted, which however, result in significant changes in  $P^*$ . Fig. 2 illustrates the effect of these changes on the compression ratio. The upper half of the figure shows the volume-temperature relation at atmospheric pressure. The line represents the experimental data [13] and the points are derived from the theory, Equation 3,

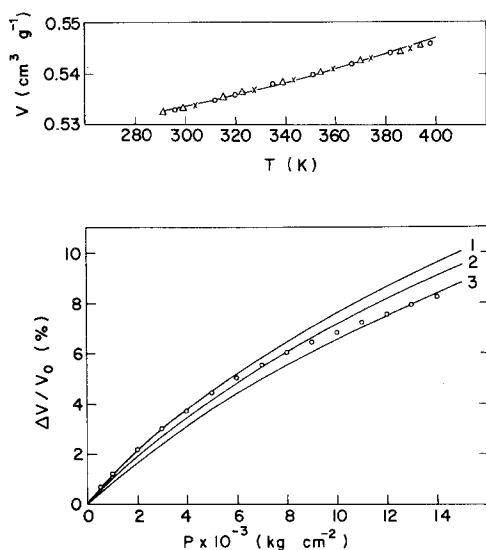


Figure 2 Isobars and isotherms for phase II. Upper part: crosses, circles and triangles, the theoretical crystal volumes with parameter sets corresponding to rows 1 to 3 in Table I respectively; line, experiment [13]. Lower part: circles, experiment [12]; lines 1 to 3, theory corresponding to respective parameter sets in Table I.

with  $\tilde{P} = 0$ , using alternatively the first three parameter sets in Table I. These may be compared with the tentative values derived earlier [8] in the absence of pressure data, namely,  $\tilde{\theta}_0 = 0.022$ ,  $V^* = 0.550$  and  $T^* = 9550$ . It will be noted that no discrimination between these alternatives is possible, based on the single isobar, since all of these yield a satisfactory agreement. The theoretical volumes  $V_0$  at  $25^\circ \text{C}$  shown correspond closely to the reported crystal densities [13, 14]. At elevated pressures such an agreement is maintained only up to  $(4 \text{ to } 5) \times 10^3 \text{ kg cm}^{-2}$  with the first set of assignments in Table I. Thereafter the theory predicts too high a compression, and this can be ameliorated only at the expense of varying the scaling pressure, or equivalently  $\tilde{\theta}_0$ .

To the best of our knowledge, no thermal expansivities are available for phase I, but only a value for the room temperature density, namely  $1.97 \text{ g cm}^{-3}$  [15]. To proceed on this basis, we retain as an assumption the previous value of  $T^*$ . Because of the lower compressibility, one anticipates then a larger  $P^*$  than for phase II. The final results are summarized by sets 4 to 6 in Table I. An equivalent reduction in the theoretical compression is accomplished by a decrease in the reduced temperature, i.e., an increase in  $T^*$ , with no significant change in  $V_0$ . This is represented by sets 7 to 9 in Table I. Fig. 3 depicts the resulting compression ratios. The general picture remains as for phase II, with departures from experiment becoming significant above  $3 \times 10^3 \text{ kg cm}^{-2}$ . No real difference between the extent of agreement, employing the sets 4 to 6 or 7 to 9, is visible. We also present in Fig. 3 theoretical isobars for  $\tilde{P} = 0$ , analogous to those shown in Fig. 2. This, of course, remains hypothetical until experimental information at atmospheric pressure becomes available

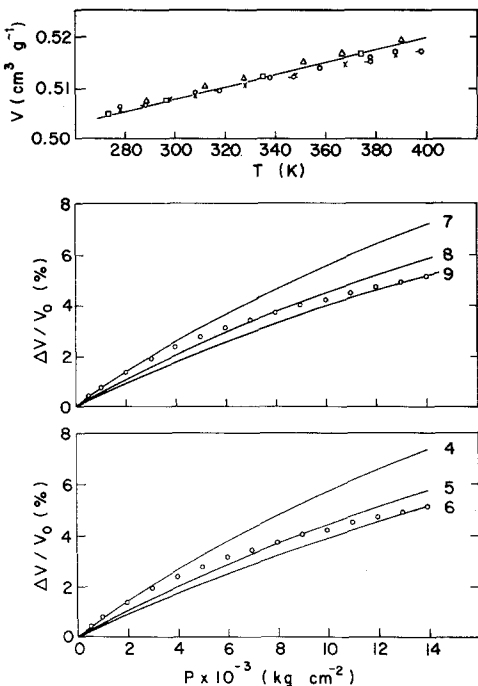


Figure 3 Isobars and isotherms for phase I. Upper part: theoretical crystal volume as a function of temperature with parameters (sets 4 to 9) in Table I; line; set 4;  $\Delta$  5;  $\square$  6;  $\times$  7;  $\circ$  8;  $\ominus$  9. Middle and lower parts: circles, experiment [12]; lines, theory, Equation 3 with parameters from the respective sets in Table I.

in order to refine the parameter values. At present we would compute a thermal expansivity  $(1/V)(\partial V/\partial T)_P$  of approximately  $1.9 \times 10^{-4} \text{ K}^{-1}$  compared with  $2.4 \times 10^{-4} \text{ K}^{-1}$  for phase II.

### 5. Further considerations and conclusions

The pressure range accounted for here by the crystal theory extends beyond that investigated by

employing the densities of the semicrystalline systems mentioned earlier [10]. However, this is significantly less than could be accomplished for LPE [9]. On the other hand, we are able to provide an empirical Tait representation, Equation 1 and Fig. 1, over the complete range of 14 kbar for both phases of PVF<sub>2</sub>. Moreover, the theoretical isotherm for LPE is well approximated by an interpolation formula of the Tait form [9]. With this in mind, it becomes of interest to investigate the Tait representation of the theory for low compressibilities as well. As an example we show in Fig. 4 three isotherms generated by varying  $T^*$  and choosing a high value of  $\tilde{\theta}_0$ . The upper and centre lines correspond to compressions slightly lower than for phase II and I respectively. All three curves are well approximated by Equation 1 with the  $C$  and  $B$  values indicated in Table II. It will be noted that the low compression curves are the result of high  $B$ s in Equation 1. In contrast, the isotherms for PVF<sub>2</sub> (see Figs. 2 and 3) are represented by considerably reduced values of  $C$ . However, at moderate pressures, the differences between the effects of  $C$  and  $B$  on the compressibility become negligible.

A physical interpretation of these two routes to a small compressibility in terms of the Tait equation is obtained by recalling the two expressions for the parameters, namely [16]:

$$\begin{aligned} V_0 C &= -(\partial P/\partial V)_T [(\partial^2 P/\partial V^2)_T]^{-1} \\ &= [(\partial \ln \beta/\partial V)_T]^{-1} \\ B &= -V_0 C(\partial P/\partial V)_T - P \\ &= (1/\beta V_0)[(\partial \ln \beta/\partial V)_T]^{-1} - P \end{aligned}$$

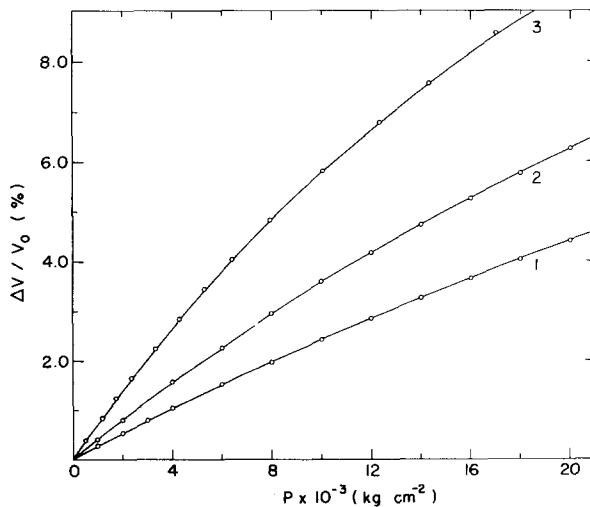


Figure 4 Theoretical isotherms: lines, theory Equation 3, with respective parameters from Table II; circles, Tait representation, Equation 2, with  $C$  and  $B$  from Table II.

TABLE II Parameter sets for Fig. 4

Set	$\tilde{\theta}_0 \times 10^3$	$V^*$ ( $\text{cm}^3 \text{g}^{-1}$ )	$T^*$ (K)	$P^*$ ( $\text{kg cm}^{-2}$ )	$V_0$ (25° C) ( $\text{cm}^3 \text{g}^{-1}$ )	$B$ ( $\text{kg cm}^{-2}$ )	$C$
1	40.3	0.5000	66 000	39 288	0.5041	14 490	0.110
2	40.3	0.5000	8 000	62 254	0.4934	25 540	0.108
3	40.3	0.5000	10 000	88 966	0.4871	38 460	0.105

The low compressibilities of the two PVF<sub>2</sub> polymers correspond, as we have seen in Equation 2, to small  $C$  values, and thus essentially signify a comparatively large dependence of the compressibility on volume. One concludes then that the theory underestimates this derivative in the higher pressure range and that a significant difference between PVF<sub>2</sub> and LPE resides in this derivative. Moreover, the higher density phase I also exhibits an increased sensitivity of the compressibility to pressure changes.

Reverting to the comparison between theory and experiment, the reasons for the departures of the former at elevated pressures are not obvious. The averaging implied by the spherically symmetrical cell potential has not limited the theory in other instances over the whole available pressure range, indeed much wider in the instance of LPE. Possibly, the asymmetry in the repeat unit of PVF<sub>2</sub> may be the cause for the discrepancies observed. Polypropylene, another polymer investigated by us employing the densities of the semi-crystalline system [10], does not involve pressures beyond about 3 kbar.

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