

SHORT COMMUNICATION

Equation of State of Polyethylene Crystal

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In a recent paper¹ an equation of state for anharmonic polymer crystals was derived on the basis of a quantum mechanical version of cell theory. Using this we explained the experimental V - T data of Davis *et al.*² for polyethylene between 200 K and its melting temperature. As regards the high pressure behaviour, only the room temperature isotherm data on polyethylene from Ito³ and Hikosaka *et al.*⁴ were available for comparison. It was found that the theory agrees closely with experiment up to 40 kbar. Recently, we came across the experimental results of Nakafuku⁵ concerning the isotherms of polyethylene, which cover a wide range of temperature. Using these data, it is now possible to subject the theory to a more stringent test of validity.

In our theory, each of the N identical chains making up the polymer crystal, is considered to consist of s segments situated on a regular lattice. Further, each chain has $3C$ volume dependent degrees of freedom and the inter-segmental potential is taken to be Lennard-Jones and Devonshire type. In the evaluation of the partition function, the effect of anharmonicity is taken up to the second order in the expansion of the cell potential. The equation of state obtained has the form,

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

where $\tilde{\theta}_0$ is the reduced quantum temperature. It was found that the best agreement with experiment

for polymers is obtained by taking $C/s = 1.6^{-9}$

In Figure 1, we show for polyethylene the theoretical¹ variation of V/V_0 with P (V_0 denotes the value of V for $P=0$) at several temperatures. To avoid overlapping, the isotherms for $T > 293$ K were shifted along the ordinate axis successively by 0.02 with respect to the preceding one at a lower temperature. In the calculations, we took $\tilde{\theta}_0 = 0.0169$ and the scaling factors for pressure, volume and temperature equal to 16.462 k bar, $1.0153 \text{ cm}^3 \text{ g}^{-1}$ and 7814 K, respectively. It should be mentioned that these parameter values for polyethylene have already been used in our earlier work.¹ The points in the figure represent the experimental data⁵ for the drawn polyethylene crystal. It is noted that the theory agrees closely with experiment up to 363 K. The departure observed at higher temperatures may be attributed to the crystalline dispersion. Nakafuku⁵ has also noted a sudden change at 363 K in the slope of the plot of experimental values of the Grüneisen constant *versus* temperature. Figure 2 shows a similar comparison between experiment⁵ and theory for an extended chain polyethylene crystal, using the above mentioned values for the characteristic parameters. With respect to temperature, the trend of agreement is similar to that observed in Figure 1. However, after the crystalline dispersion at 363 K, the extent of disagreement appears to be more pronounced in Figure 2 than in Figure 1.

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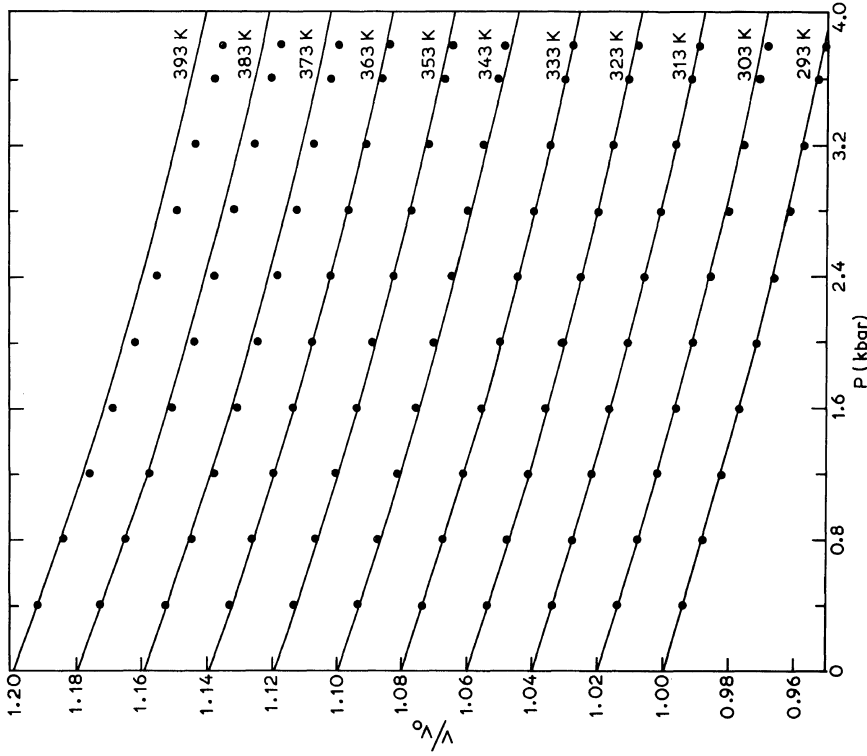


Figure 2. Comparison of theoretical and experimental isotherms for extended chain polyethylene crystal. The rest as in Figure 1.

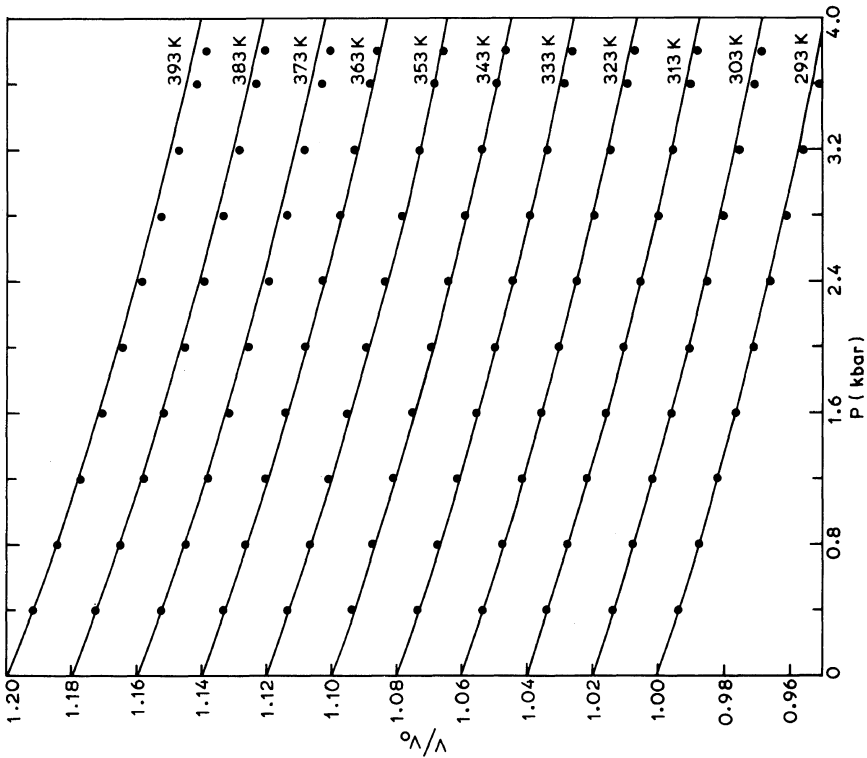


Figure 1. Comparison of theoretical and experimental isotherms for the drawn polyethylene crystal: —, theory; ●, experiment. The various curves, except for 293 K, have been shifted along the Y-axis as explained in the text.

granting a study leave to carry out this work.

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