polymer reports

Simple model for thermal pressure in molten polyethylene

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INTRODUCTION

The purpose of this report is to show that our earlier equation of state[1] for solid polyethylene can be extended to the molten state. In particular, calculations are made of the thermal pressure in molten polyethylene and these results are then used to calculate the solid–liquid phase line.

The earlier theory has been shown [2,3] to be a succesful description of the solid state of polyethylene. The assumptions of this theory break down, however, when applied to the melt. In this report, it will be shown that a simple physical model leads to reasonably accurate melt properties. The approach taken is a semi-empirical one in which physical reasoning is used to deduce the analytic form of the results and experimental measurements are used to determine the numerical values of the coefficients.

In the earlier paper, we considered solid polyethylene (PE) to be made up of both crystalline and amorphous components. For the pressure in amorphous PE, we had obtained the empirical expression

$$P_a = -\left(\frac{\partial E}{\partial V}\right)_0 + a_1 T \tag{1}$$

where E is internal energy, V is volume, T is absolute temperature, subscript zero meant $T = 0\text{K}$, and $a_1 = 9.76 \times 10^6$ dyne cm^{-2} K^{-1}. Note that the pressure is the sum of two terms: the internal pressure and the thermal pressure. The first term is the pressure along the 0K isotherm and is governed by the internal energy. The second term is the additional pressure generated by thermal motions. Since equation (1) refers to the amorphous state, one might think that it would apply to the higher temperatures encountered in the molten state. We have found, however, that the second term in equation (1), the thermal pressure contribution, is inadequate to describe the molten state and a new expression is derived here. In other words, the linear temperature dependence of equation (1) cannot be extrapolated all the way into the melt. While physically the amorphous and molten states are equivalent, we distinguish between them as a matter of convenience in distinguishing between two temperature regimes.

PHYSICAL MODEL

The functional form of the thermal pressure in molten PE can be derived from a simple physical mode. We assume that a polymer chain consists of approximately linear sections joined at arbitrary angles of fluctuating value resulting in a random coil of varying conformation. Consider a typical section of chain with length L. This length is a measure of the short range order in the liquid. Further, we assume that a polymer chain occupies a cylindrical volume equal to the volume per chain in the liquid. In addition, we assume that the chain within this volume moves in a constant potential except at the cylinder wall, at which point the potential becomes infinite. In this picture, transverse, normal vibrational modes of the chain which have too small an amplitude to allow any chain segment to reach the cylinder wall, will contribute nothing to the pressure on the wall. A mode of larger amplitude, however, will produce a pressure which is proportional to the average momentum possessed by the segments which reach the wall and inversely proportional to the period of the oscillation for the given mode.

We do not expect this model to be appropriate to all ranges of pressure and temperature. This is because the assumption of constant potential implies that the chain motion is essentially unperturbed as long as no chain segment reaches the cylinder wall. This assumption can only be correct if the chain energy (*i.e.*, the temperature) is sufficiently large so that large potential variations within the cylinder do not appreciably affect the motion or if these potential variations are themselves very small because the chains are widely separated (*i.e.*, the volume is large). We, therefore, apply this result only to the molten state, in which one might expect volumes and temperatures to be sufficiently high for the model to be reasonably accurate.

CALCULATION OF THERMAL PRESSURE

Assume a linear section of chain to be stretched along the x axis of a Cartesian coordinate system with its endpoints pinned at $x = 0$ and $x = L$. If the chain oscillates harmonically with displacements in the y axis, the

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displacement $y_n(x)$ for the n th normal mode is

$$y_n = y_{on} \sin k_n x \sin w_n t \qquad (2)$$

where $k_n = 2\pi/\lambda_n$, $w_n = 2\pi f_n$, λ_n is the wavelength and f_n is the frequency. We estimated the pressure, P_n, which this n th mode of oscillation should apply to the walls of a rigid cylinder of radius R_o, placed symmetrically about the x axis. We first calculated the average value of $\dot{y}_n(R_o)$, the velocity of the nth mode evaluated on the surface of the cylinder. The result is

$$\langle|\dot{y}_n(R_o)|\rangle = (w_n y_{on}/\Delta x)\int_0^{\Delta x} (\cos^2 k_n x^1 - R_o{}^2/y_o{}^2)^{1/2} \mathrm{d}x^1 \qquad (3)$$

where Δx is the range of x for which $y_{on} \sin k_n x \geqslant R_o$. If the chain elements have mass, m, then when they reach the cylinder wall they will be reflected transferring to the wall a momentum

$$\bar{P}_n = 2_m \langle|\dot{y}_n(R_o)|\rangle \qquad (4)$$

This momentum is transferred every 1/2 cycle in time $\tau_n = \pi/w_n$. The outward force, F_n, is then $\bar{P}_n/\tau_n$ and the pressure exerted is

$$P_n = F_n/2\pi R_o L \qquad (5)$$

If the chain is in thermal equilibrium with its surroundings at temperature T, the average kinetic energy in the n th mode $(L/8\sigma)(m\, w_n{}^2\, y_{on}{}^2)$ should equal $kT/2$, where σ is the separation of the chain segments. Setting these two quantities equal leads to the relation

$$y_{on}{}^2 = 4\sigma kT/mLw_n{}^2 \qquad (6)$$

This equation shows that the lowest frequency modes have the largest values of y_{on}. Let the N th mode be the one for which y_{on} is just equal to R_o. Then it follows that

$$N = (L/C_o \pi R_o)(4\sigma kT/mL)^{1/2} \qquad (7)$$

where C_o is the propagation speed and is given by

$$w_n{}^2 = C_o{}^2 k_n{}^2 = C_o{}^2 n^2 \pi/L^2$$

In order to find the total pressure, P, produced by the chain at temperature T, all of the modes must be summed from $n=1$ to $n=N$ (i.e., over all the modes which have $y_{on} \geqslant R_o$). The result is

$$P = (4\sigma kT/mL)^{1/2}\,(4C_o m\pi/\pi^3 \sigma R_o L) \sum_{n=1}^{N} n\varphi_n I_n(\varphi_n) \qquad (8)$$

where $\varphi_n = k_n \Delta x_n$, $I_n = \varphi_n{}^{-1}\int_0^{\phi_n} (\cos^2\theta - \cos^2\varphi_n)^{1/2}\, \mathrm{d}\theta$, and $\theta = k_n x$.

In this report, we are only interested in the functional form of the thermal pressure, and we will lump all of the constants together. The only variables are T and R_o (since R_o depends on volume). In equation (8), the two prefactors are proportional to $T^{1/2}/R_o$. The summation in equation (8) is found to be proportional to N^2, which by equation (7) is proportional to $T/R_o{}^2$. Therefore P is proportional to $(T/R_o{}^2)^{3/2}$. If one considers that the chain is relatively incompressible along its length, then one expects $R_o{}^2$ is proportional to X_l, where X_l is the volume of the liquid at any pressure divided by the volume at zero pressure and temperature. The thermal pressure is then given by

$$P \propto (T/X_l)^{3/2} \qquad (9)$$

which is the final desired result.

EXPERIMENTAL COMPARISONS

As a result of the above calculations, we propose that the total pressure in molten PE is given by

$$P_l = \left(\frac{\partial E}{\partial V}\right)_0 + a_2\left(\frac{T}{X_l}\right)^{3/2} \qquad (10)$$

where a_2 is a constant to be determined from experimental measurements. Equation (10) should be compared with our starting point, equation (1).

A direct verification of equation (10) can be made by comparing experimental isotherms with those predicted by equation (10). In *Figure 1*, we compare the theoretical isotherms with the experimental data of Matsuoka[4] as well as some measurements of our own. The constant was evaluated by fitting to the experimental data and found to be $a_2 = 6.9869 \times 10^5$ dyne cm^{-2} K$^{-2/3}$. The value of this constant explicitly includes a number of parameters such as segment size and mass, short range order length, and sound speed. Implicitly included in a_2 are any other temperature dependent quantities, such as coordination number, not otherwise specified in this model.

The agreement shown in *Figure 1* is quite reasonable. The poorer agreement for $X_l > 1.28$ results from a breakdown in the theoretical equation of state due to the fact that the internal energy function used is incorrectly

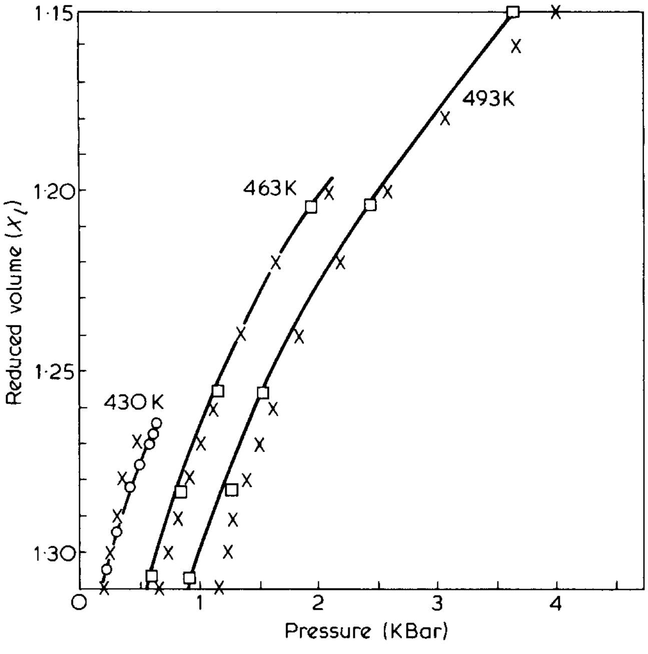

Figure 1 **Predicted and measured liquid state isotherms. (X), predicted; (□), Matsuoka; (O), this work**

approaching an inflexion point near this value of X_l. The same problem arises for the crystalline equation of state for $X_s > 1.07$. One should note that the separation in the isotherms at constant X_l, in *Figure 1*, is proportional to the thermal pressure. Had equation (1) been used for P_l, the general agreement would have been poor.

Another prediction that can be based on these theoretical expressions is the solid–liquid phase line. The condition that determines the phase line is that the Gibbs energy, G, of the solid must equal the Gibbs energy of the liquid. It is convenient to work with the Helmholtz energy, A, which is related to the Gibbs energy by the relation $G = A + PV$ and A can be obtained by integration of the thermodynamic identities

$$P = -\left(\frac{\partial A}{\partial V}\right)_T \tag{11}$$

$$E = A - T\left(\frac{\partial A}{\partial T}\right)_v \tag{12}$$

Using the results in this paper and our earlier one[1], we have the input for equation (11). These results must be supplemented by internal energy expressions for equation (12). Specifically, what is needed is the temperature dependence of the energy difference, ΔE, between solid and liquid. Expressions for ΔE have been given by Wunderlich[5]. Using these results, the phase line can be evaluated to within two constants of integration. The two constants were evaluated by means of experimental data for the zero pressure melting temperature, for which we used[6] 415K and the initial slope of the phase line, which we took to be 0.033 kbarK^{-1} (evaluated from the Clausius–Clapeyron equation, $\mathrm{d}P/\mathrm{d}T = \Delta S V$, with experimental values[6,7] for ΔS and ΔV).

The resulting theoretical phase line is compared with the experimental measurements of Bassett and Turner[8] and of Matsuoka[4] in *Figure 2*. As mentioned earlier, the theory breaks down for $X_s > 1.07$, which corresponds to the pressure range 0 to 2 kbar. Therefore no prediction is made in this region. The predicted melting temperatures appear to be about five to ten percent lower for a given pressure but, overall, the agreement is quite reasonable and tends to substantiate the validity of our approach.

It should be noted that while all of the results presented here are for polyethylene, the functional form of the thermal pressure, equation (9), should have more general applicability. We have already shown[9] that the theoretical expressions for the pressure in solid polyethylene can be extended to other polymers by way of corresponding states relations. Preliminary results indicate that the same is true for calculations of the phase line.

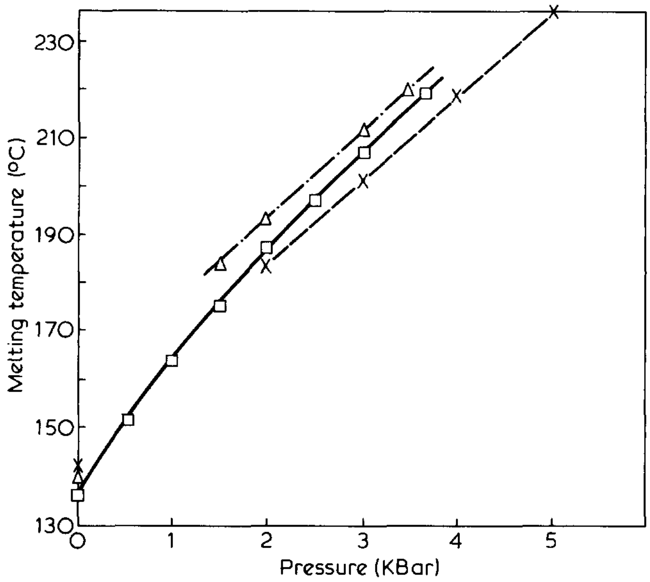

Figure 2 Predicted and measured phase lines. (X), predicted; (□), Matsuoka; (△), Bassett and Turner

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