Equation of State for a Polymer Crystal

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ABSTRACT: A quantum-mechanical version of the cell theory, including the effect of anharmonicity in the cell potential, is developed. It is applied to explain the observed volume–temperature relationship at atmospheric pressure for polyethylene crystal phase in the temperature range from 90 to 333 K. The observed agreement is very satisfactory except below about 100 K where the effects of low-frequency modes, not included in a cell-type theory, are expected to dominate the thermal behavior. A similar comparison between 233 and 388 K in the case of poly(chlorotrifluoroethylene) shows consistently good agreement. It is further found that the theory is successful in explaining the volume–pressure relationship for polyethylene crystal generated from the observed isotherms for semicrystalline samples on the basis of some plausible assumptions.

(I) Introduction

It is now generally recognized that the cell theory of Lennard-Jones and Devonshire[1] (L-J–D) which was developed to explain the thermal properties of liquids is actually more suited for solids.[2] This is due to the fact that this theory makes use of a lattice structure as its basis and has therefore too much built-in order to serve as a realistic model for the complex semiordered state of a liquid. During the fifties, Prigogine et al.[3] extended the L-J–D theory to chain liquids. Once again, comparison with experiment showed[4] that the theoretical results could not satisfactorily explain more than a few observed thermal properties and that over a too limited range of temperature. Simha and Somcynsky[5] have sought to remedy this situation with some success by allowing for the occurence of holes.

Since the original L-J–D form of the cell theory has been found to be suitable for monomeric solids, it seems natural to expect similar behavior in the case of Prigogine et al.'s version for polymeric solids. Simha et al.[6] showed that the observed expansivity of several polymeric glasses at very low temperatures can be explained by a simple quantum formulation of the cell theory in the harmonic approximation. Systematic departures between theory and experiment, however, were observed well within the expected range of the harmonic theory for all the polymers investigated. Attempts were made by these authors to associate the discrepancies with the available information on location and intensity of low-frequency mechanical relaxation processes.

For polyethylene, accurate crystal volume–temperature (V–T) data between 90 and 333 K have been reported by Davis et al.[7] In our attempt to explain these results, it became quite clear that in the quantum formulation of the cell theory anharmonic effects would also have to be incorporated. This posed a new problem as the energy eigenvalues for an anharmonic three-dimensional oscillator have not been determined so far. However, through a suitable approximation, the results for the one-dimensional anharmonic oscillator[8] have been used to deduce the desired energy eigenvalues in the three-dimensional case.

(II) Assumptions and the Cell Field

In the sequel we adopt the physical picture similar to that of Prigogine et al.[3] Thus the polymer system will be assumed to be homogenous and a chain regarded as a set of connected point centers each of which is subjected to central forces exerted by the centers of the neighboring chains. The lattice of the polymer system is defined such that each point center of the chain is situated at a lattice point at the absolute zero of temperature. A point center of the chain can interact with its neighbors through intermolecular as well as intramolecular forces. Since only intermolecular forces contribute to the configurational partition function (PF), the effective number of nearest neighbors of a chain is less than the number of neighboring sites. If z denotes the number of nearest sites of a point center, out of these only $(z - 2)$ contribute to intermolecular interactions. Thus the number $\mathcal{V}z$ of such sites for a chain with s centers would evidently be given by $\mathcal{V}z = (z - 2)s + 2$. It will be further assumed that the interaction between point centers at a distance a apart is given by the L-J–D potential

$$\phi(a) = \epsilon^*[(a/r^*)^{-12} - 2(a/r^*)^{-6}] \tag{1}$$

where ϵ^* and r^* are the usual potential parameters.

If a point center is displaced from its equilibrium position through a distance r, the interaction energy can be written in the form[9]

$$U(r) = U(0) + (r/a)^2U_1 + (r/a)^4U_2 + \ldots \tag{2}$$

where a denotes the equilibrium distance between the neighboring point centers while

$$U(0) = \frac{\mathcal{V}z\epsilon^*}{s}[A(v/v^*)^{-4} - 2B(v/v^*)^{-2}] \tag{2a}$$

$$U_1 = \frac{\mathcal{V}z\epsilon^*}{s}[A_1(v/v^*)^{-4} - 2B_1(v/v^*)^{-2}] \tag{2b}$$

and

$$U_2 = \frac{\mathcal{V}z\epsilon^*}{s}[A_2(v/v^*)^{-4} - 2B_2(v/v^*)^{-2}] \tag{2c}$$

Here v is the volume of the cell and v^* is the characteristic volume parameter; these are related to a and r^* by the relations

$$v = (a^3/\zeta) \tag{3a}$$

$$v^* = (r^{*3}/\zeta) \tag{3b}$$

where A's, B's and ζ are numerical factors depending on the geometry of the lattice.

Equation 2 can be used for the formulation of the cell PF. The first term on the rhs of this equation represents the energy of interaction when the point center is located at the center of the cell while the second term corresponds to harmonic oscillations about the mean position whose frequency

$$\nu_0 = (1/2\pi)\{2U_1/(ma^2)\}^{1/2} \tag{4}$$

where m is the mass associated with the point center; the third and the following terms represent the effect of anharmonicity.

(III) Classical Equation of State with Anharmonic Effects

In the classical case the energy can be assumed to vary continuously and the cell PF is given by

$$g_c = 4\pi \int e^{-\{U(r)-U(0)\}/kT} r^2 \,\mathrm{d}r$$

Substituting from eq 2 in the above equation and considering only the first-order anharmonic term, we may write

$$g_c \simeq 4\pi \int_0^\infty e^{-U_1 r^2/(a^2kT)} \left\{1 - \frac{U_2 r^4}{a^4 kT}\right\} r^2 \,\mathrm{d}r$$

Evaluation of the integral using eq 2a and 2b gives

$$g_c = \pi^{3/2} v^* \zeta \left(\frac{kT}{z\epsilon^*}\right)^{3/2} (v/v^*)^4 \times [A(v/v^*)^{-2} - 2B_1]^{-3/2} \left[1 - \frac{15}{4}\frac{U_2}{U_1{}^2} kT\right]$$

The configurational PF G_c for an assembly of N identical chains, each having $3c$ external degrees of freedom, would be given by

$$G_c = e^{-NsU_0/2kT} (g_c)^{cn} \tag{5}$$

Using the thermodynamic relation

$$P = kT \left\{\frac{\partial}{\partial V} \log G_c\right\}$$

the equation of state can be cast in the form

$$\tilde{P}\tilde{V} = 2(A\tilde{V}^{-4} - B\tilde{V}^{-2}) + 3\gamma_0 \tilde{T} - {}^{15}\!/_2\,(s/c)\tilde{T}^2\tilde{V}^2\alpha\beta \tag{6}$$

where $v^* = v/\tilde{V}$ is the volume scale factor per point center, $P^* = P/\tilde{P}$ $(= \mathcal{V}z\epsilon^*/sv^*)$ is the pressure scale factor, and $T^* = T/\tilde{T}$ $(= \mathcal{V}z\epsilon^*/ck)$ is the temperature scale factor; γ_0, the Gruneisen constant, is given by

$$\gamma_0 = -\frac{\partial \log \nu_0}{\partial \log V} = \frac{1}{3}\left[4 + \frac{3A_1\tilde{V}^{-2}}{A_1\tilde{V}^{-2} - 2B_1}\right] \tag{6a}$$

while

$$\alpha = 1 + \frac{2A_1\tilde{V}^{-2}}{(A_1\tilde{V}^{-2} - 2B_1)} - \frac{A_2\tilde{V}^{-2}}{(A_2\tilde{V}^{-2} - 2B_2)} \tag{6b}$$

and

$$\beta = \frac{A_2\tilde{V}^{-2} - 2B_2}{(A_1\tilde{V}^{-2} - 2B_1)^2} \tag{6c}$$

The harmonic approximation corresponds to taking account of only the first two terms on the rhs of eq 2 and eq 6. It may be noted that in this case the theory predicts the validity of the principle of corresponding states (PCS) for diverse polymers without any subsidiary condition. However, in the presence of anharmonic effects the ratio (c/s) must also assume a universal value so that PCS applies.

(IV) Quantum Mechanical Equation of State with Anharmonic Effects

In this section we deduce the equation of state which may be expected to apply from the low-temperature region up to the melting point of the polymer. Consider the Hamiltonian

$$H = \frac{1}{2m}(p_x{}^2 + p_y{}^2 + p_z{}^2) + (r/a)^2 U_1 + (r/a)^4 U_2 \tag{7}$$

The corresponding energy eigenvalue problem has not been solved. Thomas,[8] however, has worked out the problem of the linear anharmonic oscillator. According to his result the energy eigenvalues for the Hamiltonian

$$H = \frac{p_x{}^2}{2m} + {}^1\!/_2 m\omega^2 x^2 + C_4 \epsilon^2 x^4 \tag{8}$$

are given by

$$E_n = (n + {}^1\!/_2)\hbar\omega + {}^3\!/_4 C_4 \frac{\epsilon^2\hbar^2}{m^2\omega^2}(n^2 + n + {}^1\!/_2) \tag{9}$$

To determine the energy eigenvalues of the Hamiltonian of eq 7, we first write

$$r^4 = x^4 + y^4 + z^4 + x^2(y^2 + z^2) + y^2(z^2 + x^2) + z^2(x^2 + y^2) \simeq x^4 + y^4 + z^4 + x^2(\bar{y}^2 + \bar{z}^2) + y^2(\bar{z}^2 + \bar{x}^2) + z^2(\bar{x}^2 + \bar{y}^2)$$

Here the assumption is that the anharmonic effects are small so that to a good approximation the terms within the parentheses in the above expression may be replaced by their average in the harmonic approximation. The Hamiltonian in (7) can thus be replaced by an effective Hamiltonian

$$H = H_x + H_y + H_z \tag{10}$$

where

$$H_{\mathcal{V}} = (p_{\mathcal{V}}{}^2/2m) + (\mathcal{V}/a)^2 \left\{U_1 + 2U_2 \frac{\overline{\mathcal{V}^2}}{a^2}\right\} + (\mathcal{V}/a)^4 U_2 \tag{10a}$$

The average $\overline{\mathcal{V}^2}$ can be obtained by making use of the expectation value of $\mathcal{V}^2$ for the nth state

$$\langle n|\mathcal{V}^2|n\rangle = \frac{\hbar}{2\pi m\gamma_0}(n + {}^1\!/_2)$$

This gives

$$\overline{\mathcal{V}^2} = \frac{a^2}{2U_1} h\nu_0 \left(\frac{1}{2} + \frac{1}{e^{h\nu_0/kT} - 1}\right) \tag{11}$$

where ν_0 is given by eq 4. One obvious effect of the anharmonicity in (10a) is to replace ν_0 by ν' which is given by

$$\nu' = ({}^1\!/_{2\pi}) \left\{2\left(U_1 + \frac{2U_2}{a^2}\overline{\mathcal{V}^2}\right) \Big/ (ma^2)\right\}^{1/2} \tag{12}$$

Since the Hamiltonians in (8) and (10a) are formally identical, the energy eigenvlaues using eq 9 have the form

$$E_n = (n + {}^1\!/_2)h\nu' + (n^2 + n + {}^1\!/_2)\eta \tag{13}$$

where

$$\eta = \frac{3}{2}\frac{h^2 U_2}{(2\pi)^4 m^2 a^4 \nu'^2} \tag{13a}$$

The PF for each degree of freedom may now be written, using eq 13, in the form

$$g_{\mathrm{QM}} \simeq \sum_{n=0}^{\infty} e^{(n+0.5)x}\{1 - n^2 y\} \tag{14}$$

where $x = (\eta + h\nu')/kT$, and $y = \eta/kT$. The summations over n are easily carried out yielding the result

$$g_{\mathrm{QM}} = \left\{\frac{e^{-x/2}}{1 - e^{-x}}\right\}\left\{1 - y\frac{e^x + 1}{(e^x - 1)^2}\right\} \tag{15}$$

Because of the form of eq 15, it is convenient to define now an effective harmonic frequency ν by the relation

$$\nu = \nu'\,[1 + {}^3\!/_8\,(s/c)\,(h\nu'/kT^*)\beta\tilde{V}^2] \tag{16}$$

so that $x = h\nu/kT$.

The PF G_{QM} for an assembly of N chains now has the form

$$G_{\mathrm{QM}} = e^{-NsU_0/2kT}(g_{\mathrm{QM}})^{3cN} \tag{17}$$

On substitution from eq 2a and 15 this leads to the equation of state

$$\tilde{P}\tilde{V} = 2(A\tilde{V}^{-4} - B\tilde{V}^{-2}) + 3\gamma F_1(\tilde{\theta},\tilde{T}) + {}^9\!/_8\left(\frac{s}{c}\right)\gamma\beta\tilde{V}^2\tilde{\theta}^2\left[\frac{1}{2} + \frac{3e^{\tilde{\theta}/\tilde{T}} + 1}{(e^{\tilde{\theta}/\tilde{T}} - 1)^2} - \frac{\tilde{\theta}}{\tilde{T}}\frac{e^{2\tilde{\theta}/\tilde{T}} + 3e^{\tilde{\theta}/\tilde{T}}}{(e^{\tilde{\theta}/\tilde{T}} - 1)^3} - \frac{9}{4}\left(\frac{s}{c}\right)\alpha\beta\tilde{V}^2\tilde{\theta}^2\left[\frac{1}{2} + \frac{2e^{\tilde{\theta}/\tilde{T}}}{(e^{\tilde{\theta}/\tilde{T}} - 1)^2}\right] \tag{18}$$

Table I
Values of Various Parameters of Equation 18 Needed for Obtaining the Best Fit between Theoretical and Experimental Results[a]

Sample	(s/c)	$\tilde{\theta}_0$	$V^*/\mathrm{cm^3\,g^{-1}}$	T^*/K	P^*/kbar
(1) Polyethylene					
(i) Crystallized for 2.5 h	3	0.018	1.022	8100	18.00
	2	0.031	1.011	7120	
	1	0.054	0.9954	6918	
	0	0.054	0.9915	7396	
(ii) Quenched	1	0.054	0.9954	6782	
(iii) Crystallized for 32 days	1	0.054	0.9965	7079	
(2) Poly(chlorotrifluoroethylene)	1	0.054	0.4634	8750	

[a] The values of ratio (s/c) are assigned first and other parameters optimized.

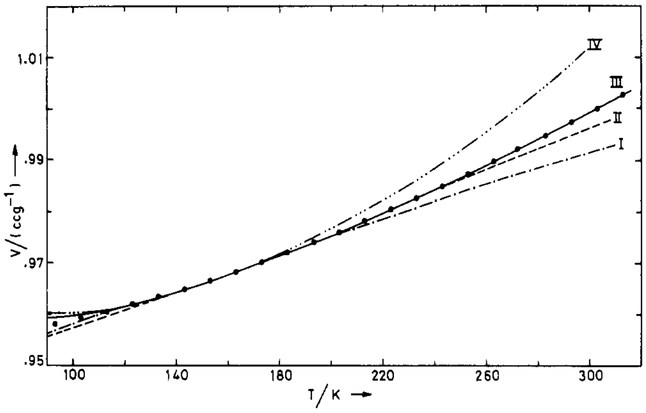

Figure 1. Comparison of theoretical V–T results of eq 18 for different values of (s/c) with experimental data for polyethylene.[7] Curve I: $s/c = 3$. Curve II: $s/c = 2$. Curve III: $s/c = 1$. Curve IV: $s/c = 0$. (●) Experimental results for sample crystallized for 2.5 h.

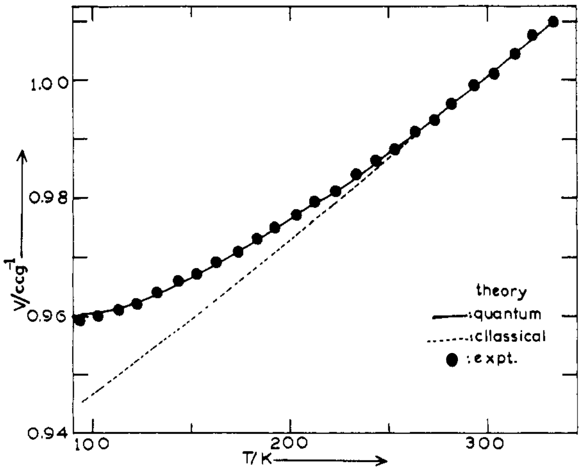

Figure 2. Comparison of theoretical V–T results with experimental data for quenched sample of polyethylene. The full curve and the dashed curve are obtained respectively from eq 18 and 6 for $s/c = 1$; (●) experimental data.[7]

where

$$\gamma = \gamma_0\left[1 + {}^1\!/_2\,(s/c)\beta\tilde{V}^2\left\{F_1(\tilde{\theta}_0,\tilde{T}) - \frac{\tilde{\theta}_0{}^2}{\tilde{T}}\frac{e^{\tilde{\theta}_0/\tilde{T}}}{(e^{\tilde{\theta}_0/\tilde{T}}-1)^2}\right\}\right] - (s/c)\alpha\beta\tilde{V}^2F_1(\tilde{\theta}_0,\tilde{T})$$

$$\theta = \frac{h\gamma}{kT^*} = \tilde{\theta}_0\left\{1 + {}^3\!/_8\left(\frac{s}{c}\right)\beta\tilde{\theta}_0\tilde{V}^2\right\}\left\{1 + \left(\frac{s}{c}\right)\beta\tilde{V}F_1(\tilde{\theta}_0,\tilde{T})\right\}$$

and

$$F_1(\tilde{\theta},\tilde{T}) = \tilde{\theta}\left[\frac{1}{2} + \frac{1}{e^{\tilde{\theta}/\tilde{T}}-1}\right]$$

It may be noted that parameter $\tilde{\theta}$ is a function of volume as well as temperature unlike $\tilde{\theta}_0$ which, according to eq 4, is an explicit function only of volume.

Davis et al.[7] have reported accurate V–T data for three polyethylene samples prepared under different conditions of crystallization. In order to compare their results with eq 18, the numerical assignments of certain parameters is required. These are the two scale factors V^*, T^* (since $\tilde{P} = 0$), θ_0, and the ratio (s/c). In our comparisons the value of (s/c) was arbitrarily selected and then a net V, T was constructed by evaluating eq 18 for an appropriate range of $\tilde{\theta}_0$ values. By superposition of experimental log V and log T values with the theoretical log V vs. log T plots, the appropriate values of V^* and T^* were determined. The numerical values of the constants employed in calculations were: $A = 1.011$, $B = 1.2045$, $A_1 = 22.1060$, $B_1 = 5.2797$, $A_2 = 200.653$, and $B_2 = 14.334$. The results of our analysis for three different values of s/c are summarized below.

Case I. $s/c = 3$. This choice has also been made by Simha and Somcynsky.[5] The best fit with experimental data for a polyethylene sample allowed to crystallize from the melt for 2.5 h is obtained for $\tilde{\theta}_0 = 0.018$. As will be seen from Figure 1 this agreement is confined over a small temperature range lying between 130 and 200 K. The corresponding values of the parameters V^* and T^* are given in Table I.

Case II. $s/c = 2$. In this case the best fit is obtained by taking $\tilde{\theta}_0 = 0.031$. Curve II of Figure 1 shows that theory is now in better agreement with experiment and spans roughly the temperature range from 120 to 240 K. The values of the parameters V^* and T^* employed are listed in Table I.

Case III. $s/c = 1$. This choice with $\tilde{\theta}_0 = 0.054$ provides the best representation of the experimental data. This is shown by curve III of Figure 1. The slight departure on the low-temperature side might be ascribed to the appreciable effect of low-frequency modes involving cooperative movement of several force centers. These are not covered in the cell theory description. The values of the parameters used are given in Table I.

Case IV. $s/c = 0$. This extreme choice corresponds to the supression of the anharmonic effects in the equation of state. Once again the choice $\tilde{\theta}_0 = 0.054$ is found appropriate. But the agreement is confined, as expected, to the low-temperature region. The results are shown by curve IV of Figure 1; the values of parameters used are listed in Table I.

The foregoing comparisons show clearly that the choice $s/c = 1$ provides the best representation of the experimental data by the theoretical expression 18. Using this value, we have also evaluated the other parameters for the representation of the crystal V–T data[7] obtained from polyethylene samples which

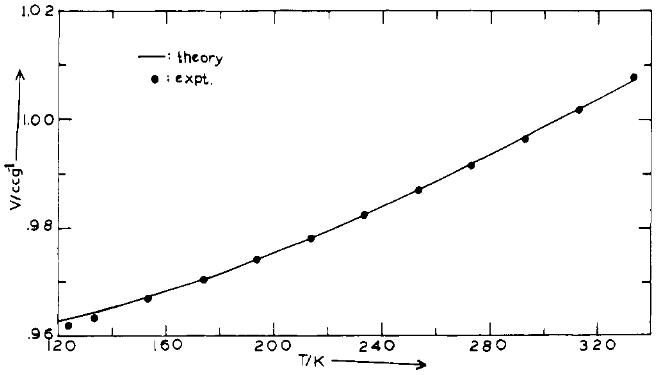

Figure 3. Same as in Figure 2; sample annealed for 32 days.

were (i) quenched and (ii) allowed to crystallize for 32 days at an appropriate temperature. The values of the parameters are listed in Table I from which it is seen that once again $\tilde{\theta}_0 = 0.054$ while V^* and T^* differ slightly. The nature of the agreement is shown in Figure 2 (quenched sample) and Figure 3 (sample crystallized for 32 days). In the latter case the departure of theory from experiment begins to show up at a somewhat higher temperature for which no reason can be assigned at present.

The theoretical expression 18 has also been tested in the case of poly(chlorotrifluoroethylene). Here direct V–T results through x-ray measurements are not available. However, the V–T data for the crystal have been generated in the range 233 to 388 K by Hoffman and Weeks.[10] The value $s/c = 1$, which showed the best agreement in the case of polyethylene, was also tried in the present case. Once again it turned out that $\tilde{\theta}_0 = 0.054$ provides a very satisfactory agreement with experiment. This choice was supplemented with $T^*/K = 8750$ and $V^*/(\mathrm{cm}^3\,\mathrm{g}^{-1}) = 0.4634$. The goodness of fit with these values is shown in Figure 4.

As a further check on eq 18, the pressure dependence of crystal volume has been considered in the case of polyethylene. Unfortunately no x-ray measurements of crystal volume under pressure have been reported for polyethylene so far.[16] However, by following a procedure similar to that of Hoffman and Weeks,[10] the isotherms have been generated.

Calculations of the degree of crystallinity of linear polyethylene samples as a function of temperature show that this value saturates below 60 °C.[11] This may be ascribed to the difficulty of segment rearrangement at temperatures sufficiently below the melting point. Assuming that the crystallinity is also independent of pressure below 60 °C, the V–P data for the crystal can be generated from the observed V–P results for semicrystalline polymer samples. For this we employed the well-known relation for the degree of crystallinity

$$x = \frac{V_a - V}{V_a - V_c} \tag{19}$$

where V, V_c, and V_a represent the specific volumes of the semicrystalline sample, crystal phase, and the amorphous phase, respectively, at a given temperature. In this equation V is an experimental quantity[12] while x is known from the zero-pressure values of all the other quantities involved. For the determination of V_c as a function of pressure at a certain temperature the only other unknown, V_a, was calculated through the equation of state given by Nanda and Simha.[11] The V–P data for polyethylene crystal at 19.4, 32.3, and 59.6 °C have been compared with the theoretical results in Figure 5, taking $P^*/(\mathrm{kbar}) = 18.00$. Once again the agreement is found to be quite satisfactory.

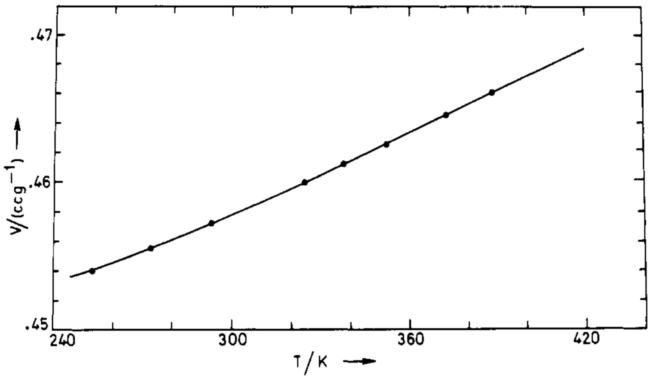

Figure 4. Comparison of theoretical V–T results of eq 18 for $s/c = 1$ (full curve) with the data for poly(chlorotrifluoroethylene).[8]

Discussion of Results

The quantum-mechanical equation of state (18) is of the form

$$\tilde{P} = \tilde{P}(\tilde{V},\tilde{T},\tilde{\theta}_0,s/c) \tag{20}$$

On the other hand, the classical form of the equation of state for monomeric materials, based on cell theory, can be cast in the form

$$\tilde{P} = \tilde{P}(\tilde{V},\tilde{T}) \tag{21}$$

and thus predicts the validity of PCS. Out of the two additional parameters (s/c) and $\tilde{\theta}_0$ appearing in eq 20, the former arises because of the polymeric nature of the material. If it can be assumed that the ratio s/c has a universal value, it drops out of consideration and eq 20 may be regarded as a quantum extension of the classical PCS.[13] The variable $\tilde{\theta}_0$ in eq 20 is proportional to $(\epsilon^* m)^{-1/2}$. Thus for heavy and strongly interacting force centers $\tilde{\theta}_0 \rightarrow 0$ and eq 20 effectively reduces to the form of eq 21. This result would apply at sufficiently high temperatures even for finite values of $\tilde{\theta}_0$ provided the condition $\tilde{\theta}/\tilde{T} \ll 1$ is satisfied.

Though there is no apparent reason to expect that $\tilde{\theta}_0$ should have the same value for diverse polymers, nevertheless the limited analysis of this paper for crystals shows $\tilde{\theta}_0 = 0.054$. Thus it seems that PCS, inspite of quantum effects, may still hold for the crystalline phase. This belief is strengthened because of a similar result obtained by Simha et al.[6] for polymeric glasses with widely different structures. However, the observed value of $\tilde{\theta}_0 = 5 \times 10^{-3}$ for glasses appears comparatively too low but can be rationalized. It is easily verified that $\tilde{\theta}_0 \propto c/(m\epsilon^*)^{1/2}$. For glasses, as compared to crystals, c is intutively expected to be lower while the product $m\epsilon^*$ should be larger on structural grounds. Both these factors working in the same direction result in the observed lowering of $\tilde{\theta}_0$ value for glasses.

We now take up the question about the need for the quantum form of the equation of state for polymer crystals in the temperature region considered. This seems necessary as the parameters T^*, V^*, and P^* are not independently known. In Figure 6, using eq 18, $\tilde{V}$–$\tilde{T}$ curves for different $\tilde{\theta}_0$ values are plotted for $s/c = 1$. It may be observed that on the high-temperature side, the various curves differ very little in slope. Thus, it should be possible in principle to fit the experimental V–T results over a limited temperature range for an arbitrary $\tilde{\theta}_0$ value. Even the dashed curve for $\tilde{\theta}_0 = 0$ (which corresponds to the classical case of section II) would provide some region of agreement. However, the widest coverage is obtained with $\tilde{\theta}_0 = 0.054$. It may be noted from Figure 2 that in the classical case noticeable deviations from experiment are observed below 260 K. The need for inclusion of anharmonic effect in theory has been brought out in Figure 1 through the plot

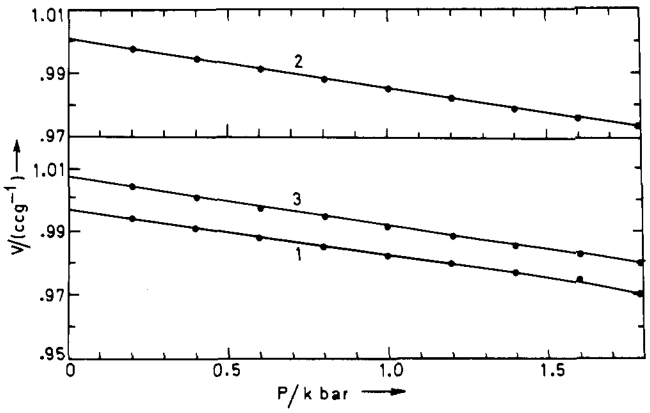

Figure 5. Comparison of theoretical V–T results of eq 18 for $s/c = 1$ with the V–P data for polyethylene crystal generated from experimental results for semicrystalline polyethylene.[12] Curve 1: $t = 19.4$ °C. Curve 2: 32.3 °C. Curve 3: 59.6 °C.

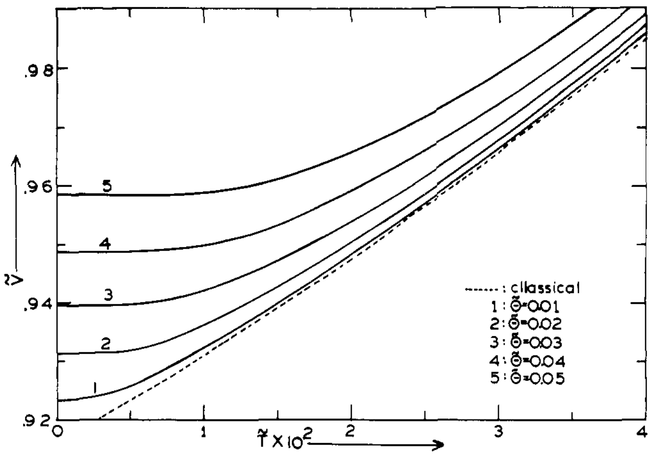

Figure 6. Theoretical $\tilde{V}$–$\tilde{T}$ plots for different values of $\tilde{\theta}$ for $\tilde{P} = 0$. Dashed curve is for the classical case, eq 6.

corresponding to $s/c = 0$ which begins to show departure from experiment for polyethylene above 170 K.

In the end it may be emphasized again that in the crystal theory the assignment of value to the ratio s/c plays an important role in determining the range of agreement with experiment. On the other hand, Simha and Somcynsky[5] observed that the cell theory with holes, applied to chain liquids, was not sensitive to the value of s/c. In fact in their case it was possible to represent the experimental PVT results equally well for widely different values of this ratio. The present investigation shows conclusively the success of the assignment $s/c = 1$ for the crystalline phase. This value may be interpreted to mean that each of the force centers has three degrees of freedom and therefore describes a motion similar to that of a monomer molecule around the equilibrium position located at the center of the cell. It should not, however, be concluded that all the degrees of freedom possessed by a chain are volume dependent since s is expected to be smaller than the number of monomer repeat units in a chain.[14] It seems that the effect of covalent connectivity is felt in the present theory essentially through the involvement of a number of monomer units in each force center. A more detailed analysis of this question and a comparison of the present theory with Pastine's work[15] will be given in a subsequent publication.

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(16) We are grateful to one of the referees for drawing our attention to a recent paper by Sham et al. (*J. Mater. Sci.*, **12**, 771 (1977)) in which PVT data for polyethylene crystal have been reported. This journal is not available here so far, therefore comparison of these results with the present theory will be taken up later.