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Hypothetical Thermodynamic Properties: The Boiling and Critical Temperatures of Polyethylene and Polytetrafluoroethylene

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The normal ($p = 101.325$ kPa) boiling-temperature behavior of a homologous series, T_B, as a function of the number of repeat units, N, is fit by a hyperbolic function whose limiting value asymptotically approaches $T_B(\infty) = (1217 \pm 246)$ K for series related to polyethylene and approximately $T_B(\infty) = 915$ K for those related to polytetrafluoroethylene. Normal boiling temperatures have been fit to the function $T_B = T_B(\infty)[1-1/(a_BN + b_B)]$ where a_B and b_B are constants characteristic of the series investigated. Similar behavior is observed for the critical temperature, T_C. As the number of repeat units, N, approaches infinity, T_B and T_C are found to converge. This provides an indirect method of determining $T_C(\infty)$. Combined with a few other experimentally determined critical temperatures, the T_C of an entire series can be predicted. Consistent with the convergence of T_B and T_C, the limiting critical pressure, $P_C(\infty)$, is found to approach 1 atm as N approaches infinity. The vaporization enthalpy and entropy at the boiling temperature, $\Delta_l^gH_m(T_B)$ and $\Delta_l^gS_m(T_B)$, used initially to suggest hyperbolic behavior of T_B, show complex behavior with increasing N. This behavior is discussed in terms of a simple mathematical model proposed previously.

Introduction

Hypothetical thermodynamic properties have been shown to provide information useful in the evaluation of thermochemical properties. For example, subcooled vaporization enthalpies evaluated at $T = 298.15$ K have been used to validate sublimation enthalpies of solids;[1] the distribution of polyaromatic hydrocarbons between the gas and particulate phase has been found to be proportional to the hypothetical subcooled liquid vapor pressure.[2] Melting temperatures of compounds that decompose before reaching the liquid state can be evaluated from solubility measurements and used to obtain estimates of fusion enthalpies; these values can be used subsequently in various other thermodynamic cycles.[3]

Most textbooks describing the physical properties of organic compounds point out that a homologous series shows regular increases in both normal melting and boiling temperatures as the size of the molecule increases. It has been shown, previously, that the melting temperature of the *n*-alkanes does not increase indefinitely but asymptotically approaches a limiting value, $T = 411$ K, as characterized by the melting temperature of polyethylene.[4,5] In this article, the question of whether the normal boiling temperature of a homologous series, T_B, increases indefinitely or whether it too asymptotically approaches a limiting value is discussed.

The increase in the normal boiling temperature of a homologous series decreases with increasing size, requiring the use of nonlinear expressions to fit experimental data. Both third-order polynomials and exponential functions have been previously used to model this property.[6,7] The polynomial expressions increase with increasing repeat unit, and therefore the boiling temperature is unbound. The exponential expression, eq 1, predicts that, as the number of carbon atoms M approaches infinity, the boiling temperature approaches a finite limiting value, $T_B(\infty)$. The numerical values of the constants, c and d, determined experimentally, result in a value $T_B(\infty) = 1078$ K. The vaporization enthalpies at the normal boiling temperature ($\Delta_l^gH_m(T_B)$), the critical temperature (T_C), and critical pressure (P_C) were also found to approach finite limits as the size of the molecule increases.[7] Equation 1 was empirically derived by Kreglewski and Zwolinski[7] using results of Kurata and Isida[8] on hole theory treatment of *n*-paraffin liquids. Kurata and Isida found that the effective length of a carbon skeleton should be proportional to the two-thirds power of the number of carbon atoms when $M > 5$.

$$T_B(M) = T_B(\infty) - ce^{-d}M^{2/3} \qquad (1)$$

This paper reports a mathematical relationship empirically derived from Gibbs' equation that suggests that boiling temperatures of homologous series related to polyethylene and polyperfluoroethylene may asymptotically approach finite limits. Application of a model and the corresponding protocol recently used to predict the melting temperatures of homologous series is also applied to their boiling temperature and critical temperature and pressure.[4] The limiting temperatures obtained are remarkably similar to those previously derived. The results support the previous model that suggested that boiling temperature, vaporization enthalpy at the boiling temperature, and the critical temperature and pressure of polymers are finite.

Sources of Data

The boiling-temperature data used in this study were obtained from a variety of sources. The major sources of data for each series reported are cited in the supplementary tables. Boiling temperatures for a few individual compounds have been obtained from some of the commercial chemical catalogs and handbooks. Vaporization enthalpies used in this study at the boiling temperature, $T = T_B$, are those from the API 44-TRC Handbook.[9] Boiling tempera-

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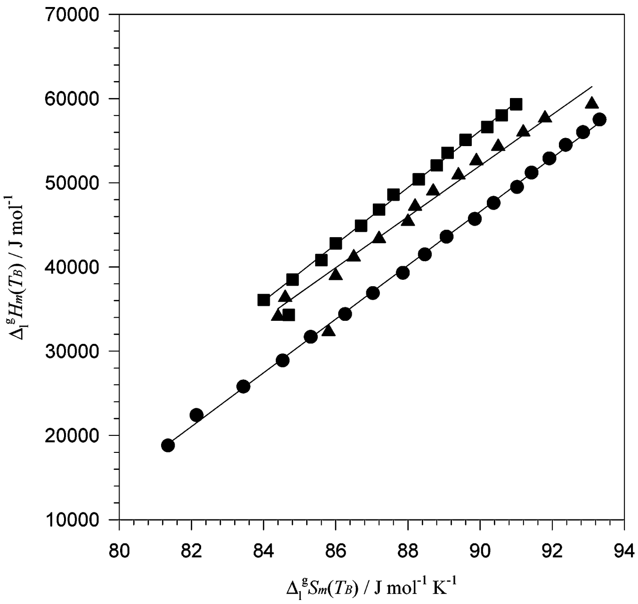

Figure 1. A plot of the $\Delta_l^gH_m(T_B)$ measured at $T = T_B$ vs the $\Delta_l^gS_m(T_B)$ also calculated at $T = T_B$ of ●, the *n*-alkanes (C_3 to C_{20}); ▲, *n*-alkylcyclopentanes (C_7 to C_{21}); ■, and *n*-alkylcyclohexanes (C_8 to C_{24}). The lines drawn through the data were obtained by a linear regression analysis. All the data were used for the *n*-alkanes; the triangle and square clearly off each respective line represents the value for ethylcyclopentane (C_7) and ethylcyclohexane (C_8), and each was not included in the regression analysis. The equations for each line are reproduced in Table 1.

tures for the *n*-alkanes are available from C_1 to C_{100}. Many of these are values that have been extrapolated from a variety of different mathematical relationships and are estimated. Experimental values for boiling temperature and vaporization enthalpy up to *n*-C_{20} have been used.[9,10] Recommended critical properties were used when available.[11] Values from other sources were used to verify some of the data. Data for many of the same compounds can be found in the various compendia cited in the Supporting Information. Boiling temperature values differ depending on the source; qualitatively, the same conclusions were reached regardless of the source.

Is the Boiling Temperature of a Polymer Finite?

The model proposed to evaluate the limiting boiling temperatures of any homologous series related to polyethylene is similar to the one used in the evaluation of melting temperatures. In the limit, regardless of whether the parent compound is an alcohol, carboxylic acid, ester, halide, etc., if the boiling temperature of polyethylene is finite, the limiting boiling temperature of a homologous series of alcohols, carboxylic acids, esters, etc. should asymptotically approach the same finite limit, the boiling temperature of polyethylene. Evidence that suggests that the boiling temperature of a polymer may be finite is provided in Figure 1. In this figure, the vaporization enthalpies of the *n*-alkanes from C_3 to C_{20} (●), *n*-alkylcyclopentanes from C_7 to C_{21} (▲), and *n*-alkylcyclohexanes from C_8 to C_{24} (■) at their normal boiling temperatures are plotted against their corresponding entropy of vaporization, $\Delta_l^gS_m(T_B)$. With the exception of the first few members of each series, the plots are remarkably linear as indicated by their respective correlation coefficients, r^2, reproduced in Table 1. The vaporization enthalpy of each of these compounds and a few other examples are expressed in linear form as a function of the entropy of vaporization by the equations listed in Table 1. Since Gibbs' energy of vaporization at equilibrium conditions (T_B, $p = 101.325$ kPa) is zero, $\Delta_l^gS_m(T_B)$ may be replaced by $\Delta_l^gH_m(T_B)/T_B$ in the equations presented in Table 1. Solving for T_B results in eq 2 where *m* and *C* represent the slopes and intercepts of the lines in Figure 1. The slopes (*m*) and intercepts (*C*) are listed in Table 1. Equation 2 is the equation of a hyperbola that asymptotically approaches *m* as $\Delta_l^gH_m(T_B)$ approaches infinity. The slopes obtained from the equations in Figure 1 are different but similar in magnitude as are the intercepts; the intercepts are also large. If the vaporization enthalpy of an increasing chain is boundless, then the average of the slopes reported in Table 1 suggest a limiting boiling temperature, $T_B(\infty) \approx 3000$ K. This is discussed in more detail below.

$$T_B = m\Delta_l^gH_m(T_B)/(\Delta_l^gH_m(T_B) - C) \qquad (2)$$

If the normal boiling temperature, T_B, of a homologous series is truly modeled by a hyperbolic function, as suggested by eq 2, and similar to what has been observed with melting temperature,[4] then a plot of the function $1/[1 - T_B(N)/T_B(\infty)]$ against the number of repeat units of the homologous series, *N*, where $T_B(N)$ represents the normal boiling temperature of each member of the series, should result in a straight line.[4] For series that converge to "polyethylene", *N* represents the number of methylene groups. Initial calculations using $T_B(\infty) = 3000$ K resulted in nonlinear plots; however, allowing $T_B(\infty)$ to vary resulted in the representative plots shown in Figure 2. The linear relationship observed between *N* and $1/[1 - T_B(N)/T_B(\infty)]$ for the compounds plotted in Figure 2 (and for all the compounds of Table 2) provided analytical expressions that could be solved for T_B in terms of $T_B(\infty)$, *N*, and two parameters, a_B and b_B, the slope and intercept of the plots in Figure 2, respectively. Solving for T_B in terms of $T_B(\infty)$, *N*, a_B, and b_B results in eq 3

$$T_B = T_B(\infty)(1 - 1/(a_BN + b_B)) \qquad (3)$$

Experimental boiling-temperature data were then fit to this expression by a nonlinear least-squares program. Input parameters included T_B and *N*, the normal boiling temperature and the number of repeat units, respectively. The best values of a_B and b_B were calculated for each value of $T_B(\infty)$. The value of $T_B(\infty)$ was allowed to vary until a minimum in the sum of the squared differences between calculated and experimental was realized. This procedure was repeated for each series of compounds for which sufficient T_B data could be found. For most of the calculations described below, $T_B(\infty)$ was minimized in increments of 5 K. The results are summarized in Table 2.

According to the model proposed, if in the limit the homologous series chosen ultimately converges to the same "polymer", then the same limiting boiling temperature, $T_B(\infty)$, would be expected. Experimental boiling temperatures are available up to approximately 650 K. Since in many instances this requires relatively few repeat units to reach this limit ($N < 20$), the uncertainty in $T_B(\infty)$ evaluated in this manner would be expected to be significant. However, the results obtained for $T_B(\infty)$ for various homologous series related to polyethylene (column 2, Table 2) show remarkable constancy in this value. Some series such as the 1-alkanols and the *n*-alkyl cyanides do show larger values for $T_B(\infty)$. However, the *n*-alkanoic acids and the 2-alkanols are fit by more normal values of $T_B(\infty)$, suggesting that the values calculated for the 1-alkanols and *n*-alkyl cyanides are not anomalies but rather more indica-

Table 1. Correlation Equations of Figures 1 and 2 Obtained by Plotting $\Delta_l{}^gH_m(T_B)$ vs $\Delta_l{}^gS_m(T_B)$

n-alkanes	$\Delta_l{}^gH_m(T_B) = (3190.7 \pm 22.6)\ \Delta_l{}^gS_m(T_B) - (240583 \pm 350)$	$r^2 = 0.9992$
n-1-alkenes	$\Delta_l{}^gH_m(T_B) = (2469.3 \pm 109.7)\ \Delta_l{}^gS_m(T_B) - (169585 \pm 951)$	$r^2 = 0.9806$
n-alkylbenzenes	$\Delta_l{}^gH_m(T_B)) = (3370.5 \pm 37.3)\ \Delta_l{}^gS_m(T_B) - (169585 \pm 951)$	$r^2 = 0.9806$
n-alkylcyclopentanes	$\Delta_l{}^gH_m(T_B) = (3028.8 \pm 97.4)\ \Delta_l{}^gS_m(T_B) - (220567 \pm 926)$	$r^2 = 0.9877$
n-alkylcyclohexanes	$\Delta_l{}^gH_m(T_B) = (3717.8 \pm 87.3)\ \Delta_l{}^gS_m(T_B) - (284890 \pm 999)$	$r^2 = 0.9918$
n-alkanethiols	$\Delta_l{}^gH_m(T_B) = (2268.7 \pm 162.6)\ \Delta_l{}^gS_m(T_B) - (161693 \pm 1728)$	$r^2 = 0.9558$

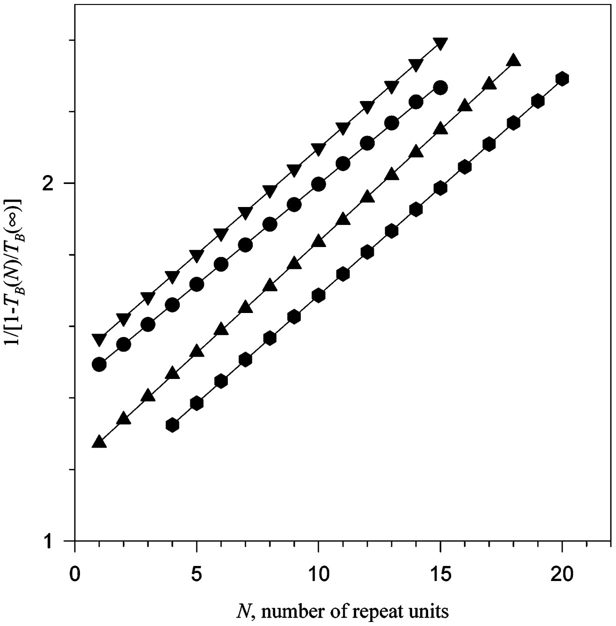

Figure 2. A plot of $1/[1 - T_B(N)/T_B(\infty)]$ against the number of repeat units, *N*; ⬢, *n*-1-alkenes; ▲, *n*-alkanes; ●, *n*-alkylcyclopentanes; ◆, *n*-alkylcyclohexanes.

tive of the uncertainty in $T_B(\infty)$ evaluated in this manner. Averaging all the limiting temperatures results in a value of $T_B(\infty) = (1217 \pm 246)$ K. This value compares quite favorably to the value of $T_B(\infty) = 1078$ K reported by Kreglewski and Zwolinski (1021 K by Somayajulu)[10] for the *n*-alkanes using eq 1.[7] Table 2 summarizes the values of a_B and b_B obtained by the nonlinear least-squares program associated with each value of $T_B(\infty)$ obtained by best fit and the standard deviation between experimental and calculated values that results (columns 3−5). Also included in the table are the results obtained by using the average value $T_B(\infty) = (1217 \pm 246)$ K (columns 6−8). This results in the averaged values a_{Bm} and b_{Bm} The number of data points associated with each correlation is indicated in the last column. A comparison of the standard deviation between experimental and calculated boiling temperature for both series of correlations (columns 5 and 8) suggests that for most compounds the calculated boiling temperature is within the experimental uncertainty of the measurement and that using the mean value for $T_B(\infty)$ does not significantly affect the quality of the fit.

A value of $T_B(\infty) = (1217 \pm 246)$ K is considerably less than $T_B(\infty) = 3000$ K, the value suggested from the slopes of the lines in Table 1 according to eq 2. A limiting value of $T_B(\infty) = 3000$ K would be approached only if $\Delta_l{}^gH_m(T_B)$ is boundless. However, if $\Delta_l{}^gH_m(T_B)$ also remains finite as $N \rightarrow \infty$, this limiting value may not be approached. Rearranging eq 2 and solving for $\Delta_l{}^gH_m(T_B)$ results in eq 4

$$\Delta_l{}^gH_m(T_B)_{max} = CT_B/(mT_B) \tag{4}$$

The limiting value of the vaporization enthalpy, $\Delta_l{}^gH_m(T_B)_{max}$, can be obtained by substituting $T_B(\infty) = (1217 \pm 246)$ K and the values of *m* and *C* from the equations in Table 1. Doing so results in a mean value of $\Delta_l{}^gH_m(T_B)_{max} = (147 \pm 30)\ \text{kJ·mol}^{-1}$. Since, in the limit, the structure of the compounds in Table 1 are most closely related to polyethylene, this value must approximate the maximum vaporization enthalpy experienced by an increasing chain of methylene groups, provided the maximum occurs at fairly large values of *N*. Furthermore, the fact that $\Delta_l{}^gH_m(T_B)_{max}$ is finite suggests that the ascending portion of the vaporization enthalpy may also be modeled by a hyperbolic function of the number of repeat units. If this is the case, a plot of $[1/(1 - \Delta_l{}^gH_m(T_B)/\ \Delta_l{}^gH_m(T_B)_{max}\ )]$ vs *N* should result in a linear correlation; alternatively, the vaporization enthalpy of each member of a homologous series should be related to $\Delta_l{}^gH_m(T_B)_{max}$ by eq 5

$$\Delta_l{}^gH_m(T_B) = \Delta_l{}^gH_m(T_B)_{max}(1 - 1/(a_HN + b_H)) \tag{5}$$

Figures 3 and 4 illustrate the behavior observed. Typical plots of $[1/(1 - \Delta_l{}^gH_m(T_B)/\ \Delta_l{}^gH_m(T_B)_{max})]$ vs *N* for the *n*-1-alkenes (●) and *n*-alkylcyclohexanes (■) are shown in Figure 3 and Figure 4 shows the experimental (symbols) and calculated vaporization enthalpies (lines) for the *n*-alkanes (●), *n*-alkanethiols (▲), and *n*-alkylcyclopentanes (■). Values of the adjustable parameters of eq 5 and the standard deviation of each fit associated with a $\Delta_l{}^gH_m(T_B)_{max} = 147\ \text{kJ·mol}^{-1}$ is provided in Table 3. Additional discussion of the behavior of vaporization enthalpy with increasing *N* is provided below.

Is the Critical Temperature of a Polymer Finite?

Ambrose's equation for the critical temperature of the *n*-alkanes, T_C, is given by eq 6.[12] The terms *c* and *d* refer to constants, and *N* represents the number of methylene groups. Though not intended to be applied to high molecular weight alkanes,[10] this equation relates the critical temperature to boiling temperature. This equation predicts that $T_C \rightarrow T_B$ as $N \rightarrow \infty$. If T_B can be fit by a hyperbolic function, then it seemed reasonable according to eq 6 that this approach should also work for T_C. Substitution of T_C for T_B in eq 3 results in eq 7

$$T_C = T_B + T_B/[c + d(N + 2)] \tag{6}$$

$$T_C = T_C(\infty)(1-1/(a_CN + b_C)) \tag{7}$$

Using the critical temperatures of the *n*-alkanes from propane ($N = 1$) to docosane ($N = 20$),[11] a nonlinear least-squares treatment provided values of a_C and b_C as a function of $T_C(\infty)$. Allowing $T_C(\infty)$ to vary by the nonlinear least-squares procedure described above resulted in $T_C(\infty) = 1050$ K, a value in good agreement with limiting boiling temperature of $T_B(\infty) = (1217 \pm 246)$ K. Similar results were obtained for several other homologous series that included the *n*-alkanals, the alkanoic acids, the 2- and 3-alkanones, the 1-alkenes, 1-alkanols, etc. The best-fit values of a_C and b_C derived for all the series examined are listed in the first five columns of Table 4. The limiting values of $T_C(\infty)$ are all well within the uncertainty of the

Table 2. Results Obtained by Treating T_B of a Series of Homologous Compounds as Function of the Number of Repeat Units, *N*, and Allowing $T_B(\infty)$ to Vary According to Equation 3; a_{Bm}, b_{Bm}: Values of a_B and b_B Obtained by Using the Mean Value of $T_B(\infty)$ = 1217 K

polyethylene series	$T_B(\infty)$/K	a_B	b_B	$\pm\sigma$/K	a_{Bm}	b_{Bm}	$\pm\sigma$/K	data points
n-alkanes	1076	0.06231	1.214	0.9	0.04694	1.1984	3.6	18
2-methyl-*n*-alkanes	1110	0.05675	1.3164	0.2	0.0461	1.2868	0.3	8
n-alk-1-enes	1090	0.06025	1.265	0.4	0.04655	1.242	2.7	17
n-alkylcyclopentanes	1140	0.05601	1.4369	0.6	0.04732	1.4037	1.3	15
n-alkylcyclohexanes	1120	0.05921	1.5054	0.1	0.04723	1.4543	1.2	13
n-alkylbenzenes	1140	0.05534	1.5027	1.1	0.05684	1.5074	1.4	15
1-amino-*n*-alkanes	1185	0.04893	1.274	3.4	0.04607	1.267	3.4	15
1-chloro-*n*-alkanes	1125	0.05717	1.2831	0.3	0.04775	1.2628	1.6	13
1-bromo-*n*-alkanes	1125	0.05740	1.3264	1.0	0.0481	1.2993	1.5	12
1-fluoro-*n*-alkanes	1075	0.05833	1.2214	0.4	0.04495	1.1987	2.1	9
1-hydroxy-*n*-alkanes	1820	0.01806	1.220	0.8	0.03953	1.3559	3.6	12
2-hydroxy-*n*-alkanes	1055	0.05131	1.4923	1.8	0.03732	1.4031	1.8	7
n-alkanals	910	0.08139	1.4561	1.4	0.04277	1.3177	2.5	7
2-alkanones	1440	0.03071	1.2905	1.6	0.0430	1.3613	1.7	8
n-alkane-1-thiols	1090	0.06170	1.3322	0.2	0.042	1.3635	2.8	14
sym *n*-dialkyl disulfides	1190	0.08720	1.4739	0.4	0.08207	1.4608	0.6	9
n-alkylnitriles	1855	0.01907	1.2294	2.6	0.04295	1.3869	3.4	11
n-alkanoic acids	1185	0.0440	1.4964	1.3	0.04100	1.4790	1.3	16
methyl *n*-alkanoates	1395	0.03158	1.3069	2.6	0.04200	1.3635	2.8	10

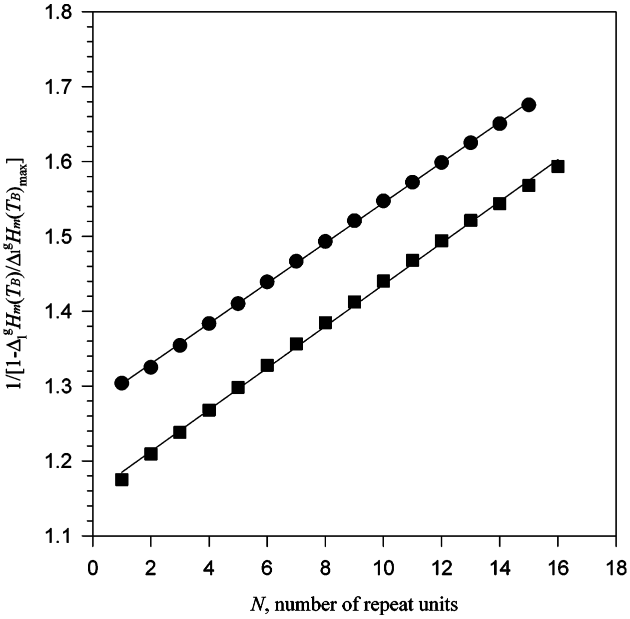

Figure 3. A plot of $1/[1 - \Delta_l{}^gH_m(T_B)/\Delta_l{}^gH_m(T_B)_{max}]$ vs the number of repeat units for the: ●, 1-alkenes; and ■, *n*-alkylcyclohexanes using a value of $\Delta_l{}^gH_m(T_B)_{max}$ = 147 kJ·mol^{-1}.

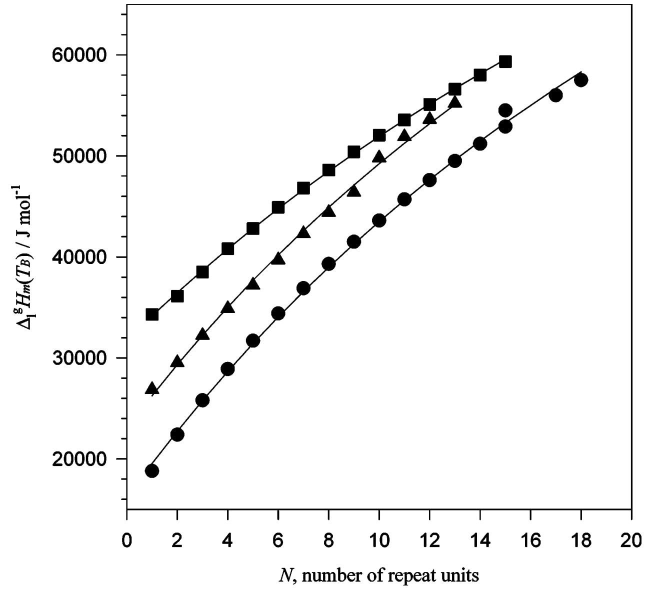

Figure 4. Vaporization enthalpies at the normal boiling temperature of the ●, *n*-alkanes; ▲, 1-alkanethiols; and ■, alkylcyclopentanes as a function of the number of repeat units. The lines were calculated with the aid of eq 5 using the value $\Delta_l{}^gH_m(T_B)_{max}$ = 147 kJ· mol^{-1}.

Table 3. Values of the Parameters of a_H and b_H Generated in Fitting $\Delta_l{}^gH_m(T_B)$ of Several Homologous Series Using Equation 5 and a Value of $\Delta_l{}^gH_m(T_B)_{max}$ = 147 kJ·mol^{-1}

	a_H	b_H	$\pm\sigma$/kJ·mol^{-1}	data points
n-alkanes	0.02960	1.1235	0.4	18
n-alkylbenzenes	0.02741	1.284	0.5	15
n-alkylcyclohexanes	0.02697	1.2754	0.2	15
n-alkylcyclopentanes	0.02821	1.2475	0.2	15
n-alk-1-enes	0.02796	1.1554	0.4	17
n-alkane-1-thiols	0.03172	1.1854	0.5	13

method. A mean value of $T_C(\infty)$ = (1068 ± 68) K was obtained. A comparison of the limiting $T_B(\infty)$ and $T_C(\infty)$ values and their uncertainties suggest that the values are within experimental error of each other; both appear to converge at approximately 1150 K. Since the data available for T_C is likely to be more uncertain, the limiting value derived from boiling temperatures, $T_C(\infty) = T_B(\infty)$ = (1217 ± 246) K, has been used in all subsequent calculations. The use of this value resulted in fits to experimental T_C data by the lines drawn in Figure 5 for several of the series examined. Additional details are provided in the caption associated with Figure 5. Columns 5 and 9 of Table 4 compare the standard deviation obtained by a nonlinear least-squares fit and the results calculated using $T_C(\infty)$ = 1217. In most cases the errors are comparable. A similar value, $T_C(\infty)$ = 1021 K, has been reported by Somayajulu using a different mathematical approach.[10]

The convergence of T_C with T_B has several further implications. As T_C approaches T_B, $\Delta_l{}^gH_m(T_B)$ must approach zero.[10] The fact that the $\Delta_l{}^gH_m(T_B)$ first increases as a function of *N* suggests that there must be some point at which it reaches a maximum before decreasing to zero as the temperature approaches 1217 K. Even the value of $\Delta_l{}^gH_m(T_B)_{max}$ suggested by the slope of eq 5 may not be realized; $\Delta_l{}^gH_m(T_B)$ must begin to decrease at some point with increasing T_B. Equation 8 reported by Somayajulu[10] provides a means of describing the possible behavior of $\Delta_l{}^gH_m(T_B)$ as a function of T_B and T_C

Table 4. Results Obtained for the Constants a_C and b_C by Treating T_C as a Function of the Number of Repeat Units, N, According to Equation 7 and Allowing $T_C(\infty)$ to Vary; a_{Cm}, b_{Cm}: Values of a_C and b_C Obtained by Using the Mean Value of T_c = 1217 K

polyethylene series	$T_C(\infty)$/K	a_C	b_C	$\pm\sigma$/K	$T_C(\infty)$/K	a_{Cm}	b_{Cm}	$\pm\sigma$/K	data points
n-alkanes	1050	0.1292	1.4225	1.7	1217	0.07445	1.4029	9.8	16
n-alkanals	1070	0.11708	1.7753	1.0	1217	0.077557	1.6355	1.8	8
alkanoic acids	1105	0.0961	2.1137	3.4	1217	0.06456	1.9329	3.9	31
1-alkanols	1045	0.11567	1.8362	3.6	1217	0.06773	1.6639	4.7	11
2-alkanones	1105	0.10063	1.8371	1.3	1217	0.071932	1.718	1.9	11
3-alkanones	1185	0.07827	1.8168	1.3	1217	0.07158	1.7811	1.3	10
1-alkenes	1035	0.1327	1.5496	0.3	1217	0.08278	1.4518	3.1	8
2-methylalkanes	950	0.16282	1.7767	0.6	1217	0.078619	1.53289	1.7	5

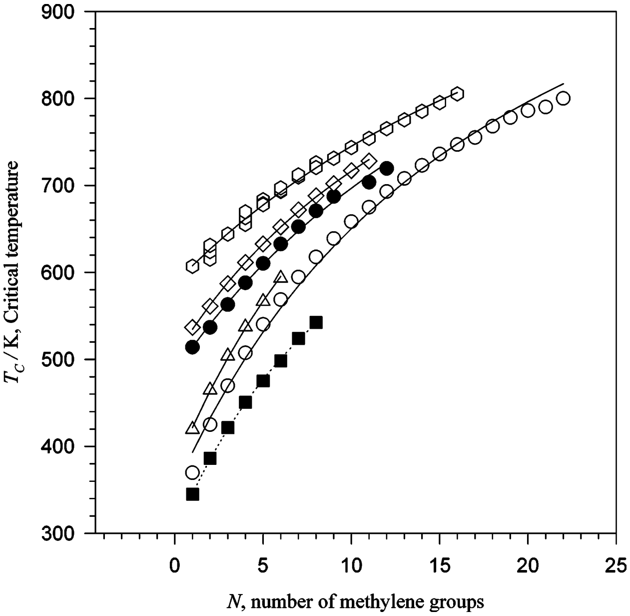

Figure 5. A plot of experimental critical temperatures vs N, the number of methylene groups for (top to bottom) the ⬡, alkanoic acids; ◇, 2-alkanones; ●, 1-hydroxalkanes; △, 1-alkenes; ○, the *n*-alkanes; and ■, *n*-perfluoroalkanes. The lines were calculated using eq 7 and values of $T_C(\infty)$ = 1217 K for the hydrocarbons and derivatives and $T_C(\infty)$ = 915 K for the fluorocarbons (squares); values of a_C and b_C are listed in columns 7 and 8 of Tables 4 and 8, respectively.

$$\Delta_l^gH_m(T_B) = e_1X + e_2X^2 + e_3X^3 + e_4X^4 \quad \text{where} \quad X = (T_C - T_B)/T_C \quad (8)$$

To calculate the anticipated behavior of $\Delta_l^gH_m(T_B)$ as a function of N according to this model, values of T_B and T_C for the *n*-alkanes were calculated using eqs 3 and 7; values for a_C and b_C that correspond to the limiting temperature, $T_B(\infty) = T_C(\infty)$ = 1217 K (columns 6−8, Table 4), were also used. Experimental $\Delta_l^gH_m(T_B)$ values for the *n*-alkanes were then fit to eq 8 using calculated values of T_B and T_C and allowing the constants e_1−e_4 to vary through a least-squares process. The resulting values of e_1−e_4 for both the *n*-alkanes and 1-alkenes are listed in Table 5.

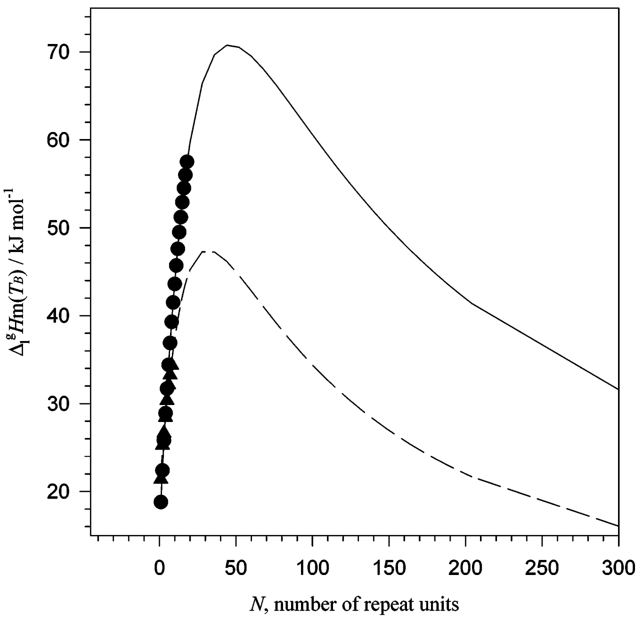

Figure 6. Values of $\Delta_l^gH_m(T_B)$ as a function of the number of repeat units. *n*-Alkanes: solid line, calculated values; ●, experimental values. *n*-Perfluoroalkanes: dashed line, calculated values; ▲, experimental values.

The behavior of $\Delta_l^gH_m(T_B)$ calculated as a function of both the number of repeat units, N, and $\Delta_l^gS_m(T_B)$ according to eq 8, is illustrated in Figures 6 and 7. The circles represent experimental data for the *n*-alkanes, and the fitted lines correspond to the behavior predicted by eq 8. According to Figure 6, a maximum of approximately 70 kJ·mol^{-1} is predicted at about N = 50 for $\Delta_l^gH_m(T_B)$. The results obtained for the 1-alkenes (not shown) were similar as were the results obtained by Somayajulu[10] using eq 8; both calculations used the same experimental data but different equations for calculating T_B and T_C. The linear behavior between $\Delta_l^gH_m(T_B)$ and $\Delta_l^gS_m(T_B)$ observed in Figure 1 for the *n*-alkanes is also evident in Figure 7. The experimental points cover only a small portion of this curve. The largest linear portion is experimentally inaccessible and therefore speculative.[13]

Critical Pressures

The convergence of T_C with T_B as $N \rightarrow \infty$ has a further implication. Since T_B represents the normal boiling temperature, P_C must approach one atmosphere as the two temperatures converge. Critical pressures are known to decrease with molecular size. A variety of different functions can be used to model the data, each resulting with a different quality of fit and somewhat different predictions. We have chosen to use a minimum number of adjustable

Table 5. Constants of Equation 8 Used in Fitting $\Delta_l^gH_m(T_B)$

	e_1	e_2	e_3	e_4	$\pm\sigma$/kJ·mol^{-1}
n-alkanes	1418.385	−9269.807	21935.55	−18508.375	0.1
n-1-alkenes	1427.21	−9194.337	21978.0	−19492.425	0.1
n-perfluoroalkanes	1091.54	−8393.756	25093.20	−27838.635	0.3

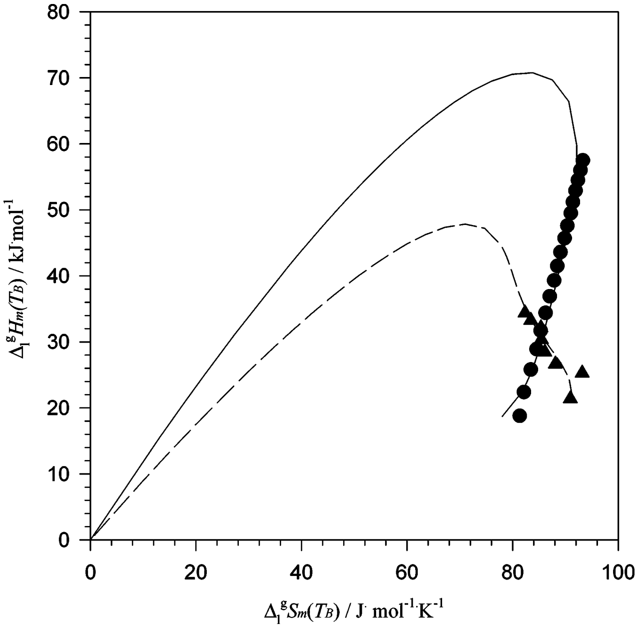

Figure 7. Experimental values of $\Delta_l{}^gH_m(T_B)$ as a function of $\Delta_l{}^gS_m(T_B)$. *n*-Alkanes: ●, experimental values; solid line, calculated values. *n*-Perfluoroalkanes: ▲, experimental values; dashed line, calculated values.

parameters to fit the data. An additional restriction was that the function converge to some limiting value with increasing *N*. Ambrose's equation provides an empirical basis for using a hyperbolic function to model both T_B and T_C. Of interest was whether a similar simple function could fit the experimental data and also approach a limiting pressure of $P_C(\infty) = 101.325$ kPa. A plot of $1/[1 - P_C(\infty)/P_C]$ vs *N* resulted in satisfactory linear plots for each of the series investigated when $P_C(\infty) = 101.325$ kPa. This suggested that the data could be fit with only two adjustable parameters. Solving for P_C as a function of *N* resulted in eq 9. Similar hyperbolic functions were used to model T_C and $\Delta_l{}^gH_m(T_B)$. The experimental critical pressures[11,12]

$$P_C = P_C(\infty)/[1 - 1/(a_{PC}N + b_{PC})] \tag{9}$$

plotted as a function of the number of repeat units are reproduced in Figure 8 for the 1-alkanols, the *n*-alkanes, and the 2-methylalkanes. The lines characterize the calculated fit. Figure 9 illustrates the fits obtained for the alkanoic acids and the 1-alkenes. The a_{PC} and b_{PC} parameters reported in Table 6 were evaluated by a nonlinear least-squares analysis. The number of entries, *N*, the standard deviation associated between experimental and calculated values for each series, and the correlation coefficients, r^2, are also provided. Given the uncertainty in experimental P_C values (see Figure 9), a limiting pressure of 0.101 MPa is certainly plausible according to this analysis.

Modeling T_B and $\Delta_l{}^gH_m(T_B)$ of Series Related to Polytetrafluoroethylene

The series examined thus far all converge experimentally in the limit to polyethylene. If the boiling temperatures of liquids with structures related to polyethylene converge to a finite value, then similar boiling temperature behavior would be expected for series converging to other polymers. Unfortunately experimental thermochemical data for many other series are not available. Sufficient data for the *n*-perfluorinated alkanes, 14 entries from C_3 to C_{16}, and the *n*-perfluorinated carboxylic acids, 8 entries ranging from C_1 to C_{14}, were found in the literature. If these series behave similarly to those just examined, the boiling temperatures of both these materials would be expected to

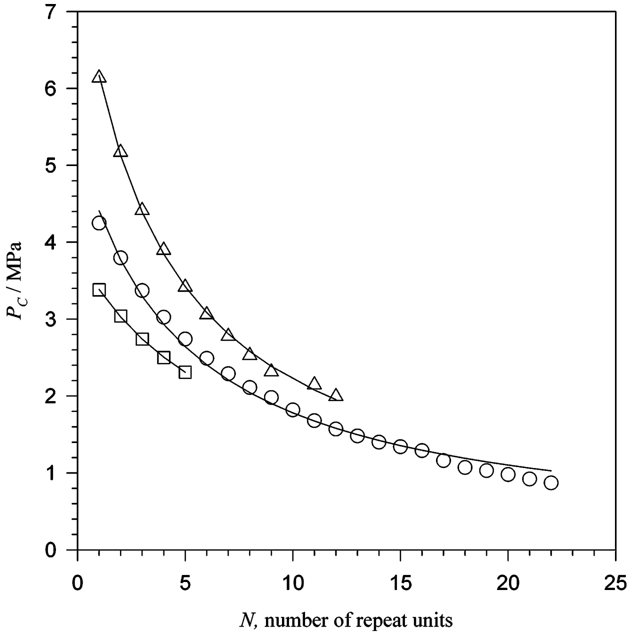

Figure 8. A plot of the critical pressure versus the number of repeat units for (top to bottom): △, the 1-alkanols; ○, the *n*-alkanes; and □, the 2-methylalkanes.

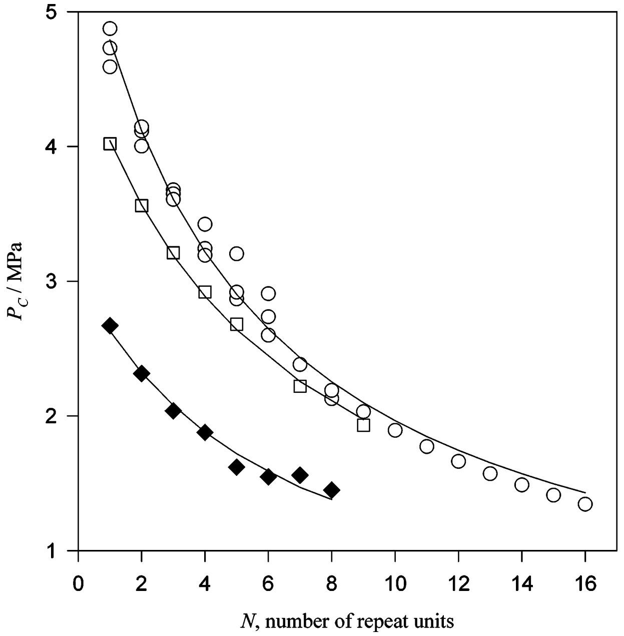

Figure 9. A plot of the critical pressure vs the number of repeat units for: ○, *n*-alkanoic acids; □, 1-alkenes; and ◆, perfluoroalkanes. The data for the alkanoic acids includes a few multiple determinations to give the reader a sense of the scatter in the experimental data.

Table 6. Values of the Parameters of a_{PC} and b_{PC} Generated in Fitting P_C of Several Homologous Series Using Equation 9 and $P_C(\infty)$ = 0.101325 MPa

	a_{PC}	b_{PC}	$\pm\sigma$/MPa	*N*	r^2
n-alkanals	0.003181	1.017	0.08	8	0.9911
n-alkanes	0.004089	1.019	0.09	22	0.9970
alkanoic acids	0.003643	1.018	0.11	16	0.9937
1-alkanols	0.003454	1.013	0.05	11	0.9953
1-alkenes	0.003555	1.022	0.03	7	0.9975
2-methylalkanes	0.003763	1.027	0.20	5	0.9997

Table 7. Values of the Parameters of a_B and b_B Generated in Fitting T_B of Several Homologous Perfluorinated Series Using Equation 3 and Allowing $T_B(\infty)$ to Vary in 5 K Increments; a_{Bm}, b_{Bm}: Values of a_B and b_B Using an Average Value of $T_B(\infty) = 915$ K

	$T_B(\infty)$/K	a_B	b_B	$\pm\sigma$/K	$T_B(\infty)$/K	a_{Bm}	b_{Bm}	$\pm\sigma$/K	N
n-perfluoroalkanes	880	0.07679	1.2905	2.1	915	0.06965	1.2816	2.2	13
n-perfluoroalkanoic acids	950	0.06313	1.5765	1.2	915	0.07053	1.6085	1.3	8
methyl *n*-perfluoroalkanoates					915	0.06637	1.5000	1.6	4
1-iodo-*n*-perfluoroalkanes					915	0.07409	1.3751	1.8	5

Table 8. Results Obtained for the Constants a_C and b_C by Treating T_C as Function of the Number of Repeat Units, *N*, According to Equation 7; a_{Cm}, b_{Cm}: Values of a_C and b_C Obtained by Using the Mean Value of $T_C(\infty) = 915$ K

polyperfluoroethylene series	$T_C(\infty)$/K	a_C	b_C	$\pm\sigma$/K	$T_C(\infty)$/K	a_{Cm}	b_{Cm}	$\pm\sigma$/K	N
n-perfluoroalkanes	920	0.1166	1.4813	1.1	915	0.1203	1.487	1.6	8

Table 9. Results Obtained for the Constants a_{PC} and b_{PC} by Treating P_C as Function of the Number of Repeat Units, *N*, and Using $P_C(\infty) = 0.101$ MPa According to Equation 9

polyperfluoroethylene series	$P_C(\infty)$/MPa	a_C	b_C	$\pm\sigma$/MPa	r^2	data points
n-perfluoroalkanes	0.1013	0.003555	1.0344	0.06	0.9703	8

converge to boiling temperature of polyperfluoroethylene.

Treating the experimental boiling points of the *n*-perfluorinated alkanes and carboxylic acids according to eq 3, and minimizing the error by allowing $T_B(\infty)$ to vary using the nonlinear least-squares procedure described above again resulted in similar values; $T_B(\infty) = 880$ and 950 K, respectively. The values are considered to be within experimental uncertainty of each other. These two values were averaged resulting in $T_B(\infty) = 915$ K and used to fit the boiling points of a few other homologous series for which only a few boiling points are available. The results are reported in Table 7. A similar limiting boiling temperature of 899 K for the *n*-perfluoroalkanes using a different empirical approach has been reported.[14]

The critical temperatures[15] of perfluoropropane through to perfluorodecane were analyzed according to eq 7 by nonlinear least squares. Allowing $T_C(\infty)$ to vary resulted in a minimum when $T_C(\infty) = 920$ K, 5 K from the mean value of $T_B(\infty)$. For the perfluorinated alkanes, the critical and boiling temperatures of the perfluorinated series also converge in the limit. A value of $T_C(\infty) = 915$ K was used in all subsequent calculations requiring $T_C(\infty)$ and $T_B(\infty)$ for the perfluorinated series. The quality of the fit using this value is illustrated in Figure 5 by the solid squares that represent the experimental values and the dotted line (calculated). The two sets of values for a_C and b_C in eq 7 are reported in Table 8.

Critical pressures for the perfluorinated alkanes are available for C_3 to C_{10}. Application of eq 9 to model P_C using a value for $P_C(\infty) = 0.101$ MPa results in the fit reproduced as the solid diamonds in Figure 9. The adjustable parameters a_{PC} and b_{PC} derived from the nonlinear least-squares treatment are reported in Table 9 along with the standard deviation associated with the fit. As with series related to polyethylene, a limiting pressure of 0.1 MPa is certainly plausible for the perfluorinated hydrocarbons as well.

Far fewer vaporization enthalpies are available for the *n*-perfluoroalkanes. Only eight are reported in a recent compendium.[16] These vaporization enthalpies, measured at different temperatures, were adjusted to their respective boiling points using eq 10[17]

$$\Delta_l^g H_m(T_B) = \Delta_l^g H_m(T_m) + [10.58 + 0.26C_{pl}][T_m - T_B] \tag{10}$$

The second term in eq 10 has usually been used to adjust vaporization enthalpies from the mean temperature of measurement, T_m, to $T = 298.15$ K and should be applicable in adjusting vaporization enthalpies to T_B provided the term $[T_m - T_B]$ is not large. The largest temperature correction was 78 K; most were considerably smaller. The C_{pl} term refers to the heat capacity of the liquid fluorocarbon, and this term was estimated using a group additivity approach.[18]

The behavior of $\Delta_l^g H_m(T_B)$ of the *n*-perfluoroalkanes according to the predictions of eq 8 is illustrated by the dashed lines in Figures 6 and 7; the triangles represent experimental data. According to Figure 6, eq 8 predicts that the maximum in $\Delta_l^g H_m(T_B)$ for the perfluorinated alkanes will be reached just slightly below 50 repeat units and will be lower than the maximum value for the *n*-alkanes. A maximum value of about 50 kJ·mol^{-1} is predicted by eq 8. The *n*-perfluoroalkanes also behave differently in Figure 7. Unlike the corresponding hydrocarbons, $\Delta_l^g S_m(T_B)$ of the *n*-perfluoroalkanes decreases with increasing number of repeat units, *N*. It is not known whether similar behavior will be observed for other homologous series that converge to polytetrafluoroethylene).

Boiling Temperature, Critical Temperature, and Pressure Estimations of Homologous Series

There is considerably more boiling temperature data than critical data available in the literature. The empirical observation that the boiling temperature and critical temperature converge according to this model can be quite useful in estimating critical temperatures using eq 7. For the two series investigated, $T_B(\infty)$ and $T_C(\infty)$ have been evaluated; all that is needed are a few experimental boiling and /or critical temperatures to evaluate the *a* and *b* terms in eq 3 and 7. Values of T_B and T_C for the remaining members of any homologous series related to polyethylene and polytetrafluoroethylene can then be estimated. Estimations of critical pressures can also be achieved in a similar manner using eq 9 and $P_C(\infty) = 0.101$ MPa.

Figure 10 illustrates the correlation observed between calculated and experimental boiling temperatures using eq 3 and $T_B(\infty) = 1217$ K for hydrocarbons related to polyethylene (●) and $T_B(\infty) = 915$ K for the perfluorinated analogues (▲). The correlation obtained between calculated and experimental critical temperatures using eq 7 and $T_C(\infty) = 1217$ K for hydrocarbons related to polyethylene (●) and $T_C(\infty) = 915$ K for the perfluorinated analogues (▲) is reproduced in Figure 11. Similarly, Figure 12 illustrates the correlation between calculated and experimental critical pressures assuming a limiting critical pressure of 1 atm. The standard deviation between experimental and

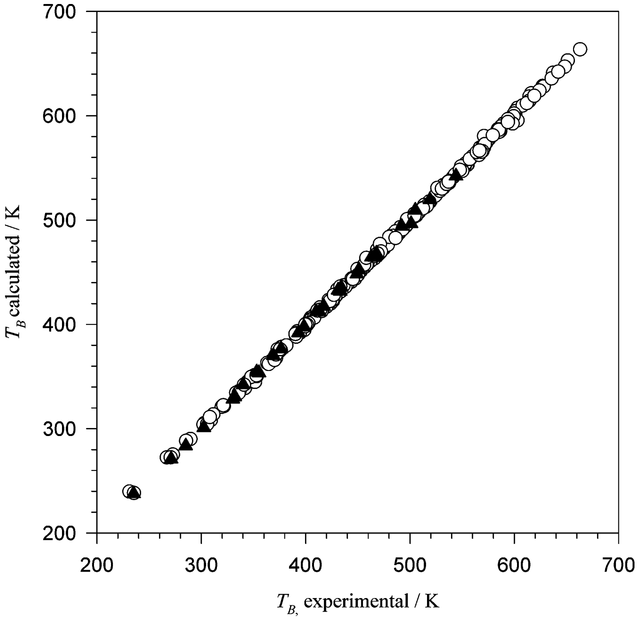

Figure 10. Calculated boiling temperatures, T_B, vs experimental values: ○, series related to polyethylene using $T_B(\infty) = 1217$ K; ▲, series related to polytetrafluoroethylene using $T_B(\infty) = 915$ K. The equation of the line is given by: $T_{B(calc)} = (1.000 \pm 0.001)T_{B(expt)} + (0.117 \pm 2.23)$; correlation coefficient $r^2 = 0.9994$ for 262 observations.

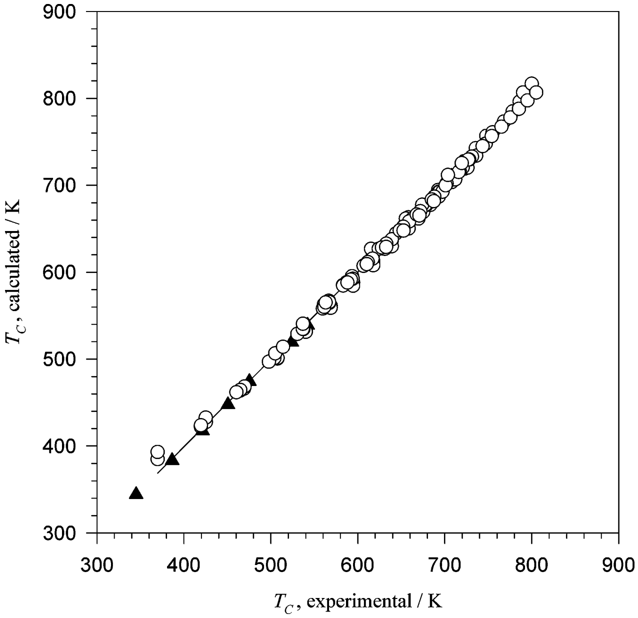

Figure 11. Calculated critical temperatures, T_C, vs experimental values: ○, series related to polyethylene using $T_C(\infty) = 1217$ K; ▲, series related to polytetrafluoroethylene using $T_C(\infty) = 915$ K. The equation of the line is given by: $T_{C(calc)} = (1.003 \pm 0.006)T_{C(expt)} - (2.07 \pm 5.22)$; correlation coefficient $r^2 = 0.9968$ for 106 observations.

boiling temperatures calculated using $T_B(\infty) = 1217$ for series related to polyethylene was ±2.3 K (232 entries); for series related to polytetrafluoroethylene using $T_B(\infty) = 915$ K, the uncertainty was ±1.8 K (30 entries). Critical temperatures and pressures could be reproduced with a standard deviation of ±5.2 K (106 entries) and ±0.056 kPa (77 entries), respectively.

Boiling temperatures are relatively easy to measure; measurement of critical temperatures and pressures is more challenging. It appears that use of boiling temperatures to evaluate $T_C(\infty)$ and a few carefully spaced critical temperature and pressure measurements can result in reasonable estimates of a homologous series for intermediate and extrapolated values of N provided the extrapolation is kept reasonably close to the experimental values.

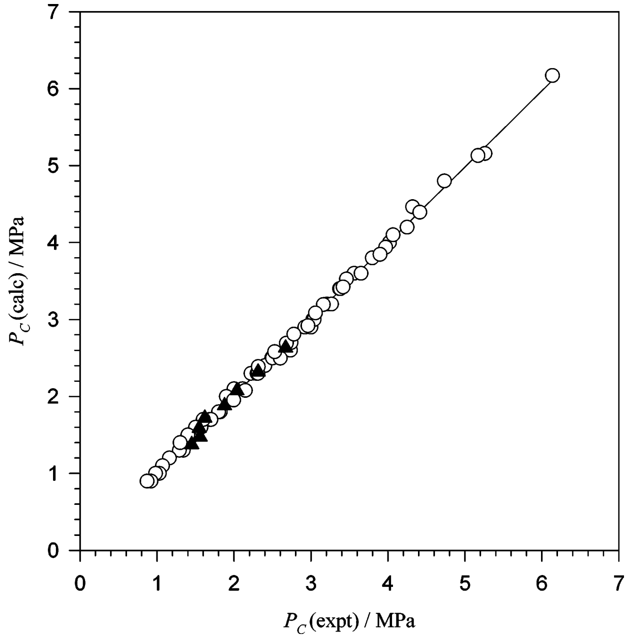

Figure 12. A comparison of calculated vs experimental critical pressures, P_C, using eq 9 and a value of $P_C(\infty) = 0.101$ MPa: ○, series related to polyethylene; ▲, series related to polytetrafluoroethylene. The equation of the line is given by: $P_{C(calc)} = (0.9909 \pm 0.006)T_{C(expt)} - (0.028 \pm 0.055)$; correlation coefficient $r^2 = 0.9975$ for 77 observations.

Discussion

The behavior predicted for T_B, T_C, and $\Delta_l^g H_m(T_B)$ of an increasing chain of repeat units, N, is not intuitively obvious. These properties are molecular properties whose physical meaning may change as the size of the molecule increases. Take $\Delta_l^g H_m(T_B)$ as an example. Vaporization enthalpy at the boiling temperature is a measure of the energy necessary to break attractive intermolecular forces at work. Consider an increasing chain of repeat units. Provided the chain is flexible, the chain will coil back on itself as it becomes larger.[7] The proportion of intramolecular interactions will eventually increase at the expense of the intermolecular ones if the molecule gets large enough. Thus it does not seem unreasonable that $\Delta_l^g H_m(T_B)$ may begin to decrease as some point. On the molecular level, $\Delta_l^g H_m(T_B)$ focuses only on the interplay between inter- and intramolecular interactions, both of which are short range. Longer-range interactions are ignored, and in the limit, the concept of intermolecular interactions becomes moot when $N \rightarrow \infty$. Nevertheless, the model seems useful in mimicking the behavior of T_B, T_C, and P_C as a function of N at the level of interest to chemists and the conclusions reached by treatment of the experimental T_B, T_C, and P_C data appear to be internally self-consistent.

Summary

The behavior of T_B, T_C, and $\Delta_l^g H_m(T_B)$ observed in this study suggests that these properties can be successfully treated as asymptotically approaching finite limits. The results do suggest that the linear behavior first observed in plots of $\Delta_l^g H_m(T_B)$ vs $\Delta_l^g S_m(T_B)$ that suggested hyperbolic behavior of T_B as a function of N, however, must be more complex. Hyperbolic eqs 3 and 7, prompted by the linearity observed between $\Delta_l^g H_m(T_B)$ and $\Delta_l^g S_m(T_B)$, successfully model T_B and T_C and appear useful in estimating them. A limiting critical pressure of 0.1 MPa is also plausible according to this analysis. The boiling temperatures of polyethylene and polytetrafluoroethylene have been evaluated as approximately 1200 and 900 K, in good agreement with earlier work.[10] For homologous series that approach the structures of polyethylene and polytetrafluoroethylene in the limit, only a few experimental values are necessary to provide estimates for most of the series experimentally accessible. More useful perhaps is the use of boiling temperatures to obtain estimates of $T_B(\infty)$ of a series; used as a model for $T_C(\infty)$, this together with a few experimental critical temperatures and pressures can afford these critical properties for much of the series. In summary, the use of the hyperbolic functions described above to model T_B, T_C, and P_C provide some predictive advantages over the use of other polynomials that result in functions that initially approach each other but ultimately diverge as $N \rightarrow \infty$.

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Supporting Information Available:

Tables including the experimental boiling temperatures, vaporization enthalpies, and references and boiling temperatures calculated using the protocols described in the text are available free of charge via the Internet at http://pubs.acs.org.

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