

A *VSE* Equation of State for Liquids. V. Poly(tetrafluoroethylene), 600–725 K

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Synopsis

Our volume–entropy–energy (*VSE*) equation of state for liquids, first proposed in 1973 for use with low molecular weight homogeneous liquids, is here applied for the first time to a high molecular weight liquid that is heterogeneous in molecular weight, namely, a molten polymer. Four thermodynamic quantities, T , s , c_p , and ϵ , are calculated over the range of 600–725 K at ambient pressure and are compared with experimental values, with excellent results. The grand average of the standard percentage errors (S.P.E.) for the 24 points is 0.1100%.

INTRODUCTION

The purpose of this paper is to show that systems containing molecules of high molecular weight, heterogeneous with respect to size, do not affect the successful application of our *VSE* equation of state to the calculation of thermodynamic quantities in what we call “the region of regular performance.” Since the application of external pressure broadens the “region of *irregular* performance,” our equation is not recommended for use with polymeric systems under high pressure. Many other thermodynamic quantities can be calculated from our equation, but we chose to present only those quantities for which corresponding experimental values are available in the literature for comparison with the calculated values. This is done merely to demonstrate the capabilities of the equation.

Our *VSE* equation of state¹ is

$$\epsilon = f_1 s f_2 + f_3 \quad (1)$$

where ϵ is specific energy, s is specific entropy, and f_1 , f_2 , and f_3 are volume-dependent functions, defined below.

We have proposed² that in every liquid there is a region over which the fractional change in entropy is directly proportional to the fractional change in temperature. We call this “the region of regular performance.” We have shown³ that this region extends from a temperature somewhat above the melting temperature all the way to the critical temperature. Our equation has been applied to a variety of homogeneous liquids of low molecular weight,² such as aliphatic and aromatic organic liquids, polar and nonpolar liquids including water, and liquid metals.^{2,4} This paper reports on our first study of a high molecular weight liquid heterogeneous with respect to molecular weight, namely, poly(tetrafluoroethylene). Since the results of the calculations here reported are uniformly excellent (grand average standard percentage error 0.11%), they confirm the well-known fact that thermodynamics applies only to a system, not to a substance.

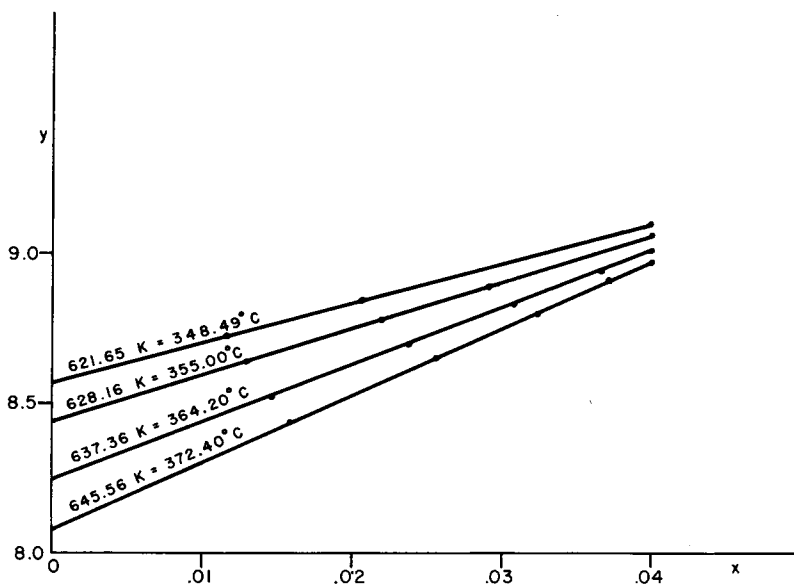


Fig. 1. Idealized Hudleston plot. Smoothed values of the Hudleston A and B parameters are obtained by individually plotting $y = \bar{P}v^{2/3}/x = A + Bx$ where $x = (v^0)^{1/3} - v^{1/3}$, at $T = 621.25, 628.16, 637.36,$ and 645.50 K. The slopes and intercepts of the idealized plots are obtained from least-squares fits according to eqs. (22) and (23). From data of Zoller.⁸

THEORETICAL

Our VSE equation of state follows directly from the assumption expressed by eq. (2) of reference 1, namely,

$$\left(\frac{\partial T}{T}\right)_v = K_1 \left(\frac{\partial s}{s}\right)_v$$

Derivation of eq. (1) of this paper from eq. (2) of reference 1 is given in the earlier paper and will not be repeated here.

The present study of poly(tetrafluoroethylene) and our current study of polyethylene have added considerably to our prior understanding of the nature of the liquid state. Thus, it appears that in the region of regular performance of polymers the liquid behaves in several ways like an ideal gas. For example, $v = f(T)$ is strictly linear in this region, and a van der Waals-type equation of state properly describes the PVT relationships of both of these polymers. Also, our study of polyethylene provides a visual criterion distinguishing the two regions. In the region of regular performance, polyethylene is clear and transparent. In the irregular region it is translucent or opaque. Thus, the transition point which we define² by u_d now clearly represents the point at which all crystallites have melted as heat is applied. With low molecular weight liquids this transition point is not visible.

The similarity between the molten polymer and an ideal gas suggests a parallel that lends more credence to our original assumption. Thus, in an ideal gas at constant volume,

$$c_v = \left(\frac{\partial \epsilon}{\partial T}\right)_v = c_p - R \quad (2)$$

from which

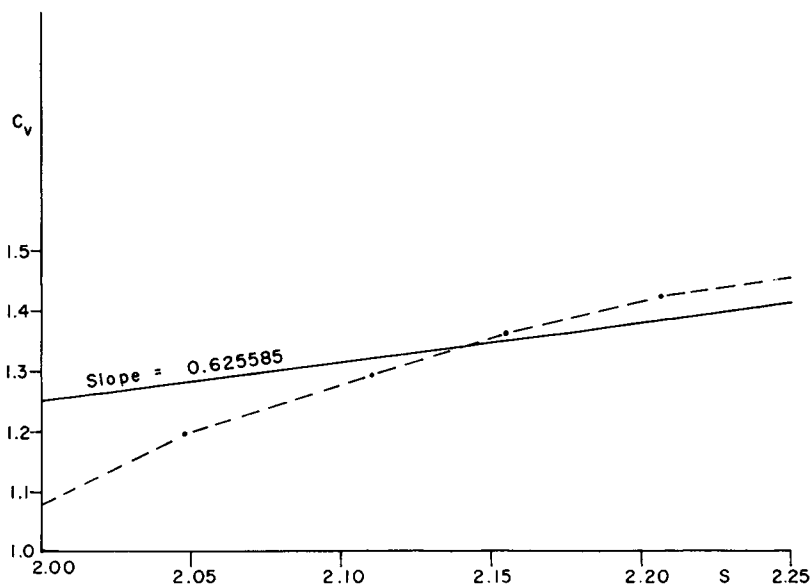


Fig. 2. First approximation of c_v vs s . Heat capacity at constant volume, c_v , is obtained from eq. (27), as explained in the text. The first approximation uses β_T from eq. (19) and α from eq. (16). Subsequent approximations use γ from eq. (24). (---), experimental $c_v = c_p - T\nu\alpha\gamma$ vs. s , $\gamma = \alpha/\beta_T$; $\beta_T = 30\nu_0^{1/3}/e^A$, eq. (19); (—) $c_v = (\Sigma y/\Sigma x)s$

$$\partial \epsilon_v = c_v \partial T_v \quad (2a)$$

Also,

$$\partial \epsilon_v = T_v \cdot \partial s_v \quad (3)$$

where $s_v = s_p - R \ln T_v$.

Values of c_p and s_p are listed in the API 44 tables⁵ for many gases. Conversion to c_v and s_v by use of eqs. (2) and (3) enables one to plot c_v versus s_v . Examination of many such plots shows that for every gas there is a region over which

$$c_v = (\text{const}) \cdot s_v \quad (4)$$

Thus, with *n*-heptane, for example,

$$c_v = 0.537128s_v, \text{ 700 to 1000}^\circ\text{C} \quad (4a)$$

Combining eqs. (2) and (3), one writes

$$\left(\frac{\partial T}{T}\right)_v = \left(\frac{\partial s}{c_v}\right) \quad (5)$$

Substituting $1/K \cdot s_v$ for c_v in eq. (5) gives the assumption originally proposed, eq. (2) of reference 1.

While we do not claim this to be a rigorous derivation of our equation of state, the similarity between the liquid region of regular performance and the ideal gas lends considerable credence to the fundamental nature of our relationship.

In reference 2, there are eight plots of c_v versus s for various systems. From these plots, the regions of "regular" and "irregular" performance are clearly evident, since the plot deviates from the straight line (direct proportionality)

In the region of regular performance, the volume-dependent functions f_1 , f_2 , and f_3 are defined in terms of their derivatives as follows:

$$\frac{df_1}{du} = c_2 \quad (6)$$

$$\frac{df_2}{du} = 0 \quad (7)$$

$$\frac{d^2 \ln f_3}{du^2} = u^p e^w \quad (8)$$

where $p = \text{a constant}$ and $w = A + Bu + Cu^2$.

Since the above exact definition of f_3 involves a double integration and requires five parameters (p , A , B , C , and the integration constant K) it is a great simplification to use an approximation equation, eq. (12), which could be defined in terms of its derivative as

$$\frac{d \ln f_3}{d \ln u} = c_5 \quad (9)$$

We hasten to point out, however, that this approximation equation is not sufficiently precise to extrapolate beyond the range of the data, and it is not safe to use its derivatives in the calculation of thermodynamic quantities involving partial and/or successive derivatives of f_3 .

In the region of regular performance all thermodynamic quantities obtained from constant-volume derivatives of eq. (1) can be calculated with great accuracy as far as our studies have gone. Such calculations involve only three parameters, c_1 , c_2 , and c_3 . Somewhat less precise calculations of energy from eq. (1) require two more parameters, c_4 and c_5 .

In the region of irregular performance, we have shown² how the deviations can

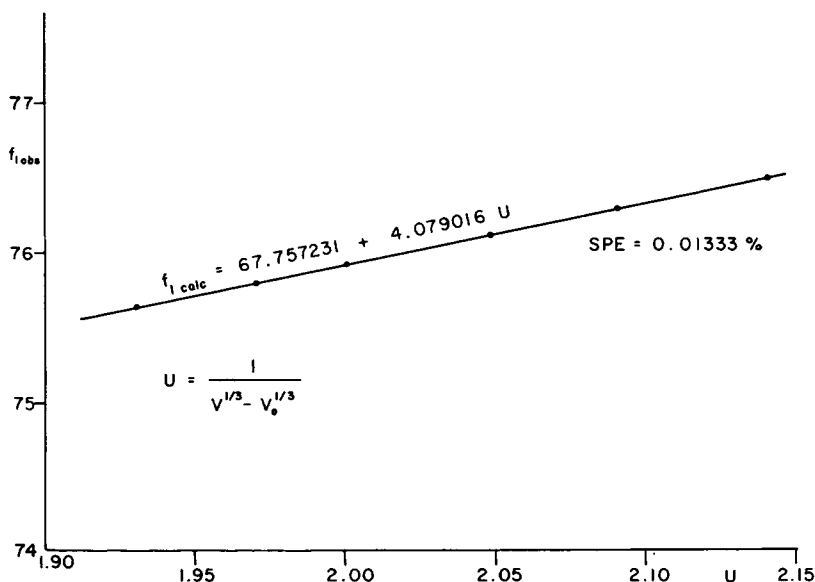


Fig. 4. Third approximation of f_1 vs u . Again, f_1 comes from eq. (29), using c_3 from the second approximation of c_3 vs s .

be evaluated with reasonable accuracy by introducing corrections in f_1 , f_2 , and f_3 , as explained in reference 2. Since this paper considers only the region of regular performance of poly(tetrafluoroethylene), no further reference to these corrections need be made here. The region of regular performance of the poly(tetrafluoroethylene) samples measured by the experimenters whose data we have used⁶⁻⁸ appears to start at about $u_d = 1.73$, or 600 K. Data are available up to 725 K.

Integration of eqs. (6), (7), and (9) gives

$$f_{1\text{calc}} = c_1 + c_2 u \quad (10)$$

$$f_{2\text{calc}} = c_3 \quad (11)$$

$$\ln f_{3\text{calc}} = c_4 + c_5 \ln u \quad (12)$$

where

$$u^{-1} = v^{1/3} - v_0^{1/3} \quad (13)$$

The physical constant v_0 , which we sometimes refer to as the "occupied volume," may be obtained directly from viscosity data by using our viscosity equation⁹:

$$\eta = A e^{B \left(\frac{v_f}{v_0} \right)} \quad (14)$$

where $v_f = v - v_0$ and v = specific volume.

When viscosity data are not available, other methods of estimating v_0 can be used. In the case of poly(tetrafluoroethylene), determination of v_0 was relatively simple since the specific volumes were found to be linear with T , and the y -intercept therefore is v_0 . Because of this linearity, $v\alpha$ is a constant, see eq. (17).

GENERAL CALCULATIONS

The data used in the present study are the calorimetric data of Douglas and Harman⁶ and the *PVT* data of Lupton⁷ and Zoller.⁸

We have frequently employed the Hudleston equation as a tool to obtain accurate specific volumes from *PVT* data.¹⁰ This criterion, explained more fully below, was used to check the atmospheric pressure-specific volumes of Zoller,⁸ Table I, and of Lupton⁷ [by calculation from his eq. (2)]. Zoller's ambient pressure values appear to be accurate to three significant figures.

Very slight modifications of four of Zoller's higher pressure values were made (our Table I) to provide more perfect agreement with the idealized Hudleston plots (Fig. 1). These very minor modifications are shown in Table I, which lists the *PVT* data we have used.

To the best of our knowledge, the samples of poly(tetrafluoroethylene) used by both Douglas and by Zoller were sufficiently alike so that the data from the two laboratories are compatible with each other. The four-place calorimetric data of Douglas and Harman⁶ appeared to us to be excellent and were used without modification.

EVALUATION OF ACCURACY OF EXPERIMENTALLY DETERMINED SPECIFIC VOLUMES

Earlier reference to Zoller's data⁸ indicated that the published values of specific volumes at ambient pressures are accurate to three significant figures. Our evaluation of the accuracy of *PVT* data uses the Hudleston equation as a tool to calculate the most probable low-pressure values. This can be done because in high-pressure technique the higher-pressure measurements are more accurate than the low-pressure ones. This is fully discussed in references 10 and 11. If one determines the Hudleston line by means of the high-pressure values, then the low-pressure values can be corrected by putting the points on this line.

By following this method it was determined that Zoller's ambient pressure-specific volumes are indeed accurate to three significant figures. When plotted against *T*, the relationship $v = f(T)$ was found to be linear. The deviations alternated, and the standard percentage error was only 0.0875%, leaving no doubt about the linearity of *v* versus *T*. The *y*-intercept was 0.06013, which, as mentioned above, must be v_0 . The equation is

$$v = 0.06012997 + 0.0009553T \quad (15)$$

From eq. (15), $\alpha = (1/v)[(\partial v/\partial T)_p]$ becomes

$$\alpha = \frac{0.0009553}{v} \quad (16)$$

and

$$v\alpha = 0.0009553 \quad (17)$$

The specific volumes were calculated at intervals of 25 from 575 K to conform to the calorimetric data, Table 5 of reference 6.

CALCULATION OF PARAMETERS c_1 , c_2 , AND c_3

There are many ways to calculate the parameters of eq. (1), but the simplest way is to first plot c_v versus *s* and obtain c_3 from the slope of the straight line from the origin through the points. Then

$$c_3 = \frac{1}{\text{slope}} + 1 \quad (18)$$

TABLE II
Slopes of c_v vs *s* and f_1 vs *u* Lines

	c_v vs <i>s</i>	f_1 vs <i>u</i>	SPE % ^a
1st Approximation	0.625583	3.964482	0.01342
2nd Approximation	0.625098	4.066381	0.01339
3rd Approximation ^b	0.624471	4.079016	0.01333
4th Approximation	0.624001	4.127895	0.02742

^a S.P.E. = $100[\Sigma(y_i - y)^2/n]^{1/2}$, where y_i = observed value, *y* = calculated value, and *n* = number of observations.

^b The 3d approximation is obviously the correct one.

The heat capacity at constant volume c_v is obtained from the measured value at constant pressure c_p by use of a relationship, eq. (27), involving γ . The isothermal coefficient of compressibility β_T , sometimes abbreviated "compressibility," can be estimated roughly from a Hudleston equation plot by use of the following equations:

$$\beta_T = \frac{30(v^0)^{1/3}}{e^A} \quad (19)$$

where A is the Hudleston intercept from

$$y = \frac{Pv^{2/3}}{x} = A + Bx \quad (20)$$

$$x = (v^0)^{1/3} - v^{1/3} \quad (21)$$

where v^0 = specific volume before compression and v = specific volume after compression.

It is generally conceded by those familiar with high-pressure research that β_T cannot usually be determined accurately from PVT data at ambient pressure. This situation arises from the fact that the numerical value of β_T increases rapidly as the external pressure is reduced to the neighborhood of 1 bar. Thus, a small error in v makes a large error in β_T . At least four or preferably five significant figure specific-volume data are required to enable the accurate calculation of β_T from PVT data. Other measurements, such as velocity of sound or internal pressure, are generally preferred for the accurate determination of β_T .

Because we had only three-place PVT data to work with, it was necessary to make "idealized" plots of the Hudleston equation in order to ensure accurate specific volumes at 1 bar. This was done by plotting the actual A and B values versus T and smoothing the observed quantities by applying least-squares fits as represented by eqs. (22) and (23):

$$A = 21.255096 - 0.020408T \quad \text{S.P.E.} = 0.0749\% \quad (22)$$

and

$$B = -225.469776 + 0.383583T \quad \text{S.P.E.} = 0.5448\% \quad (23)$$

Although this procedure did not greatly improve the accuracy of β_T as calculated from eq. (19), this failure was not important because accurate values of β_T can be obtained through the use of γ , since $\beta_T = \alpha/\gamma$ and α is known with high accuracy, eq. (16).

Reference to part III of this series³ will show that γ can be calculated with high accuracy over the entire region of regular performance by use of the following equation:

$$\gamma = F \frac{s_{\text{obs}}}{c_3 - 1} \left[\frac{c_2}{f_{1\text{calc}}} \right] \quad (24)$$

where

$$F = -\frac{du}{dv} = \frac{(u/v^{1/3})^2}{3} \quad (25)$$

and

$$f_{1\text{calc}} = c_1 + c_2u \quad (26)$$

Obviously, c_1 , c_2 , and c_3 must be known to apply eqs. (24)–(26), and these parameters are determined for poly(tetrafluoroethylene) as follows:

Heat capacity at constant pressure, c_p , and entropy at constant pressure, s_p , are available from reference 6. Therefore, c_v can be obtained from eq. (27) if γ is known:

$$c_v = c_p - Tv\alpha\gamma \quad (27)$$

For poly(tetrafluoroethylene),

$$Tv = 0.0009533T \frac{\alpha}{\beta_T} \quad (28)$$

Using the approximate values of β_T obtained from eq. (19) and the smoothed values of the Hudleston A values, one can calculate a set of approximate c_v values. Figure 2 shows such a set plotted versus s . The slope of the best line from the origin through these points is given by $\Sigma y/\Sigma x = 0.625583$. This "average" slope gives a starting point for subsequent approximations that ultimately lead to highly accurate values of c_v . Thus from the average slope found in approximation 1, one calculates a value of 3.964482 for c_3 . This approximate value is used in the following equation to calculate the first $f_{1\text{obs}}$:

$$f_{1\text{obs}} = \frac{T_{\text{obs}}}{c_3 s_{\text{obs}}^{c_3-1}} \quad (29)$$

Now, one plots $f_{1\text{obs}}$ versus u for the first approximation of f_1 , which provides the first approximation of c_2 from eq. (26). Knowing $f_{1\text{calc}}$ and c_2 , a much more precise value of γ may now be calculated from eq. (24), again using s_{obs} obtained from reference 6.

With the new value of γ , one may repeat the calculation of c_v from eq. (27) and go through the same process again. Four approximations were made with the results listed in Table II. The third approximation is evidently the correct one, whence $c_1 = 67.757231$, $c_2 = 4.079016$, and $c_3 = 2.601356$.

CALCULATION OF PARAMETERS c_4 AND c_5

Many thermodynamic quantities are obtained from the partial and/or successive derivatives of energy at constant volume. In all of these instances, only three parameters, c_1 , c_2 , and c_3 , are required. To calculate energy from eq. (1), however, the value of f_3 must be found, and this requires two more parameters, c_4 and c_5 . These are obtained directly from calorimetric data (and the three primary parameters) as follows: From eq. (1), one writes

$$f_{3\text{obs}} = \epsilon - f_{1\text{calc}} s_{\text{calc}}^{c_3} \quad (30)$$

TABLE III
Parameters

$c_1 = 67.757231$ $c_2 = 4.079016$ $c_3 = 2.601356$ $c_4 = 5.099462$ $c_5 = -0.502806$	}	determined from PVT data
$v_0^{1/3} = 0.391769$ (physical constant)		

TABLE IV
Calculation of T , s , c_p , and ϵ at Atmospheric Pressure

T_{obs}, K	Given \rightarrow $v, \text{ml/g}$	$T_{\text{calc}}, \text{K}$	v, s $\Delta T, \text{K}$	T, v		T, v		T, v		T, v		$\Delta \epsilon, \text{J/g}$
				$s_{\text{obs}}, \text{J/g-deg}$	$s_{\text{calc}}, \text{J/g-deg}$	$\Delta s, \text{J/g-deg}$	$c_{\text{pobs}}, \text{J/g-deg}$	$c_{\text{pcalc}}, \text{J/g-deg}$	$\Delta c_p, \text{J/g-deg}$	$\epsilon_{\text{obs}}, \text{J/g}$	$\epsilon_{\text{calc}}, \text{J/g}$	
600	0.6333	599.91	0.0900	1.992	1.992	0	1.331	1.323	0.0080	571.2	571.17	0.0312
625	0.6572	625.05	-0.0500	2.047	2.047	0	1.361	1.357	0.0040	604.9	604.92	-0.0175
650	0.6811	650.11	-0.1100	2.101	2.101	0	1.391	1.391	0	639.3	639.36	-0.0629
675	0.7050	675.05	-0.0500	2.154	2.154	0	1.421	1.424	-0.0030	674.4	674.45	-0.0539
700	0.7289	699.86	0.1400	2.206	2.206	0	1.451	1.457	-0.0060	710.3	710.14	0.1628
725	0.7528	725.02	-0.0200	2.258	2.258	0	1.480	1.489	-0.0090	747.0	747.08	-0.0828
				S.P.E. ₆ = .0132		0		0.4149		0.0119		
				grand av. S.P.E. ₄ = 0.1100								

A very good approximation for $f_{3\text{calc}}$ is eq. (12), and a least-square calculation gives c_4 and c_5 .

For poly(tetrafluoroethylene) the values were found to be $c_4 = 5.099462$ and $c_5 = -0.502806$. The fit is excellent over the range of the data (S.P.E. = 0.0163), but eq. (12) is still only an approximation that fails in the neighborhood of T_c . Generally speaking, the derivatives of eq. (12) cannot be used safely to calculate thermodynamic quantities directly. Other methods are available to obtain f_3' and f_3'' [ref. 2, eq. (15) and (16)] should they be required.

Table III lists all parameters involved in the present study.

CALCULATION OF FOUR THERMODYNAMIC QUANTITIES PERTAINING TO THE SYSTEM "LIQUID POLY(TETRAFLUOROETHYLENE)"

Calculations of T , s , c_p , and ϵ over the range of 600–725 K were made from the following equations and the results compared with the observed values:

$$T_{\text{calc}} = f_{1\text{calc}} c_3 s_{\text{calc}}^{c_3-1} \quad (31)$$

where $f_{1\text{calc}}$ is from eq. (10) and

$$\ln s_{\text{calc}} = \frac{\ln T_{\text{obs}} - \ln f_{1\text{calc}} - \ln c_3}{c_3 - 1} \quad (32)$$

The s_{calc} value is obtained from eqs. (31) and (32).

The $c_{p\text{calc}}$ value is obtained from

$$c_{p\text{calc}} = \frac{s_{\text{calc}}}{c_3 - 1} + T v \alpha \gamma_{\text{calc}} \quad (33)$$

where γ_{calc} is from eq. (24), using s_{calc} in place of s_{obs} . [The values of s_{obs} and s_{calc} are identical in the case of poly(tetrafluoroethylene) over the range of these studies.]

The ϵ_{calc} value is obtained from

$$\epsilon_{\text{calc}} = f_{1\text{calc}} s_{\text{calc}}^{c_3} + f_{3\text{calc}} \quad (34)$$

where $f_{3\text{calc}}$ is from eq. (12).

Table IV lists the results.

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