RICE UNIVERSITY

AN IMPROVED THEORETICAL BASIS FOR THE EQUATION
OF STATE OF PURE FLUIDS

by

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\(v\) Modified potential function
\(x\) Reduced radial distance
\(Z\) Partition function
\(z\) Compressibility factor

**Greek Symbols**

\(\alpha\) Potential steepness parameter
\(\beta\) Inverse temperature parameter
\(\gamma\) 0.57721566...
\(\epsilon\) Lennard-Jones potential parameter
\(\pi\) 3.14159...
\(\rho\) Density
\(\phi\) Reduced length
\(\eta\) Dimensionless density
\(\sigma\) Lennard-Jones potential parameter
\(\psi^t\) Molecular translational partition function
ABSTRACT

AN IMPROVED THEORETICAL BASIS FOR THE EQUATION OF STATE OF PURE FLUIDS

by Kurt Ernest Suchsland

The theoretical perturbation equation of state developed by McQuarrie and Katz is considered. The equation is

\[
\left( \frac{P}{\rho kT} \right) = \left( \frac{P}{\rho kT} \right)_{hs} + \frac{3}{n} (\gamma + 1 \ln \frac{A}{T^*}) n^* \frac{\partial}{\partial n^*} \left( \frac{P}{\rho kT} \right)_{hs}
\]

\[- \frac{12A^*}{T^*} \frac{\partial}{\partial n^*} \left[ n^* \int_0^\infty x (2^{-m}) g_{hs}(x, n^*) \, dx \right],
\]

where \( n, m, \) and \( A \) are Lennard-Jones parameters; \( T^* \) is the reduced temperature; \( n^* \) is a reduced density; \( x \) is the reduced radial distance; and \( g_{hs}(x, n^*) \) is the hard sphere radial distribution function for a system of diameter equal to sigma. An improved equation developed by Carnahan and Starling is used for the hard sphere compressibility factor. Instead of using tables of the hard sphere radial distribution function to evaluate the integral, the quadrature of the integral's Laplace transform is used for which an analytic
form exists. A computer program was written to evaluate the quadrature numerically.

The effective hard sphere diameter, \( c_\sigma \), was determined from experimental methane data at temperature \( T_0 \), which is the temperature for which \( (\partial^2 P/\partial T^2)_{N,V} \) is zero. From the equation of state it is possible to calculate an effective hard sphere diameter over a range of temperature. This effective hard sphere diameter was determined over the temperature range of 200 to 2000°K. The hard sphere diameters which were calculated are compared with the effective hard sphere diameters predicted by Rowlinson and Barker and Henderson for the repulsive contribution of the intermolecular potential and with the experiment values.

The deviation of the pressure of a linear van der Waals isochor from the actual experimental pressure was used to test the equation of state. It was found that the \( \ln T^* \) term can not account for the deviation from a linear isochor observed experimentally. The diameter becomes negative for very large temperatures due to the \( \ln T^* \) term, which originates from the Lennard-Jones potential. To predict the correct diameter and compressibility factor at very high temperatures a potential containing a hard core term is required.
I. SURVEY OF RECENT WORK

At high temperatures the equation of state of a simple fluid approaches that of a hard sphere due to the dominance of repulsive forces. At lower temperatures the attractive forces may be treated as a perturbation on the repulsive forces.

Recent work in statistical thermodynamics has provided a theoretical basis for calculating the coefficients of the virial expansion

\[ z(\rho, T^*) = a(\rho) + b(\rho)/T^* + c(\rho)/T^{*2} \]

\[ + O(\frac{1}{T^{*3}}), \quad (1) \]

where \( z \) is the compressibility factor; \( a, b, \) and \( c \) are coefficients which are functions of density; and, \( T^* \) is the reduced temperature. Zwanzig [1] states that the form of virial expansion in equation (1) satisfactorily fits experimental data for the inert gases and has shown that it reproduces data for argon and nitrogen over a temperature range of 0° to 150°C up to six or seven hundred amagat units.
Zwanzig developed a high-temperature equation of state for nonpolar gases in 1954 by a perturbation expansion on the system's partition function. A system's thermodynamic properties may be determined from its partition function. The partition function for an assembly of N particles is

\[ Z = (\psi^t/V)^N Q, \]  \hspace{1cm} (2)

where \( \psi^t \) is the molecular translational partition function and \( Q \) is the configuration integral (or configurational partition function) [2].

The configuration integral for a classical assembly of molecules for which there is a pair potential is

\[ Q = \frac{1}{N!} \int_\mathcal{V} \cdots \int_\mathcal{V} \exp \left\{ - \frac{1}{kT} \sum_{i<j}^N u(r_{ij}) \right\} \, dr_1 \ldots dr_N, \]  \hspace{1cm} (3)

where \( dr_i \) is the differential volume element located at \( r_i \) and \( u(r_{ij}) \) is the potential energy of interaction of a pair of molecules.

Zwanzig assumed the potential energy could be divided into two parts such that

\[ u(r) = u_0(r) + u_1(r). \]  \hspace{1cm} (4)

\( u_0(r) \) is the potential of the unperturbed system and \( u_1(r) \) is the perturbation. For \( u_0(r) \) Zwanzig used
\[
u_0(r) = \begin{cases} \infty & r < c \sigma \\ 0 & r > c \sigma \end{cases}, \quad (5)
\]

which is the hard sphere potential, where \(c\sigma\) is the diameter of the hard sphere reference system. For \(u_1(r)\) Zwanzig used

\[
u_1(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right], \quad (6)
\]

which is the Lennard-Jones (12-6) potential, where \(\varepsilon\) is the well depth and \(\sigma\) is the distance at which \(u_1(r) = 0\). Figure 1 shows the form of Zwanzig's potential.

Figure 1. Variation of the intermolecular pair potential of Zwanzig with distance.

The equation of state and the solution of the Born-Green equation for the radial distribution function were used...
for the hard sphere reference system [3]. His work was truncated after the $1/T^*$ term. The first term is the hard sphere compressibility factor.

One of the drawbacks of Zwanzig's method is that it treats the potential as being infinitely steep. It also necessitates the determination of a hard sphere diameter to which the results are very sensitive.

Frisch, Katz, Praestgaard, and Lebowitz [5] published an article in 1966 on a high-temperature equation of state for argon using the same form for the potential as Zwanzig. For the hard sphere distribution function the Percus-Yevick approximation was used, which is good to higher densities than other approximations [6]. Like Zwanzig, they truncated their equation at the $1/T^*$ term. The first term $a(\rho)$ is the hard sphere compressibility factor as determined by Theile [7] (and by Wertheim [8]) for the Ornstein-Zernike equation

$$a(\rho) = \frac{1+n+\eta^2}{(1-\eta)^3}, \quad (7)$$

where $\eta$ is the dimensionless density

$$\eta = \frac{n}{6} \rho (c\sigma)^3 \quad (8)$$

with $\rho$ being the number density. The second term $\frac{b(\rho)}{T^*}$, is
\[
\frac{b(\rho)}{T^*} = \frac{12n}{kT} \int_0^\infty f(s,n) U(s) \, ds,
\]

where \( f(s,n) \) is a known function and \( U(s) \) is the Laplace transform of the intermolecular pair potential. By slight adjustment of accepted values of \( \sigma \) and \( \epsilon \) and by adjusting \( c \) the hard sphere cutoff parameter, the \( b(\rho) \) term was accurately predicted for Argon at \( 0^\circ \) and \( 150^\circ \)C for densities of 40 to 600 amagats.

Rowlinson [9] has expanded the partition function in terms of \( 1/n \) by a Taylor expansion to take into account the steepness of the repulsive potential. The intermolecular potential Rowlinson used in his article was a Lennard-Jones potential of the form

\[
u(r) = \epsilon \left[ \left( \frac{r_m}{r} \right)^n - 2 \left( \frac{r_m}{r} \right)^{n/2} \right], \tag{9}\]

where \( r_m \) is the distance at which the potential is minimum and \( n \) is a steepness parameter. Rowlinson's results show the repulsive portion of the intermolecular potential to be dominant at high temperatures and densities.

Rowlinson suggests several potentials for which his method may be used, all of which go to the hard sphere potential as \( n \) goes to infinity.
McQuarrie and Katz [4] chose a pair potential

\[ u(r) = A \epsilon \left[ \left( \frac{\sigma}{r} \right)^{n} - \left( \frac{\sigma}{r} \right)^{6} \right] \]  

(10)

and expanded the partition function in \(1/n\) to obtain an equation which includes the attractive portion of the potential and takes into account the steepness of the repulsive portion of the potential. The constant \(A\) is

\[ A = \left( \frac{n}{n-6} \right) \left( \frac{n}{6} \right)^{\frac{6}{n-6}}. \]  

(11)

For \(n = 12\) Equation (10) becomes merely the Lennard-Jones (12-6) potential. As \(n\) goes to infinity the potential becomes the potential shown in Figure 2.

![Figure 2. The intermolecular potential of McQuarrie and Katz for infinite n](image-url)
The equation for the compressibility factor which McQuarrie and Katz arrived at has the form

\[ z(p, T^*) = a(p) + \frac{b(p)}{T^*} + c(p) \ln T^*. \quad (12) \]

The \( a(p) \) and \( c(p) \) terms involve the hard sphere compressibility factor. McQuarrie and Katz used the Pade approximation calculated by Ree and Hoover [10] for the hard sphere compressibility factor, which is

\[ z_{hs} = \frac{\rho^*(1+0.065507\rho^*+0.017329\rho^{*2})}{1-0.561493\rho^*+0.081313\rho^{*2}}, \quad (13) \]

where \( \rho^* = \frac{2}{\pi} \sigma^3/3 \) \hspace{1cm} (14)

and

\[ z_{hs} = \left( \frac{p}{\rho kT} \right)_{hs} - 1. \quad (15) \]

The \( b(p) \) term involves the integral

\[ I_1 = \int_0^\infty x^{-4} g_{hs}(x, \rho^*) \, dx, \quad (16) \]

where \( g_{hs}(x, \rho^*) \) is the hard sphere radial distribution function and \( x \) is \( r/\sigma \). To evaluate \( I_1 \), McQuarrie and Katz used the values Throop and Bearman tabulated for the Percus-Yevick radial distribution function.
Using a Lennard-Jones (14-6) potential McQuarrie and Katz were able to calculate compressibility factors which agree with experimental results for reduced temperature as low as 3 and densities as high as 40 moles per liter. Their results are better for a Lennard-Jones (15-6) potential than for a Lennard-Jones (12-6) potential, but this does not mean the Lennard-Jones (15-6) potential is a more accurate representation of the true intermolecular potential. The terms of order \((1/n)^2\) and \(\beta/n\) were truncated in the expansion of the configurational partition function, and these may be less significant for a Lennard-Jones (15-6) potential.

A procedure which led to satisfactory results at high densities and low temperatures has been developed by Barker and Henderson [11]. They assumed an arbitrary intermolecular potential \(u(r)\) such that as \(r\) became small, \(u(r)\) effectively goes to infinity. Barker and Henderson defined a modified potential \(v(d, \sigma, \alpha, \gamma, r)\) to be

\[
v(d, \sigma, \alpha, \gamma, r) = \begin{cases} u(d+(r-d)/\alpha), & d+(r-d)/\alpha < \sigma \\ 0, & \sigma < d+(r-d)/\alpha < d+(\sigma-d)/\alpha \\ \gamma u(r), & \sigma < r. \end{cases}
\]

The modified potential function becomes a hard sphere potential of diameter \(d\) for \(\alpha = \gamma = 0\) and Equation (17) becomes
the original potential for \( \alpha = \gamma = 1 \). Barker and Henderson expanded the natural logarithm of the configurational partition function in a Taylor series in powers of \( \alpha \) and \( \gamma \) about \( \alpha = \gamma = 0 \). The resulting equation for the Helmholtz free energy is

\[
\frac{F}{NkT} = \ln Q
\]

\[
= \frac{F_{hs}}{NkT} - \alpha 2\pi \rho d^2 g_{hs}(d) \{ d - \int_0^\sigma \{ 1 - \exp(-\beta u(z)) \} dz \}
\]

\[
+ \gamma 2\pi \rho \beta \int_0^\infty g_{hs}(r)u(r)r^2 dr + \text{higher order terms}
\]

(19)

for the \( v(d, \sigma, \alpha, \gamma, r) \) intermolecular pair potential function, where \( \beta = 1/kT = 1/\epsilon T^* \). For \( \alpha = \gamma = 1 \) Equation (19) corresponds to the Helmholtz free energy of a system with a potential \( u(r) \). Choosing \( d \) in Equation (19) to be

\[
d = \int_0^\sigma \{ 1 - \exp(-\beta u(z)) \} dz
\]

(20)

removes the \( \alpha \) term. For a simple fluid with potential \( u(r) \), the Helmholtz free energy is
The last term in Equation (21) is an estimate of the $\gamma^2$ terms, which were omitted from Equation (19). The $\sigma^2$ and $\alpha_1\gamma$ terms are believed to be small due to the choice of $d$.

The compressibility factor is given by

$$\frac{F_{\text{NkT}}}{NkT} = \frac{F_{\text{hs}}}{NkT} + 2\pi \rho \beta \int_{\sigma}^{\infty} g_{\text{hs}}(r) u(r) r^2 \, dr$$

$$- \pi \rho \beta \left( \frac{\partial \rho}{\partial p} \right) \frac{\partial}{\partial \rho} \rho \int_{\sigma}^{\infty} g_{\text{hs}}(r) u^2(r) r^2 \, dr \quad . \quad (21)$$

Barker and Henderson made numerical calculations for the compressibility factor using a Lennard-Jones (12-6) potential. An analytic form of the Percus-Yevick equation was used for the hard-sphere radial distribution function over $d < r < 2d$; the Throop and Bearman tables were used for $2d < r < 3.95d$; and $g_{\text{hs}}(r)$ was approximated by 1.0 for $r > 3.95d$. The Padé approximation was used for $(\frac{p}{\rho kT})_{\text{hs}}$.

Mansoori, Provine, and Canfield [12] using Barker and Henderson's approach have developed an analytic equation for the compressibility factor, where no tabular tables were necessary.
II. DEVELOPMENT OF THE EQUATION OF STATE

A. The Hard Sphere Compressibility Factor

The radial distribution function is proportional to the probability of a particle center being a distance \( r \) from another particle center [13]. The total correlation function is defined as

\[
h(r) = g(r) - 1 .
\]  

(23)

The total correlation function then becomes a measure of the effect one particle has on the position of another. If the effect of other particles on the pair occupation probability is neglected, the total correlation function becomes equal to the direct correlation probability \( c(r) \) [14].

Percus and Yevick [15] proposed an approximation in 1958, which has led to an analytic solution to the hard sphere compressibility factor. Percus and Yevick's assumption yields an equation for hard spheres which relates the direct correlation function to the pair distribution function. The equation is [16]

\[
c(r) = (1 - e^{6u(r)}) g(r) .
\]  

(24)
Solving the virial theorem [17]

$$\frac{p}{\rho kT} = 1 - \frac{2\pi \rho}{3kT} \int_0^\infty u'(r) g(r) r^3 \, dr$$  \hspace{1cm} (25)$$

and the Ornstein-Zernicke equation [14]

$$\phi(r_{12}) = c(r_{12}) + \rho \int c(r_{12}) \phi(r_{23}) \, dr_3$$ \hspace{1cm} (26)$$

using the exact pair distribution function would yield the same compressibility [16]. Thiele [8] solved both equations using the Percus-Yevick equation. Thiele's result from the virial theorem is

$$\left( \frac{p}{\rho kT} \right)_{HS} = \frac{1+2n+3n^2}{(1-n)^2}$$

$$= \frac{1+n+n^2-3n^3}{(1-n)^3} \hspace{1cm} (27)$$

which is slightly lower than Monte Carlo calculations of the hard sphere compressibility factor. His solution to the Ornstein-Zernicke equation is

$$\left( \frac{p}{\rho kT} \right)_{HS} = \frac{1+n+n^2}{(1-n)^3} \hspace{1cm} (28)$$

which is slightly higher than Monte Carlo calculations.
An averaging of Equations (27) and (28) would be expected to give very good agreement with Monte Carlo calculations. Starling and Carnahan [18] found that one-third Equation (27) plus two-thirds Equation (28) produced an equation

\[ \left( \frac{p}{\rho kT} \right)_{\text{hs}} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3}, \]  

which is better than any existing analytic form.

The virial expansion of Equation (29) and of the Pade approximation which was developed by Ree and Hoover based on known virial coefficients are

\[ \left( \frac{p}{\rho kT} \right)_{\text{hs}} = 1 + 4\eta + 10\eta^2 + 18\eta^3 + 28\eta^4 + 40\eta^5 + \ldots \]  

and

\[ \left( \frac{p}{\rho kT} \right)_{\text{hs}} = 1 + 4\eta + 10\eta^2 + 18.36\eta^3 + 28.2\eta^4 + 39.5\eta^5 + \ldots \]  

The two expansions show very good agreement. Equation (29) will be used for the hard sphere compressibility factor.
B. Derivation of the Equation of State

The following derivation is primarily due to McQuarrie and Katz [4]. As stated earlier, the configurational partition function of a $N$ molecular system is

$$Q = \frac{1}{N!} \int \cdots \int_V \exp\{-\beta \sum_{1 \leq i < j} u(r_{ij})\} \, dr_1 \cdots dr_N. \quad (3)$$

The intermolecular potential is assumed to have the Lennard-Jones form

$$u(r_{ij}) = A\varepsilon \left\{ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^{6} \right\}, \quad (32)$$

where $A$ is a constant. Setting the derivative of the potential with respect to $r$ equal to zero and the potential equal to $\varepsilon$ at $r = r_m$, $A$ is found to be

$$A = \left( \frac{n}{n-m} \right)^{1/2} \left( \frac{m}{m} \right)^{m-1} \quad (33)$$

The partition function may be expanded in a Taylor series in terms of $1/n$ such that

$$Q(n) = Q(n=\infty) + \left( \frac{\partial Q}{\partial 1/n} \right)_{n=\infty} \frac{1/n}{1!} + \cdots$$

$$+ \left( \frac{\partial^2 Q}{\partial (1/n)^2} \right)_{n=\infty} \frac{(1/n)^2}{2!} + \cdots \quad (34)$$
The expansion in $1/n$ should satisfactorily treat the repulsive steepness as the $(\frac{\sigma}{r})^n$ term is dominant in the repulsive portion of the potential. The expansion is truncated at the $1/n$ term as higher order terms are very difficult to determine. Since $n$ is large the terms of $(1/n)^2$ and higher should be small.

Let

$$u_n(r) = \varepsilon A \left( \frac{\sigma}{r} \right)^n$$  \hspace{1cm} (35)$$

$$u_m(r) = \varepsilon A \left( \frac{\sigma}{r} \right)^m$$  \hspace{1cm} (36)$$

and

$$u_\infty(r) = \lim_{n \to \infty} u_n(r)$$  \hspace{1cm} (37)$$

$$= \begin{cases} \infty & r < \sigma \\ 0 & r > \sigma \end{cases}$$  \hspace{1cm} (38)$$

Then the configurational partition function as $n$ goes to infinity becomes

$$Q(n=\infty) = \frac{1}{N!} \int \cdots \int_V \exp\{-\beta \sum_{i<j}^N u_\infty(r_{ij})\} \exp\{-\beta \sum_{i<j}^N u_m(r_{ij})\} \, dz_1 \cdots dz_N.$$  \hspace{1cm} (39)$$
Expanding the exponential

\[ \exp\{-\beta \sum_{i<j}^{N} u_m(r_{ij})\} \]

in a Taylor expansion in \( \beta \), the configurational partition function for \( n \to \infty \) is

\[
Q(n=\infty) = \frac{1}{N!} \int \cdots \int \exp\{-\beta \sum_{i<j}^{N} u_\infty(r_{ij})\}\{1-\beta \sum_{i<j}^{N} u_m(r_{ij})
\]

\[ + 0(\beta^2) d_{r_1} \cdots d_{r_N} \]  \( (40) \)

The series is truncated before the \( 0(\beta^2) \) term. The summation of \( u_m(r_{ij}) \) from \( 1 \leq i < j \leq N \) consists of \( N(N-1)/2 \) terms, which upon integration yields the same result.

Therefore

\[
Q(n=\infty) = \frac{1}{N!} \int \cdots \int \exp\{-\beta \sum_{i<j}^{N} u_\infty(r_{ij})\}d_{r_1} \cdots d_{r_N}
\]

\[ - \beta \frac{N(N-1)}{2N!} \int \cdots \int u_m(r_{ij}) \exp\{-\beta \sum_{i<j}^{N} u_\infty(r_{ij})\}
\]

\[ d_{r_1} \cdots d_{r_N} \]  \( (41) \)

The first term is the hard sphere configurational partition function, so that
Q(n=∞) = Q_{hs} - \frac{\beta}{2(N-2)!} \int \cdots \int u_m(r_{12}) \exp{-\beta} \\
\sum_{i<j}^N u_{\infty}(r_{ij}) dr_1 \cdots dr_N 
(42)

= Q_{hs} - \frac{\beta}{2(n-2)!} \int \cdots \int u_m(r_{12}) \exp{-\beta} \\
\sum_{i<j}^N u_{\infty}(r_{ij}) dr_3 \cdots dr_N \, dr_1 dr_2 
(43)

The probability of finding \( h \) molecules in \( h \) volumes is

\[ n^{(h)}(r_1 \cdots r_h) = \frac{1}{Q(N-h)!} \int \cdots \int \exp{-\beta} \sum_{i<j}^N u(r_{ij}) ] \\
\, dr_{h+1} \cdots dr_N, \text{ } (44)\]

which is the general distribution function [2]. For \( h = 2 \), \( n^{(h)} \) becomes the pair distribution function and is related to the radial distribution function by

\[ n^{(2)}(r_1, r_2) = \left( \frac{N}{V} \right)^2 g^{(2)}(r_1, r_2) \text{ } (45) \]

\[ = \left( \frac{N}{V} \right)^2 g^{(2)}(r_{12}) \text{ } (46) \]
for an isotropic fluid. Therefore

\[ g(r) = \left( \frac{V}{N} \right)^2 \frac{1}{(N-2)!} \frac{1}{Q} \int \cdots \int \exp\{-\beta \sum_{i<j} u(r_{ij})\} \]

\[ dr_3 \cdots dr_N \]  \hspace{1cm} (47)

and the configurational partition function as \( n \to \infty \) is

\[ Q(n=\infty) = Q_{hs} - \frac{Q_{hs} \beta N^2}{2V^2} \int \int u_m(r_{12}) g_{hs}(r_{12}) dr_1 dr_2. \]

Choosing molecule 2 as the origin, \( dr_1 \) becomes \( dr_{12} \).

Integrating over \( dr_2 \) gives

\[ Q(n=\infty) = Q_{hs} - (V) \frac{Q_{hs} \beta N^2}{2V^2} \int u_m(r_{12}) g_{hs}(r_{12}) dr_{12}. \]

\[ \int \]  \hspace{1cm} (49)

as the integral of \( dr_2 \) is simply the volume. In spherical coordinates \( dr_{12} \) is

\[ dr_{12} = 4 r_{12}^2 dr_{12}. \]

Dropping the subscripts and defining \( x \) as

\[ x = r/\sigma \]  \hspace{1cm} (51)
Equation (49) becomes

\[ Q(n=\infty) = Q_{hs} \]

\[ - \frac{2\pi Q_{hs} \beta N^2 \sigma^3}{V} \int_0^\infty x^2 u_m(x) g_{hs}(x) \, dx. \]  \tag{52}

The potential approaches zero very rapidly, which allows the upper limit to be taken as infinity.

Taking the derivative of the configurational partition function with respect to \(1/n\) gives

\[ \frac{\partial Q}{\partial 1/n} = - \frac{n^2 \beta A \varepsilon \sigma^3 N}{2(N-2)!} \int \cdots \int x_{12}^{-n} \ln x_{12} \exp\{-\beta \sum_{i<j}^N u_n(x_{ij}) \}
\]

\[ + \beta \sum_{i<j}^N u_m(x_{ij}) \, dx_1 \cdots dx_N \]  \tag{53}

where

\[ \frac{\partial}{\partial 1/n} \sum_{i<j}^N u_n(x_{ij}) \]

has been taken as

\[ \frac{\partial}{\partial 1/n} \left[ \frac{N(N-1)}{2} u_n(x_{12}) \right]. \]
By neglecting terms of order $\beta$ and higher, the exponent of $u_m(r_{ij})$ becomes unity. Following the procedure used to find $Q(n = \infty)$,

\[
\frac{\partial Q}{\partial 1/n} = -n^2 \frac{A e^x}{2(n-2)!} \int \cdots \int x_{12}^{-n} \ln x_{12} \exp\{-\beta \sum u_n(x_{ij})\}
\]

\[
\frac{V/n^3}{x_{12}} \sum x_{12} \sum x_{12} \exp\{-\beta \sum u_n(x_{ij})\}
\]

\[
\frac{n^2}{V} \sum x_{12} \sum x_{12} \exp\{-\beta \sum u_n(x_{ij})\}
\]

For $n$ large, the integrand is zero except when $x$ is approximately one.

The radial distribution function has a discontinuity at $1/n$ equal to zero. Define a function $y(x)$ by the equation

\[
g(x) = y(x) \exp[-\beta u_n(x)]
\]

\[
y(x) = y(x) \exp[-\beta Ae^x^{-n}]
\]

as was done by Rowlinson [9]. The integrand becomes then
\[ I_2 = y(1) \int_0^\infty x^{-n} \ln x \exp[-\beta A \varepsilon^{-n}] x^2 \, dx. \] (59)

Letting
\[ x^{-n} = z \] (60)

\[ (\frac{\partial Q}{\partial 1/n})_{n\to\infty} = \lim_{n\to\infty} \frac{-2\pi N^2 \beta A \varepsilon^3 Q_n y(1)}{V} \int_0^\infty z^{-3/n} \ln z \exp(-\beta A \varepsilon z) \, dz. \] (61)

\[ = -2\pi N^2 \beta A \varepsilon Q_{hs} y(1) \int_0^\infty \ln z \exp(-\beta A \varepsilon z) \, dz \] (62)

\[ = -2\pi N^2 \beta A \varepsilon^3 Q_{hs} y(1)(\gamma + \ln \beta A \varepsilon)/V. \] (63)

The configurational partition function may be written as

\[ Q(n) = Q_{hs} \{1 - \frac{2\pi A^3 \beta N^2}{V} \int_0^\infty x^2 u_m(x) g_{hs}(x) \, dx \]

\[ -2\pi N^2 \beta A \varepsilon^3 y(1)(\gamma + \ln \beta A \varepsilon)/Vn \} + \text{higher order terms.} \] (64)
Assuming the $\beta$ and $1/n$ terms in Equation (64) are small gives as the expanded logarithm

$$
\ln Q(n) = \ln Q_{hs} - \frac{2\pi^3 \beta N^2}{V} \int_0^\infty x^2 u_m(x) g_{hs}(x) \, dx
$$

- $\frac{2\pi N^2 A \epsilon \sigma^3}{nV} \gamma(1)(\gamma + \ln \frac{A}{T^*}) \, . \quad (65)

Defining $\eta^*$ as

$$
\eta^* = \frac{\pi}{6} \sigma^3 \left( \frac{N}{V} \right) \, , \quad (66)
$$

which is $\eta$ for $c$ equal to one, and using the relation for $\gamma(1)$ in an assembly of hard spheres [9]

$$
\gamma(1) = \frac{3V}{2\pi N \sigma^3} \{ \left( \frac{pV}{NkT} \right)_{hs} - 1 \} \quad (67)
$$

allows Equation (65) to be written as

$$
\ln Q(n) = \ln Q_{hs} - 12\beta N \eta^* \int_0^\infty x^2 u_m(x) g_{hs}(x) \, dx
$$

- $\frac{3N}{n} \left[ \left( \frac{pV}{NkT} \right)_{hs} - 1 \right] (\gamma + \ln \frac{A}{T^*}) \, . \quad (68)

Using the well known equation relating the configurational partition function to pressure
\[ P = kT \left( \frac{\partial \ln Q}{\partial V} \right)_{N,T} \] (69)

to find the compressibility factor yields

\[ z = -\frac{1}{N} \eta^* \left( \frac{\partial \ln Q}{\partial \eta^*} \right)_{N,T} \] (70)

\[ = \left( \frac{pV}{NkT} \right)_{hs} + 12\beta \eta^* \frac{3}{\partial \eta^*} \left[ \eta^* \int_0^\infty x^2 u_m(x) g_{hs}(x) \, dx \right] 
+ \frac{3}{n} (\gamma + \ln \frac{A}{T^*}) \eta^* \frac{3}{\partial \eta^*} \left[ \left( \frac{pV}{NkT} \right)_{hs} \right] \] (71)

which, after substitution of Equation (29) for the hard sphere compressibility factor, becomes

\[ z = \frac{1+n^*+n^*2-n^*3}{(1-n)^3} + \frac{6}{n} (\gamma + \ln \frac{A}{T^*}) \frac{\eta^*(2+2n^*-n^*2)}{(1-n)^4} \]

\[ + 12\beta \eta^* \frac{3}{\partial \eta^*} \left[ \eta^* \int_0^\infty x^2 u_m(x) g_{hs}(x) \, dx \right]. \] (72)

Since \( g_{hs}(x) \) is 0 for \( x < \sigma \) the limits of integration on the \( \beta \) term may be changed to 1.0 to \( \infty \), so that

\[ 12\beta \eta^* \frac{3}{\partial \eta^*} \left[ \eta^* \int_0^\infty x^2 u_m(x) h_{hs}(x) \, dx \right] \]
The two integrals may be expressed as quadratures of their Laplace transforms to give \([5,12]\)

\[
12\beta n^* \frac{2}{\partial n^*} \int_0^\infty x^2 u_m(x) g_{hs}(x) \, dx \\
= 12\beta n^* [ \int_0^\infty x^2 u_m(x) g_{hs}(x) \, dx ]
\]

\[
= 12 \frac{n^*}{T^*} \int_0^\infty G(s) U(s) \, ds + \int_0^\infty f(s) U(s) \, ds
\]

\[\text{(74)}\]

where

\[
G(s) = s L(s) e^{-s} / (12n^* L(s) e^{-s} + S(s)),
\]

\[\text{(75)}\]

\[
f(s) = \frac{s^4 e^{-s} [s(1+n^*-an^2)+(2n^*+1)^2]}{[12n^* L(s) e^{-s} + S(s)]^2},
\]

\[\text{(76)}\]

\[
U(s) = - A \left[ \frac{s^{n-2}}{(n-2)!} \right],
\]

\[\text{(77)}\]

\[
L(s) = (1 + n^*/2) s + 1 + 2n^*
\]

and
\[ S(s) = (1-n)^2 s^3 + 6n^*(1-n^*) s^2 + 18n^*2 s \]

- \(12n^*(1+2n^*) \). \hspace{1cm} (78)

The final equation for the compressibility factor is then

\[
z = \frac{1+n^*+n^*2-n^*3}{(1-n^*)^3} + \frac{6}{n}(\gamma + \ln \frac{A}{T^*}) \frac{n^*(2+2n^*-n^*2)}{(1-n^*)^4} \\
+ 12 \frac{n^*}{T^*} \int_0^\infty [G(s) + f(s)] U(s) \, ds \]. \hspace{1cm} (79)
III. APPLICATION OF THE EQUATION
OF STATE TO METHANE

A. Determination of Sigma from Experimental Data
and The Equation of State

The compressibility factor is very sensitive to the value used for sigma in Equation (79) and is very sensitive to the hard sphere diameter in many other theoretical perturbation equations of state. A method is discussed here which will be used to determine sigma for high density methane. The PVT data used is taken from an article by Venix, Kobayashi, and Leland [19] on low temperature volumetric properties of methane.

The first term of Equation (1), \( a(\rho) \), can be determined from experimental data by a least squares fitting of the data using successive polynomials, extrapolation of the isochores to 1/T equal to zero in a plot of \( z \) versus 1/T, or by use of the slope \( \left( \frac{\partial P}{\partial T} \right)_{N,V} \) at high temperatures where higher order terms become small. The hard sphere diameter can be evaluated from \( a(\rho) \) using Equation (29).

When the configurational partition is expanded about a potential's steepness parameter, such as Rowlinson's
1/n or Barker and Henderson's $\alpha$, the effective hard sphere diameter, $d$, becomes a function of temperature. The term $a(\rho,d)$ expressed in terms of sigma and temperature is

$$a(\rho,d) = a(\rho,\sigma) + \frac{3}{n}(\gamma + \ln \frac{A_{\text{T}}}{\text{T}_{\text{w}}^2})\eta^* \frac{\partial}{\partial \eta^*}[a(\rho,\sigma)]$$

in Equation (71). Methods used to find the hard sphere diameter of Zwanzig may not be satisfactory for temperature dependent diameters.

It should be noted that Equation (79) predicts negative compressibility factors as the temperature becomes very large. Therefore Equation (79) must be considered as breaking down at very high temperatures. It would be expected from the assumptions made in the derivation that Equation (75) would be most accurate at high temperatures, where the truncated inverse temperature terms become small. Because of the failure of Equation (75) to predict the compressibility factor successfully at very high temperatures, more moderate temperatures must be used to determine sigma. It will be seen in the following two sections that there is no difficulty due to high temperature application of Equation (79) to methane as all experimental data are well below temperatures at which the diameter becomes negative.

The greatest linearity of each isochor occurs in the region of the van der Waals isochor. At temperature $T_0$,
for which the pressure of the van der Waals isochor equals the experimental pressure, \( \frac{\partial^2 p}{\partial T^2} \) is zero. Figure 4 shows the deviation of the actual pressure of methane from the linear van der Waals isochor. It is obvious that the first two terms of an expansion of the form suggested by Zwanzig would represent the compressibility quite well over the temperature and pressure range of the data. To account for the deviation from the van der Waals isochor more terms are needed. Assuming the compressibility factor for methane in the region near \( T_0 \) can be expressed by

\[
z = \frac{1}{\rho k} \{ A(\rho) + \frac{B(\rho)}{T} + \frac{C(\rho)}{T^2} + D(\rho) \ln T \},
\]

which is the form Equation (79) would have if it had been truncated after the \( \beta^2 \) term it is found

\[
C = -\frac{D T_0^2}{2}
\]

and the difference between the van der Waals pressure and the experimental pressure would be given as

\[
P_{VDW} - P_{exp} = D[ T \ln(\frac{T_0}{T}) + \frac{3}{2}T - 2T_0 + \frac{T_0^2}{2T} ] .
\]

Plotting \( P_{VDW} - P_{exp} \) vs \( T \ln(\frac{T_0}{T}) + \frac{3}{2}T - 2T_0 + \frac{T_0^2}{2T} \) should
yield linear isochores of slope D. Sigma can then be determined by use of the coefficient of the natural logarithm term in Equation (79). Unfortunately the isochores are not linear as is evident from Figure 3, which shows $P_{VDW} - P_{exp}$ vs $T \ln\left(\frac{T_0}{T}\right) + \frac{3}{2}T - 2T_0 + \frac{T_0^2}{2T}$. Therefore Equation (81) can not satisfactorily reproduce experimental data well enough to predict the deviation from the van der Waals isochor.

At $T_0$ the temperature dependent term of Equation (80) is small for large $n$ and $a(\rho,d)$ is approximately $a(\rho,\sigma)$. At $T_0$ truncated higher order terms may be expected to be small due to the linearity of each isochor in the region near $T_0$. The value of sigma may be determined therefore using the slope $(\frac{\partial P}{\partial T})_{N,V}$ at $T_0$, which is tabulated for various densities in the article by Venix, Kobayashi, and Leland. The values obtained for sigma are listed in Table 1. The values calculated are the best value of sigma to describe the experimental data for each isochor for a Lennard-Jones $(n,m)$ potential.

The value used for $\varepsilon/k$ was $137^\circ K [22]$ for the Lennard-Jones (12-6) potential and $310^\circ K [23]$ for the Lennard-Jones (28-7) potential. These are values for methane for which there is a value of sigma already associated. The Lennard-Jones (28-7) potential is suggested by Hamann and Lambert for methane and other tetrahedral molecules.
**TABLE 1**

CALCULATED VALUES OF SIGMA FOR METHANE

<table>
<thead>
<tr>
<th>Density gm/cc</th>
<th>Sigma (12-6) Angstroms</th>
<th>Sigma (28-7) Angstroms</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.341</td>
<td>3.2257</td>
<td>3.3724</td>
</tr>
<tr>
<td>0.321</td>
<td>3.2190</td>
<td>3.3611</td>
</tr>
<tr>
<td>0.297</td>
<td>3.2085</td>
<td>3.3477</td>
</tr>
<tr>
<td>0.282</td>
<td>3.2032</td>
<td>3.3406</td>
</tr>
<tr>
<td>0.265</td>
<td>3.2015</td>
<td>3.3354</td>
</tr>
<tr>
<td>0.240</td>
<td>3.2030</td>
<td>3.3324</td>
</tr>
<tr>
<td>0.221</td>
<td>3.2203</td>
<td>3.3406</td>
</tr>
<tr>
<td>0.206</td>
<td>3.2255</td>
<td>3.3433</td>
</tr>
<tr>
<td>0.189</td>
<td>3.2007</td>
<td>3.3306</td>
</tr>
<tr>
<td>0.179</td>
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<td>3.3291</td>
</tr>
<tr>
<td>0.164</td>
<td>3.1936</td>
<td>3.3334</td>
</tr>
<tr>
<td>0.158</td>
<td>3.1932</td>
<td>3.3354</td>
</tr>
<tr>
<td>literature</td>
<td>3.822</td>
<td>3.57</td>
</tr>
</tbody>
</table>
FIGURE 3: DEVIATION OF EXPERIMENTAL PRESSURE FROM THE LINEAR VAN DER WAALS VALUE.
**FIGURE 4** DEVIATIONS FROM LINEARITY FOR SELECTED METHANE ISOCHORES

*Figure 4 is taken from Reference [19].
B. The Hard Sphere Cut-off Parameter

1. The Cut-off Parameter from the Equation of State

The hard sphere cut-off parameter is defined as

\[ c = \frac{d}{\sigma} \]  \hspace{1cm} (84)

Expanding \( a(\rho, d) \) by a Taylor series in \((c-1)\) gives

\[ a(\rho, d) = a(\rho, \sigma) + 3 \frac{\partial z(\rho, \sigma)}{\partial n^*} n^*(c-1) + \ldots \]  \hspace{1cm} (85)

Comparison of Equation (85) with Equation (80) shows that the hard sphere cut-off parameter is

\[ c = 1 + \frac{1}{n} (\gamma + \ln \frac{A}{T^*}) \]  \hspace{1cm} (86)

Equation (86) is the cut-off parameter corresponding to Equation (79). The hard sphere diameter may be determined using Equation (86) and the value of sigma determined previously.

At very high temperatures, Equation (86) is not valid as the cut-off parameter becomes negative. From physical reasoning it would be expected that the cut-off parameter would always be less than one for a Lennard-Jones potential as \( u(d) \) would be expected to be in the repulsive region; however, it must be remembered that the
configurational partition function was expanded only about the repulsive potential and that terms of $\beta/n$ were truncated, so that the cut-off parameter in Equation (85) is dependent only upon the repulsive potential. For temperatures where Equation (86) is greater than unity, expansion of the configurational partition function about only the repulsive potential may lead to unsatisfactory values for the compressibility factor.

2. The Cut-off Parameter of Rowlinson

In Rowlinson's article, since a Lennard-Jones potential was expanded, the cut-off is a function of both the repulsive and attractive potentials. Rowlinson [22] introduced a reduced length

$$\phi = (x)^{1/n} (1 + \frac{F(x)}{n})$$  \hspace{1cm} (87)

where

$$x = 1/T^*$$ \hspace{1cm} (88)

and

$$F(x) = \gamma - 2 \pi x^{1/2} \sum_{l=0}^{\infty} \frac{x^l}{(2l+1)l!}$$

$$- \sum_{m=1}^{\infty} \frac{(m-1)! 2^{m} x^{m}}{(2m)!}$$ \hspace{1cm} (89)
Rowlinson's reduced length is defined by

\[ \phi = \frac{d}{r_m} \]  

(90)

so that

\[ c = A^{1/n} \phi \]  

(91)

and

\[ c = \left( \frac{A}{T^*} \right)^{1/n} \left( 1 + \frac{F(x)}{n} \right). \]  

(92)

It can be found that for any large \( n \) the maximum cut-off parameter for a Lennard-Jones \( (n, \frac{n}{2}) \) potential occurs at \( x = 0.12 \) and that

\[ c_{\text{max}} = (0.12A)^{1/n} \left( 1 - \frac{0.646}{n} \right) \]  

(93)

which for a Lennard-Jones \( (12-6) \) potential gives a maximum cut-off parameter of 0.89.

The repulsive potential

\[ u(r) = Ae \left( \frac{\sigma}{r} \right)^n \]  

(35)

is a special case of Rowlinson's work. When the potential is of the form given in Equation (35), the cut-off parameter becomes
\[ c = \left( \frac{A}{T^*} \right)^{1/n} \left( 1 + \frac{\gamma}{n} \right), \] (94)

which is the same as the high-temperature limit of Equation (92).

Equation (94) predicts an effective hard sphere diameter of zero as \( T \to \infty \) as compared to a negative diameter predicted by Equation (86). A system of molecules with soft exponential repulsive (and attractive) forces with no hard core diameter would be expected to behave more ideally as temperature increases. Equation (94) predicts that the isochors in Figure 3 are not linear as \( 1/T \) goes to zero, but decreases very rapidly to unity.

It should be noted that expansion of \( (A/T^*)^{1/n} \) gives as the cut-off parameter in Equation (94)

\[ c = (1 + \frac{\gamma}{n})[1 + \frac{1}{n} \ln(\frac{A}{T^*}) + \frac{1}{2n^2} \ln^2(\frac{A}{T^*})+...], \] (95)

which to the order of \( 1/n \) is the same as Equation (86). In the derivation of both Equations (86) and (94), terms of order greater than \( 1/n \) were truncated. Equation (95) is not valid as \( T \to \infty \).

Sigma may be found by applying Equation (94) to the diameter obtained from Equation (29) at \( T_0 \). The values obtained are in Appendix A and will be used to compare the
hard sphere diameter at various temperatures in the next section.

3. The Cut-off Parameter of Barker and Henderson

Barker and Henderson used as their diameter

\[ d = \int_{0}^{\sigma} \{1 - \exp[-\beta u(r)]\} \, dr \tag{20} \]

The cut-off parameter corresponding to Equation (20) is

\[ c = \int_{0}^{1} \{1 + \exp[-\beta u(x)]\} \, dx \tag{96} \]

The integral can be determined easily numerically. Barker and Henderson's cut-off parameter will be used in the next section to compare diameters. The values predicted for sigma are listed in Appendix B.

C. Comparison of the Hard Sphere Diameter of Methane

In this section, the hard-sphere diameter of methane will be compared for various isochors over a range of temperatures using Equations (86), (94), and (96).

The variation of diameter with temperature is shown for \( n = 28 \) in Figure 5 and for \( n = 12 \) in Figure 6. The
value of sigma calculated for the density of 0.240 gm/cc was used. Since the cut-off parameter is not dependent on density the diameter predicted for only one isochor need be compared. All other isochors will have diameters, which show a similar variation with temperature. There is a shift in the diameter with density, which depends on the equation used to determine sigma. This shift in diameters will be investigated in the next section when the variation of the predicted value of sigma is discussed.

All three equations predict a decrease in diameter with increasing temperature. Since Equations (86) and (94) were both arrived at by the Taylor expansion of the configurational partition function in powers of 1/n, they would be expected to predict approximately the same diameter over moderate temperatures. Equation (95) indicates that Equations (86) and (94) do approximate each other over a moderate temperature range. Figure 5 shows a difference in the predicted diameters, while Figure 6 shows very close agreement. The reason there is not better agreement in Figure 5 is the value of sigma used for Equation (86) was calculated from Equation (80), which Equation (86) approximates to the order (c-1) while the value of sigma used for Equation (94) was determined by applying Equation (94) to the hard sphere diameter at T_0. The values of the cut-off
parameter for \( n = 28 \) are listed in Table 2 for temperatures of 200°K to 2000°K. From Table 2 it is obvious that for the same sigma Equations (86) and (94) predict close to the same diameter over the temperature range investigated.

### TABLE 2

**THE METHANE CUT-OFF PARAMETER**

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>Equation 86</th>
<th>Equation 94</th>
<th>Equation 96</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>1.063044</td>
<td>1.064851</td>
<td>0.999711</td>
</tr>
<tr>
<td>300</td>
<td>1.048563</td>
<td>1.049542</td>
<td>0.998771</td>
</tr>
<tr>
<td>400</td>
<td>1.038289</td>
<td>1.038814</td>
<td>0.997318</td>
</tr>
<tr>
<td>600</td>
<td>1.023808</td>
<td>1.023880</td>
<td>0.993718</td>
</tr>
<tr>
<td>800</td>
<td>1.013533</td>
<td>1.013496</td>
<td>0.989926</td>
</tr>
<tr>
<td>1200</td>
<td>0.999053</td>
<td>0.998926</td>
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<tr>
<td>1600</td>
<td>0.988778</td>
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<tr>
<td>2000</td>
<td>0.980809</td>
<td>0.989867</td>
<td>0.971519</td>
</tr>
</tbody>
</table>

In order to compare the Barker and Henderson diameter given in Equation (96) with the diameters predicted by Equations (86) and (94), the hard sphere diameter was
FIGURE 5: EFFECTIVE HARD SPHERE DIAMETER OF METHANE FOR \( \rho = 0.24 \text{ g/cm}^3 \) AND \( N = 28 \).
FIGURE 6: EFFECTIVE HARD SPHERE DIAMETER OF METHANE FOR $\rho = 0.24$ GM/CC AND $N = 12$. 
determined not for the Lennard-Jones (12-6) and (28-7) potentials, but for the repulsive potential given in Equation (35), which is the same potential used to arrive at Equations (86) and (94). The hard sphere diameter predicted by Equation (96) is zero for 1/T equal to zero. Unlike the diameter predicted by Equations (86) and (94) the Barker and Henderson diameter is never greater than sigma, which would not be correct for a purely repulsive potential.

D. Dependency of Sigma Upon Density

As is evident from the previous sections, the calculated value of sigma is dependent on density and consequently the effective hard sphere diameter predicted changes with density. The variation of the calculated values of sigma with density are shown in Figure 7 for n = 12 and n = 28. Equation (80) was used to determine the values of sigma used in Figure 7.

Part of the variation may be due to truncated terms of order 1/n² and β/n. The values of sigma predicted for n = 28 are slightly more consistent than those for n = 12. The reason for the values of sigma being more consistent for n = 28 may be that the truncated terms of order 1/n², β/n, and higher may be less significant than for n = 12. The values of the cut-off parameters are greater than unity
for both values of n indicating that the expansion in 1/n of the potential given in Equation (32) does not satisfactorily approximate the configurational partition function at the low temperatures of the methane data. Expansion of the configurational partition function in 1/n and 1/m, which is similar to Rowlinson's expansion when m = n/2, would yield a better value of sigma for methane, but would remove the attractive term from the equation of state.

The Lennard-Jones potential does not adequately describe the true intermolecular pair potential. Even if the configurational partition function was expanded in 1/n and 1/m a density dependence would still prevail due to an inadequate potential. Better representations of the intermolecular potential have been proposed. Among these are the Kihara, which possesses a parameter to take into account the molecular core size; the numerically tabulated potential of Dymond and Alder [23], which uses a multivariational technique to find the optimum potential function; and the Mason and Rice [24] exp-six potential.

The temperature $T_0$ at which the slope $\left( \frac{\partial P}{\partial T} \right)_{N,V}$ is taken varies with density. The effect of the variation can be seen in Figure 7 as $T_0$ is greatest for the densities of 0.206 gm/cc and 0.221 gm/cc. There is a slight rise in the curve in Figure 7 for both $n = 12$ and $n = 28$ at the above densities. The reasons variations in $T_0$ effect the predicted
value of \( \sigma \) are the slope \( \left( \frac{\partial P}{\partial T} \right)_{N,V} \) only approximates \( a(\rho,d) \) over the range of temperature at which \( T_0 \) is found and more significantly the expansion has left out significant terms which vary with temperature and density. Figure 8 shows the variation of the effective hard sphere diameter at \( T_0 \) with density. If the temperature dependent terms had been neglected in calculating \( \sigma \), \( \sigma \) would have varied as the diameter in Figure 8. It is obvious from Figure 8 that without the correction for temperature the calculated values of \( \sigma \) would change more with density.

Even with the exact potential function and without significant truncation errors at high density there would still be a variation in the calculated values of \( \sigma \). Equation (29) is not an exact representation of the hard sphere diameter. The variation in \( \sigma \) would be small however. With the exact potential and without significant truncation errors \( \sigma \) could be determined accurately directly from the compressibility factor.

E. Calculation of the Compressibility Factor

The first term of the compressibility factor, \( a(\rho,d) \), was calculated over a temperature range of 150 to 600°K for the twelve densities for which the value of \( \sigma \) has been evaluated. The leading term was calculated using Equation (80)
FIGURE 7: VARIATION OF THE CALCULATED SIGMA WITH DENSITY.
FIGURE 8: EFFECTIVE HARD SPHERE DIAMETER AT T₀.
for both \( n = 12 \) and \( n = 28 \). The values are listed in Appendix C.

To compare the calculated values to the experimental data \( a(\rho,d) \) is assumed to remain constant over the temperature range of the date and a least squares fitting of the equations

\[
    z = a(\rho,d) + b(\rho)/T^* \tag{97}
\]

and

\[
    z = a(\rho,d) + b(\rho)/T^* + c(\rho)/T^{*2} \tag{98}
\]

was performed. From the values of \( a(\rho,d) \) in Appendix C it does not appear that \( a(\rho,d) \) is very constant over the temperature range of 150 to 275°K over which the experimental data was taken. The correct value would be much more constant however.

The values calculated decrease more rapidly with increasing temperatures than the actual due to the expansion of the configurational partition function about the repulsive potential only, which is not satisfactory at the low temperatures of the methane data.

Table 3 lists the values determined for \( a(\rho,d) \) for the least squares fittings of Equations (97) and (98) and for the calculated \( a(\rho,d) \) at 150 and 300°K. Since \( (1/\rho k) \left( \partial P/\partial T \right)_{N,V} \) at \( T_0 \) is very close to the least squares value of
the constant term there is naturally fair agreement between the calculated $a(\rho,d)$ and the least squares value of the constant term. $T_0$ is between 150 and 300°K for the densities investigated.

The value of $b(\rho)$ was calculated using Equation (74). The integration was performed numerically using Simpson's rule. The value used for sigma corresponds for each density to the value tabulated in Table 1. The results are tabulated in Tables 4 and 5. To obtain an idea of the actual magnitude of $b(\rho)$ the values obtained in the least squares fitting of Equations (12), (97), and (98) are also listed.

The values calculated for $b(\rho)$ are all much larger than indicated by the least squares fitting of the experimental data. The calculated values of $b(\rho)$ are so large that combining $a(\rho,d)$ and $b(\rho)/T^*$ yields a negative value for the compressibility factor up to several hundred degrees Kelvin.

The calculated values of $b(\rho)$ are larger for $n = 28$ than for $n = 12$, while the actual $b(\rho)$ should be smaller for $n = 28$ as the reduced temperature is smaller for $n = 28$. The cause of the reversal is that the value of sigma for $n = 28$ was calculated as being greater than for $n = 12$, while the opposite is true when sigma is determined from the Boyle temperature and volume. The values of sigma are not the only cause of $b(\rho)$ being incorrect. If the literature values
listed in Table 1 were used $b(\rho)$ would have been calculated as being even larger. The potential $u_m(r)$ does not sufficiently describe the attractive portion of the potential.
### Table 3

**The Leading Term \(a(\rho, d)\) for Methane**

<table>
<thead>
<tr>
<th>Density (gm/cc)</th>
<th>Experimental</th>
<th>Equation (97)</th>
<th>Equation (98)</th>
<th>Equation (8)</th>
<th>Equation (8)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>T=150°K</td>
<td>T=300°K</td>
<td>T=150°K</td>
<td>T=300°K</td>
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<tr>
<td>0.158</td>
<td>1.766</td>
<td>1.797</td>
<td>1.811</td>
<td>1.749</td>
<td>1.847</td>
</tr>
<tr>
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<td>1.852</td>
<td>1.786</td>
<td>1.892</td>
</tr>
<tr>
<td>0.179</td>
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<td>2.263</td>
<td>1.960</td>
<td>1.885</td>
<td>2.011</td>
</tr>
<tr>
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<td>1.954</td>
<td>2.094</td>
<td>2.042</td>
<td>1.959</td>
<td>2.103</td>
</tr>
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<td>0.206</td>
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<td>2.208</td>
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<td>2.299</td>
</tr>
<tr>
<td>0.221</td>
<td>2.197</td>
<td>2.447</td>
<td>2.343</td>
<td>2.231</td>
<td>2.438</td>
</tr>
<tr>
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<td>3.048</td>
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</tr>
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<td>3.271</td>
<td>3.682</td>
<td>3.424</td>
<td>3.736</td>
</tr>
<tr>
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<td>--</td>
<td>4.094</td>
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<td>4.116</td>
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<table>
<thead>
<tr>
<th>Density (gm/cc)</th>
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<th>Equation (98)</th>
<th>Equation (12)</th>
<th>Calculated From Equation (74)</th>
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</thead>
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<td>-2.15</td>
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<td>-3.01</td>
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<td>-3.74</td>
<td>-3.56</td>
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<td>-10.794</td>
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TABLE 5

$b(p)$ FOR n = 28

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<th>Equation (97)</th>
<th>Equation (98)</th>
<th>Equation (12)</th>
<th>Calculated From Equation (74)</th>
</tr>
</thead>
<tbody>
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<td>0.158</td>
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<td>-0.86</td>
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</tr>
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<td>-1.53</td>
<td>-0.61</td>
<td>- 5.273</td>
</tr>
<tr>
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<td>-1.26</td>
<td>-0.85</td>
<td>- 5.663</td>
</tr>
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<td>-1.13</td>
<td>-1.47</td>
<td>-0.82</td>
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<td>-1.22</td>
<td>-1.58</td>
<td>-0.88</td>
<td>- 7.037</td>
</tr>
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<td>0.240</td>
<td>-1.34</td>
<td>-1.67</td>
<td>-1.07</td>
<td>- 7.788</td>
</tr>
<tr>
<td>0.265</td>
<td>-1.50</td>
<td>-1.69</td>
<td>-1.33</td>
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<td>-1.57</td>
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<td>-1.83</td>
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<td>0.341</td>
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<td>--</td>
<td>--</td>
<td>-13.589</td>
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IV. CONCLUSIONS

The effective hard sphere diameter is the diameter which when used in the hard sphere equation of state (Equation (29)) predicts the repulsive portion of the potential's contribution to the compressibility factor. It was found that the effective hard sphere diameter of methane can be determined by applying the equation of state (Equation (79)) to experimental data for methane at $T_0$, the temperature for which $(\frac{\partial^2 P}{\partial T^2})_{N,V}$ is zero. At $T_0$ truncated errors in the equation of state can be considered small as isochors are very linear over a range of temperatures in the region near $T_0$. The contribution of the repulsive portion of the potential of a Lennard-Jones $(n,m)$ potential to the equation of state was found to equal the slope $(\frac{\partial P}{\partial T})_{N,V}$ divided by $\rho k$.

Sigma is the radial distance at which the potential is zero. From the equation of state and the effective hard sphere diameter at $T_0$ it was possible to determine the best value of sigma for a Lennard-Jones $(n,m)$ intermolecular pair potential. The values calculated for sigma were found to depend on the isochor used. Part of the dependency is due to small truncation errors, however also significant is the
inadequacy of the intermolecular potential used. The values of sigma calculated are around 3.34 Å for a Lennard-Jones (28-7) potential and 3.21 Å as compared to 3.57 and 3.82 Å for sigma determined from the second virial coefficient.

By applying the equation of state to the values of sigma calculated from the experimental data, it was possible to calculate the effective hard sphere diameter over a range of temperatures. The diameters calculated were compared with the diameters predicted by applying the cut-off parameter of Rowlinson and by the cut-off parameter of Barker and Henderson for the repulsive portion of the Lennard-Jones potential. The cut-off parameter is the effective hard sphere diameter divided by sigma. It was found that the effective diameter decreases with increasing temperature. There is close agreement between the effective hard sphere diameter predicted by the equation of state and the Rowlinson cut-off parameter. This agreement is due to the moderate temperature range investigated.

At very high temperatures the cut-off parameter predicted by the equation of state is negative, (while Rowlinson's cut-off parameter goes to zero). A negative cut-off parameter corresponds to a negative diameter. At high temperatures the equation of state is unsatisfactory. To correctly predict the cut-off parameter at very high temperature a
potential possessing a hard core term is necessary. Using a potential containing a hard core term would lead to a limiting value of the cut-off parameter at high temperatures related to the hard core size.

It was found that an equation of the form of the equation of state, that is an equation for the compressibility factor with an inverse temperature expansion and a \( \ln T^* \) term, cannot satisfactorily describe the deviation of the experimental pressure from the pressure of a linear van der Waals isochor. The natural logarithm arises due to the choice of a Lennard-Jones potential.

Because of the inadequacy of the Lennard-Jones potential it would be of interest in future work to replace it by a more adequate potential. Choice of an adequate potential would depend upon not only the ability to describe the true potential and its hard core term, but the difficulties encountered in expanding the configurational partition function.
REFERENCES


APPENDIX A

VALUE OF SIGMA CALCULATED FROM ROWLINSON'S CUT-OFF PARAMETER

This appendix lists the values of sigma calculated applying Equation (94), which is the Rowlinson cut-off parameter for the repulsive potential given in Equation (35). The diameter was first determined by setting $a(\rho,d)$ in Equation (29) equal to $(1/\rho k)(\frac{\partial p}{\partial T})_N,V$ at $T_0$ for each density. Sigma is then given by Equation (84).

### TABLE 6
CALCULATED VALUE OF SIGMA METHANE USING EQUATION (94)

<table>
<thead>
<tr>
<th>Density gm/cc</th>
<th>Sigma (28-7) Angstroms</th>
<th>Sigma (12-6) Angstroms</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.158</td>
<td>3.3135</td>
<td>3.1188</td>
</tr>
<tr>
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<td>3.3117</td>
<td>3.1206</td>
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<td>3.1243</td>
</tr>
<tr>
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<td>3.1327</td>
</tr>
<tr>
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<td>3.3253</td>
<td>3.1668</td>
</tr>
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<td>0.221</td>
<td>3.3209</td>
<td>3.1560</td>
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<td>3.3066</td>
<td>3.1079</td>
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<td>3.0983</td>
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<td>3.3200</td>
<td>3.0882</td>
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<tr>
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<td>3.3240</td>
<td>3.0734</td>
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</tbody>
</table>
APPENDIX B

CALCULATION OF SIGMA FOR METHANE USING BARKER AND HENDERSON'S CUT-OFF PARAMETER

As was done to find sigma in Appendix A, the diameter was determined by setting Equation (29) equal to \((1/\rho k) \left( \frac{\partial P}{\partial T} \right)_{N,V} \) at \( T_0 \). To find sigma Equation (96) was evaluated numerically for the Barker and Henderson cut-off parameter. The repulsive potential given in Equation (35) was used for \( u(r) \).

TABLE 7

CALCULATED SIGMA USING EQUATION (96)

<table>
<thead>
<tr>
<th>Density gm/cc</th>
<th>Sigma (12-6) Angstroms</th>
<th>Sigma (28-7) Angstroms</th>
</tr>
</thead>
<tbody>
<tr>
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<td>3.5102</td>
</tr>
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APPENDIX C

CALCULATED VALUES OF THE LEADING TERM $a(p,d)$

The values of $a(p,d)$ are listed in Tables 8 and 9 for temperatures between 150 and 600°K. Equation (80) was used to determine $a(p,d)$ with $a(p,\sigma)$ being

$$a(p,d) = a(p,d)\bigg|_{c=1}$$

$$= \frac{1+\eta^*+\eta^*^2-\eta^*^3}{(1-\eta^*)^3}.$$  

The value of $\sigma$ used to calculate $\eta^*$ were taken from Table 1.
TABLE 8

\[ a(\rho, d) \text{ for } n = 12 \]

<table>
<thead>
<tr>
<th>Density gm/cc</th>
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<th>250</th>
<th>300</th>
<th>350</th>
<th>400</th>
<th>450</th>
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<th>550</th>
<th>600</th>
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<td>1.879</td>
<td>1.852</td>
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</table>
TABLE 9

\( a(\rho, d) \) for \( n = 28 \)

<table>
<thead>
<tr>
<th>Density ( \text{gm/cc} )</th>
<th>150</th>
<th>200</th>
<th>250</th>
<th>300</th>
<th>350</th>
<th>400</th>
<th>450</th>
<th>500</th>
<th>550</th>
<th>600</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.158</td>
<td>1.811</td>
<td>1.784</td>
<td>1.765</td>
<td>1.749</td>
<td>1.735</td>
<td>1.723</td>
<td>1.712</td>
<td>1.703</td>
<td>1.695</td>
<td>1.687</td>
</tr>
<tr>
<td>0.164</td>
<td>1.852</td>
<td>1.825</td>
<td>1.804</td>
<td>1.786</td>
<td>1.772</td>
<td>1.759</td>
<td>1.748</td>
<td>1.738</td>
<td>1.729</td>
<td>1.721</td>
</tr>
<tr>
<td>0.179</td>
<td>1.960</td>
<td>1.929</td>
<td>1.905</td>
<td>1.885</td>
<td>1.868</td>
<td>1.854</td>
<td>1.841</td>
<td>1.829</td>
<td>1.819</td>
<td>1.809</td>
</tr>
<tr>
<td>0.189</td>
<td>2.042</td>
<td>2.008</td>
<td>1.981</td>
<td>1.959</td>
<td>1.941</td>
<td>1.925</td>
<td>1.910</td>
<td>1.898</td>
<td>1.886</td>
<td>1.876</td>
</tr>
<tr>
<td>0.206</td>
<td>2.208</td>
<td>2.167</td>
<td>2.135</td>
<td>2.109</td>
<td>2.087</td>
<td>2.068</td>
<td>2.051</td>
<td>2.036</td>
<td>2.023</td>
<td>2.010</td>
</tr>
<tr>
<td>0.221</td>
<td>2.343</td>
<td>2.297</td>
<td>2.261</td>
<td>2.231</td>
<td>2.206</td>
<td>2.185</td>
<td>2.166</td>
<td>2.149</td>
<td>2.133</td>
<td>2.119</td>
</tr>
<tr>
<td>0.240</td>
<td>2.517</td>
<td>2.463</td>
<td>2.421</td>
<td>2.387</td>
<td>2.359</td>
<td>2.334</td>
<td>2.312</td>
<td>2.292</td>
<td>2.274</td>
<td>2.258</td>
</tr>
<tr>
<td>0.265</td>
<td>2.802</td>
<td>2.736</td>
<td>2.685</td>
<td>2.643</td>
<td>2.607</td>
<td>2.577</td>
<td>2.550</td>
<td>2.525</td>
<td>2.503</td>
<td>2.483</td>
</tr>
<tr>
<td>0.282</td>
<td>3.028</td>
<td>2.952</td>
<td>2.893</td>
<td>2.845</td>
<td>2.804</td>
<td>2.768</td>
<td>2.737</td>
<td>2.709</td>
<td>2.684</td>
<td>2.661</td>
</tr>
<tr>
<td>0.297</td>
<td>3.257</td>
<td>3.170</td>
<td>3.103</td>
<td>3.048</td>
<td>3.001</td>
<td>2.961</td>
<td>2.925</td>
<td>2.894</td>
<td>2.865</td>
<td>2.839</td>
</tr>
</tbody>
</table>
APPENDIX D

The following program is the program used to determine the effective hard sphere diameter of methane at $T_0$. $S(I)$ is the slope $(\partial P/\partial T)_N,V$ of the $I^{th}$ isochor at $T_0$ in atm per °K. $\rho(I)$ is the density of the $I^{th}$ isochor in gm per cc. The upper and lower limits of $\eta$ are one and zero. To calculate the slope from the hard sphere equation of state $\eta$ is taken as the average of the two limits. The calculated slope is then compared to the experimental. If agreement is not within a specified value, the limit furtherest from the correct $\eta$ is redefined as the average and the procedure is repeated until the correct $\eta$ is found. Once $\eta$ is known the diameter may be calculated.
C PROGRAM TO FIND H. S. DIA. OF METH., ANGSTROMS

DIMENSION S(12), PHD(12)
B=16.043/0.0552
READ 1,(S(I), I=1,12)
READ 1, (PHD(I), I=1,12)
DO 2 I=1,12
AEXP=H*S(I)/RH(1,I)
ETA1=0.
ETA2=1.
ETA=(ETA1+ETA2)/2.
ACAL=(1.0+ETA*ETA+2.*ETA**3)/(1.0-ETA)**3
TEST=ABS(AEXP-ACAL)
IF (0.0001<TEST), 5,4
IF (AEXP<ACAL), 6,7
6 ETA2=ETA.
GO TO 3
7 ETA1=ETA.
GO TO 3
8 D=(60.*ETA*16.043/(3.14159*PHD(I)*6.0225)**(1./3.))
2 PRINT A,D,PSD(I)
1 FORMAT(12.6,3)
8 FORMAT(2X, 2PD=F10.6, 3X, 4HRH0=F10.6)
STOP
END
The next program solves for sigma and the effective hard sphere. Equations (29) and (80) are used to determine sigma. From the value of sigma the hard sphere diameter is predicted using Equation (86) to calculate the cut-off parameter over a temperature range of 150 to 2775°K. RHO(I) is the density in gm per cc. S(I) is \( \left( \frac{\partial P}{\partial \Omega} \right)_{N,V} \) at \( T_0 \) in atm per °K. TEMP(I) is the temperature \( T_0 \) in °K. It is necessary to specify the Lennard-Jones parameters \( \alpha_N, \alpha_M \), and \( ESPK ( = \varepsilon/k) \).
C PROGRAM TO FIND SIGMA + H S DIA OF METHANE

C U(R) = A * E * (SIGMA/R)**AN - (SIGMA/R)**AM

AN = 12
AM = 6

ESPK = 137

DIMENSION RHOD(12), S(12), TEMP(12)

READ 1, (RHOD(I), I=1, 12)
READ 1, (S(I), I=1, 12)
READ 1, (TEMP(I), I=1, 12)

GAMMA = .57721566

CN = AM / (AN - AM) * (AN / AM) * (AN / (AN - AM))

DO 2 I = 1, 12

ALNC = ALOG(CN * ESPK / TEMP(I))

D1 = 2
D2 = 4

RD = .60225 * RHOD(1) / 16.03

SEXP = S(1) * 16.043 / 82.0552 / RHOD(1)

8 D = (D1 + D2) / 2,

XI = 3.14159265 * RD * N**3 / 6,

ZHS = 2. * XI * (2. * XI) / (1. - XI)**3

DZHS = 4. * (1. + XI**5 * XI**2) / (1. - XI)**4

SCAL = 1. * ZHS + 3. * (GAMMA + ALNC) * XI * DZHS / AN

TEST = ABS(SEXP * SCAL)

IF (.0001 = TEST) 4, 5, 5

4 IF (SXP * SCAL) 6, 7, 7

D2 = D

D1 = D

GO TO 8

6 GO TO 8

7 D1 = D

GO TO 8

5 PRINT 11, D, RHOD(1)

T = 125

DO 2 J = 2, 100

T = T + 25

ALNC = ALOG(CN * ESPK / T)

DD = D * (1. + (GAMMA + ALNC) / AN)

PRINT 9, DD, T

2 CONTINUE

1 FORMAT (12F6.3)

9 FORMAT (X, 4HD14=F10.6, 3X, 2HT=F8.2)

11 FORMAT (2X, 6HSIGMA=F10.6, 2X, 4HRHOD=F10.6)

STOP

END
The third program determines the coefficient of the inverse temperature term in the equation of state (Equation (79)). It is necessary to specify the Lennard-Jones parameters $AN$, $AM$, and $ESPK$ ($=\varepsilon/k$). The integration is performed using Simpson's rule. While the upper limit of the actual integral is infinity, $(FS+GS)\times U(S)$ goes to zero rapidly, so that using 60 as the upper limit is satisfactory. $RII(I)$ is the density in gm per cc and $SIGMA(I)$ is the value of sigma in angstroms.
PROGRAM TD CALC R FOR METHANE, Z=A*B/T+CLN(T)  D-6

U(R)=A*E*((SIGMA/R)*AN*(SIGMA/R)*AM)

AN=12.
AM=6.

DIMENSION RH(12),SIGMA(12)
READ 1B*(RH(I),I=1,12)
READ 1B*(SIGMA(I),I=1,12)
GAMMA=577215*6
FM=1.
PM=0.
HM=M=2
DO 2 I=1,MM
PM=PM+1.
2 FM=FM*PM
PN=0.
N=6.
FN=1.
NN=N=2
DO 3 I=1,NN
PN=PN+1.
3 FN=FN*PN
AN=AN/(AN*AM)*(AN/AM)**(AN/(AN-AM))
DO 15 III=1,12
RHO=H(III)
D1A=SIGMA(III)
RD=60025*RHO/16.043
C BINT=INT= INT OF INTERVALS=2N+4
INT=1000.
BINT=1000.
C BB=UPPER LIMIT
BB=60.
C AA=LOWER LIMIT
AA=5.
S=0.
SUM=0.
RH=(RB-AA)/BINT
DO 7 I=1,INT
S=S+RH
US=S*MM/FM
DS=S*S*XI/(2.0*XI+1.0)**2+2.0*S*XI*XI
ALS=S*S*XI/2.0+1.0+2.0*XI
SS=12.*XI*(1.0+2.0*XI)
SS=S*S*S*(1.0+XI)**2+6.0*XI*(1.0+XI)*S**2+16.*S**2*XI**2-SSS
Y=EXP(-SS)
DEN=12.*XI*Y+ALS+SS
FS=DS+S*4*Y/(DEN**2)
GS=ALS*S*Y/DEN
FLL=(FS+GS)*US
ALT=(-1.)*I
IF(ALT).LT.11,11,12
11 SUM = SUM + 2 * FLI
   Go To 7
12 SUM = SUM + 4 * FLI.
   7 Continue

   B = A * A * B * H * SUM * X1
   PRINT 4, B, RH0
   15 Continue

   4 FORMAT (6X, 2HE=F10.6, 3X, 4HRHO=F10.6)
   18 FORMAT (12E6, 3)
   Stop
   End