i = counter
o = outside or feed condition
R = symbol for monoethyl adipate, $(CH_2)_4(COONa)(COOC_2H_5)$
s = shell
S = adipate, $(CH_2)_4(COONa)_2$
t = tube

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Manuscript received June 25, 1973; revision received July 26 and accepted July 30, 1973.

A Note on the Blasius Problem for Viscoelastic Fluids

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Denn (1967) considered the fundamental problem of boundary-layer flow over a semi-infinite flat plate with zero pressure gradient for a class of power-law viscoelastic fluids satisfying a constitutive relation of the Rivlin-Ericksen type. A perturbation about the inelastic flow was made by assuming a solution of the form

$$f(x,\eta) = f_0(\eta) + \epsilon\, x^{-s/n+1} f_1(\eta) + \text{higher order terms} \tag{1}$$

where n and s are the power-law exponents for shear-stress and normal-stress, respectively, and ϵ is an elastic parameter. Equation (1) may also be viewed as an inverse coordinate expansion valid for large x. The equations for f_0 and f_1 are found to be the following:

$$f_0''' + \frac{1}{n(n+1)} f_0 f_0''^{(2-n)} = 0 \tag{2}$$

$$\begin{aligned} f_1''' &+ \frac{2-n}{n(n+1)} f_0 f_0''^{(1-n)} f_1 \\ &+ \frac{s}{n(n+1)} f_0' f_0''^{(1-n)} f_1' + \frac{1-s}{n(n+1)} f_0''^{(2-n)} f_1 \\ &= \frac{1}{n(n+1)} \left[\frac{s+1}{n(n+1)} f_0 f_0' f_0''^{(s+1-2n)} \right. \\ &\left. + \frac{n-s}{n^2(n+1)^2} f_0^3 f_0''^{(s+2-3n)} - (3-2s)\, f_0''^{(n+s-1)} \right] \end{aligned} \tag{3}$$

$$f_0(0) = f_0'(0) = 0; \quad f_0'(\infty) = 1 \tag{4}$$

$$f_1(0) = f_1'(0) = f_1'(\infty) = 0 \tag{5}$$

In these equations primes denote total derivatives. Denn obtained solutions for the cases ($n = 1$, $s = 2$) and ($n = 1$, $s = 1.5$) having values of $f_1''(0) = 0.03$ and -0.082, respectively.

Lockett (1969) showed that in the special case of a second-order fluid ($n = 1$, $s = 2$) there exists an infinite number of solutions to Equation (3) satisfying the boundary conditions (5). The difficulty is due to an eigensolution of the classical Blasius problem of the form

$$f_1(\eta) = A[f_0(\eta) - \eta f_0'(\eta)] \tag{6}$$

which satisfies the homogeneous version of (3) for any value of the constant A. This eigensolution, which is the first of an infinite, discrete set (see, for example, Van Dyke, 1964b), was first encountered by Alden (1948) in connection with the third-order boundary-layer approximation for the flat plate.

The correct solution for the second-order fluid was given by Davis (1967) who showed that a logarithmic term occurs in the expansion for $f(x, \eta)$. Thus, (1) must be replaced by

$$f(x,\eta) = f_0(\eta) + \frac{\epsilon}{x}\left[\log \frac{x}{\epsilon} f_{11}(\eta) + f_{12}(\eta) \right] + \text{higher order terms} \tag{7}$$

The solution for $f_{11}(\eta)$ is found to be the eigensolution (6) with the constant A determined by the condition of exponential decay of vorticity. However, as in the analogous problem of Newtonian boundary-layer flow far downstream on a parabola (Van Dyke, 1964a), a unique solution for $f_{12}(\eta)$ cannot be obtained due to the presence of the eigensolution.

Consider now the general case of arbitrary (positive)

Table 1. Summary of Calculations; $n = 1$, $s = 1.5$

$f_1''(0)$		$\eta = 5$	$\eta = 10$	$\eta = 15$
10	$f_1 =$	0.569381×10^2	0.649677×10^2	0.669350×10^2
	$f_1' =$	0.515655×10^1	0.577827×10^0	0.273355×10^0
1	$f_1 =$	0.621493×10^1	0.741261×10^1	0.762405×10^1
	$f_1' =$	0.771544×10^0	0.626665×10^{-1}	0.293355×10^{-1}
0	$f_1 =$	0.579026×10^0	0.101760×10^1	0.103394×10^1
	$f_1' =$	0.284321×10^0	0.542649×10^{-2}	0.222220×10^{-2}
−.0820	$f_1 =$	0.117107×10^0	0.493461×10^0	0.4938118×10^0
	$f_1' =$	0.244388×10^0	0.735096×10^{-3}	-0.957544×10^{-8}
−10	$f_1 =$	-0.557801×10^2	-0.629325×10^2	-0.648671×10^2
	$f_1' =$	-0.458791×10^1	-0.566974×10^0	-0.268911×10^0

Table 2. Summary of Calculations; $n = 1$, $s = 2$

$f_1''(0)$		$\eta = 5$	$\eta = 10$	$\eta = 15$
10	$f_1 =$	0.510249×10^2	0.525263×10^2	0.525316×10^2
	$f_1' =$	0.251100×10^1	0.177904×10^{-2}	0.647880×10^{-3}
1	$f_1 =$	0.564136×10^1	0.588648×10^1	0.589183×10^1
	$f_1' =$	0.355328×10^0	0.177676×10^{-2}	0.647880×10^{-3}
0	$f_1 =$	0.598752×10^0	0.704284×10^0	0.709630×10^0
	$f_1' =$	0.115808×10^0	0.177650×10^{-2}	0.647880×10^{-3}
−10	$f_1 =$	-0.498274×10^2	-0.511177×10^2	-0.511124×10^2
	$f_1' =$	-0.227938×10^1	0.177396×10^{-2}	0.647880×10^{-3}

n and s. The first eigensolution of the classical Blasius problem is the x-derivative of the Blasius solution (Van Dyke, 1964b; Stewartson, 1967; Libby and Fox, 1963). For the power-law fluid, it is readily verified that the x-derivative of the flat-plate solution is again an eigensolution, and it is reasonable to assume that it is the first eigensolution in the non-Newtonian case also. Thus, one obtains

$$\psi_1 = Ax^{-n/n+1}\,[f_0(\eta) - \eta f_0'(\eta)] \tag{8}$$

$$f_1(x, \eta) \equiv x^{-\frac{1}{n+1}}\psi_1 = Ax^{-1}[f_0(\eta) - \eta f_0'(\eta)] \tag{9}$$

which again yields the eigenfunction (6). Clearly, this eigensolution, being of order x^{-1}, belongs to the second term of the expansion (1) only when $s = n + 1$. For $s < n + 1$, the eigensolution is relegated to a higher order term. For $s > n + 1$, the first eigensolution (and possibly a higher order eigensolution as well) precedes the term of order $x^{-s/n+1}$. Thus, for $s < n + 1$ the asymptotic expansion for $f(x, \eta)$ begins as in Equation (1) while Equation (7) applies for $s = n + 1$.

Numerical solutions to Equations (2) to (5) were computed for the case $n = 1$. In accordance with the above analysis, unique solutions were obtained for $s < 2$. Table 1 summarizes the results for the case $s = 1.5$, for which a value of $f_1''(0) = -0.0820$ was obtained, in agreement with Denn's calculation. Similarly, solutions were obtained for $s = 1.75$ and 1.25 having values of $f_1''(0) = -0.260$ and $+0.129$, respectively. For comparison, the computations for $s = 2$ are summarized in Table 2. Here the presence of the eigensolution is evident as different values of $f_1''(0)$ yield different solutions, each having the same asymptotic form for $f_1'(\eta)$ as $\eta \to \infty$.

It follows from the above results that the conclusions originally reached by Denn are valid. In particular, the wall shear stress may be either increased or decreased due to the presence of fluid elasticity, depending on the value of s. This result stands in contradiction to a solution obtained by the momentum integral method (White, 1966). In addition, as pointed out by Davis (1967) in the case of the second-order fluid, the asymptotic solution for $f(x, \eta)$ indicates that the flow of a power-law viscoelastic fluid approaches the Blasius flow of a power-law inelastic fluid far downstream on the plate.

ACKNOWLEDGMENT

The author wishes to thank the referee for his valuable comments in the review of this note.

NOTATION

A = arbitrary constant
f = transformed stream function
f_0, f_1, f_{11}, f_{12} = functions of η in asymptotic expansion for $f(x, \eta)$
n = power-law exponent for shear stress
s = power-law exponent for normal stress
x = streamwise coordinate
ϵ = elastic parameter
η = similarity variable
ψ = stream function

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Manuscript received April 6, 1973; revision received August 30 and accepted September 4, 1973.

A Correlation for the Thermodynamic Properties of Supercritical Fluids at Very High Pressures

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Recently Breedveld and Prausnitz (1973) applied corresponding states theory to the *PVT* data of several simple fluids at very high pressures and developed generalized tables and charts for density, fugacity, enthalpy, and internal energy for the reduced temperature range 1 to 50 and for reduced pressures from 1 to 2000. This work extended the earlier work of Dodge (1944), Hougen et al. (1964), and Pitzer et al. (see Lewis et al., 1961) with respect to both T_R and P_R.

It is interesting to note that the several species, whose data were analyzed by Breedveld and Prausnitz in compiling their extensive tables and charts, are simple molecules of spherical or almost spherical geometry (Ar, N_2, He, H_2, Ne, Xe, CO, CH_4). In this note we propose a correlation with a statistical mechanical basis which allows calculation of pressures from densities and temperatures with results which agree very well with those in the supercritical region of the tables and charts of Breedveld and Prausnitz. It is quite general, with only three temperature-dependent parameters, and provides excellent predictions particularly in the region $T_R \geqq 4$, a situation no doubt due to the absence of the inflection of the isotherms that occurs at temperatures closer to $T_R = 1$. This note presents the correlation and comments on its accuracy and usage in predicting thermodynamic properties. The utility of such a correlation is that a large region of high temperature state data at all pressures and densities becomes available in the form of an equation of state which can be used to predict thermodynamic properties with the aid of a computer. With proper combinatorial rules (see Breedveld and Prausnitz, 1973; Leland and Chappelear, 1968), the correlation could be useful too for predicting the properties of mixtures.

THEORETICAL EQUATION OF STATE

The square-well intermolecular potential can be written

$$\begin{aligned} u(x) &= +\infty, & x &\leq 1 \\ &= -\epsilon, & 1 &< x \leq R \\ &= 0, & x &> R \end{aligned}$$

where x is a reduced length r/σ, σ being the hard-sphere diameter, ϵ an energetic parameter denoting strength of attractive potential energy of an interacting pair of molecules, and R a parameter denoting extent of the interaction, or more specifically, the width of the attractive well is (R-1) in reduced coordinates. Schrodt et al. (1972a, 1972b) derived an equation of state for $P = P(v, T)$ from statistical mechanics for fluids interacting with a square-well potential for $R = 1.85$ and showed that it could predict features of the liquid-gas coexistence region and the critical region qualitatively well. (See Kozak et al., 1972.)

It should be noted that the choice of the square-well potential model is based on expediency. It is the simplest potential representation that still incorporates the features required for real, condensable fluids. Certainly the square-well potential is not meant to be a precise representation of the intermolecular nature of fluids but the mathematical simplicity attendant to its usage compensates for this shortcoming. Added incentive for undertaking the construction of a correlation for the high temperature regime was provided by the intuitive feeling that the impulsive nature of the intermolecular forces for the square-well model (due to its step-function form) would more closely represent reality in this thermodynamic regime. Experience has shown that a value of $R = 1.85$ represents the nature of spherical molecules (Hirschfelder et al., 1954; Palyvos et al., 1967) for the square-well potential model.

The prediction of pressure via statistical mechanics is one of the more sensitive predictions, in that the pair correlation function $g(x)$ is weighted by the derivative of

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