Acoustic nonlinearity calculations using the Tait equation of state

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Abstract: Beyer's B/A parameter of acoustic nonlinearity was calculated for a series of n-alkane liquids using the Tait equation of state supplemented with specific heat data. Calculations of sound speed, sound speed derivatives, the two components of B/A, and the value of B/A itself were compared with experimental data taken from the literature. In addition, a comparison of the results with Ballou's rule (linear relation of B/A vs reciprocal sound speed) was made. It is concluded that an analytical equation of state is a convenient method of calculating acoustic properties and that this calculation is a sensitive technique for evaluating equations of state. The physical reason for this is that the acoustic parameters involve derivatives of volume and thus are a more stringent probe than an evaluation of the volume itself.

INTRODUCTION

Beyer's nonlinearity parameter B/A for a liquid, as a function of pressure, P, and absolute temperature, T, can be expressed as

\[ \frac{B}{A} = 2\rho \left( \frac{\partial^2 c}{\partial P} \right)_T + \frac{2cT\alpha}{C_p} \left( \frac{\partial c}{\partial T} \right)_P = \left( \frac{B}{A} \right)' + \left( \frac{B}{A} \right)'' \]  

(1)

in terms of the liquid density \( \rho \), sound speed \( c \), thermal expansion coefficient \( \alpha \), and specific heat at constant pressure, \( C_p \). Sound speed can be expressed as \( \sqrt{B_sV} = \sqrt{(C_p/C_v)B_T} = \sqrt{\gamma B_sV} \) where \( V = 1/\rho \) is specific volume, \( B_s \) is the adiabatic bulk modulus, \( B_T \) is the isothermal bulk modulus, and \( C_p \) and \( C_v \) are the specific heat capacities at constant pressure and constant volume respectively. All the required information to calculate B/A can be obtained from a pressure-volume-temperature (PVT) equation of state except \( C_p \). Experimental values of \( C_p \) will be used here. Note that only the heat capacity at zero pressure is required since \( C_p(T,P) \) can be calculated from \( C_p(T,0) \) using the equation of state. This method of calculating B/A from an equation of state and \( C_p \) has already been demonstrated using our equation of state and compared with experimental data for a series of n-alkane liquids and molten polyethylene [2]. The purpose of this paper is to follow the same procedure using the Tait equation to determine the sensitivity of the calculations to the form of the equation of state.

The Tait equation will be used in the form [3]

\[ V(T,P) = V_0 \exp(\alpha_0 T) [1 - C \ln(1 + P/(B_0 \exp(-B_1 T))] \]  

(2)

where \( V(T,P) \) is specific volume and there are five adjustable parameters: \( C, V_0, \alpha_0, B_0, \) and \( B_1 \). Using this equation, one can calculate analytical expressions for the first derivatives of volume (thermal expansion coefficient and bulk modulus) as well as the higher derivatives needed to evaluate the temperature and pressure derivatives of sound speed.

COMPARISON WITH EXPERIMENT

The first step is to determine the Tait equation parameters for the n-alkanes by fitting to experimental PVT data. Data for \( n = 7, 8, 9, 12, \) and 16 was taken from Boelhouwer [5] and for \( n = 5 \) from Belinskii and Ikramov [6]. For polyethylene melt, data was taken from Olabisi and Simha [7]. Fitting parameters are listed in Table 1. The calculated volumes differ from the experimental values by no more than 0.1 per cent. Experimental values of \( C_p(T,0) \) for the n-alkanes [8] and molten polyethylene [9] were taken from published values. Having all the needed input parameters, the sound speed for the n-alkane liquids can now be calculated. Calculated values at room temperature and zero pressure differ from experimental values by 2 to 5 per cent. Evaluating the derivatives of the sound speed and substituting into eq. 1, values of B/A were then determined. Results are listed in Table 1 along with experimental values calculated from Boelhouwer [10]. Calculated values at room temperature and zero pressure differ from experimental values by 3 to 16 per cent. These differences are judged to be approximately the same as uncertainty of the experimental measurements.
There is an empirical observation known as Ballou's rule that $B/A$ is a linearly increasing function of $1/c$ [11]. While only roughly true, this rule is useful in understanding how data on different material types is related. Some theoretical justifications of this rule have been presented [12,13]. The calculated results here tend to cluster around Ballou's rule but there is considerable scatter. The experimental results show similar scatter of roughly the same magnitude. In both cases, the pentane data is the furthest from the line.

Table 1. Tait parameters and $B/A$ (at $T = 293$ K and $P = 0$) for n-alkanes of varying chain length

<table>
<thead>
<tr>
<th>n</th>
<th>C</th>
<th>$V_0$ (cm$^3$/g)</th>
<th>$\alpha_0$ (10$^{-4}$/K)</th>
<th>$B_0$ (MPa)</th>
<th>$B_1$ (10$^{-4}$/K)</th>
<th>$B/A$ calc</th>
<th>$B/A$ exp</th>
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<tbody>
<tr>
<td>5</td>
<td>0.095125</td>
<td>0.99932</td>
<td>16.11</td>
<td>506.79</td>
<td>84.329</td>
<td>8.61</td>
<td>7.41</td>
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<tr>
<td>7</td>
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<td>0.96825</td>
<td>14.117</td>
<td>738.01</td>
<td>84.624</td>
<td>8.88</td>
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<td>8</td>
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<td>0.96816</td>
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<td>872.39</td>
<td>84.123</td>
<td>7.82</td>
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<td>9</td>
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<td>0.9772</td>
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<td>0.98028</td>
<td>10.498</td>
<td>752.32</td>
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<td>16</td>
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<td>9.4975</td>
<td>579.37</td>
<td>59.494</td>
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<td>45.185</td>
<td>9.38</td>
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</tbody>
</table>

CONCLUSIONS

The Tait equation gives a fair representation of the nonlinear acoustic behavior of n-alkane liquids. While the Tait equation fits volume data within an error of 0.1 per cent, the error in sound speed (based on first derivatives of volume) is about 5 per cent, and the error in $B/A$ (based on second derivatives of volume) is about 10 per cent. This uncertainty in $B/A$ is about the same as the accuracy of direct acoustic measurements. Ballou's rule is seen to apply only very crudely to these liquids.

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REFERENCES


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