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# Analysis of ultrasonic velocities in hydrocarbon mixtures

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## ABSTRACT

Ultrasonic velocity data on hydrocarbon mixtures was shown by Wang and Nur [JASA **89**, 2725 (1991)] to agree quite well with the predictions of a simple mixing rule (volume average of velocity). The same data is reanalyzed using Wood's formula and the time average approximation. Wood's formula for acoustic velocity is shown to be always less than the time average formula, which is itself always less than the simple mixing rule result. Although the volume average rule agrees best with the data on binary mixtures of 1-decene and 1-octadecene, all these formulas agree with the data to within 1% and, therefore, it is not possible to distinguish among the formulas using this data set. Similar results are also found for six multicomponent hydrocarbon mixtures.


## INTRODUCTION

Wang and Nur (1991) have published a series of measurements on ultrasonic velocities of liquid hydrocarbons and mixtures. They found that their data on hydrocarbon mixtures could be adequately explained using a simple mixing rule having the form of a volume average over the velocities of the pure hydrocarbon constituents

$$\langle V \rangle = \sum x_i V_i, \tag{1}$$

where the $x_i$s are the volume fractions of the constituents and the $V_i$s are their acoustic velocities. This result is somewhat surprising since the formula (1) has no known theoretical standing. Instead, I would have expected that a liquid mixture should obey Wood's formula (Wood, 1955)

$$V_W = (K_R/\rho)^{\frac{1}{2}}\,, \tag{2}$$

where the effective bulk modulus of the fluid mixture should be given by the harmonic mean (or Reuss average)

$$\frac{1}{K_R} = \sum \frac{x_i}{K_i} \tag{3}$$

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of the constituents' adiabatic bulk moduli ($K_i = \rho_i V_i^2$) and the average density is just

$$\rho = \sum x_i \rho_i. \tag{4}$$

Wood (1955) states that the formula (2) is "... applicable to a mixture of any two fluid media, which do not react chemically."

Wood's formula (2) is based on the fact that (3) is an exact result for the effective bulk modulus of a fluid mixture during quasistatic (isothermal) deformations, while the corrections needed to change from isothermal to adiabatic moduli are generally negligible at moderate temperatures. Wood's formula is therefore known to be correct for mixtures of Newtonian fluids at low frequencies, and should also give an adequate description of the ultrasonic data on hydrocarbons if the acoustic wavelengths in the fluid mixtures are sufficiently large. The center frequency of the transmitter in the Wang and Nur (1991) experiments was 2.25 MHz and a typical value of the wave speed was 1.3 km/s, so the wavelength is approximately 0.6 mm. Whether this wavelength is large or small depends on the manner of the fluid mixing: If the fluid is well-mixed at the microscopic level, then this is a large wavelength. However, if the fluid mixture typically contains blobs of one fluid floating in the other liquid, then the relative size of the wavelength depends on the size of these blobs. The mixtures were described as being "well-stirred" by Wang and Nur (1991). How this translates into the microstructure of the fluid mixture is unknown to the author, but if the hydrocarbons are miscible [as is most likely (Orr, 1992)] then the blobs should be of molecular size and Wood's formula should apply.

Another well-known estimate that might be suspected to work well in describing these data is the time average formula of Wyllie *et al.* (1957)

$$\left\langle \frac{1}{V} \right\rangle^{-1} = \left( \sum \frac{x_i}{V_i} \right)^{-1}. \tag{5}$$

Although this formula is not exact in any nontrivial limit, it is based in part on Fermat's principle of least traveltime through a mixture. The average traveltime will generally be greater than the minimum traveltime. Therefore, we expect the velocity estimate (5) to be a lower bound on the true velocity, whenever this formula applies. Applicability of the formula depends again on the wavelength, but this time the wavelength should be short compared to the inclusion size – since Fermat's principle may be derived from the eikonal equation which is a high frequency approximation.

To the author's knowledge, general relationships among these three estimates of the mixture velocity have not been noted before. The main purpose of this paper is to point out that these estimates are ordered, *i.e.*, Wood's formula always gives a smaller velocity than the time average, which is in turn always smaller than the volume average. The secondary purpose is to show that all three estimates give an adequate description (within 1%) of the ultrasonic data on hydrocarbon mixtures presented by Wang and Nur (1991).

## RELATIONS AMONG THE VELOCITY ESTIMATES

First, the general relationship between (1) and (5) is trivial, because it is well-known that the harmonic mean is always less than or equal to the mean (Abramowitz, 1972). Thus, I find

$$\left\langle \frac{1}{V} \right\rangle^{-1} \leq \langle V \rangle \,. \tag{6}$$

Then, for a binary mixture with $x_1 = x$ and $x_2 = 1 - x$, consider the difference

$$\left\langle \frac{1}{V} \right\rangle^2 - \frac{1}{V_W^2} = 2x(1-x) \left[ \left( \frac{\rho_1 \rho_2}{K_2 K_1} \right)^{\frac{1}{2}} - \frac{1}{2} \left( \frac{\rho_1}{K_2} + \frac{\rho_2}{K_1} \right) \right] \leq 0. \tag{7}$$

The fact that the right hand side is less than or equal to zero follows from the fact that the geometric mean is always less than or equal to the mean (Abramowitz, 1972). This result establishes the general relation for binary mixtures that

$$V_W \leq \left\langle \frac{1}{V} \right\rangle^{-1} . \tag{8}$$

Finally, to establish the result (8) for multicomponent mixtures, I consider

$$\left\langle \frac{1}{V} \right\rangle^2 = \left[ \sum x_i \left( \frac{\rho_i}{K_i} \right)^{\frac{1}{2}} \right]^2 = \left[ \sum (x_i \rho_i)^{\frac{1}{2}} (x_i / K_i)^{\frac{1}{2}} \right]^2 \leq \sum x_i \rho_i \sum x_i / K_i = \frac{1}{V_W^2}, \tag{9}$$

where the inequality in (9) follows from Cauchy's inequality (Abramowitz, 1972) for sums $(\sum a_i b_i)^2 \leq \sum a_i^2 \sum b_i^2$. Thus, (9) shows that (8) is a general result for multicomponent mixtures.

Combining these results, I obtain the set of inequalities

$$V_W \leq \langle 1/V \rangle^{-1} \leq \langle V \rangle \,. \tag{10}$$

These results have been derived for arbitrary multicomponent fluid mixtures, including but not restricted to binary mixtures.

## COMPARISON TO DATA

Table 1 presents the velocity data of Wang and Nur (1991) on 14 pure hydrocarbons, together with the known densities (Rossini et al, 1953; Weast and Grasselli, 1989), and the adiabatic bulk moduli computed from these values at 20° C. The estimated uncertainty in all the measured velocities (pure hydrocarbon as well as hydrocarbon mixtures) is stated to be 0.2 %. Including possible errors in the density values, an error propagation analysis shows that the error in computing the effective bulk modulus

needed in Wood's formula from the the measured velocities is about 0.5 %. It follows that the error in the computed velocities for the mixtures using Wood's formula is about 0.3 %. Table 2 compares the measured velocities of binary alkene mixtures as a function of volume fraction to the computed velocities using Wood's formula, the time average estimate, and the volume average estimate. All three computed values lie within 0.6 % of the measured values for all values of volume fraction. The volume average estimate is generally closer to the measured values than either of the other two estimates. However, when measurement errors in both the mixture velocities and the two pure hydrocarbon velocities used to compute these values are considered ($0.3 + 0.2 = 0.5$ %) together with the fact that the nominally "pure" hydrocarbon samples may have only been 90–96 % pure (Wang, 1988), the remaining differences are in fact too small to allow us to distinguish the three formulas – except for the fact that they are ordered, as I have shown. Note that the time average estimate does appear to be a lower bound on the measured values in all cases. The significance of this observation is unclear however, since the wavelengths are long compared to the expected scale of the mixed fluid microstructure.

Table 3 compares the measured velocities of multicomponent hydrocarbon mixtures to the same three velocity estimates. All three estimates are again within 1 % of the measured values, but now the volume average estimate is not always the one closest to that observed. The more complex fluid mixtures seem to agree somewhat better with Wood's formula. In all but one case, Wyllie's time average velocity is again observed to be a lower bound on the measured velocities. However, the main conclusion appears to be that the three estimates are again virtually indistinguishable for this data set.

## CONCLUSION

My conclusion is that the volume average formula used by Wang and Nur (1991) apparently gives good agreement with the velocity data for these hydrocarbon mixtures because in all cases the spread in velocities and densities is so small that Wood's formula, Wyllie's time average, and the volume average all give virtually the same results (within probable experimental error). In general, Wood's formula is expected to give reliable estimates even when the fluid constituents have widely differing acoustic speeds and densities (as in the case of liquid/gas mixtures), whereas the volume average formula is expected to have more limited applicability.

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Table 1. Measured ultrasonic velocities (Wang and Nur, 1991) and densities (Rossini et al, 1953; Weast and Grasselli, 1989) at 20° C and computed bulk moduli of various hydrocarbons.

| *Hydrocarbon* | $V_{meas}$ (km/s) | $\rho$ (g/cm$^3$) | $K$ (GPa) |
|---|---|---|---|
| Alkanes | | | |
| $C_8H_{18}$ | 1.194 | 0.7025 | 1.002 |
| $C_{10}H_{22}$ | 1.247 | 0.7301 | 1.135 |
| $C_{12}H_26$ | 1.294 | 0.7487 | 1.254 |
| $C_{14}H_{30}$ | 1.333 | 0.7628 | 1.355 |
| $C_{16}H_{34}$ | 1.354 | 0.7734 | 1.418 |
| | | | |
| Alkenes | | | |
| $C_8H_{16}$ | 1.188 | 0.7149 | 1.009 |
| $C_{10}H_{20}$ | 1.247 | 0.7408 | 1.152 |
| $C_{12}H_{24}$ | 1.290 | 0.7584 | 1.262 |
| $C_{14}H_{28}$ | 1.321 | 0.7713 | 1.346 |
| $C_{16}H_{32}$ | 1.349 | 0.7811 | 1.421 |
| $C_{18}H_{36}$ | 1.369 | 0.7888 | 1.478 |
| | | | |
| Naphthenes | | | |
| $C_6H_{12}$ | 1.276 | 0.7785 | 1.268 |
| $C_7H_{14}$ | 1.358 | 0.8098 | 1.493 |
| $C_8H_{16}$ | 1.402 | 0.8349 | 1.641 |

Table 2. Measured ultrasonic velocities (Wang and Nur, 1991) for a sequence of binary hydrocarbon mixtures at 20° C compared to velocities computed using Wood's formula, the time average equation, and a simple mixing rule. Data required for computing Wood's formula may be found in Table 1. The formula for the 1-decene/1-octadecene hydrocarbon mixture is $(C_{10}H_{20})_x(C_{18}H_{36})_{(1-x)}$, where $x$ is the volume fraction of 1-decene. Units of all velocities are km/s.

| $x$ | $V_{meas}$ | $V_W$ | $\langle 1/V\rangle^{-1}$ | $\langle V\rangle$ |
|---|---|---|---|---|
| 0.00 | 1.369 | 1.369 | 1.369 | 1.369 |
| 0.10 | 1.358 | 1.354 | 1.356 | 1.357 |
| 0.20 | 1.348 | 1.340 | 1.343 | 1.345 |
| 0.294 | 1.336 | 1.328 | 1.331 | 1.333 |
| 0.40 | 1.321 | 1.314 | 1.317 | 1.320 |
| 0.50 | 1.307 | 1.301 | 1.305 | 1.308 |
| 0.60 | 1.298 | 1.290 | 1.293 | 1.296 |
| 0.70 | 1.286 | 1.279 | 1.281 | 1.284 |
| 0.80 | 1.275 | 1.267 | 1.270 | 1.271 |
| 0.90 | 1.260 | 1.257 | 1.258 | 1.259 |
| 1.00 | 1.247 | 1.247 | 1.247 | 1.247 |

Table 3. Measured ultrasonic velocities (Wang and Nur, 1991) of six multicomponent hydrocarbon mixtures at 20° C compared to velocities computed using Wood's formula, the time average equation, and a simple mixing rule. Data required for computing Wood's estimate may be found in Table 1. Units of all velocities are km/s.

| *Hydrocarbon Mixture* | $V_{meas}$ | $V_W$ | $\langle 1/V \rangle^{-1}$ | $\langle V \rangle$ |
|---|---|---|---|---|
| $(C_{10}H_{22})_{.2}(C_{12}H_{26})_{.2}(C_{14}H_{30})_{.2}(C_{16}H_{34})_{.4}$ | 1.319 | 1.313 | 1.315 | 1.316 |
| $(C_8H_{18})_{.2}(C_{10}H_{22})_{.2}(C_{12}H_{26})_{.2}(C_{14}H_{30})_{.2}(C_{16}H_{34})_{.2}$ | 1.286 | 1.278 | 1.282 | 1.284 |
| $(C_{12}H_{24})_{.3}(C_{14}H_{28})_{.3}(C_{16}H_{32})_{.4}$ | 1.326 | 1.322 | 1.322 | 1.323 |
| $(C_8H_{16})_{.1}(C_{10}H_{20})_{.1}(C_{12}H_{24})_{.2}(C_{14}H_{28})_{.1}(C_{16}H_{32})_{.5}$ | 1.312 | 1.303 | 1.306 | 1.308 |
| $(C_{10}H_{20})_{.1}(C_{14}H_{28})_{.1}(C_{16}H_{32})_{.2}\times$ $(C_6H_{12})_{.1}(C_7H_{14})_{.2}(C_8H_{16})_{.3}$ | 1.343 | 1.341 | 1.341 | 1.346 |
| $(C_8H_{18})_{.04}(C_{10}H_{22})_{.08}(C_{12}H_{26})_{.08}(C_{14}H_{30})_{.08}(C_{16}H_{34})_{.12}\times$ $(C_8H_{16})_{.02}(C_{10}H_{20})_{.06}(C_{12}H_{24})_{.1}(C_{14}H_{28})_{.1}(C_{16}H_{32})_{.2}\times$ $(C_6H_{12})_{.02}(C_7H_{14})_{.04}(C_8H_{16})_{.06}$ | 1.309 | 1.308 | 1.312 | 1.314 |