Thermal Scattering Must Be Accounted for in the Determination of Adiabatic Compressibility

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Sound velocity measurement is a widely used method for determining the compressibility of liquids, solutions, solutes, and macromolecules[1−9] and for the determination of a wide range of thermodynamic parameters.[10] Hitherto, the compressibility determined from sound velocity measurement has been interpreted as being adiabatic, and thermal scattering has been neglected. It is shown here that thermal scattering can be very significant and may be calculated by scattering theory. However, results indicate that the very large number density of scatterers in solutions, even at low mole fraction or volume fraction, causes additional scattering effects which are not yet included in scattering theory. It has previously been suggested that the heat flow associated with thermal scattering may produce a significant departure from adiabatic conditions.[9] However, it is shown that propagation remains adiabatic in the presence of thermal scattering, under the usual experimental conditions.

Introduction

The measurement of sound velocity in solutions and suspensions is commonly used to determine the compressibility of particles, macromolecules, and solutes.[1−10] The question arises as to whether the compressibility determined in this way is the adiabatic or isothermal value. The nature of the thermal conditions affects the conclusions drawn in terms of molecular structure, hydration properties, etc. In this Letter, we discuss the heat flow in the region of a particle or solute molecule to show that the calculated compressibility is adiabatic but that the effects of thermal scattering must be accounted for.

Measurements of sound velocity and density in liquids are related to compressibility through an equation named after Laplace[11]

$$\nu = (\kappa_a \rho)^{-0.5} \tag{1}$$

where ν is the (magnitude of) velocity of compressional sound, ρ is the density (mass per volume), and κ_a is the adiabatic compressibility.[12] This is also called the Wood equation. In a solution or suspension, the compressibility of the sample is determined as a function of the concentration of solute or dispersed phase, in order to calculate the compressibility contribution from that component. It is this contribution which is related to the hydration structure of the solute in the solvent.

Discussion

Pierce[13] shows that propagation is adiabatic below about 10^{13} Hz in pure water, and Zemansky[12] derives the condition for adiabatic propagation in pure liquids as

$$\frac{2\tau f}{\nu^2 \rho C_\nu} \ll 1 \tag{2}$$

where τ is the thermal conductivity, C_ν the specific heat capacity at constant volume, and f the frequency of sound. The left-hand side of this equation has the value 1.3×10^{-7} at 20 °C

for 1 MHz ultrasound in water, clearly satisfying the adiabaticity condition. Equation 2 is equivalent to the condition that the acoustic wavelength be much greater than the thermal wave decay length, which is given by

$$\left(\frac{2\tau}{\rho C_p \omega}\right)^{0.5} \tag{3}$$

where ω is the angular frequency of the acoustic wave and C_p the specific heat capacity at constant pressure. For water, the thermal decay length is 0.2 μm at 1 MHz, where the acoustic wavelength is 1.5 mm (at 20 °C).

In the presence of inhomogeneity (e.g. solute molecules or suspended particles), it is essential to account for the thermal term which gives rise to scattering of the acoustic wave.[11,14−19] As a result, a modification of eq 1 which simply accounts for changes in the partial molar volume of the dispersed phase in solvent will be incorrect. On the other hand, it is also incorrect to conclude that the ratio of the temperatures between the particle and its surroundings defines whether the acoustic propagational mode is adiabatic or not, as Nölting[9] suggests. Isothermal conditions require heat to flow from the compression half-cycle to the expansion half-cycle of the acoustic wave, as Zemansky concluded.[12] Equation 2 therefore also defines the adiabatic limit for solutions and dispersions, provided the attenuation of the acoustical mode is small.

We have shown[20] that in the long wavelength ($\lambda \rightarrow \infty$) limit that applies here, the velocity of sound in a liquid dispersion is given, according to scattering theory, by

$$\frac{1}{\nu^2} = \frac{1}{\nu_1^2}(1 + \alpha\phi + \delta\phi^2) \tag{4}$$

where

$$\alpha = \left[\frac{\kappa_{a2} - \kappa_{a1}}{\kappa_{a1}} + \theta + \frac{\rho_2 - \rho_1}{\rho_1}\right]$$

and

$$\delta = \left(\frac{\kappa_{a2} - \kappa_{a1}}{\kappa_{a1}} + \theta\right)\left(\frac{\rho_2 - \rho_1}{\rho_1}\right) + \frac{2(\rho_2 - \rho_1)^2}{3\rho_1^2}$$

$$\theta = (\gamma - 1)\frac{\rho_2 C_{p2}}{\rho_1 C_{p1}}R^2$$

where

$$R = \left[\frac{\dfrac{\beta_2}{\rho_2 C_{p2}} - \dfrac{\beta_1}{\rho_1 C_{p1}}}{\dfrac{\beta_1}{\rho_1 C_{p1}}}\right]$$

Here ν_1 is the velocity in the pure solvent, ϕ is the volume fraction of the solution occupied by solute, and α and δ are coefficients defined above, which can be related to the monopole and dipole scattering coefficients a_0 and a_1.[21] Quantities referring to the solvent are subscripted 1, and those referring to the solute are subscripted 2. β is the volume thermal expansivity and γ the ratio of the specific heat capacities.

Experimental evidence for the validity of scattering theory extends to particle sizes as small as 130 nm,[22] and it seems reasonable to apply it to solute molecules in solution. The heat flow between the particle and the solvent is related to the ratio R, the fractional difference in the temperature change in each substance caused by a given pressure field. R can be negative, corresponding to heat flow between solute and solvent in antiphase to the pressure fluctuation. Although the acoustic field is still adiabatic, the thermal scattering due to the heat flow near the particle is sufficient to affect significantly the measured sound velocity. This effect is partially accounted for by scattering theory (eq 4). However, if the scattering particles are molecules, then the high number density of scatterers even at extremely low concentrations by volume may lead to multiple scattering effects not included as yet in the theory. These arise from the influence on a molecule of the combined scattered thermal fields of its neighbors. The solute parameters will also be altered in nonideal solutions, by hydration[23] and by the heat of mixing.[24]

A test of eq 4 in two very different binary mixtures—ethanol/water and *n*-heptane/cyclohexanol—is summarized in Table 1. Thermal expansivity data for water has been taken from Zemansky.[12] Other data[25,26] are referenced in Table 1. The minimum number of points (three) for a quadratic fit (in concentration) were taken in the case of the (relatively) concentrated ethanol/water and concentrated *n*-heptane/cyclohexanol in order to approach the dilute limit as closely as the data allowed. The temperature dependence of the expansivity and heat capacity of water was included, 20 °C data was used for ethanol, and the excess enthalpy of water + ethanol was not accounted for. The approximations made do not significantly affect the conclusions. In the case of the dilute ethanol/water data, the 12 points in the data set were accurately (standard error 6×10^{-6}) fitted by a quadratic function of concentration and no improvement was obtained by the use of a cubic polynomial. This is strong evidence for the validity of the modified Urick equation approach.

The sequence of calculation is as follows: the thermal term θ is calculated from the thermal properties of the two components, allowing the compressibility to be determined from the linear coefficient α; as a comparison, the expected thermal component θ' is determined from the quadratic coefficient δ using the compressibility already calculated from the linear term. The difference between θ and θ' is consistent with concentration dependent multiple scattering of the thermal wave, which introduces an additional component into the quadratic term. We have therefore based our calculation of the compressibility on the linear term only.

The compressibility computed using the method of Gekko and Yamagami[5] agrees well with that calculated from an unmodified Urick equation, which neglects thermal scattering (κ_{u2}, using $\theta = 0$). The adiabatic compressibility calculated from the linear term and accounting for thermal scattering (κ_{a2}) is significantly different. In the case of solutions of water, in which the temperature ratio R can exceed -25, the compressibility of a dissolved solute like ethanol may be very significantly altered from the value determined without accounting for thermal scattering.

TABLE 1: Velocity and Density Data in Binary Mixtures with Parameters Calculated by the Modified Urick Equation, Including Adiabatic Compressibility[a]

T	x_{max}	α	δ	θ	θ'	R	κ_{u2}	κ_{a2}	$\overline{\kappa_{a2}}$	ref
					Ethanol in Water					
0	0.051	−1.68	2.03	0.18	−12.74	−25.87	−2.7E−10[b]	−3.6E−10	−2.7E−10	20
10	0.051	−1.23	1.08	0.165	−6.15	17.72	−4.1E−11	−1.2E−10	−5.4E−11	20
20	0.051	−0.99	1.02	0.157	−5.35	7.13	7.7E−11	4.9E−12	5.3E−11	20
30	0.051	−0.78	0.90	0.142	−5.23	4.48	1.6E−10	1.0E−10	1.4E−10	20
					Cyclohexanol in *n*-Heptane					
30	0.488	−0.24	0.11	2E−04	1.06	0.03	7.5E−10	7.5E−10		21
					Dilute Ethanol in Water					
5	0.008	−1.2	−0.95	0.172	7.96	*21.0*	−2.7E−11	−1.1E−10		20
15	0.008	−0.95	−0.81	0.16	6.38	*11.0*	9.4E−11	1.9E−11		20
					Water in Ethanol					
0	0.4	−1.33	1.44	0.272	4.14	−1.03	−7.5E−10	−9.7E−10		20
10	0.4	−1.35	1.37	0.235	3.92	−0.96	−8.4E−10	−1.0E−09		20
20	0.4	−1.41	1.45	0.208	4.03	−0.91	−9.8E−10	−1.2E−09		20
30	0.4	−1.59	1.86	0.186	4.82	−0.87	−1.2E−09	−1.4E−09		20
					n-Heptane in Cyclohexanol					
30	0.242	0.13	0.20	3E−04	−1.7	−0.03	1.1E−09	1.1E−09		21

[a] T is the temperature (in °C); α, δ, θ, and R are defined in eq 4; x_{max} is the molar fraction of solute over which the compressibility was determined. All compressibilities are in Pa^{-1}. Italicized values have been interpolated. κ_{u2} is the compressibility calculated from α by setting $\theta = 0$. κ_{a2} is the compressibility determined from α using compressibility and density data for the pure solvent and the partial molar volume of the solute computed from density data using a polynomial adaptation of the method of intercepts.[27] θ' is the value of θ determined from the quadratic term δ using κ_{a2} determined from α. $\overline{\kappa_{a2}}$ is the partial specific adiabatic compressibility calculated by the method of Gekko and Yamagami.[5] [b] Read as -2.7×10^{-10}.

Conclusions

The measurement of sound velocity in solutions and emulsions can be used to determine the compressibility of the solution, solute molecules, or dispersed particles. This compressibility is adiabatic under the usual experimental conditions. However, thermal scattering of the acoustic wave at the solute molecules or particles can have a large effect on the measured sound speed and must be included in the calculation of adiabatic compressibility. Some multiple scattering effects which may be significant in solutions are not yet included in scattering theory.

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