Topic2540

Newton-Laplace Equation

The Newton-Laplace Equation is the starting point for the determination of isentropic compressibilities of solutions [1,2] using the speed of sound u and density ρ; equation (a) [3].

$$u^2 = (\kappa_S \cdot \rho)^{-1} \qquad \text{(a)}$$

Densities of liquids and speeds of sound at low frequencies can be precisely measured [4,5] .The isentropic condition means that as the sound wave passes through a liquid the pressure and temperature fluctuate within each microscopic volume but the entropy remains constant. The condition 'at low frequencies' is important because at high frequencies (e.g. > 100 MHz) there is a velocity dispersion and absorption of sound as the sound wave couples with molecular processes within the liquid [2,6,7].

Several points emerge from a consideration of equation (a). For example one might ask --- is it just assumed that the correct term is κ_S and not κ_T? The point is that in their examination of the properties of aqueous solutions and aqueous mixtures authors often write something along the following lines -- 'we used the Newton-Laplace equation to calculate κ_S from measured speeds of sound'. One might then ask-- can one prove equation (a) and is the proof thermodynamic? Rowlinson states that the speed of sound defined by equation (a) is, and we quote, 'of course a purely thermodynamic quantity' [1]. This comment raises the issue as to whether or not the defined quantity equals the measured speed of sound.

Intuitively the task of measuring the isothermal property K_T [= $-(\partial V/\partial p)_T$] might seem less problematic than measuring the isentropic property, K_S [= $-(\partial V/\partial p)_S$] . K_T would be obtained by measuring the change in volume following an increase in pressure. However as Tyrer warned [8] in 1914, the isothermal condition is difficult to satisfy and estimated compressions and compressibilities reported up to that time and in the majority of cases were certainly between isentropic and isothermal values. Tyrer did in fact measure κ_T and calculated κ_S using equation (b).

$$\kappa_S = \kappa_T - T \cdot [\alpha_p]^2 / \sigma \qquad \text{(b)}$$

Other authors [9,10] have measured κ_T directly by, for example, the volume increase on sudden decompression of a liquid from high to ambient pressure. Nevertheless the conventional approach uses the Newton-Laplace equation. Historically this subject has its origins in the attempts initiated in the 17th Century to measure the speed of sound in air [11].

A sound wave travelling through a fluid produces a series of compressions and rarefactions. Consequently planes of molecules perpendicular to the direction of the sound waves are displaced. The displacement ε depends on both position x and time t.

Thus $\varepsilon = \varepsilon[x,t]$ (c)

The speed of the sound wave u is related to the displacement ε using equation (d), the wave equation.

$$(\partial^2\varepsilon / \partial x^2) = (1/u^2)\cdot(\partial^2\varepsilon / \partial t^2) \quad \text{(d)}$$

A classic analysis [12] in terms of equation (d) and stress-strain relationships for an isotropic phase using Hooke's Law yields equation (a).

At this stage we could consider both the isothermal compressibility κ_T and the isentropic compressibility κ_S. If equation (a) is correct then, either (a) the speed of sound can be calculated knowing κ_S and ρ, or (b) κ_S can be calculated by measuring speed of sound u and density ρ.

Another line of argument states that equation (a) defines the speed of sound in terms of κ_S and density ρ. The question arises -- is the speed of sound calculated using equation (a) equal to the measured speed of sound?

The analysis up to and including equation (d) was familiar to Newton (I. Newton 1642-1727) [13]. Newton using Boyle's Law assumed that the fluid is an ideal gas and that the compressions and rarefactions are isothermal (and in a thermodynamic sense, reversible);

Hence $u^2 = p/\rho$ (e)

Equation (e) was particularly important to Newton because the three quantities in equation (e) can independently determined for (dry) air. Using the density ρ for air at pressure p one can calculate the speed of sound in air. The agreement between observed and calculated speeds was, somewhat disappointingly, only fair but encouraging. The disagreement was an underestimate by 20% as was noted by Newton.

The argument is interesting in the sense of testing if the analysis yields the measured speed of sound. Clearly the equations do not. An important contribution was made by Laplace [14] who assumed that the compressions and rarefactions are perfect and isentropic; i.e. $p \cdot V^{\gamma}$ = constant where γ is the ratio of isobaric and isochoric heat capacities. This is the assertion made by Laplace. The overall condition is isentropic for a gas at temperature T. The condition refers to macroscopic properties. Within each microscopic volume both temperature and pressure fluctuate but the entropy remains constant. [The equilibrium and isentropic conditions mean that there is no loss of heat on compression and no gain of heat on rarefaction when the sound wave passes through the system; everything is in phase.] Assuming that γ is independent of p,

$$u^2 = \gamma \cdot p / \rho \qquad \text{(f)}$$

The point is that Laplace knew γ for (dry) air at 273 K and standard pressure equals 1.4. With this information Laplace obtained good agreement between theory and experiment for the speed of sound in air. In other words Laplace confirmed his assertion that for air (a fluid with low density, 1.29×10^{-3} g cm^{-3}) compressions and rarefactions are isentropic and not isothermal. Hence the fame of the Newton-Laplace equation which is based on an assertion. Laplace did not **prove** that the processes are isentropic but having shown agreement between theory and experiment one must conclude that the assertion is correct for air. Equation (a) is the Newton-Laplace Equation. The key point is that the equation emerges from an **Equation of State** for isentropic compressions of a particular gas, air. Indeed the success achieved by the Newton-Laplace equation in term of predicting the speed of sound in a gas is noteworthy. However we need to comment on the link between κ_S measured directly and obtained from measurements of κ_T , α_p and C_p using equation (b) [15]. We direct attention to a given closed system containing liquid water. From a practical standpoint, the difference between isothermal and isentropic compressibilities (cf. equation (b)) written here for the pure liquid water,

$$\frac{[\alpha^*_{p1}(\ell)]^2 \cdot V^*_1(\ell) \cdot T}{C^*_{p1}(\ell)} \; .$$

is reasonably accessible. The molar volume $V^*_1(\ell)$ is obtained from the density $\rho^*_1(\ell)$; $\alpha^*_{p1}(\ell)$ is obtained from the dependence of density on temperature at fixed pressure.

The molar isobaric heat capacity $C^*_{p1}(\ell)$ is also experimentally accessible. The most frequently cited data set for $V^*_1(\ell)$ and $\alpha^*_{p1}(\ell)$ was published by Kell and Whalley in 1965 [16]; see also reference [17]. The isothermal compressibility is less accessible . In 1967 Kell summarised[18] the results obtained by Kell and Whalley[16] and quoted that at 25 Celsius, $\alpha^*_{p1}(\ell)$ = 257.05 x l0^{-6} K^{-1} and $\kappa^*_{T1}(\ell)$ = 45.24 Mbar^{-1}. In 1969 Millero and co-workers[19] directly measured isothermal compressions of water(ℓ) drawing comparisons with the estimates made by Kell and Whalley [16,17]. They reported that for water(ℓ) at 25 Celsius, $\kappa^*_{T1}(\ell)$ = (45.94 ± 0.06) Matm^{-1}. Millero *et al.* comment [19] on the excellent agreement.

In 1970, Kell addressed the issue which is of interest here [18]. Equation (b) is the key to the debate because we obtain an estimate of $\kappa^*_{S1}(\ell)$ from measured $\kappa^*_{T1}(\ell)$, $\alpha^*_{p1}(\ell)$, $V^*_1(\ell)$ and $C^*_{p1}(\ell)$; i.e. $\kappa^*_S(\ell;\text{density})$. Alternatively we obtain $\kappa^*_{S1}(\ell)$ using equation (a); i.e. speed of sound and density yielding κ_S (acoustic) . The key question is --- are $\kappa^*_S(\ell;\text{density})$ and κ_S (acoustic) equal? How confident are we that they are equal? There are no assumptions underlying the calculation of $\kappa^*_S(\ell;\text{density})$. In the case of κ_S (acoustic), the sound wave perturbs the system isentropically; cf. Laplace analysis. Kell comments [20] that speeds of sound can be precisely measured and also a precise estimate of the defined κ_S (acoustic) is obtained. Granted the validity of equation (a) one can re-express equation (b) as an equation for $\kappa^*_{T1}(\ell)$ in terms of measured $\kappa^*_{S1}(\ell)$, $\alpha^*_{p1}(\ell)$, $V^*_1(\ell)$ and $C^*_{p1}(\ell)$. Examination of various sets of data showed that κ_S (acoustic) has less systematic errors than $\kappa^*_S(\ell;\text{density})$ but that they are effectively the same, a point confirmed by Fine and Millero [21].

Footnotes

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[3] $u^2 = \frac{1}{\kappa_s} \cdot \frac{1}{\rho} = [\text{N m}^{-2}] \cdot \frac{1}{[\text{kg m}^{-3}]} = \frac{[\text{kg m s}^{-2}\ \text{m}^{-2}]}{[\text{kg m}^{-3}]} = [\text{m}^2\ \text{s}^{-2}]$

u = [m s^{-1}]

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