THE HOT CHOCOLATE EFFECT

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Introducing bubbles into a cup with liquid changes the pitch of the sound it makes when tapped with a spoon. This is known as the hot chocolate effect. Simple experiments that can be performed at home, are presented, demonstrating the changing speed of sound in water when bubbles are present. A simplified but effective mathematical model is derived. In addition to demonstrating the effect, the experiments described provide an opportunity for students to develop skills to think like a scientist by devising and testing explanations.

POJAV VROČE ČOKOLADE

Uvajanje mehurčkov v skodelico s tekočino spremeni višino tona, ki ga slišimo, ko skodelico udarimo z žlico. To je pojav vroče čokolade. Predstavljeni so enostavni poskusi, ki jih je mogoče izvesti doma in demonstrirajo spreminjanje hitrosti zvoka v vodi, ko so prisotni mehurčki. Izpeljan je enostaven a uporaben model. Opisani poskusi ponujajo priložnost za učence in dijake, da razvijajo sposobnost znanstvenega razmišljanja s predlaganjem in testiranjem razlag.

1. Introduction

Bubbles in liquids have long fascinated physicists. William Bragg described the attenuation of sound by bubbles in his 1920 book:

> "This is very easily shown by tapping with a spoon or knife a tumbler containing beer or stout with a layer of foam on it. The sound is absolutely dead: quite different from the tinkling sound that the tumbler gives when empty or when partly filled with water. The foam absorbs the energy of the vibrating glass." [1]

Even before him, in 1910, Mallock noticed the effect in frothy liquids and proposed a model for the speed of sound and attenuation in bubble-liquid mixtures, noting that even a small amount of bubbles significantly lowered the speed of sound [2]. Later, in 1933, Minnaert studied the sounds of running water and how air bubbles in water produce those sounds [3]. He constructed a mathematical model and performed experiments investigating bubble pulsation.

A curious phenomenon was observed in the 1960s while mixing instant coffee in a mug [4]. If the bottom of the mug was tapped repeatedly with a spoon as the powder was stirred into the water, the sound emitted could be heard to rise in pitch. They also noted the effect in a glass of freshly poured beer and suggested that the release of bubbles is the cause. Later, Frank S. Crawford noticed a similar effect:

> "Put an ounce of dry hot chocolate powder in a mug; fill the mug with hot water; stir. Now start tapping on the bottom of the mug with your knuckle. Listen for a note that slowly rises in pitch. (My record: 3 1/2 –octave rise from the initial low pitch to the final high pitch.) It takes about a minute for the pitch to stop rising. Now stir again. As the spoon accidentally hits the inside of the mug you will hear the pitch descend once more and the experiment can be repeated. (With each repetition there is a smaller pitch lowering, as can be easily verified by performing the experiment while sitting at a piano.)" [5]

Crawford proposed a mathematical model and investigated the effect thoroughly. After his 1982 paper, it became known as *the hot chocolate effect*. If only Bragg had tapped his glass immediately after it was filled, before the bubbles rose to the top, he could have noticed the time-dependent pitch that constitutes the effect.

2. A simple experiment

The hot chocolate effect can be observed in a simple experiment [6], which is summarized here. The authors give the following instructions:

> "All it requires is a tall cylindrical glass, an effervescent tablet, and a spoon. Crush a small piece of the tablet to powder and drop it into the dry glass. Add tap water to fill the glass and immediately start tapping on the bottom of the glass with the spoon. Carefully listen to the pitch of the sound."

At first, the pitch will get lower, but after about $10 - 30$ s it will start to increase, finally reaching a high tone after a minute or two. To identify any patterns in observations, we can record the sound and analyse its spectrum.

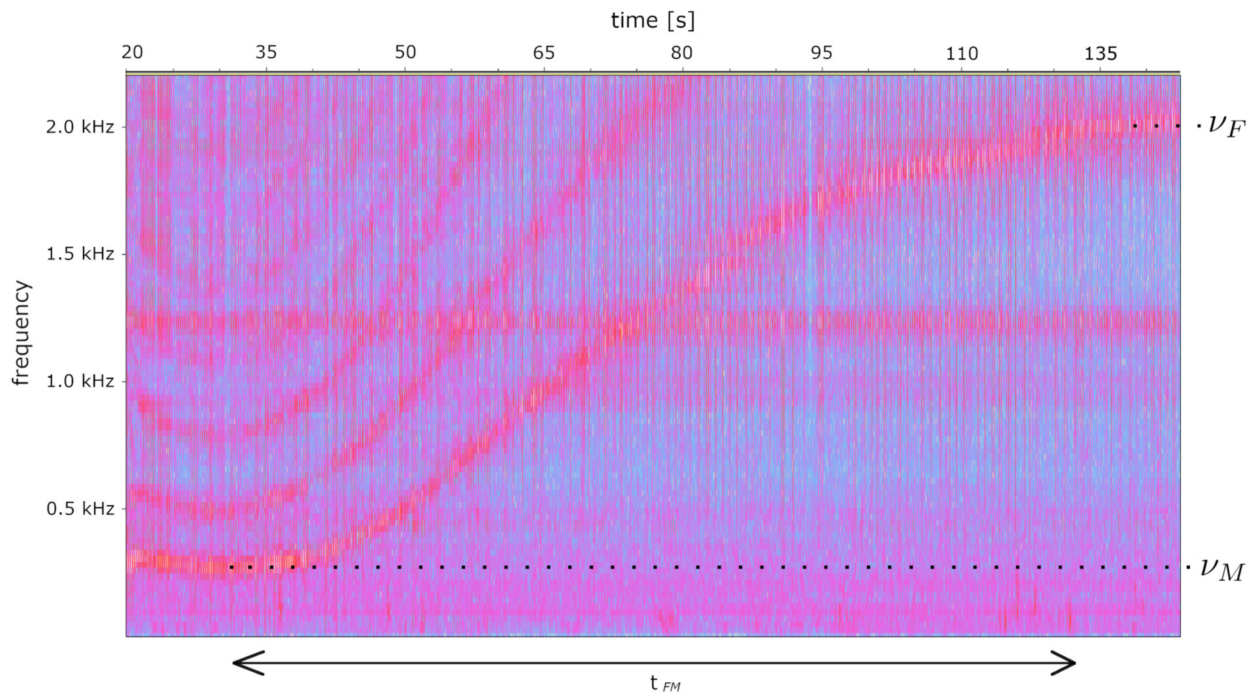

Figure 1. Time dependence of the sound spectrum obtained for the experiment with three quarters of a vitamin C tablet inside a cylindrical glass with a length of 21 cm and a diameter of 65 mm. The height of the liquid was $L = 20$ cm. Time is measured from the moment at which the water was poured into the glass. The colour scale represents the spectral density (amplitude of the sound in a particular frequency range): from blue (small amplitude) to red (medium amplitude) to white (the largest amplitude). The denoted values are explained below.

Figure 1 shows a typical example of the time variation of the sound spectrum. We can see that there are a few sounds starting at specific frequencies (about 300 Hz, 600 Hz, 1000 Hz, 1250 Hz, ...). The high-pitched sound at 1250 Hz remains constant throughout the experiment. There are sounds at higher frequencies outside the plot region, which also remain constant throughout. We can also observe, that the frequency of some sounds changes during the experiment. They get lower and reach a minimum value. Then they rise above their starting values and settle there after time t_{FM}.

First, we will focus on the sound with the lowest pitch. Its starting frequency is about 300 Hz, the minimum frequency is $\nu_M = 250$ Hz and the final frequency is $\nu_F = 2000$ Hz. Given that the tablet releases bubbles during the experiment, it is reasonable to hypothesize that the bubbles are responsible for the frequency change of the low-pitched sound. If this is true, we expect some correlation between the production of bubbles and pitch. We can test our explanation by performing the experiment using different fractions of a tablet, since a larger fraction will produce more bubbles.

fraction of tablet	ν_M[Hz]	ν_F[Hz]	t_{FM}[s]
1/4	750	1500	50
1/2	400	1500	60
3/4	250	2000	100

Table 1. The fraction of a tablet used in the experiment and corresponding minimal frequency ν_M, final frequency ν_F, time from minimum to final frequency t_{FM}.

We find, that when the fraction of a tablet we use is larger, the minimum frequency is lower. This supports our hypothesis that the production of bubbles influences pitch. By observing the glass from the side, we can see that a larger fraction of a tablet means a higher density of bubbles. We can also see how bubble density changes during the experiment.

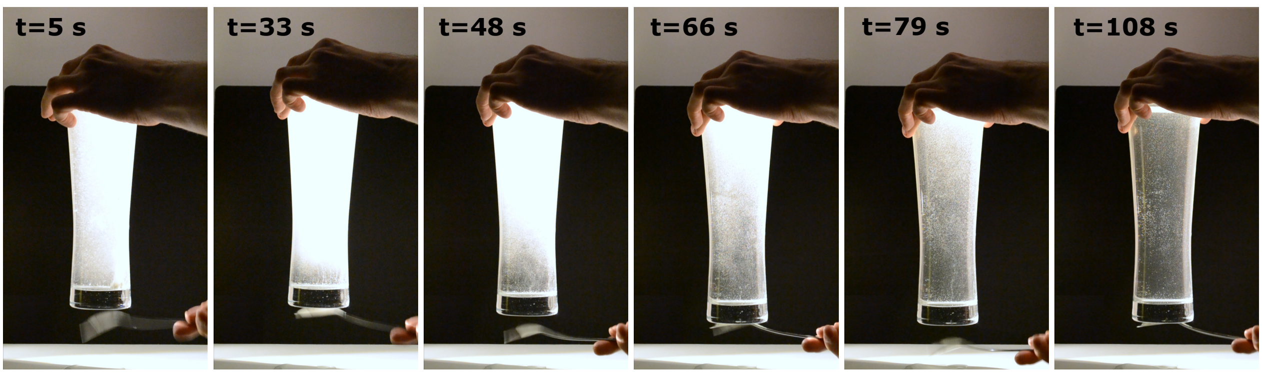

Figure 2. Bubbles in the glass during the experiment with three quarters of a vitamin C tablet. Time is measured from the moment at which the water was poured into the glass. Full video with sound is available at [7].

The sound reached the lowest frequency at about $t = 33\,\mathrm{s}$. Note that at $t = 0$ bubbles were larger than at $t = 33\,\mathrm{s}$, but there are fewer of them. As the bubble density increases (from $t = 0$ to $33\,\mathrm{s}$), the pitch gets lower. After the tablet dissolves, the bubbles start disappearing (from $t = 33\,\mathrm{s}$ onward) and the pitch increases. A higher density of bubbles is concurrent with lower pitch, which is consistent with our hypothesis that the presence of bubbles influences the pitch. The time t_{FM} from the minimum frequency to the final is longer for larger fractions of a tablet. This is also consistent with our hypothesis, since a larger amount of a tablet generates more bubbles, which were observed to remain in the water longer and so could influence the pitch longer.

So far, we have established that the frequency change of the sound with the lowest pitch is correlated with bubble density. But in Figure 1, we can also see higher-pitched sounds that exhibit similar behaviour. Their frequency appears to be a multiple of the frequency of the lowest-pitched sound. Also, why does the sound at about 1250 Hz not change with time?

One possible explanation is that the low-pitched sounds are produced by standing waves in the medium that fills the glass, which behaves like a tube closed at one end (bottom of the glass) and open at the other end (water surface). The high-pitched sounds are produced by the vibrations of the glass container and are not significantly affected by the medium in the glass. For half-open pipes, we have the well-known equation for standing wave frequencies

$$\nu_n = n\frac{c}{4L}, \tag{1}$$

where c is the speed of sound in the medium that fills the glass and L is the length of the column of the medium. This equation is an approximation assuming that there is a pressure node at the open end of the pipe. Using the height of the water $L = 20\,\mathrm{cm}$ and the approximate speed of sound in water $c = 1480\,\mathrm{m/s}$ at $20\,^\circ\mathrm{C}$, we get $\nu_1 = 1850\,\mathrm{Hz}$. Considering our accuracy, this is near the highest final frequency of 2000 Hz (Table 1). We observed that this fundamental frequency changes with time, so it is reasonable to propose, that the speed of sound in water changes due to the presence of bubbles.

We can test our explanation with additional experiments. If the low-pitched sounds are produced by standing waves, then the fundamental frequency of the empty glass should be lower than that of a glass with water, since the speed of sound is larger in water. The fundamental frequency of the bubble-water mixture should eventually approach the fundamental frequency of the full glass as the bubbles leave the water. If the non-changing high-pitched sounds are produced by the glass itself, those frequencies should be unaffected by what is going on in the water.

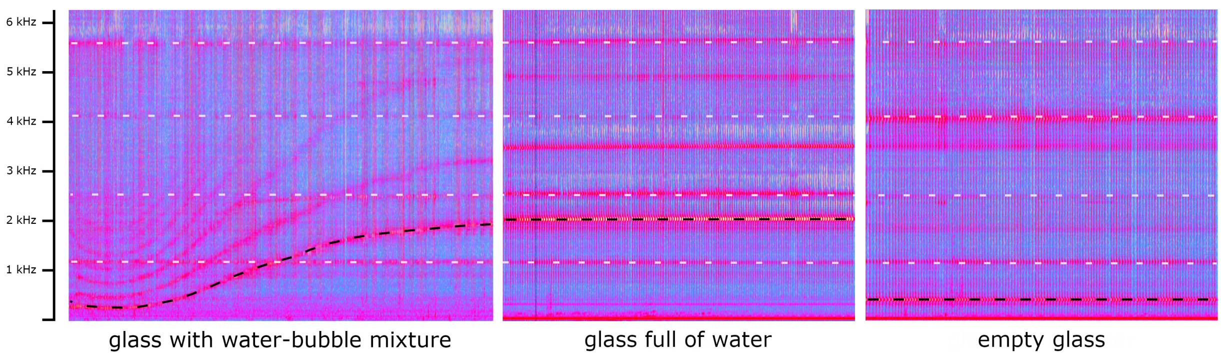

Figure 3. Time dependence of the sound spectrum for the three testing experiments obtained by tapping the bottom of the glass with a spoon. The black lines mark the fundamental frequency in the column of water, and the white lines mark frequencies that correspond to glass wall vibrations.

Figure 3 shows the results of the proposed experiments. The results match our predictions: the higher-pitched sounds are the same in all cases, and the fundamental frequencies approach the fundamental frequency in the full glass. After a minute or two the fundamental frequencies settle slightly below the fundamental frequency of the full glass. This discrepancy may be due to a small amount of tiny bubbles that remain visible in the liquid for hours. They may also be responsible for the observed differences in the final frequencies (table 1). Perhaps different amounts of a tablet cause a difference in the amount of remaining bubbles. This hypothesis would have to be tested with further experiments. While the results of the experiment support our explanation, we still need to describe the mechanism by which the bubbles change the speed of sound.

3. Mathematical model

The speed of sound in gasses and liquids is given by

$$c = \sqrt{\frac{1}{\rho\chi}}\,, \tag{2}$$

where ρ is the density of the medium and χ is its compressibility. The density of water is about 800 times larger than the density of air, but its compressibility is about 15000 times smaller. The density of a water-air mixture is approximately equal to the density of water, but its compressibility is closer to the compressibility of air since the bubbles in the mixture are easy to compress. The speed of sound can therefore be significantly lower than in air. Using (1) we can estimate the lowest speed of sound in the described experiment ($L = 20\,\mathrm{cm}$): the lowest frequency $\nu_M = 250\,\mathrm{Hz}$ gives us $c = 200\,\mathrm{m/s}$, which is much lower than the speed of sound in air $340\,\mathrm{m/s}$.

In the experiment above, the bubble density first increases, which increases the compressibility of the bubble-water mixture and only slightly decreases its density, since water still represents the majority of the volume in the mixture. This lowers the speed of sound. Eventually, the bubble density starts to decrease (as the tablet dissolves) and the speed of sound increases and therefore the sound pitch increases.

Propagation of sound through a collection of bubbles has first been examined theoretically by Mallock in 1910 [2] under the assumption that the mixture could be considered as a homogeneous liquid of the same density and mean compressibility. He obtained an approximate expression for the speed of sound and noted that bubbles are very effective at damping the sound. In 1930, Wood [8] confirmed Mallock's work but cast the results in a more useful form. The following derivation is adapted from Wilson and Roy [9], which is in turn based on Wood's derivation. We make a few assumptions, which are further justified in [5, 9, 10]:

- surface tension, liquid vapour in the bubble and dissipative effects are negligible,
- the sound frequencies and size of the bubbles are small enough, that the bubbles do not resonate and so the compressibility does not depend on the frequency,
- the wavelength of the sound is much larger than the bubble radius, and we can therefore treat the medium as homogeneous with an average density and compressibility.

This way we avoid having to tackle sound scattering on individual bubbles, however, our model only applies at low frequencies. The neglected effects only become significant for small bubbles ($r \lesssim 0.05\,\mathrm{mm}$) and at wavelengths comparable to bubble size. More widely applicable models exist but are more complex [10]. The volume fraction of the gas, known as the void fraction, is

$$f = \frac{V_g}{V}\,, \tag{3}$$

where V_g is the volume of the gas phase and V is the total volume of the mixture $V = V_g + V_l$. The subscripts l and g refer to the liquid and gas phases respectively. The effective mixture density is

$$\rho = \frac{m_l + m_g}{V_l + V_g} = \frac{\rho_l V_l + \rho_g V_g}{V} = (1-f)\rho_l + f\rho_g\,. \tag{4}$$

Since compressibility is defined as

$$\chi = -\frac{1}{V}\frac{\partial V}{\partial p}, \tag{5}$$

the effective compressibility of the mixture is

$$\begin{aligned}
\chi &= -\frac{1}{V}\frac{\partial (V_l + V_g)}{\partial p} = -\frac{1}{V}\frac{\partial V_l}{\partial p} - \frac{1}{V}\frac{\partial V_g}{\partial p}\\
&= -\frac{V_l}{V}\frac{1}{V_l}\frac{\partial V_l}{\partial p} - \frac{V_g}{V}\frac{1}{V_g}\frac{\partial V_g}{\partial p}\\
&= (1-f)\left(-\frac{1}{V_l}\frac{\partial V_l}{\partial p}\right) + f\left(-\frac{1}{V_g}\frac{\partial V_g}{\partial p}\right)\\
&= (1-f)\chi_l + f\chi_g\,.
\end{aligned} \tag{6}$$

For the speed of sound in the mixture we then get

$$\frac{1}{c^2} = \left[(1-f)\rho_l + f\rho_g\right]\left[(1-f)\chi_l + f\chi_g\right]\,. \tag{7}$$

Using equation (2) we can eliminate the compressibilities and finally get

$$\frac{1}{c^2} = \frac{(1-f)^2}{c_l^2} + \frac{f^2}{c_g^2} + f(1-f)\frac{\rho_g^2 c_g^2 + \rho_l^2 c_l^2}{\rho_l \rho_g c_g^2 c_l^2}. \tag{8}$$

An example plot of equation (8) for air bubbles in water is shown in Figure 4.

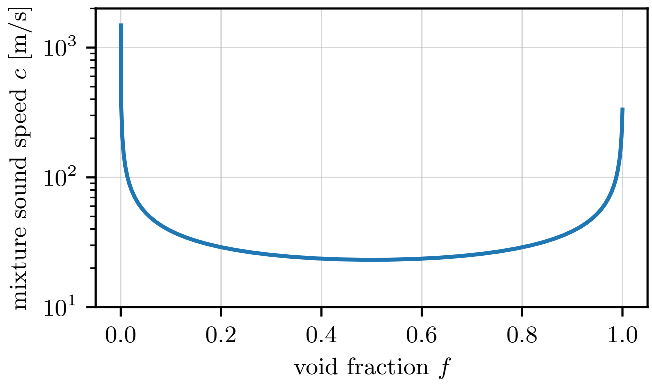

Figure 4. The speed of sound for the mixture of air bubbles in water given by equation (8). Parameter values are $\rho_l = 998\,\mathrm{kg/m^3}$, $\rho_g = 1.21\,\mathrm{kg/m^3}$, $c_l = 1481\,\mathrm{m/s}$ and $c_g = 333\,\mathrm{m/s}$.

The equation behaves properly in the limits. As the mixture approaches pure liquid, $f \to 0$ and $c \to c_l$. Alternatively, as $f \to 1$, $c \to c_g$. Near zero volume fraction, there are only a few bubbles in the liquid and near volume fraction of one, there are only droplets in air. In these limits the medium is definitely not homogenous and the model will probably not work well. A minimum of $c = 23\,\mathrm{m/s}$ occurs at $f = 0.5$. Across much of the void fraction range, the speed of sound in the mixture is lower than the speed in either water or air. Even a small fraction of bubbles causes a large decrease in the speed of sound. The bubbles greatly increase the compressibility but affect the density much less. High compressibility and high density yield a low speed of sound.

This model has been experimentally verified [9]. The experimental apparatus consisted of a 60 cm long and 5.2 cm wide PVC pipe with about 50 cm of water inside, an air injection system that created the bubbles, a hydrophone and a data acquisition system. A small float positioned at the top of the pipe was used to determine the void fraction $f = \Delta l/(l + \Delta l)$, where l is the length of the water column without bubbles and Δl is the change in length when bubbles are present as measured by the change in the position of the float. Bubble density was controlled by the injection system, which allowed for the fundamental frequency to be determined at different void fractions. Continuous bubble production at the bottom of the tube excites acoustic standing waves that are observed with a hydrophone. The excitation is sufficiently broadband to excite the first several modes.

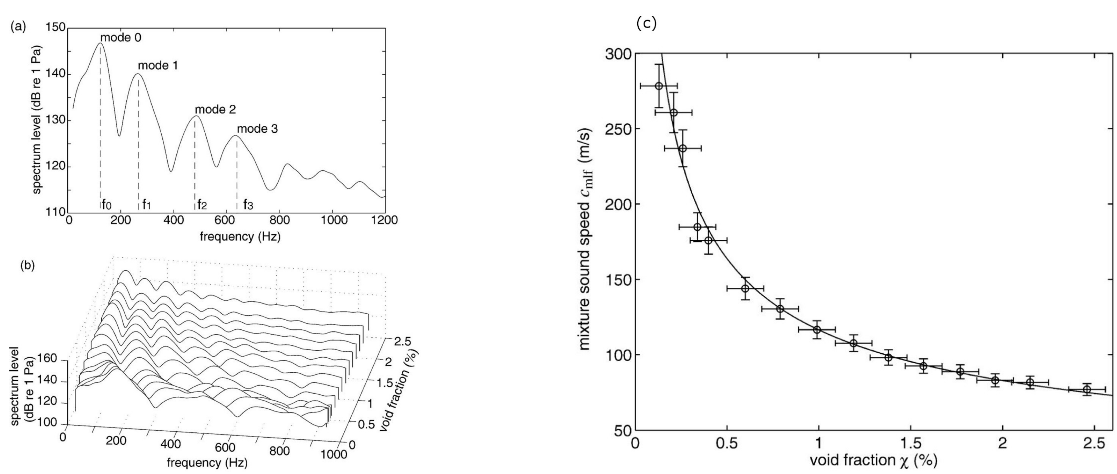

Figure 5. (a) A single spectrum at 0.4 % void fraction for which the modes have been identified. The units are decibels referenced to 1 µPa. (b) Spectra at different void fractions. (c) Experimental verification of the model at low void fractions. The solid line is the speed of sound predicted by equation (8) and the open circles are measured values. Vertical error bars represent the uncertainties due to the measurement of the column length $l + \Delta l$ and finite bandwidth resolution of the spectra. Horizontal error bars represent the uncertainties due to the measurement of Δl. Reproduced from: [9].

Figure 5b shows that increasing the void fraction causes the eigenfrequencies of the tube to compress towards lower frequencies, which results in a lower perceived pitch of sound. The measured speed of sound in Figure 5c matches the model within the experimental uncertainty in the range of tested void fractions. At very small void fractions ($f \lesssim 0.1\,\%$) the model is expected to significantly differ from measurements, since the bubbles are fewer and less homogeneously spaced throughout the tube. Due to inhomogeneity, the effective medium model breaks down and can not be used to describe such a system. A more advanced treatment of sound scattering on individual bubbles is required [10].

4. Pedagogical aspect

The process of gathering knowledge about the hot chocolate effect, which is described above, can be understood within the framework of the Investigative Science Learning Environment (ISLE) [11, 12]. ISLE is an approach to teaching and learning physics which mirrors scientific practice. Figure 6 shows the logical progression of student actions and thoughts in ISLE. Students develop physics concepts as their own ideas by repeatedly:

1. observing phenomena and looking for patterns,
2. developing explanations for these patterns,
3. using these explanations to make predictions about the outcomes of testing experiments that they propose,
4. deciding if the outcomes of the testing experiments disprove their explanations,
5. revising their explanations if necessary,
6. applying those for practical purposes.

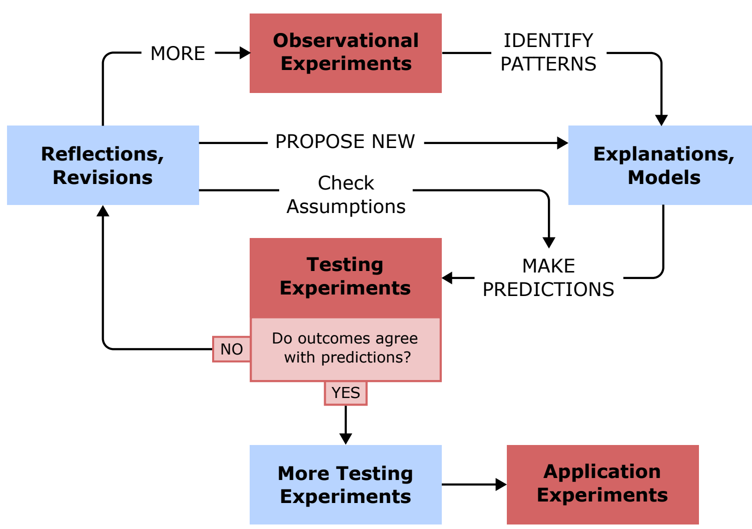

Figure 6. ISLE process diagram. Based on: [12].

The explanation of the hot chocolate effect in this paper followed this progression. We started with an *observational experiment*, where we noticed that the pitch changes when bubbles are present. Then, we analysed the spectrum of the sound. We identified patterns: sounds at some frequencies changed, while some did not. Using a larger amount of the tablet increased the change. Based on that and our knowledge of standing waves in tubes, we proposed an explanation: bubbles cause the speed of sound to change, while the fundamental frequency of the glass walls remains unchanged. We then devised *testing experiments* to test this explanation. Based on our explanation, we predicted that the sounds produced by the glass itself should remain the same if the glass is empty or full and that the changing sound should eventually approach the fundamental frequency in a full glass.

The outcomes of testing experiments were in agreement with our predictions, and we have failed to disprove the explanation. If they were not, we would have had to reevaluate the assumptions we made when making predictions or revise our explanation. After an explanation has survived many tests, we gain confidence in it. Then, we can *apply* our tested explanations to solve a practical problem or to measure some quantity.

The process is not necessarily linear or ever completed. After the outcomes of our testing experiments matched our predictions, we developed a mathematical model to quantify the change in the speed of sound. This model was then tested and measurements were compared to predictions. The model could then be subject to further revisions and improvements based on testing experiments.

The experiments described above provide an excellent opportunity for students to devise and test explanations with simple equipment. If the students understand the basic physics behind the experiments, they can be encouraged to devise explanations and suggest testing experiments after observing the initial experiment. To help students learn to reason in the ISLE way, we can encourage them to come up with multiple different explanations and propose testing experiments to differentiate between them. It would not be surprising (with some guidance) that they might associate bubbles with surface tension and follow up by wondering how decreasing the surface tension (for example, by adding a drop of soap) changes the outcome of the experiment. They could propose that when surface tension is reduced, it should be easier for the bubbles to form and we would observe lower sound frequencies. Of course, this hypothesis needs additional testing experiments. Once the students have tested their explanations and models, they could apply their knowledge to solve practical problems, such as the ones described below.

5. Applications

The hot chocolate effect has found a use in analytical chemistry for broadband acoustic resonance dissolution spectroscopy (BARDS) [13]. The dissolution of a compound results in the introduction and generation of bubbles. This is due to gases adhered or trapped within the particles. A reduction in gas solubility due to the solute causes additional bubble generation. The effect can be monitored via the frequency change of mechanically provoked acoustical resonances, as described above. The change of the fundamental frequency is strongly dependent on the physical and chemical characteristics of the solute, which allows for discrimination between compounds, particle sizes and characterizing dissolution rates. The method has been used for tracking yeast metabolism through the production of CO_2 bubbles [14], inexpensive quality control of pharmaceutical products [15, 16], to characterize tablet powder wetting behaviour [17], and since the frequency changes depend on the chemical and physical characteristics of a compound, it can be used to rapidly discern between genuine and falsified pharmaceutical tablets [18, 19].

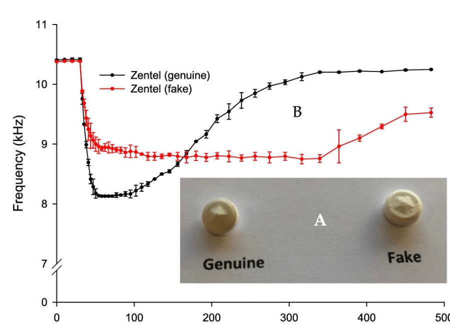

Figure 7. (A) An image of genuine and falsified albendazole tablets. (B) BARDS data of genuine and falsified tablets of albendazole dissolved in water. The time dependence of the fundamental frequency can clearly differentiate between the genuine and fake tablet. Reproduced from: [18]. License: CC BY 4.0.

6. Conclusion

The presence of bubbles in a liquid has been shown to affect the speed of sound. Even a small volume fraction of bubbles can lower the speed of sound below that of the gas that constitutes the bubbles. A simple model was presented that is in good agreement with measurements at low frequencies. More complex models are available, but even such a simple one is sufficiently accurate to be useful in some analytical and pharmaceutical applications. The described experiments can be used to help students develop the ability to think like a scientist through devising and testing explanations.

7. Acknowledgment

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