Title
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Publication Date
1980-12-01

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Physics, Computer Science & Mathematics Division

Submitted to the American Journal of Physics

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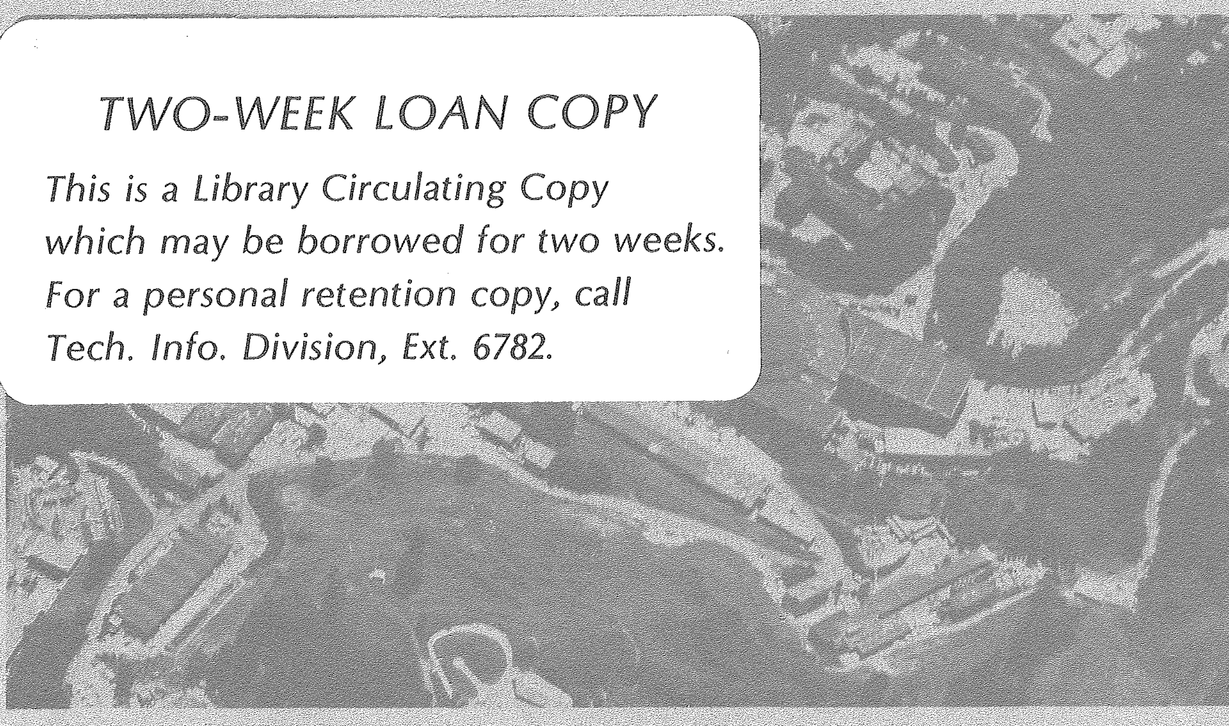
December 1980



Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48

To be submitted to Am. J. Phys.

LBL-11773
Dec. 23, 1980

THE HOT CHOCOLATE EFFECT

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ABSTRACT

The "hot chocolate effect" was investigated quantitatively, using water. If a tall glass cylinder is filled nearly completely with water and tapped on the bottom with a softened mallet one can detect the lowest longitudinal mode of the water column, for which the height of the water column is one quarter wavelength. If the cylinder is rapidly filled with hot tap water containing dissolved air the pitch of that mode may descend by nearly three octaves during the first few seconds as the air comes out of solution and forms bubbles. Then the pitch gradually rises as the bubbles float to the top. A simple theoretical expression for the pitch ratio is derived and compared with experiment. The agreement is good to within the ten percent accuracy of the experiments.

1. INTRODUCTION

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: a 3½-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.)

I discovered the effect accidentally just before Christmas, 1974, while having hot chocolate with my friend Nancy Steiner. (She noticed it first.) Several years later I found that the effect is well known.[1,2,3,4,5]

It works for any liquid into which you can introduce gas bubbles (air trapped in powder, or carbon dioxide in soft drinks or beer.) After stirring, the bubbles fill the liquid volume; the velocity of sound in the bubbly mixture is then reduced below that of the bubble-free liquid and the pitch is correspondingly reduced. As the bubbles float to the top of the mug a smaller fraction of the volume has the reduced sound velocity and the pitch rises, reaching the value for the bubble-free liquid when most of the bubbles have floated to the top.

2. OBSERVATIONS WITH HOT WATER. THE INVERSE EFFECT.

In order to have simple experiments and theoretical predictions it would help if the effect worked for the simplest case imaginable--air bubbles in water. I might therefore have been discouraged to read in Ref. 1 that "almost any powder could produce the effect in cold or hot water, but water alone would not", if I had not already tried it and found a large effect in water. Perhaps those authors did not try hot tap water. Not only does hot tap water give a fine effect, it gives something new that I call the "inverse" hot chocolate effect.

To observe the inverse effect turn on your hot water faucet and watch the water stream as you wait for the cold water to run off and the water to become hot. Suddenly you may see the water become cloudy (full of small air bubbles). At that time fill your mug rapidly, turn off the faucet and start tapping. For the first few seconds you may hear the pitch descending. That is the inverse effect. After a few seconds the pitch starts to rise--the "normal" effect. To see what is happening replace the mug by a tall transparent glass or jar. Look at a light through the glass as you tap. You will notice that during the inverse effect (descending pitch) the water is getting cloudier. That is because air that was in solution under high pressure in the hot water pipe is coming out of solution and forming bubbles. The greater the amount of air in the form of bubbles the lower the pitch. As you continue to watch and tap you will see the bubbles rise under gravity. A clear region grows at the bottom of the glass, with a rather sharp boundary between clear and cloudy regions. As the boundary rises the pitch rises (the normal effect). When the boundary has reached the top surface of the liquid the water is clear and the pitch stops rising.

No effect is seen (no cloudiness) or heard (no pitch changes) with cold tap water. That is because the dissolved air remains in solution.

Using hot tap water the largest pitch lowering that I have observed is a factor of about seven in frequency--nearly three octaves. That was achieved using a tall graduated cylinder. With a coffee mug the most I can get out of hot tap water is about one octave. That is because the bubbles have only a short distance to float to reach the top of the mug, and they reach the top before all the air has had time to come out of solution to form bubbles. With a tall cylinder the bubbles can have floated up one coffee-mug height and nevertheless still occupy most of the volume. Then there is time for the inverse (pitch lowering) effect to be nearly completed before the normal effect takes over.

The effect works on most of the hot water faucets I have tried. The largest effect (cloudiest water and greatest pitch lowering) is obtained with the faucet valve partially closed. The growth of the small bubbles is apparently triggered when the supersaturated hot water flows past a constriction (the partially closed faucet) where the pressure is suddenly released.

The bubbles are due to dissolved air, not air entrained at the nozzle. That is shown as follows: If I submerge the nozzle in water while it is emitting hot cloudy water there is no decrease in the cloudiness. Also, there is practically no effect with a cold-water faucet, even though the air entrainment should be essentially the same as for hot water.

If I open the hot water valve completely the cloudiness goes away and the water starts to run clear again. Under these circumstances there is sometimes no effect. Sometimes there is a small delayed inverse effect where the water in the rapidly filled jar remains clear with no pitch lowering for a few seconds, and then suddenly gives a small pitch lowering and bubble formation, but with fewer and larger bubbles than with the constricted valve. The question naturally arises: when I get no effect with the wide open hot water valve, is it because the bubbles have already been formed far back in the pipe somewhere and then for some reason become "lost" before I detect them? Or is the air instead still in solution in the hot water? I tried adding sand to the clear hot water to stimulate bubble growth, without success. It occurred to me to try sound waves. I borrowed a "supersonic" cleaning device having a 6-inch by 6-inch basin that can be filled three or four inches deep with water. Sound waves of about 11 kHz fill the liquid volume and agitate whatever is inserted there. I used a 250 ml volumetric flask to hold my water samples. The flask was first filled completely and then tipped sufficiently sideways so that bubbles rising in the main volume would be trapped in the domed top of the tipped main volume rather than traveling up the neck of the flask. When I filled the flask rapidly with hot cloudy water emerging from the constricted faucet the effect of the sound-wave agitation was to rapidly coalesce the small bubbles into larger bubbles which rapidly rose to the top and were trapped in the dome where I could measure the diameter of the flattened single large coalesced bubble. When I again used hot cloudy water but did not turn on the agitation I had to wait several minutes for the many small bubbles to rise and coalesce into a single trapped bubbles; but I found the same final size for that bubble as when I agitated the water. When I filled the flask with hot clear water obtained with the faucet wide open I found that after waiting for several minutes I still had practically no air bubbles, but if I agitated I immediately started to generate bubbles. After about ten minutes of agitation I got no more bubbles, At that time the total amount of trapped air in the single coalesced bubble was the same size as I got from the bubbly hot water obtained from the constricted valve. I conclude that the clear hot water from the wide open faucet is still supersaturated with air and in fact contains the same amount of air in solution as the cloudy hot water contains in the form of small bubbles. The fact that the two methods give the same result suggests that in each case all of the excess air (above that which is in equilibrium at 1 atmosphere at the hot temperature) is coming out of solution. It would be implausible for these two very different methods to have the same efficiency for getting rid of excess air unless that efficiency is close to 100%. (This expectation was later confirmed; see Sec.7.)

3. A SIMPLE MODEL: LONGITUDINAL OSCILLATIONS

Since the pitch-lowering effect works for air bubbles in water we should be able to make quantitative comparisons between experiment and theory. Unfortunately, the theory given in Ref. 1 is rather sophisticated. It involves the flexing modes of the glass container, perhaps because those authors tapped on the side of the mug rather than on the bottom in listening to the effect. Their predictions depend on the container diameter and wall thickness and on the elastic constants of the glass as well as on the properties of the liquid. Perhaps because of this complexity I did not pursue the problem for several years. But recently (1980) my interest revived. (I drink a lot of hot chocolate.) It occurred to me that whether or not the flexing modes are present I might search for other modes based on a much simpler hypothesis. I made the assumption that the pitch I hear when I tap with a soft mallet (my knuckle) on the bottom of a tall cylindrical glass container has almost nothing to do with the container but is simply the pitch expected for a cylindrical column of liquid undergoing longitudinal vibration in its lowest longitudinal mode. Since the top surface of the liquid is free, and the bottom, in contact with the glass, is fixed, I expected the height of the water column to be exactly one quarter wavelength for sound waves in the liquid, both for the case of the bubble-free liquid and for the case where the liquid is uniformly filled with bubbles (before they have had time to float to the top).

I tested this hypothesis. Since my sense of pitch can easily be wrong by an octave, I used a microphone and an oscilloscope. I found that I needed a suitably softened mallet--a piece of wood with several layers of masking tape over it--in order to avoid distracting high frequency sounds from the glass container. Starting with cold tap water ($20^{\circ}C$) in a 250 ml graduated cylinder I found that with a cylindrical water column of height 0.28 m my gentle tapping on the bottom of the cylinder excited damped oscillations having a frequency of about 1300 Hz. Assuming the water column to be one quarter wavelength gives a sound velocity $v = \lambda f = 4x0.28x1300=1460$ m/sec, which agrees well with the handbook value of 1470 m/sec. Thus my simple hypothesis was verified. (I also checked that when I poured out some of the water the frequency increased by the expected amount, and that the frequency did not depend on the diameter of the cylinder.)

Going over to hot tap water from a partially contricted faucet I found that I could get a frequency decrease by a factor of about 7 during the inverse effect. When the bubbles all rose to the top the pitch was essentially the same as for cold water. (For the same length of water column the frequency for the hot water should actually be about 8% higher than for the cold water. My oscilloscope measurements were only good to about $\pm$ 10% and I did not check that point.) Since the pitch decrease during the inverse effect has to compete with a small simultaneous pitch rise due to the rising of the bubbles, I estimate that my experimental pitch-lowering factor of 7 ± 0.7 should be corrected to 7.5 ± 0.8 , for the pitch-lowering I would get if the bubbles did not rise.

Once I had learned how to detect this longitudinal mode with the tall graduated cylinder using both my ear and the oscilloscope then I was able to recognize it also for water in a coffee mug, where I had difficulty in determining the pitch by ear alone. For a cold water column of height 6.8 cm

I observed damped oscillations of 5000 Hz. That makes the water column 0.23 wavelengths high, agreeing with the expected 0.25 within my measurement errors. That shows that the effect observed "naturally" in the kitchen (i.e., in a coffee mug) is the same as the one observed with tall glass cylinders.

4. QUALITATIVE EXPLANATION OF THE LARGE PITCH RATIO

The velocity of sound in air is about one fourth of its velocity in water. Therefore if you completely replace the water column by an air column of the same height the pitch goes down by a factor of about 4. How can it possibly be that if, instead, you replace only a tiny fraction of the water volume by air bubbles, the sound velocity goes down not by a tiny fraction of 4 but by a factor of nearly 8? That is a surprise, if we are expecting to find sound velocity in bubbly water to be given by some kind of "interpolation" between the velocities in pure air and pure water.

Further thought makes it less surprising. Sound speed in a liquid or gas depends on two physical quantities: compressibility and mass density. It helps to think in terms of slowness rather that speed. Let us define slowness = 1/speed. (Slowness is measured in units of seconds per cm, or hours per mile.) The slowness of sound is greater (i.e. the sound travels more slowly), the greater the inertia (mass density) of the gas or liquid. Greater compressibility (weaker "return force") also gives greater slowness. Slowness turns out to be the square root of the product of the density times the compressibility. Water has about 800 times the density of air, so we might expect it to have greater sound slowness than air. However, air is about 15,000 times more compressible than water. Thus air wins the "slowness race" by a factor of the square root of 15,000/800, which is 4.3, and sound travels 4.3 times slower in air than in water. Now suppose that the water is filled with air bubbles distributed homogeneously throughout the liquid but occupying only a small fraction of the total liquid volume. The density will then be essentially that of water. That gives a large slowness contribution. But the compressibility will be practically all due to the air in the form of bubbles. That also gives a large slowness contribution. It should not surprise us that by combining the large slowness contribution of the water (its inertia) with that of the air (its compressibility) we can get a slowness that is greater than that of either water or air.

5. A SIMPLE QUANTITATIVE THEORY

We need a theoretical expression for the velocity of sound in a homogeneous mixture of water and air bubbles, in order to compare with our experiments. The exact theory is rather complicated.[6] It predicts that the sound velocity in the mixture depends on the bubble radii. I made only very crude measurements of bubble radii. However, I did measure the fraction of the liquid volume occupied by bubbles. (The method is described later.) It turns out that that is all we need to know, for our sound wave frequency and our bubble-size regime. What follows is a very simple theory that can be compared with my measurements.

The velocity of sound, v, in a homogeneous liquid or gas depends on the mass density ρ and the compressibility K as follows:

$$1/v^2 = K\rho \quad , \qquad (1)$$

where the compressibility K is defined as

$$K=(dV/dp)/V . \qquad (2)$$

Here V is the volume and dV is the volume decrease due to the pressure increase dp in the sound wave. Now consider a homogeneous mixture of water and air bubbles. We will only consider sound frequencies where the wavelength is large compared with the bubble radii and the spacing between bubbles. Then Eqs.(1) and (2) should still apply. Use subscripts w and a, for water and air, and no subscript for the mixture. Since the fractional volume occupied by bubbles is very small we take the density of the mixture to be that of water: $\rho=\rho_w$. The total volume in Eq.(2) is essentially that of the water: $V=V_w$. For the volume change dV we take $dV=dV_w+dV_a$. Then Eqs.(1) and (2) give for the mixture

$$1/v^2 = (\rho_w/V_w)(dV_w/dp) + (\rho_w/V_w)(dV_a/dp). \qquad (3)$$

The first term in Eq.(3) is just $1/v_w^2$, according to Eqs.(1) and (2). Multiply Eq.(3) by v_w^2. Then multiply the numerator and donominator of the second term by V_a and define $V_a/V_w=f_a$, where f_a is the fractional volume occupied by air bubbles (for f_a small compared with unity.) The second term becomes $v_w^2\rho_w f_a K_a$, which also equals $f_a K_a/K_w$. Then Eq.(3) becomes

$$v_w/v = [1+(K_a/K_w)f_a]^{\frac{1}{2}} = [1+v_w^2\rho_w f_a K_a]^{\frac{1}{2}} . \qquad (4)$$

We now make a simplifying (and possibly wrong) assumption. We neglect the possible dependence of K_a on bubble radius, surface tension, water vapor, heat of vaporization, thermal conductivity of the air, etc., and take K_a to be the same as one takes for sound velocity in normal air, which is the adiabatic compressibility of dry air. That gives $K_a=1/\gamma p$, where $\gamma=1.40$ is the ratio of specific heats for dry air and $p=1.01\times10^6$ dyne/cm^2 at 1 atmosphere. For water we take $\rho_w=1.0$ gm/cm^3 and $v_w=1470$ m/sec. That gives

$$K_a/K_w = v_w^2\rho_w/\gamma p = 1.49\times10^4. \qquad (5)$$

Then Eq.(4) becomes

$$v_w/v = [1+1.49\times10^4 f_a]^{\frac{1}{2}} \qquad (6)$$

For $f_a=0$, Eq.(6) says that the sound velocity reduces to v_w, as it must. (The dissolved air molecules have no effect. It is only when they collect in bubbles that they increase the compressibility.) For $f_a=0.01$, Eq.(6) predicts that in the bubbly mixture the sound velocity is about 1/12 of the velocity in water, or about 1/3 the velocity in air. That agrees with our qualitative discussion in Sec. 4.

The formula for v_w/v given in the more sophisticated theory of Ref.6 reduces to my Eqs.(4), (5), and (6) in the limit where the sound frequency is small compared with the natural oscillation frequency for radial oscillation of the bubbles. That is indeed the case for my observations. (See the Appendix.)

6. COMPARISON OF THEORY AND EXPERIMENT

In order to measure f_a and the pitch ratio I separated the experiment into two parts performed one after the other with several repetitions within a few minutes, so that the hot tap water would not have time to change its properties. For measuring frequency ratios I used a 250 ml graduated cylinder. This was tall enough so that bubbles rose by only a small fraction of the height of the water column during the "inverse" effect while they were forming. To measure f_a I needed a suitable "volume magnifier", so I instead used a 250 ml volumetric flask having a tall narrow neck (the magnifier). I taped a ruler onto the neck so that I could read the position of the liquid meniscus. After first filling the flask with hot bubbly tap water I would quickly read the meniscus. This first reading was a bit difficult, since the water was cloudy with bubbles and the meniscus was "frothing" with the arrival of new bubbles floating up from below. (An improved method described later eliminated the need for this difficult first reading.) Nevertheless I could read it to about $\pm$ 1 mm. After most of the bubbles had risen to the top (it takes two or three minutes) I found that the meniscus had dropped by about 4 mm. That corresponded to a volume decrease of 0.8 cm^3, which I take to be the volume of air that was in the form of air bubbles when I first read the meniscus immediately after filling the flask. That gives f_a=0.8/250 =(3.2$\pm$ 0.8)x10^{-3}. Inserting this value of f_a into Eq.(6) gives a predicted velocity ratio v_w/v = 7.0$\pm$0.8. Since I assume the column of liquid is one quarter wavelength, both for the pure water and for the mixture, the predicted velocity ratio is the same as the predicted frequency ratio. My measured frequency ratio was 7.5$\pm$0.8. Thus I found good agreement between my observations and the simple theory. (An improved measurement of f_a is described in Sec.7.)

7.EXPECTED VALUE OF f_a.

Some weeks after measuring f_a it occurred to me that I should be able to predict its value. Assume the air goes into solution at the cold water temperature of 20°C and reaches the equilibrium concentration for water at 20°C in contact with air at 1 at pressure. After the water gets into the pipes it sees no more air, The dissolved air fraction remains constant. (These assumptions were supported by conversations with East Bay Municipal Utilities District engineers.) When the water is in my hot water pipes it is under gauge pressure of about 50 psi. Therefore the air remains in solution. When it emerges from the hot water faucet it is suddenly again at 1 at pressure and is supersaturated with air, because the hot water cannot hold as much dissolved air as the cold water. If suitably "triggered", the excess air will come out of solution in the form of rapidly growing bubbles. When all of the excess air has come out of solution the bubbles stop growing. (That terminates the inverse effect.) We then have a calculable fraction f_a of the volume in the form of air bubbles.

Here is the calculation. According to the Handbook of Chemistry and Physics (35th Edition) for pure N_2 at 760 mm Hg pressure in contact with water at $20^{o}C$, the equilibrium amount of N_2 in solution is 0.01545 cc of N_2 gas when reduced to STP (standard temperature and pressure, $0^{o}C$ and 760 mm Hg) for each cc of water. At $40^{o}C$ it is 0.01184 cc (at STP) per cc of water. Taking the difference we find 0.0145-0.01184 = 0.00361 cc (at STP) per cc of H_2O , that should come out as bubbles. The bubbles are not at $0^{o}C$ but at $40^{o}C$ so they occupy a large volume in the ratio (273+40)/273=1.146. Also, when the N_2 went into solution the partial pressure of N_2 was not 760 mm Hg but only 78% of that, for normal air. Thus the amount in solution is reduced by a factor of 0.78. Also, at $40^{o}C$ the vapor pressure of water is 55 mm Hg. The total pressure of air plus water vapor in the bubble should be 760 mm Hg, so the air need only furnish 760-55= 705 mm Hg pressure. That increases the volume of the bubble by the ratio 760/705=1.078. (Surface tension may contribute an additional correction to the pressure. See the Appendix.) The amount of N_2 I expect to come out as bubbles is therefore

$$f_a(N_2) = 0.00361 \times 1.146 \times 0.78 \times 1.078 = 3.5 \times 10^{-3}. \qquad (7)$$

For pure oxygen at 760 mm Hg pressure the equilbrium amount in solution at $20^{o}C$ is 0.03102 cc of O_2 (at STP) per cc of H_2O. At $40^{o}C$ it is 0.02306. Taking the difference, converting to volume at $40^{o}C$ and 705 mm Hg, and multiplying by the fractional partial pressure of oxygen in air, 21%, we get a predicted value

$$f_a(O_2) = (0.03102-0.02306)\times 1.146 \times 0.21\times 1.078= 2.1 \times 10^{-3} . \qquad (8)$$

We can compare the preditions (7) and (8) with my observed value of $f_a=(3.2\pm 0.8)\times 10^{-3}$. My observed value was just (57±14)% of the predicted total , $f_a=5.6\times 10^{-3}$, given by the sum of (7) plus (8).

At first I was delighted by this fairly good agreement. But then I was struck by the fact that my observed value would be in excellent agreement with the predicted excess for N_2 alone, as given by (7). Was it possible that my bubbles were pure nitrogen, with no oxygen? I received support for this fascinating hypothesis by noticing that at both 20^o and 40^o the solubility per molecule of oxygen is twice that of nitrogen. (For example at 20^o the ratio of the two numbers 0.03102 and 0.01545 given above is 2.01.) If water "likes" oxygen twice as well as it does nitrogen, might not that inhibit the speed of diffusion of the oxygen through the water to reach the surface of the growing bubble, relative to that of nitrogen, or inhibit its evaporation into the volume of the bubble, relative to nitrogen?

Perhaps I should have just asked a chemist, but I was afraid the answer might discourage me. I needed to learn how to measure oxygen content in water and air. Fortunately I soon contacted Prof. David Jenkins and Mr. Bruce Jacobsen of the U.C. Sanitary Engineering Departmemt, who are experts at that measurement. Rather than bring samples of water to their laboratory I worked with Mr. Jacobsen, using samples from their faucet, since their faucet gave nice cloudy hot water (when the valve was constricted) and a fine pitch-lowering effect. We found that the cold tap water at 22^oC had the predicted amount of DO (dissolved oxygen) for water saturated with air at 22^oC and 1 atmosphere. The hot water at 56^oC that had been "debubbled" by passing it through the constricted faucet had exactly (within measurement errors) the reduced amount of DO expected for water at 56^o saturated with air at 1 at. That is, a supersaturated oxygen residue was not being left behind in the water when the bubbles formed. This showed that the debubbling was practically 100% efficient at removing excess oxygen, and "shot down" my fascinating hypothesis. As a further check we measured the oxygen fraction of the gas that came off as bubbles from the water emerging from the constricted hot water faucet. The gas was not pure nitrogen. It had the normal fraction of oxygen found in air. This "drove the last nail in the coffin" and my fascinating conjecture was laid to rest.

That left unanswered the question as to why I was only getting about 60% of the predicted amount of air in bubbles when I measured f_a. I suspected that I was losing air in larger than average bubbles that were floating up and being lost either before I made my first meniscus measurement (the difficult "frothy" one) or during it. To eliminate this first meniscus measurement I designed an improved flask for measuring f_a. The flask was made by joining a pear shaped flask at its narrow end to a 5 mm (inside diameter)calibrated pipette. The flask is stoppered at its broad end, which I'll call the bottom. The pipette can be corked at its end (the "top"). The end of the cork defines the end of the pipette volume.
In use the flask is corked at the top, inverted, filled to overflow through the bottom, stoppered to overflow at the bottom, reinverted so the top is up, immersed in a hot bath at the temperature of the hot tap water until all the bubbles have risen (five minutes), and then read. Only one meniscus reading is needed because the cork defines the end of the pipette and its location replaces the "frothy meniscus" measurement. The magnification is also larger on this flask; the air occupies about 50 mm along the pipette rather than the 4 mm of the earlier technique.

With the improved flask I find(for 20^o cold and 40^o hot water)

$$f_a = (4.1 \pm 0.4)\times 10^{-3}. \qquad (9)$$

Inserting this value of f_a into Eq.(6) gives a predicted pitch ratio $v/v_w = 7.9 \pm 0.4$, which is still in good agreement with my measured value of 7.5 ± 0.8. My "efficiency" for catching the excess air, with the improved flask, is found by dividing (9) by (7)+(8), to get 4.1/(3.5+2.1)=0.73. Part of the "missing" 27% may be lost during the filling of the flask, before it gets stoppered, since this is a somewhat turbulent process and large bubbles released during the filling can rise rapidly and be lost before I finish filling, and insert the stopper. Another possibility is that the predictions (7) and (8) are too high, because I have not corrected the pressure (and hence the volume) for surface tension. (See the Appendix.) Whatever losses that may occur during measurement of f_a should also occur during the filling of my graduated cylinder to make the pitch-lowering measurements; therefore no correction factor need be applied to the result (9) before using it to predict the pitch ration.

8. FURTHER OBSERVATIONS

If one starts with an empty graduated cylinder and taps the bottom with a knuckle the pitch heard by ear (or observed on the oscilloscope) is of course that of the air column, with the length of the air column being approximately one quarter wavelength for sound in air. As one adds cold water to the cylinder the air column shortens and its pitch rises. One can now start to listen for a high note due to longitudinal vibrations in the water column. But this note is difficult to hear until the cylinder is nearly full. It is masked by the much louder note from the air column. If instead one starts with the cylinder completely full of water then there is no air column and one can easily identify the pitch of the note due to the water column. As one now pours out water a little at a time one can keep track of this note as its pitch ascends, and can start to hear a note from the air column. Since the velocity of sound in air is roughly one quarter of the velocity in water, then, when the air column at the top of the cylinder is about one quarter the height of the water column the pitch of the water vibrations will equal the pitch of the air vibrations. For even less water the louder and lower air vibrations make it difficult to hear the water vibrations. In order to hear the water vibration it now helps to ruin the air column by stuffing a wet paper towel into the air space so as to damp the air vibrations. Alternatively one can use a stethoscope with its detector just under the water surface, to enhance the water note.

By judicious tuning of the water level in the region where the air column is about one quarter of the water column one can, using the oscilloscope, observe beats between the simultaneous air and water notes when the bottom of the cylinder is tapped. Because of the poor impedance match at the water-air surface it is hard to get the water note out of the water, and the water note is weak compared with the air note. Therefore the beats are not strongly modulated. I can see them with a microphone and oscilloscope but cannot hear them by ear.

In the Appendix, I examine the dependence of the sound velocity on bubble radius and conclude that for our regime of bubble radii and sound frequency the assumption of adiabatic oscillation of the air bubbles is probably not valid. If that is indeed the case and the oscillations are isothermal that would increase my predicted pitch ratio by about 18%. Experiments more accurate than those I report here could settle that question. I also show in the Appendix that surface tension can probably be neglected for our bubble sizes. I also show that a model where the number of bubbles remains roughly constant while each bubble grows with time agrees both with the appearance of the water (increasing cloudiness during the inverse effect) and also the time duration (of order 10 seconds) of the inverse effect.

9. APPENDIX. DEPENDENCE OF SOUND VELOCITY ON BUBBLE DYNAMICS

The radial oscillation of gas bubbles in water was investigated theoretically and experimentally by Minnaert.[7] By equating the maximum potential energy (at maximum compression) to the maximum kinetic energy (at the equilibrium radius, a), and assuming that the compressibility was the adiabatic compressibility of dry air, namely $K_a=1/\gamma p$, Minnaert derived the expression

$$\omega_R^2=3\gamma p/a^2\rho_w, \qquad (10)$$

where $\omega_R=2\pi f_R$, and f_R is the natural oscillation frequency. Minnaert verified Eq.(10) experimentally for bubbles having radii between 1.5 and 3 mm. He also verified the need for the factor $\gamma=1.4$ for air bubbles, and verified the dependence on the factor γ by using other gases besides air. If the oscillations had been isothermal the factor $\gamma=1.4$ would be replaced by unity in Eq.(10). More generally we let γ denote the "polytrope" index, which should equal the ratio of specific heats, 1.4, if the oscillations are adiabatic, should equal 1.0 if they are isothermal, and may lie somewhere between if they are neither. Minnaert's experiments demand $\gamma=1.4$ and rule out 1.0, for his bubble sizes.

Medwin[6] gives a formula for v/v_w which is the same as our Eq.(4), except that his expression for K_a depends on frequency. If we neglect his damping term (which is only important close to the resonance frequency f_R) his result can be written

$$K_a=[Z^2/(Z^2-1)](3/a^2\rho_w\omega_R^2) \qquad (11)$$

where $Z=\omega_R/\omega$, and $\omega=2\pi f$, where f is the driving frequency. If we substitute Minnaert's value of ω_R from Eq.(10) we obtain

$$K_a=(1/\gamma p)Z^2/(Z^2-1). \qquad (12)$$

For driving frequency f much smaller than the resonance frequency f_R we have $Z>>1$. Then Eq.(12) becomes $K_a=1/\gamma p$ and Medwin's formula reduces to my Eq.(6).

My observations were at sound frequency f=1.3 kHz. For a bubble radius 0.1 mm, Eq.(10) predicts f_R=33 kHz. Most of the bubbles that contribute to my observations appear by eye (with a pocket magnifier) to have radii about 1/50 mm. Thus my measurements at 1.3 kHz should lie in the low frequency regime of Eq.(12) and I expect my Eq.(6) to be sufficiently accurate at my level of experimental accuracy.

Should one use the adiabatic compressibility in calculating the resonant frequency f_R when the bubble radius is less than 0.1 mm? Minnaert verified γ=1.4 in Eq.(10) for bubbles with radii greater than 1.5 mm. But for sufficiently small bubbles and for sufficiently low frequency f there will be time for heat to flow by diffusion from the center to the surface of the bubble during a half period T/2 = 1/2f. Air molecules can there quickly exchange energy with the water. Thus for sufficiently small bubbles we should replace γ=1.4 by 1.0 in Eq.(10), and therefore in Eq.(12) and in my Eqs. (5) and (6). If we replace γ=1.4 by 1.0 in Eq.(5) that replaces the "1.49" in Eq.(6) by 2.09, and changes the predicted pitch lowering in my experiment from 7.9$\pm$0.4 to 9.3$\pm$0.5. I cannot quite distinguish between those two predictions with my experimental accuracy; partly that is because of uncertainty in my technique for measuring f_a (where is the "missing" 27%?) and partly because it is difficult to determine the lowest frequency to better than 10% during the simultaneous frequency decrease (as bubbles form) and increase (as they rise).

At what bubble radii do we expect heat flow to become important at our sound frequency? Let the collision mean free path for the air molecules be λ ; let the rms molecular velocity be c, and let the molecules diffuse for a time t. Then the mean square radius R^2 of diffusion of an air molecule is given by

$$R^2=\lambda ct. \qquad (13)$$

Taking $\lambda=6\times10^{-6}$ cm, c=300 m/s, and $t=T/2 = 3.9\times10^{-4}$ sec for f=1.3 kHz gives R=0.08 mm. This is four times greater than our estimated average bubble radius of about 0.02 mm. Therefore for our bubbles the adiabatic assumption should break down, whereas at Minnaert's radii of greater than 1.5 mm the adiabatic assumption should be valid. (I reach this same conclusion when I substitute into the more complete formulas derived in the thorough theoretical discussion of oscillating gas bubbles by C. Devin, Jr.[8])

Experiments less crude than those reported here could examine the transition between adiabatic and isothermal oscillation.

What role does surface tension play? That depends on the bubble radii. The gauge pressure $p-p_o$ inside an air bubble of radius a, when applied to the cross sectional area πa^2 of a slice through a bubble great circle, must balance the force $\sigma 2\pi a$ due to surface tension exerted across the perimeter $2\pi a$. That gives $(p-p_o)\pi a^2=\sigma 2\pi a$, or

$$p=p_o+(2\sigma/a)=p_o[1+(2\sigma/a_o p_o)(a_o/a)], \qquad (14)$$

where a_o is the final bubble radius. For water we have σ=75 dyne/cm. Taking $a_o=2\times10^{-3}$ cm (my estimate using a pocket magnifier), and p_o= 1 at = 1.0×10^6 dyne/cm^2, Eq.(14) becomes

$$p=[1+(0.075)(a_o/a)]p_o. \qquad (15)$$

Let us first apply Eq.(15) to the predicted value of f_a. For $a=a_o$, Eq.(15) predicts that the pressure inside the bubble is 1.075 at. We neglected that factor in the main text. The predicted volume is therefore reduced by a factor of 1/1.075. The sum of (7)+(8), multiplied by 1/1.075, is $[(3.5+2.1)/1.075]\times10^{-3} = 5.2\times10^{-3}$, which is to be compared with my measured value of $(4.1\pm0.4)\times10^{-3}$. Suppose now that my estimate of a_o was biased in that I notice the largest bubbles most easily. If the average value of a_o is, say, 0.5×10^{-3} cm instead of 2×10^{-3} cm then the 0.075 should be replaced by 0.30 in Eq.(15). In that case the predicted value of f_a becomes 4.3×10^{-3}, in by diffusion a region of radius R_o. According to Eq.(13) that time is given by

$$t_o = R_o^2/\lambda c. \qquad (19)$$

The chance that during the exploration of this region the air molecule will be captured in the bubble should be proportional to the time spent in the bubble volume; that time should be proportional to the bubble volume. Thus, without worrying about factors of two (the bubble volume is not constant) we multiply Eq.(19) by the volume ratio R_o^3/a_o^3. That gives our estimated clean-out time t:

$$t = R_o^5/a_o^3\lambda c. \qquad (20)$$

Since the ratio R_o/a_o is fairly well known (it depends only on our fairly well measured value of f_a) but a_o is poorly measured, we put in our value $R_o/a_o=5$ and write Eq.(20) as $t = 5^5 a_o^2/\lambda c$. For the mean free path λ of the air molecule diffusing in water we take the edge length of the cube occupied by one water molecule in the liquid: $\lambda=3\text{x}10^{-8}$ cm. Taking c=300 m/sec (thermal velocity), and our crude value $a_o = 2 \times 10^{-3}$ cm, we find an estimated bubble growth time

$$t = 5^5(2\text{x}10^{-3})^2/(3\text{x}10^{-8})(3\text{x}10^4) = 14 \text{ sec.} \qquad (21)$$

Because of the large uncertainty in a_o, the better-than-order-of-magnitude agreement of (21) with my observations has to be pure luck. But the order-of-magnitude agreement is not, and supports the model with practically constant number of bubbles, each growing larger with time because of the capture of diffusing air molecules.

Finally, what is it that determines the initial number of bubbles per unit volume, N_v? (That is what determines the final bubble radius a_o.) I believe there is a very simple concept that would enable me to predict N_v. But I haven't found the concept.

ACKNOWLEDGEMENTS.

I would like to thank Bruce Jacobsen, David Jenkins, Jordin Kare, Phil Lubin, Terry Mast, Richard Muller, and Peter Tans for helpful comments and suggestions. This work was supported by the Physics Division of the U. S. Department of Energy under contract No. W-7405-ENG-48.

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5. W. Bragg, "The World of Sound", (Dover, 1968), p.158, describes the attenuation of sound by bubbles in a liquid. He says "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." If only he had tapped his glass immediately after it was filled, before the bubbles rose to the top, he would have noticed the time-dependent change of pitch that constitutes the hot chocolate effect. It might then have been called the cold beer effect.

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