FYS2160/LAB Fall term 2019: GAS THERMODYNAMICS

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The sound of air, argon, and CO_2. By exploiting interference (resonance) in Kundt's tube to measure the speed of sound we can extract some thermodynamic quantities. We will examine how these depend on temperature, and by comparing our measurements with the expected behaviour of ideal gases we can find the number of thermodynamic degrees of freedom, and determine if the gas is ideal or not.

Sections I – V summarize the most important ideas to be investigated in this lab. Results that are necessary to complete the assignment in Section VI may be found in the five numbered boxes.

An appendix is devoted to explaining why numbers in physics are completely different from mathematical numbers, and how to treat experimental data (numbers) with the respect they deserve. A comparison of experimental numbers and theoretical (mathematical) numbers is meaningless unless you have a "stick" ("ruler") to measure the distance between them. This measuring stick is the "error" or "uncertainty" of your measurement.

I. WHAT IS A PHYSICAL THEORY?

A theory should be as simple as possible, but not simpler. Albert Einstein

Real materials consist of atoms, which are made of electrons, protons and neutrons, which are made of quarks and gluons, which are .... How can we do physics when matter is so complicated? The answer is that we can model the "cosmic onion" one layer at a time. Physics is the art of simplification, i.e., of ignoring those details that are irrelevant for what one has chosen to model.

This is possible because most of the details that are important (relevant) for microphysics are unimportant (irrelevant) for macrophysics. Consider the Solar system. Compared to a planet you are microscopic, and completely irrelevant for the planet's trajectory through space and time. Planetary trajectories can be determined to very good accuracy by modelling the Sun and planets as points obeying Newtonian mechanics.

It is not unusual that macroscopic concepts have no microscopic meaning. An atom has neither pressure nor temperature. This phenomenon, that the whole (collective behaviour) is more than (or at least different from) the sum of its parts, is called *emergence*. That the "collective" (the gas) forgets the "personality of its individuals" (microscopic details of the molecules) is called *universality*. Without these concepts we cannot understand physics or any other natural science. *The prime example of this is thermodynamics and statistical mechanics.*

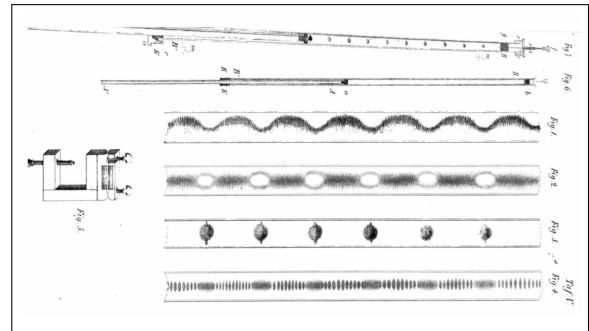One of the purposes of this lab is to encourage you to

Figure 1. Original illustration from the article by August Kundt in *Annalen der Physik* in 1866, which shows standing waves inside *Kundt's tube*.[1] We shall here repeat his experiment with modern equipment, with one of the objectives being to test thermodynamic gas theory.

reflect on what is important, and what is not, in thermodynamic gas theory. Our first task is find out how to model the molecules in a gas: what is relevant, and what is not? We wish to find out how thermodynamic variables like pressure and temperature capture the collective macroscopic behaviour of the myriad of microscopic constituents (atoms or molecules).

II. FROM MOLECULES TO MOLES

The simplest model of a molecule is that atoms are represented by indivisible mathematical points *(rigid balls or spherical "stones")* without "personality" (i.e., no other physicially measurable attributes), which are connected by "sticks" with no structure. This *sticks&stones* molecule can move and rotate in space, but that is all. A better model is to replace the sticks with springs, so that the molecule also can vibrate (*ball&spring* model). An even better model is to replace the balls with Bohring atoms, where the electrons can be excited to various states with distinct, discrete (quantized) energies (*quantum oscillator&spring* model), but we will not consider this model here.

At room temperature ($T \simeq 300\,K$) the *sticks&stones* model of air works surprisingly well. In this model air molecules do not interact, which means it is treated as

an *ideal gas.* For ideal gases we have a very direct bridge between micro- and macro-physics, via the *heat capacity.* The only information that thermodynamics retains about this "mathematical" gas is how many *thermodynamic degrees of freedom* f the molecules have, and how heavy they are. The more degrees of freedom the molecules have, the more heat they can store. This is measured by the molar heat capacities c_p (constant pressure; *isobaric* process) and c_V (constant volume; *isochoric* process).

In an ideal gas at normal temperature (less than $1000\,K$) every degree of freedom contributes $R/2$ to c_V:

$$c_V = f\,\frac{R}{2}, \quad c_p = (f+2)\,\frac{R}{2},$$

where R is the *molar gas constant* (a.k.a. the *universal* or *ideal* gas constant):[2]

$$c_p - c_V = R = 8.314\,4598(48)\ \text{J/(K} \cdot \text{mol).}$$

The *adiabatic index* (a.k.a. the *heat capacity ratio,* the *ratio of specific heats, Laplace's coefficient,* or the *isentropic expansion factor*) for an ideal gas is

$$\boxed{\gamma = \frac{c_p}{c_V} = \frac{f+2}{f}} \tag{1}$$

This ratio determines the macroscopic *adiabatic equations* for an ideal gas, which assert that $p\,V^\gamma$, $T\,V^{\gamma-1}$, and $T\,p^{1/\gamma-1}$ are constants. For an ideal gas the *equation of state* is

$$pV = n_{\text{mol}}RT,$$

where n_{mol} is the amount of matter measured in the SI unit mol. The number of moles of gas molecules is $n_{mol} = m/M_{\text{mol}} = N/N_A$, where m is the mass of the gas, M_{mol} is the mass of one mole of the gas (the *molar mass*), N is the number of molecules in the gas, and N_A is Avogadro's number.

The connection to statistical mechanics is evident from an examination of the equation of state:

$$pV = Nk_BT, \quad k_B = 1.380\,648\,52(79) \times 10^{-23}\ \text{J/K}$$

where k_B is Boltzmann's constant.[2] The thermodynamic gas constant R is proportional to Boltzman's constant k_B in statistical mechanics, and their ratio is Avogadro's constant:[2]

$$N_A = R/k_B = 6.022\,140\,857(74) \times 10^{23}/\text{mol.}$$

Thermodynamics is universally true (anywhere, at any time), provided that a few simple conditions are satisfied.

III. COUNTING DEGREES OF FREEDOM

We must distinguish between the number of mechanical degrees of freedom (f_{mech}) and the number of thermodynamic degrees of freedom (f), because they usually do not coincide at high temperature.

If the temperature T is significantly lower than the *characteristic temperaure* $\Theta \simeq 1000K$ where the atoms in a molecule start to vibrate, then the molecule will behave like a rigid body. Three numbers are needed to specify the location of the center of mass (3 translational degrees of freedom). In addition there are at most three rotations of the molecule that can store energy, but if the molecule has one or more axes of rotational symmetry ($s > 0$), then these rotations cannot store energy, and the number of rotational degrees of freedom relevant for thermodynamics is $f_{rot} = 3 - s$. For $T << \Theta$ the number of "rigid" degrees of freedom is therefore given by

$$\boxed{f_{rig} = 3 + f_{rot} = 6 - s} \tag{2}$$

where s is the number of rotational symmetries of the molecule. Every rigid degree of freedom contributes $R/2$ to the heat capacity. So, for rigid molecules (i.e., at low temperature[4]) the number of atoms does not matter, only which shape the molecule has (and its total mass).

Confusing vibes

This section is not relevant for this lab, but is intended to clarify a topic of much confusion that you may encounter elsewhere.

If $T \gtrsim \Theta \simeq 1000K$ we must include other degrees of freedom. The total number of *mechanical* degrees of freedom for n atoms is always $f_{mech} = f_{rig} + f_{vib} = 3n$, because we need three coordinates to determine the position of each of the n points, no matter how they move. The number of mechanical vibrational degrees of freedom is therefore $f_{vib} = 3n - 6 + s$. Each of these can be modelled by replacing the rigid rods between pairs of atoms with springs, i.e., harmonic oscillators.

Each vibration mode contributes an amount R to the heat capacity, so we can write the total heat capacity as $c_V = fR/2$, where we will call $f = f_{rig} + 2f_{vib} = 6(n-1) + s$ the number of *thermodynamic* degrees of freedom. At high temperature the number of thermodynamic degrees of freedom does *not* equal the number of mechanical degrees of freedom if $n \geq 2$: $f = f_{mech} = 3$ for $n = 1$, but $f > f_{mech} = 3n \geq 6$ for $n \geq 2$.

If these concepts are confused, as sometimes happens even in textbooks, then the counting of relevant degrees of freedom will be wrong. Since a vibrational mode can not be excited at room temperature, in this lab there will be *no* confusion: $f = f_{rig} = 6 - s$ for $T_{room} << \Theta \simeq 1000K$.

The reason that we have to double the counting of vibrational modes is that an oscillator has both kinetic and potential energy. If we model the bond between two atoms with a spring of a given stiffness ν_k (which is determined by how strong the bond is), then the molecule can store potential energy proportional to ν_k in the spring when it is stretched or compressed. At sufficiently high temperature each spring can store equal amounts of kinetic and potential energy (the *equipartition theorem*), so

each vibration contributes twice as much as translations and rotations to the capacity of the gas to store energy (the heat capacity c_V).

We define Θ_k ($k = 1, 2, \ldots, f_{\text{vib}}$) to be the *characteristic temperature* that must be exceeded in order to excite the vibration mode labeled by k. The value of $\Theta_k \propto \nu_k/k_B$ is determined by the spring constant ν_k. For normal molecules Θ_k is over a thousand degrees, and by "room temperature" we mean $T_{\text{room}} << \Theta_k$ (for all k).

IV. SOUND WAVES

Sound is a longitudinal pressure wave, and the speed of this wave depends on temperature, pressure, and other thermodynamic quantities. We are here going to use Kundt's tube to measure the speed of sound (cf. Fig. 1), use this to investigate how the heat capacity $c_*(s, M_{\text{mol}}, T)$ depends on molecular structure and temperature, and compare and contrast this with the theory of ideal gases.

A comparison of experimental data and theoretical results is meaningless unless you have a "stick" to measure the distance between them. This measuring stick is the "error" or "uncertainty" of your measurement!

It makes no difference whether the theoretical model is analytical or numerical. You may be able to solve a sufficiently simple model analytically and thereby obtain exact theoretical values of observables, but this has no value unless you have experimental data with error bars that can be used measure how well the model simulates reality.

In the absence of "the untimely intrusion of reality" (experiments), no matter how hard you work on your model this will only teach you something about the model, nothing at all about the real world.

Furthermore, since all models have limited validity, it is not sufficient to only rely on the experimental data that led to the construction of the model in the first place: it may break down at any time, so you must keep checking the model with new experiments adapted to your needs.

In other words, in physics an experimental number without units and error bars is worthless, and a theoretical number detached from reality is equally worthless.

A. Experimental determination of the speed of sound by finding resonances in the tube

We can determine the speed of sound in a gas by identifying the resonance frequencies of standing waves inside a tube, since we know that the velocity c of a wave always is given by $c = \lambda\nu$, where λ is the wavelength. From wave mechanics we know that a standing wave in a closed tube with resonance frequency ν_n has wavelength $\lambda_n = 2L/n$, where L is the length of the tube and n is an integer

($n = 1, 2, 3, \ldots$). Combining these results we obtain the linear function

$$\nu_n = an + b, \qquad a = \frac{c}{2L} \tag{3}$$

where the speed of sound is determined by the slope a. To get a better linear fit for the slope we leave the value of b undetermined.[3]

The uncertainty δc of your best estimate $\bar{c} = 2\bar{L}\bar{a}$ of the speed of sound is obtained by using the "Pythagorean method" (described in the appendix) for calculating how the uncertainties of a and L propagate through the function $c(a, L) = 2La$. The value of L and δL is given on each tube (they are not all the same).

B. Theoretical calculation of the speed of sound in ideal gases

From wave mechanics we know that the speed of sound c depends on the density ρ of the material (gas) and the *adiabatic compression modulus* K:[5]

$$K = -V\frac{dp}{dV} = \gamma p \implies$$
$$c = \sqrt{\frac{K}{\rho}} = \sqrt{\frac{\gamma p}{\rho}} = \sqrt{\frac{(f+2)p}{f\rho}},$$

where we have used that $K = \gamma p$ follows from the adiabatic equation $p \propto V^{-\gamma}$ and Eq. (1).

Example: The density of air is $\rho_0 \approx 1.29\,\text{kg/m}^3$ at $T_0 = 0°\text{C}$ at sea level, where the air pressure is $p_0 = 1$ atmosphere $\approx 1.0125 \times 10^5\,\text{Pa}$. If air is an ideal gas, then $f = f_{rom} = 3 + 3 - 1 = 5$ gives the speed of sound $c_0 \approx 331.5\,\text{m/s}$, which is in good agreement with the experimental value.[2]

From $\rho = m/V = nM_{\text{mol}}/V$ and $pV = nRT$ we get a thermodynamic equation for c in an ideal gas:

$$c_{\text{id}}(T) = \sqrt{\frac{(f+2)RT}{fM_{\text{mol}}}} \tag{4}$$

where T is the *absolute temperature* (measured in K).

Notice that the molar mass M_{mol} determines the speed of sound: the lighter the gas, the faster sound waves move through it. Compare for example the speed of sound in helium, which at room temperature ($20°\text{C}$) is more than 1000 m/s (cf. inset in Fig. 2), with the speed of sound in air. An exception from this rule is neon, which is a bit heavier than ammonia and water: $M_{\text{mol}}(\text{NH}_3) = 17.03\,\text{g/mol} < M_{\text{mol}}(\text{H}_2\text{O}) = 18.02\,\text{g/mol} < M_{\text{mol}}(\text{Ne}) = 20.12\,\text{g/mol}$. The reason is that neon has fewer degrees of freedom, which in this case is enough to overcome the small difference in molecular masses.
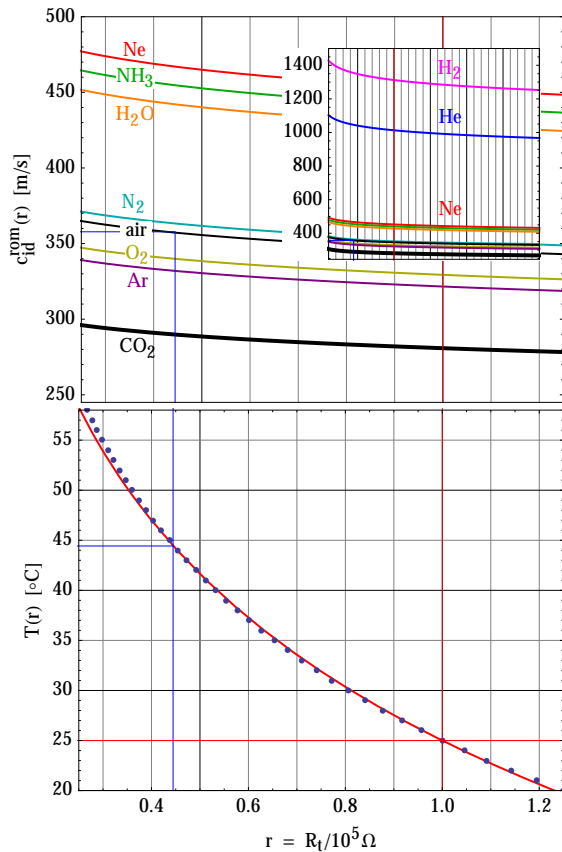
Figure 2. By measuring the electrical resistance $R_t[\Omega]$ in a thermistor, we can read off the temperature T_C [°C] from this diagram. Bottom: The red graph is our approximate (empirical) thermistor function $T_C(r) \approx 25 - 24\ln r$ [$r = R_t/(10^5\,\Omega)$], which has been fitted to the manufacturer's table (blue dots).

V. THERMISTOR PHYSICS

The purpose of this part of the lab is to emphasize that the apparatus (sensors) we use for mesurements also are physical systems. They are therefore only useful to the extent that we understand their physics. Often we use tables and graphs to convert the independent variable we actually measure to the dependent variable we need.

A good example that we have encountered before is the *Hall effect*, which appears when an electrical current in a solid encounters a magnetic field. This is an interesting phenomenon that we studied in FYS1120: *Electromagnetism* to get a better understanding of both electromagnetism and the (quantum mechanical) band structure of semiconductors. Having understood the physics of this phenomenon, we can then use it to make devices that measure magnetic fields with great precision, by measuring the Hall potential transverse to the current. Such *Hall probes* are now widely used, and so cheap and tiny that you probably have a handful in your phone.

To give a quantitative comparison of our sound data

with thermodynamic gas theory we must be able to measure the temperature accurately. We do this by measuring the electrical resistance R_t of a particular type of semiconductor called a *thermistor*. The "thermistor function"

$$T_C(r) \approx 25 - 24\ln r \qquad (5)$$

where $r = R_t/(10^5\,\Omega)$ and R_t is the Ohmic resistance of the thermistor,[6] is plotted in Fig. 2. Notice that it gives the temperature in *Celsius* (°C), not in *Kelvin* (K)!

We see that this empirical formula (best fit to manufacturer's data over a small range of temperatures) deviates slightly from tabulated values at high temperatures, but since it fits very well (with the uncertainties of our measurements) in the temperature range we are going to study, it is sufficient for our purposes.[6]

VI. EXERCISES

Exercise 1: What is sound?
(reminder of wave physics)

The purpose of this exercise is to remind ourselves what sound is (Fig. 3), what plane and standing pressure waves inside a tube are (Figs. 8 and 9), and how the resonance condition depends on boundary conditions, i.e., whether we plug the ends or not.

1.1 *Plane pressure waves*

Use the appended analog pressure wave simulator #1 (Fig. 8) to remind yourself what a *plane longitudinal pressure wave* is.

1.2 *Standing pressure waves*

Use the appended analog pressure wave simulator #2 (Fig. 9) to remind yourself what a *standing longitudinal pressure wave* is.
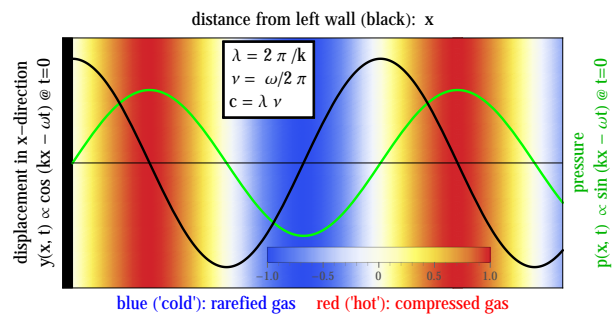

Figure 3. Three ways to "visualize" sound.

1.3 Resonance condition

From earlier courses (FYS2130: *Svingninger og bølger*, or similar) we know that the condition for resonance and standing waves inside a tube of length L that is plugged at both ends is $\lambda_n = 2L/n$, where n is an integer. Discuss this, and deduce a formula for the difference $\Delta\nu_k = \nu_k - \nu_0$ between the resonance frequencies $\nu_k \propto n_k = n_0 + k$ and an arbitrary reference resonance ν_0 determined by an unknown resonance number n_0 [cf. Eq. (3)]. We will extract the speed of sound from the slope of the graph of $\Delta\nu_k$.

Exercise 2: Measuring the speed of sound
(experimental part of this lab)

We are going to use standing waves to measure the speed of sound, with an apparatus sketched in the diagram shown in Fig. 4.

The gas is contained inside a long tube (with a specified internal length L with uncertainty $\delta L = \pm 1.5\,\text{mm}$, measured with a laser), which is plugged at both ends with massive metal disks. One of the plugs has a small hole in the center that emits sound waves from a loudspeaker attached to the outside of the plug. The speaker is driven by an alternating harmonic current delivered by a signal generator, which has a number of knobs on the right hand side where the amplitude (signal strength) can be adjusted so that the sound detector does not "clip" the signal.

The plug at the other end of the tube is equipped with a miniature microphone, which is connected to a battery driven amplifier attached to the outside of the plug (cf. Fig. 5). The signal from this amplifier, which is proportional to the pressure in the gas at the microphone, is sent to an oscilloscope. Make sure that both the input and output signals are unclipped harmonics (sines).

Our task is to identify resonance frequencies where the signal is much stronger than neighboring frequencies. The advanced signal generator can deliver frequencies with a precision of 10^{-3} Hz, but we cannot determine the maximum peaks on the oscilloscope with anything like this precision. Estimate the uncertainty in your readings.

There will be four groups analysing the speed of sound in four different tubes: [ATTENTION: You are not allowed to fill any gas other than air by yourself!]

K1: contains air at $T = T_{\text{room}}$

K2: contains air at $T > T_{\text{room}}$ ($I_{\text{max}} = 0.3\text{A}$)

K3: contains air at $T \gg T_{\text{room}}$ ($T_{\text{max}} \simeq 70°\text{C}$)

K4: contains argon or CO_2 at $T = T_{\text{room}}$

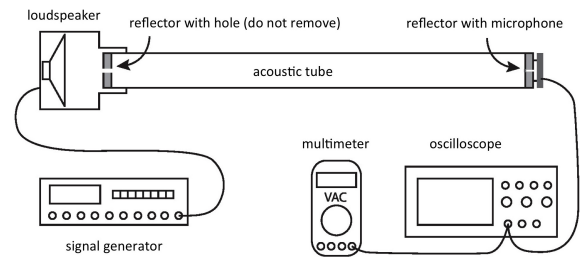*All results from K1 - K4 will be shared, so that you can compare and contrast them. After completing the next*

Figure 4. Sketch of the device used to measure the speed of sound in a gas (air, argon or CO_2 in this lab). The temperature inside the tube is monitored by inserting a tiny thermistor (not shown here) that does not obstruct the sound waves. Some of the tubes are wrapped with a heating cable and insulation (not shown here) so that the gas can be heated to at most 70°C. OBS: the heating current should not exceed $I_{\text{max}} = 0.3\,\text{A}$.
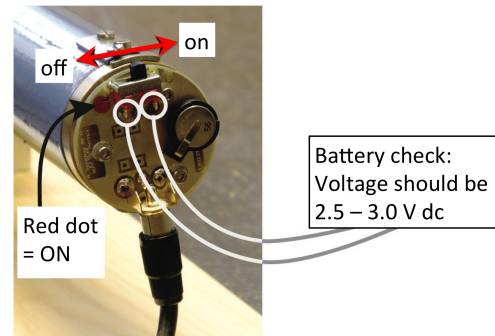

Figure 5. Photograph of the circuit board with on/off switch for the microphone amplifier, which runs on a small battery (round disk on the right hand side) that should have a nominal voltage of at least 2.3 V.

excercise you will compare these experimental results with theoretical expectations for ideal gases.

2.1 Resonances

Find all resonance frequencies in K1 - K4 in the frequency interval from about 200 Hz up to about 2 kHz. You may find a resonance below 200 Hz, but that one is so uncertain that it is better to use higher frequencies. Each reading should be as accurate as you can manage with about 30 seconds of "fine-tuning" for each resonance. Estimate (roughly) the uncertainty in each frequency measurement. Since it is difficult to find the longest wave (how long?) it is better to plot differences. This eliminates any systematic mislabeling of the data, i.e., use $\Delta\nu_k$ from the previous exercise.

Find the best linear fit to the data, and use Eq. (3) to find the speed of sound. What is the most important contribution to the uncertainty?

You may find the PYTHON code in the appendix useful. It will return the least squares fit to the data, includ-

ing the uncertainty in the slope. Verify that including more points shrinks this uncertainty.

2.2 *Temperature dependence*

If your tube is not wrapped up in a shiny thermal blanket, try to change the temperature inside the tube by placing your $(2, 4, 6, \ldots)$ hands on the tube, or blow on it. Is the temperature change measurable? Estimate the uncertainty in the temperature measurement.

Exercise 3: Sound of molecules

We first analyse how the number of microscopic degrees of freedom depends on molecular structure.

3.1 *Geometry*

How many rotational symmetries s_n can a molecule made of $n = 1, 2, 3, \ldots$ point-like atoms have?

3.2 *Atomic physics* Use your results from Exercise 3.1 and the periodic table of the elements to construct a table giving the molar masses and number of mechanical and thermodynamic degrees of freedom for noble gases, air, hydrogen, water, carbon dioxide and ammonia. Draw all the rotational and vibrational modes that can store energy in diatoms and CO_2. (Hint: The symmetry of the molecule depends on which group each atom belongs to.)

3.3 *Temperature dependence*

Use the theory of ideal gases to make a diagram showing the speed of sound in hydrogn, helium, neon, argon, nitrogen, oxygen, air, carbon dioxide and ammonia, as a function of temperature.

3.4 *Comparison of experiment and theory*

Compare your experimental data from Exercise 2 with your theoretical results from Exercise 3.3. What can you conclude about air (mostly N_2 and O_2) and about carbon dioxide?

Exercise 4: Thermistor thermometer
(metrology, semiconductors and thermodynamics)

We have used that the electrical resistance of a semiconductor has a strong temperature dependence, which we exploit to make a sensitive thermometer. This phenomenon is itself a consequence of thermodyamics, which we wish to understand better.

4.1 *Resistance and temperature dependence*

Electrical resistance in a metal increases approximately linearly with temperature, $r(T) = \alpha + \beta T + \ldots$, because the atoms in the crystal act as "barrage balloons" that obstruct electron flight through the metal lattice.

We have in this lab observed the opposite behaviour in semiconductors. Why does resistance in a semiconductor *decrease* when the temperature increases?

4.2 *Band population*

What is the physical reason that the "thermistor equation" Eq. (5) is more or less correct? In other words, can you find a qualitative explanation for why the temperature dependence of a semiconductor is logarithmic, rather than linear, as it is for metals? [Hint: What is the statistical distribution of charge carriers (electrons and holes) between the valence band and the conduction band?

APPENDIX: HOW TO TREAT YOUR DATA

In physics an experimental number without units and error bars is worthless.

This is an informal introduction to "linear regression", which is the most important and widely used method for analysing experimental data. It is essential for any physicist to quickly develop a relationship to experimental data, whether this is obtained from own work, or is being peddled by others.

A number derived from a measurement has no value unless we have some idea of how uncertain it is. The quickest and most robust method for fitting a model to data is to find a linear relationship, perhaps by changing variables and plotting the data so that hey populate the vicinity of a straight line, and then formally fitting this line to the data.

A. Linear models

In this lab the objective is to use a little knowledge from wave mechanics and a few measurements to construct a data list consisting of pairs of numbers, which can be thought of as points in a plane. Your task is to use this list to find the most probable value (the best estimate) $\bar{c}$ of the speed of sound in a gas, and the uncertainty δc of this estimate.

The simplest way to estimate $\bar{c}$ is to use a ruler. This is a slightly vague but very graphic way to illustrate how a line is fitted to a set of data. After plotting the data points on a plane a transparent ruler is placed on top of the paper in such a way that the data points a pread out "as evenly as possible" on both sides of the edge of the ruler. Intuition dictates that this is the "best fit". Linear regression is one way to make this intuition precise. All we need is a simple way to measure how "evenly" the points are spread out.

Notice that you are using the whole data set, and therefore all available information, when you shift and twist the ruler, and this is clearly a necessary requirement for a good fit. Notice also that only in rare cases does a data point sit right on the line, and it is usually not a good idea to "connect the dots", since this may be misleading as it does not combine the data set in a physically meaningful way.

A ruler is a good way to get a rough idea of the fitted line, but in reality we also use a computer to make this procedure quantitative. It tries out "all possible" lines $y = ax + b$ by changing the slope a and intercept b (constrained to a finite number by some built in numerical resolution). For each choice of line the sum of the squares of the (vertical) distances of the data points to the line is calculated. By definition, the winner (i.e., the "best fit") is the line with the smallest sum of squares. The slope $\bar{a}$ of this line contains the information about the best estimate of the speed of sound. (In other experiments we may also be interested in the best estimate $\bar{b}$ of the intercept, but not here.)

The spread of the data points around the line gives us the standard deviation. If you do not already have a favourite application that fits a line and calculates the uncertainty of this estimate automatically, you may wish to use the two lines of PYTHON code appended to this section. It does not get any simpler than that.

Without a universal line-fitting tool you cannot do physics, so if this is not already hardwired into your brain you should have that done now!

In the final part of this lab you are going to compare your experimental results with the theory of ideal gases, which asserts that $c \propto \sqrt{T}$. You must therefore also estimate the most probable value $\bar{T}$ of the average temperature inside the tube when you obtained the data. This comparison is meaningless unless you can estimate the uncertainty δc of the estimate $\bar{c}$, and the uncertainty δT of your estimate $\overline{T}$.

It has no meaning to say that two numbers are "near" each other unless you have a "measuring stick" to measure the distance between these numbers.

Is the estimated value $\bar{\pi} = 3.1415$ of the circumference to diameter ratio of any circle (obtained by wrapping wires around circles of many different sizes, say) "near" the exact value $\pi = 3.1415926535897932\ldots$ (exact if you knew all the dots), even if there are infinitely many numbers between these two (always!) distinct numbers? *The measuring stick is the variance (standard deviation) of the estimated value, so if you misplace this stick you have nothing!* If the uncertainty in the estimate of $\bar{\pi}$ is $\delta\pi = \pm0.001$, then $\bar{\pi}$ and π must be treated as the same number in physics, because we have no empirical information that allows us to say otherwise. If the uncertainty in the estimate $\bar{\pi}$ is $\delta\pi = \pm0.0001$, then $\bar{\pi}$ and π should be treated as different numbers in physics, because we do have empirical evidence allowing us to say that it is very improbable that they actually are the same number. This conclusion is not absolutely certain, but absolutes have no place in science. Our ambition is to know how uncertain our knowledge is, not to find "absolute truth".

The "uncertainty" in data that comes from unavoidable statistical variations (often called "errors", unfortunately) can be made as small as you can afford, by collecting more data. How big must the deviation be before we can say that the data do not support the model?
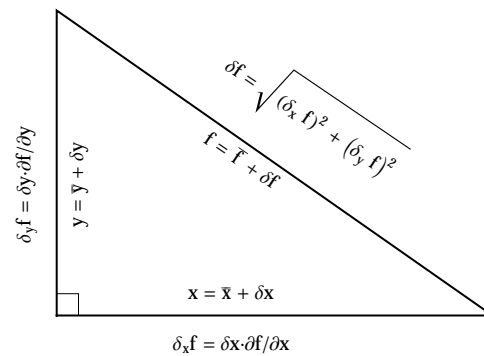

Figure 6. This "Pythagorean uncertainty triangle" is a mnemonic for addition of uncertainties.

There is no right answer to this question, but at least in particle physics the convention is that if the discrepancy is more than 5 standard deviations ("sigma") (the probability that this is a random statistical fluctuation is less than 1 in 3.5 million), then there is a real problem, and usually the model (theory) is in big trouble. However, sometimes the lack of agreement is caused by unknown *systematic errors* that often derive from an inadequate understanding of the measuring apparatus. If this is the case, then an improved experiment (rather than an improved theory), which actually measures what we think it is measuring, is what is needed. Systematic errors is the Achilles' heel of any experiment, because there is no systematic way of identifying their sources.

B. Pythagorean error propagation

When the best line has been found we can calculate the "spread" δa (*variance, standard deviation*) of the slope $\bar{a}$ of this line.

The standard deviation is defined in such a way that if you repeated the exact same experiment many times, then you would find

$a \in \langle \bar{a} - \delta a, \bar{a} + \delta a \rangle$ in ca. 68.27% of the experiments,
$a \in \langle \bar{a} - 2\delta a, \bar{a} + 2\delta a \rangle$ in ca. 95.45% of the experiments,
$a \in \langle \bar{a} - 3\delta a, \bar{a} + 3\delta a \rangle$ in ca. 99.73% of the experiments,
$a \in \langle \bar{a} - 4\delta a, \bar{a} + 4\delta a \rangle$ in ca. 99.994% of the experiments,
$a \in \langle \bar{a} - 5\delta a, \bar{a} + 5\delta a \rangle$ in ca. 99.9999% of the experiments,
etc.

The best estimate of the speed of sound is $\bar{c} = 2\bar{L}\bar{a}$, but what is the uncertainty δc of this estimate? More generally: *what is the uncertainty in the value of a function $f(x_1, x_2, \ldots)$ of one or more independent stochastic variables x_1, $x_2, \ldots$, which each has an uncertainty δx_1, $\delta x_2, \ldots$?*

Each uncertain variable x_k contributes to the uncertainty δf of f, but less than you might naively think. Heuristically, if all the measured values are independent, then they "pull in orthogonal directions", and should
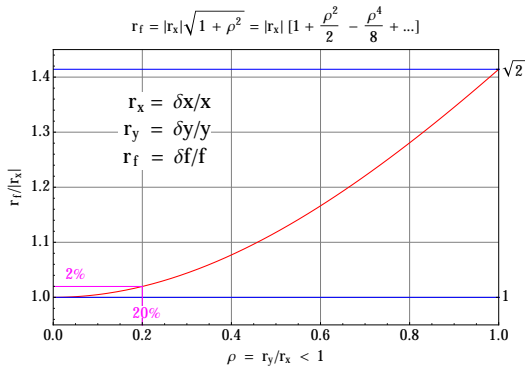
Figure 7. Relative uncertainty when $f = x \cdot y$ and $r_y < r_x$. Notice that if r_y is 20 % of r_x, then it contributes only 2 % to the relative uncertainty of f. If r_y er 10 % of r_x it contributes less 0.5 %.

therefore not be added linearly, which is the naive guess. That would give an excessively large etsimate of δf.

If there is only one variable, then the uncertainty in f if found by derivation, $\delta f = |df/dx|\delta x$. If there are two or more variables each one contributes via partial derivatives, but these should be added "in quadrature". For two variables a useful mnemonic is the "Pythogorean uncertainty triangle" shown in Fig. 6. The uncertainty δf of the best estimate $\bar{f} = f(\bar{x}, \bar{y})$ is given by the hypothenuse, which is smaller than the sum of the legs,

$$\delta f = \sqrt{(\delta_x f)^2 + (\delta_y f)^2} < \delta_x f + \delta_y f.$$

(More variables may be accomodated by an obvious generalization of this formula.) *Example:*

$$f(x, y) = xy \implies \frac{\delta f}{f} = \sqrt{\left(\frac{\delta x}{x}\right)^2 + \left(\frac{\delta y}{y}\right)^2}.$$

We see that it is the *relative uncertainties* $r_x = \delta x/x$, etc. that are relevant.

Since they are squared, a relative uncertainty that is significantly smaller than the others will not contribute much to the relative uncertainty of f. In this case we can drop one variable, and the equation simplfies to a much used form, $\delta f \approx y\delta x$. Fig. 7 shows how fast the contribution from the least significant variable, here $r_y = \delta y/y$, "dies" compared to $r_x > r_y$.

So, if you decide to use $\delta c \approx 2L\delta a$ to calculate the uncertainty in the speed of sound, then you must justify this by verifying that the relative uncertainty in a is much larger than the relative uncertainty in L.

C. Nonlinear models

The analytic process we have used here to estimate the speed of sound in a gas is typical. The method is the same for all linear functions, $f(x) = ax + b$. This is more general than it looks, because we can often swap a nonlinear function for linear one by a change of variables. Some examples are:

- $f(x) = a/x + b$: define $z = 1/x$ and study instead $g(z) = az + b$.

- $f(x) = c\exp(ax + b)$: take the logarithm on both sides and study instead $g(x) = \ln f(x) = ax + \tilde{b}$, where the new constant is $\tilde{b} = b + \ln c$.

- $f(x) = c\ln(ax + b)$: exponentiate both sides and study instead $g(x) = \exp f(x)/c = ax + b$.

- $f(x) = (ax + b)^c$: take the root on both sides and study instead $g(x) = \sqrt[c]{f(x)} = ax + b$.

If it is the uncertainty δx of a variable x that is known (usually determined by a separate fitting) then you have to use the Pythagorean method, even if there is only one independent variable x, to find the uncertainty of any quantify that is a function of x. For example,

$$f(x) = ax + b \implies \delta f = \left|\frac{\partial f}{\partial x}\delta x\right| = a\,\delta x,$$

while (see above list),

$$f(x) = a/x + b \implies \delta z = \left|\frac{\partial z}{\partial x}\delta x\right| = \frac{\delta x}{x^2}$$
$$\implies \delta g = \left|\frac{\partial g}{\partial z}\delta z\right| = \frac{a}{x^2}\,\delta x,$$

If it is the uncertainty δz of a transformed variable $z = z(x)$ that is known, usually by fitting a linear function $g(z) = az + b$, then you should use the Pythagorean method on $g(z)$, not $g(x)$: $\delta g = a\delta z$. The uncertainty in x is then $\delta x = |dz/dx|\delta z$. For example, if $z = 1/x$ then $\delta z = \delta x/x^2$ and $\delta x = \delta z/z^2$.

D. PYTHON

We find the best estimate $\bar{a}$ for the slope, as well as the uncertainty δa of this estimate, by fitting a straight line $y = ax + b$ to the list $[(1, \nu_1), (2, \nu_2), (3, \nu_1), \ldots, (n, \nu_n)]$ of n experimental data points.

The simplest way to do this in PYTHON is to download the statistics package **stats** from **scipy**, and then feed the two vectors (lists) $X = [1, 2, 3, \ldots, n]$ and $Y = [\nu_1, \nu_2, \nu_3, \ldots, \nu_n]$ to **linregress**:

> from **scipy** import **stats**
> **stats.linregress**$(\mathbf{X}, \mathbf{Y})$

The function **linregress** returns a list $[\bar{a}, \bar{b}, r, t, \delta a]$, where the first and last element gives the result we need, $a = \bar{a} \pm \delta a$.

Since the lists X og Y can be any type of data, you now have a very simple and useful tool (two lines of code!) for doing linear regression, on anything, at any time.

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[1] A. Kundt (1866). "Über eine neue Art Akustischer Staubfiguren und über die Anwendung derselben zur Bestimmung der Shallgeschwindigkeit in festen Körpern und Gasen". Annalen der Physik (Leipzig: J. C. Poggendorff.) **127** (4).

[2] The NIST Reference on Constants, Units, and Uncertainty. US National Institute of Standards and Technology. 2014 CODATA recommended values. OBS: SI units were recently redefined.

[3] Rather than acquiescing to the theoretical bias $b = 0$. This is actually the least biased thing to do, because we have made many assumptions about the geometry of the apparatus to arrive at Eq. (3). Since it is the longest wavelengths that are most sensitive to global (geometric) features, we should expect low frequency data to deviate somewhat from the simple linear relation in Eq. (3), and they do, so b is a legitimate and necessary fitting parameter.

[4] By "low" temperature we mean here $1K << T << 1000\,K$. In this case phase transitions are determined by classical thermal fluctuations. At really low temperatrues ($T << 1\,K$) quantum phase trasnitions are possible that are driven by quantum fluctuations. These are of interest in future electronics, including quantum computers.

[5] K is also called the *bulk modulus*, or *Young's elasticity modulus* in three dimensions, since it parametrizes volumetric elasticity.

[6] A log-linear fit of $T_C(r) = 25 - b\ln r$ to the factory table gives a slope $\bar{b} \approx 23.9548$. We will here use $\bar{b} \approx 24$, since this gives temperatures that deviate from the table by less than $\pm 0.05°$C. The much more complicated standard empirical (Steinhart-Hart) equation $T_K(R) = 1/(a + b\ln R + c\ln^3 R)$ usually found in the literature requires three fitting parameters (a, b, and c), and the fit is no better over the small range of temperatures we are probing here.

[7] This is not a purely academic excercise. To avoid a climate catastrophe we wish to store the greenhouse gas CO_2 inside the planetary crust. The thermodynamics of CO_2 and mixtures of CO_2 with other gases is therefore of considerable interest.

Analog computer to visualize: TRAVELING SOUND WAVE
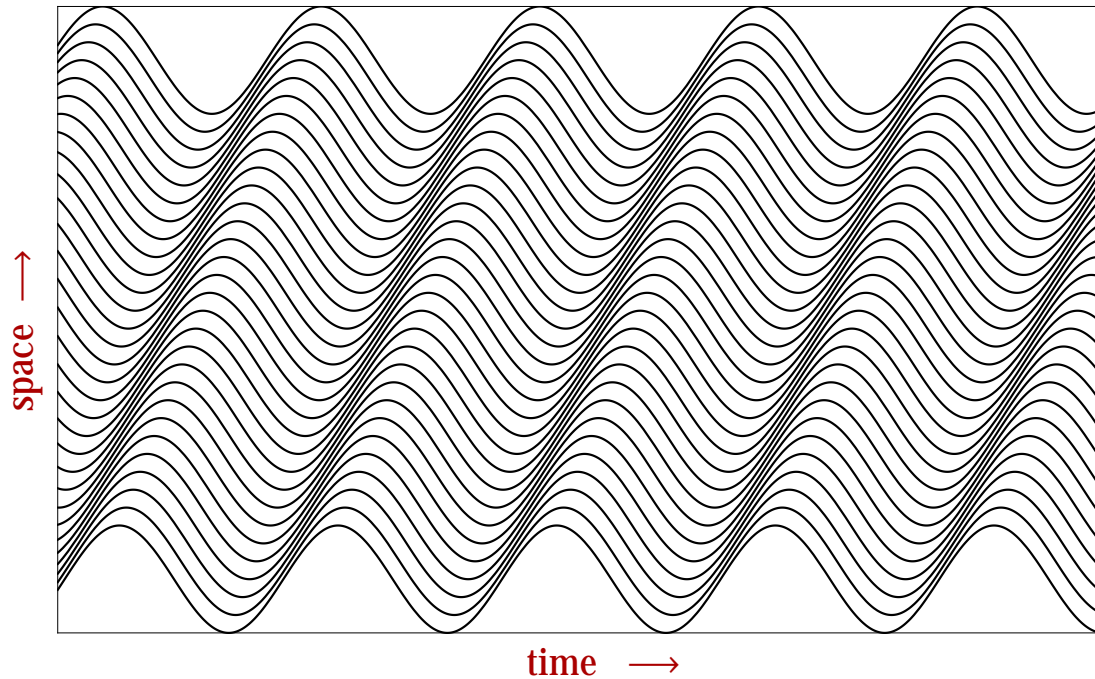### (longitudinal compression wave)

Figure 8. analog pressure wave simulator #1: visualizing plane sound waves. Glue together two stiff sheets of cardboard separated by a slit between the sheets of at most one millimeter. By pulling the slit (the "tube") in the time direction you will see a propagating pressure wave which compresses and dilutes the "gas" of black dots.

Analog computer to visualize: STANDING SOUND WAVE
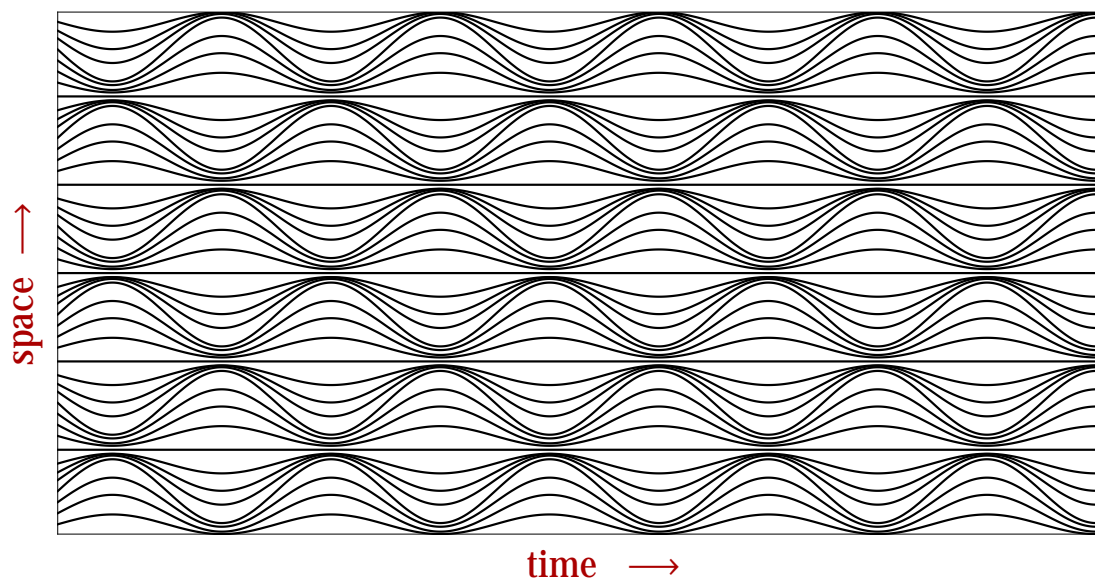### (longitudinal compression wave)

Figure 9. analog pressure wave simulator #2: visualizing standing sound waves. Glue together two stiff sheets of cardboard separated by a slit between the sheets of at most one millimeter. By pulling the slit (the "tube") in the time direction you will see a standing pressure wave which compresses and dilutes the "gas" of black dots.