

Mean speed of a gas molecule

Phys 294/5 Experiment 6

Student's manual

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1 Theory

This experiment determines the mean speed of a gas' molecules. There are two theoretical ways of deriving the typical speed of a monoatomic ideal gas: 1) using classical mechanics theory, and 2) using statistical mechanics theory. Both methods are explored here, in the theory section, and they provide the same result. From the second method, we obtain the mean speed of such particles. In the experimental details section, another method for finding the mean speed of a monoatomic gas particle is explained. We do not use a monoatomic gas, but this experiment illustrates the power of combining ingenuity and simple tools and approximations to obtain results that are far from being irrelevant. We can also get to see the agreement between classical and quantum/statistical mechanical theory and the theory-experiment dynamics in physics, from a slightly different perspective, namely, using different methods to arrive to the same conclusion.

1.1 Classical mechanics ¹

Picture a particle of mass m moving at a speed v in a single dimension ², bouncing between two walls separated by a distance L . The average time

¹Based on Finn, Chapter 3 [3] and Davis [2].

²Because we are talking of a single particle moving at a speed v , this is the same as the average speed of the particle. But this is obvious.

between two subsequent collisions of the particle with the same wall is

$$\tau = \frac{2L}{v}. \quad (1)$$

The force that the particle imparts on the wall is, on average,

$$\langle F \rangle = \frac{dp}{d\tau}, \quad (2)$$

where p is the impulse. But $dp = 2mv$, then

$$\langle F \rangle = \frac{mv^2}{L}. \quad (3)$$

Now we build the analogy for N particles of mass m moving in a 3-dimensional box of size L (i.e. the volume is $V = L^3$, and the area of one of its faces is $A = L^2$). for the i th particle,

$$\vec{v}_i = (v_{ix}, v_{iy}, v_{iz}), \quad (4)$$

then the mean squared speed of the particles is

$$\langle v^2 \rangle = \frac{\sum_{i=1}^N (v_{ix}^2 + v_{iy}^2 + v_{iz}^2)}{N}, \quad (5)$$

and the mean square speeds of the components are

$$\langle v_x^2 \rangle = \sum_{i=1}^N v_{ix}^2 / N, \langle v_y^2 \rangle = \sum_{i=1}^N v_{iy}^2 / N, \langle v_z^2 \rangle = \sum_{i=1}^N v_{iz}^2 / N. \quad (6)$$

But the choice of coordinates is arbitrary, so we can assume that

$$\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = \frac{1}{3} \langle v^2 \rangle. \quad (7)$$

The average force applied on a wall by the i th component of all the particles is, on average (deduced from Equation 3),

$$\langle F \rangle = m \frac{N \langle v_i^2 \rangle}{L} = m \frac{N \langle v^2 \rangle}{3L}, \quad (8)$$

and the pressure is

$$P = \frac{\langle F \rangle}{A} = \frac{mN \langle v^2 \rangle}{3V}. \quad (9)$$

But $N = nN_A$, where n is the number of moles and N_A is Avogadro's number, so

$$PV = 3nN_A m \langle v^2 \rangle. \quad (10)$$

For a monoatomic ideal gas, we have the ideal gas law from thermodynamics:

$$PV = nRT, \quad (11)$$

where R is the thermodynamics constant, P is the pressure (on the gas), V is the volume (of the gas), and T is the temperature of the gas/environment, assuming that they are in thermal equilibrium. Comparing with Equations 11 & 10, we obtain:

$$\frac{1}{3}N_A m \langle v^2 \rangle = RT, \quad (12)$$

which gives, defining $k_B \equiv \frac{R}{N_A}$ (this is Boltzmann's constant) and $m_m \equiv mN_a$ (this is the molar mass of the substance)

$$\langle v^2 \rangle = \frac{3RT}{N_A m} = \frac{3k_B T}{m} = \frac{3RT}{m_m}, \quad (13)$$

and the rms speed, or typical speed, of an ideal monoatomic gas with particles of mass m at a temperature T is

$$v_{rms} = \sqrt{\frac{3k_B T}{m}} = \sqrt{\frac{3RT}{m_m}}. \quad (14)$$

1.2 Statistical mechanics ³

This derivation is quite involved without some quantum mechanics. Some of the formulas here are presented without further explanation, their derivations being beyond the scope (and level) of this course.⁴

We start by looking at Boltzmann's probability distribution:

$$p(k) = \frac{e^{-E(k)/k_B T}}{Z}, \quad (15)$$

which tells the probability of finding a particle in a gas in a state of energy $E = \frac{\hbar k}{2m}$, where \hbar is Plank's constant divided by 2π , k is the magnitude of the wavevector of the (point-like) particle, and m is the mass of the particle. k_B is Plank's constant, T is the temperature of the gas and $Z = V/\lambda_D^3$,

³Based on Bowley [1], Chapter 7.

⁴If you are interested in the full derivation, see Bowley [1], Chapter 7, or Finn [3], Chapter 6, for an alternative (and simpler) derivation using statistical mechanics.

with $\lambda_D = \left(\frac{2\pi\hbar^2}{mk_BT}\right)^{1/2}$ being the thermal de Broglie wavelength, is called the partition function. Then, out of N particles in the gas, the number of particles expected to have an energy E , as above, is given by

$$N_k = Np(k) = \frac{Ne^{-E(k)/k_BT}}{Z}. \quad (16)$$

The next question to ask is how many particles are in the states with wave vector magnitudes $k + dk$. This is wave vector space. Think of a solid sphere whose layers, or shells, are described by wave vectors of magnitude k . This is very convenient for describing energy states in non-discrete values. We introduce a quantity called the density of states (in three dimensions):

$$D(k) = \frac{Vk^2}{2\pi^2}, \quad (17)$$

which tells you the amount of states per a shell of radius k in wave vector space. Then the average number of particles in states in the range k and $k + dk$ is

$$f(k)dk = \frac{Ne^{-E(k)/k_BT}}{Z} D(k)dk. \quad (18)$$

The speed of a non-relativistic particle with a wave vector of magnitude k is given by $v = \frac{\hbar k}{m}$. Rewriting $f(k) \rightarrow n(v)$, we obtain Maxwell's distribution of speeds:

$$n(v)dv = \left(\frac{N\lambda_D^3 m^3}{2\pi^2 \hbar^3}\right) v^2 e^{-mv^2/2k_BT} dv. \quad (19)$$

There is a very important formula for calculating average values:

$$\overline{A} = \frac{\int_0^\infty f(k)A(k)dk}{\int_0^\infty f(k)dk}. \quad (20)$$

We can use this to calculate the average value of $v^2(k) = \frac{\hbar^2 k^2}{m^2}$ (recalling that $E(k) = \frac{\hbar^2 k^2}{2m}$):

$$\langle v^2 \rangle = \frac{\int_0^\infty \left(\frac{N\lambda_D^3}{2\pi^2}\right) k^2 e^{-\hbar^2 k^2/2mk_BT} \left(\frac{\hbar^2 k^2}{m^2}\right) dk}{\int_0^\infty \left(\frac{N\lambda_D^3}{2\pi^2}\right) k^2 e^{-\hbar^2 k^2/2mk_BT} dk}. \quad (21)$$

Integrating gives:⁵

⁵I used Mathematica for the integration. It is a very good program, and it is very useful for Physics.

$$\langle v^2 \rangle = \frac{3k_B T}{m}. \quad (22)$$

Taking the square root gives the root-mean-square speed:

$$v_{rms} = \sqrt{\frac{3k_B T}{m}}. \quad (23)$$

Compare Equations 14 & 23: we have obtained the same result using two different methods. The typical speed of an ideal monoatomic gas of molar mass m_m and temperature T is:

$$v_{rms} = \sqrt{\frac{3RT}{m_m}}. \quad (24)$$

Now we use Equation 20 to determine the average speed of a molecule of an ideal monoatomic gas:

$$\langle v \rangle = \frac{\int_0^\infty \left(\frac{N\lambda_D^3}{2\pi^2} \right) k^2 e^{-\hbar^2 k^2 / 2mk_B T} \left(\frac{\hbar k}{m} \right) dk}{\int_0^\infty \left(\frac{N\lambda_D^3}{2\pi^2} \right) k^2 e^{-\hbar^2 k^2 / 2mk_B T} dk}. \quad (25)$$

After we integrate ⁶, we obtain:

$$\langle v \rangle = \frac{4}{\sqrt{2\pi}} \sqrt{\frac{k_B T}{m}} = \frac{4}{\sqrt{2\pi}} \sqrt{\frac{RT}{m_m}}. \quad (26)$$

Curious enough, this value is equal to [5, 4]

$$\langle v \rangle = 2 \langle v_z \rangle, \quad (27)$$

where $\langle v_z \rangle$ is the mean value of the z component of the molecular velocities of the gas particles enclosed by a (real space) (semi-)circular dome.

2 Experimental details ⁷

For this experiment you will need:

- 1 \times scale of 0.001 g sensibility with a tare subtraction device
- 1 \times Petri dish with lid

⁶Again, I used Mathematica.

⁷Based on Ganci [5].

- 300 ml of volatile liquid (isopropyl alcohol, ethanol or diethyl ether)
- Timer
- Thermometer
- Tape (optional)

Figure ?? shows a picture of the experimental setup.

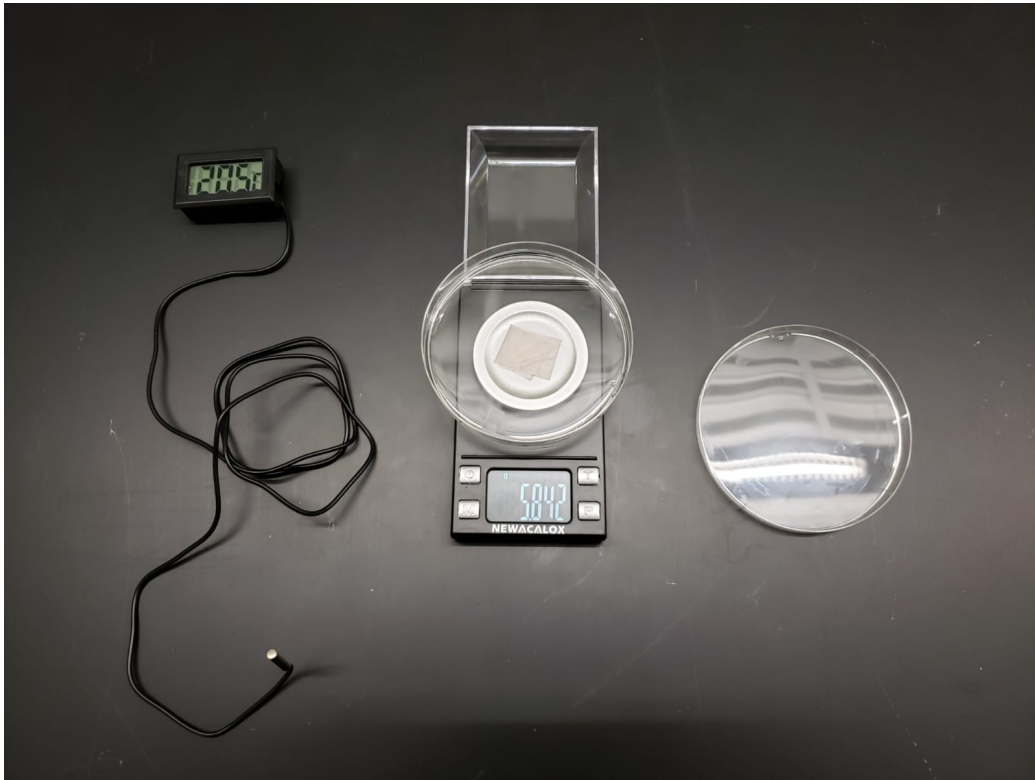


Figure 1: Experimental setup.

Before proceeding to explain how to perform the experiment, we will see an overview of what you are expected to do. The Petri dish is placed on the scale and it is filled with a volatile liquid. You will be measuring the time and change in mass of the liquid as it evaporates. At a certain point you will cover the Petri dish with a lid, and you will observe a sudden drop in the mass of the liquid. This occurs because of the momentum transfer from the gas particles of the lid. In other words, the evaporated molecules push the Petri dish upwards. This can be described as a reaction force, given by: [5, ?]

$$F = \langle v_z \rangle \frac{dm(t)}{dt} = \frac{1}{2} \langle v \rangle \frac{dm(t)}{dt}. \quad (28)$$

This formula assumes a change in speed from zero to $\langle v \rangle / 2$ in an infinitesimal time dt of a mass $m_{small} = dm$.

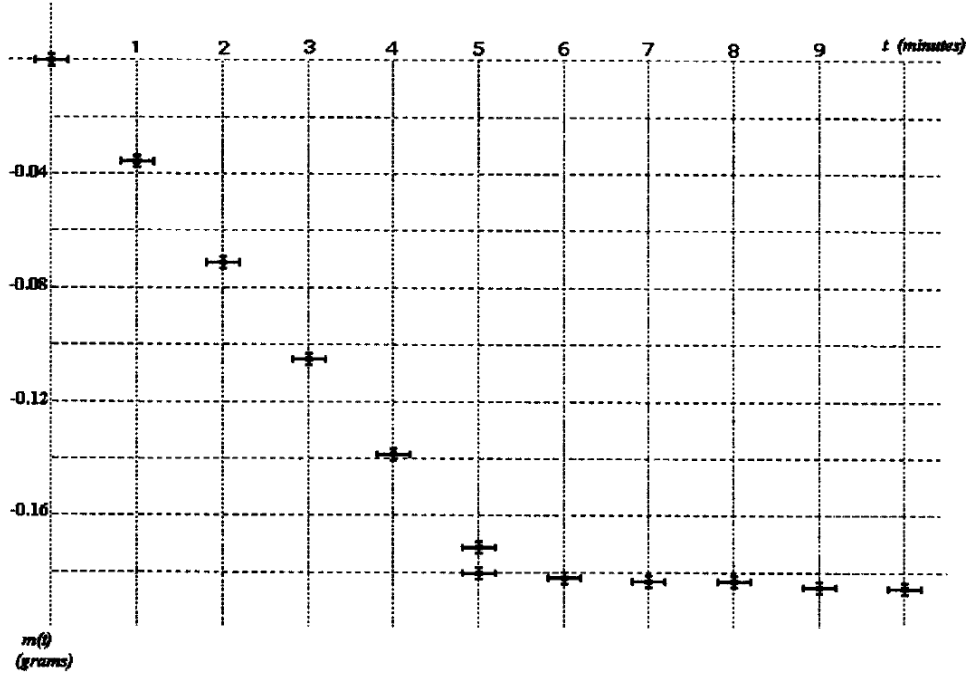


Figure 2: Graph of the change in mass readings of the scale through time.

For the linear fit analysis you will use the data point after the removal of the lid up to the point just before you place the lid on the Petri dish again, that is the point just before the ‘instantaneous’ drop in the mass reading.

Taken from Ganci [5], Figure 3.

Figure 2 shows a graph of the mass of the liquid versus the time. The sudden drop in the measured mass occurs when the lid is placed on the Petri dish. This is an instantaneous force. So dm is a measurement of the mass being accelerated upwards; this acceleration must be at least the value of g , the acceleration due to gravity. This acceleration happens continuously at infinitesimal time periods dt , and this is the reason why the measurement of the mass of the liquid does not go up after covering the Petri dish again. Taking all this into account, we rewrite the reaction force as:

$$F = \delta mg. \quad (29)$$

Equation 28 & 29 gives, with $dt \rightarrow \Delta t$ and $dm \rightarrow \Delta\mu$:

$$\langle v \rangle = \frac{2\delta m g \Delta t}{\Delta\mu}. \quad (30)$$

2.1 Experimental procedure

First take a measurement of the mass of the lid alone. Then remove the plate of the scale and stick the Petri dish to it with a tape (if you have one). Make sure the centers of the plate and the Petri dish are aligned as best as possible. Gently place the Petri dish on the scale and press (do not ever exceed the maximum mass capacity of the scale or you could damage it permanently!), then tare the scale. Let the Petri dish sit on top of the scale for about a minute, letting the tape to stretch. Place the lid and then remove it, and make sure that the reading, after removal, is zero. If it is not zero, then you have to fix it by repeating the taping procedure. If it is zero, then proceed by placing the lid on the Petri dish and take a measurement of the mass of the lid. remove the lid and quickly fill the Petri dish with sufficient volatile liquid (this amount should be small enough to see a push from the molecules against the lid and large enough to avoid working with too small numbers and how they are affected by the manipulation of the equipment; in the testing of this experiment, 5 grams of volatile liquid worked fine) volatile liquid and cover it immediately. Take a measurement of the initial mass of the liquid and lid together (you will subtract the mass of the lid later). Let the Petri dish covered for a minute. When a minute is reached, take a measurement of the mass of the liquid and lid again (this is to make sure that no molecules have escaped the system) and remove the lid. Immediately, take a measurement of the mass of the liquid alone. For at least then minutes, take a measurement of the mass of the liquid. When you are ready, after the last minute, take one last measurement of the mass of the liquid alone and cover the Petri dish as quick as possible and immediately and take a measurement of the mass of the liquid and lid (again, you will subtract the mass of the lid later). Take a measurement of the system every minute for 10 subsequent minutes. You will notice that the reading of the mass of the system drops for the first minute or two, then stays more or less stable for a couple of minutes, and then it drops again steadily. Before doing any calculation, look at the data you collected and think of which value is the best for δm write this value down and explain your reasoning.

All the data being collected, determine the experimental value of $\langle v \rangle$ with Equation 30 and compare it to the theoretical value consistent with Maxwell's distribution of speeds, Equation 26. Do they agree? Based on calculations,

which is the best value for δm ? Does this agree with your initial intuitive guess? Explore why this is the case.

Note: every time you take a measurement of the mass(es), record the time and temperature of the room. You will need these values. You will also have to press the ‘P’ button and then the ‘M’ button on the scale every minute, when you take a measurement, to avoid the scale turning off. Try making all movements as gentle as possible. Sometimes when you remove the lid, the scale adds more mass to the reading. That is why it is very important to take measurements quickly, before and after you take the lid off and before and after you put it on the Petri dish; this is so that you can compare and correct or repeat the experiment, whichever you consider necessary. Watch out for any anomalous behaviour of the scale and make note of it; add this to the uncertainties.

References

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