E2: Intensity Fluctuation Spectroscopy

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Abstract

We investigate the intensity correlation function of laser light scattered off a suspension of latex spheres in de-ionised water. After verifying the performance of our detectors, we use the technique of intensity fluctuation spectroscopy to find Boltzmann's constant by measuring the intensity correlation function. A value of $k_B = 1.26 \pm 0.14 \times 10^{-23} JK^{-1}$ was obtained.

1 Introduction

It is well known that particles in a fluid undergo small random movements, called Brownian motion, at finite temperatures. In the simplest case of non-interacting particles this is due to collisions between the atoms of the fluid and the particles. These collisions give rise to a fluctuating force on the particles which vary their position and velocity. The particles' motion is also damped by the same collisions, and these two effects are related by the fluctuation dissipation theorem:

$$\mu k_B T = \int_0^\infty < v(t)v(0) > dt \tag{1}$$

where $\mu = 1/(6\pi\eta R)$ is the mobility of the particles, η is the shear viscosity of the fluid, R is the radius of the particle, for spherical particles; k_B is Boltzmann's constant, T is the temperature, and $< v(t)v(0) >$ is the velocity autocorrelation function. The quantity $\mu k_B T$ is the diffusion constant D_0.

Thus if we can measure the velocity autocorrelation function, we can find the particle size, knowing all other variables. Since the velocity autocorrelation function is related to the positional fluctuation of the particles, we can infer it by measuring the positions of the particles over time. We do this indirectly by measuring the diffraction pattern that the particles, each acting as a single scatterer, produce when coherent (laser) light is shone on them.

This is discussed further in Section 2. This method, called Intensity Fluctuation Spectroscopy (I.F.S.) is now widely used to find the size of proteins, viruses,

polymers, colloids or sediments. In this investigation, however, we will use latex spheres of known size, measured using an environmental scanning electron microscope, to determine Boltzmann's constant.

The standard setup is to use a photomultiplier to detect the intensity of the scattered light, connected to a autocorrelator to produce the intensity correlation function. For this investigation, however, we use a photo-diode with built in voltage amplifier connected to a PC to perform the autocorrelation. The light source is a He-Ne gas laser, with a wavelength of $633nm$.

2 Theoretical Background

If a suspension of randomly moving particles is illuminated by a coherent light source, a randomly fluctuating diffraction pattern, called a speckle pattern, is produced. We can easily measure the (temporal) intensity (second order) autocorrelation function of this speckle pattern, and from that determine the velocity autocorrelation function above. The intensity autocorrelation function is given by:

$$g^{(2)}(\tau) = \frac{< I(t+\tau)I(t) >}{< |I(t)|^2 >}$$

$$g^{(2)}(\tau) = 1 + |g^{(1)}(\tau)|^2 \tag{2}$$

where the angular brackets indicate averaging over the fluctuations, and $g^{(1)}(\tau)$ is the amplitude, or first order, correlation function given by:

$$g^{(1)}(\mathbf{K},\tau) = \frac{< \mathbf{E}(\mathbf{K},t+\tau)\mathbf{E}^*(\mathbf{K},t) >}{< |\mathbf{E}(\mathbf{K},t)|^2 >} \tag{3}$$

Here, $\mathbf{K} \equiv K = 4\pi/\lambda \sin(\frac{1}{2}\theta)$ is the scattering wave-vector, θ is the scattered angle, $\mathbf{E}$ is the electric field of the scattered light, which is a sum over that scattered off each particle:

$$\mathbf{E}(\mathbf{K},t) \propto \sum_{i=1}^{N} \exp(i\mathbf{K}\cdot\mathbf{r}_i(t)) \tag{4}$$

with $\mathbf{r}_i(t)$ is the position of the ith particle at time t. Substituting this into Equations 3, we get:

$$g^{(1)}(\mathbf{K},\tau) = \frac{\sum_{i=1}^{N}\sum_{j=1}^{N} < \exp(i\mathbf{K}\cdot[\mathbf{r}_i(t) - \mathbf{r}_j(t+\tau)]) >}{\sum_{i=1}^{N}\sum_{j=1}^{N} < \exp(i\mathbf{K}\cdot[\mathbf{r}_i(t) - \mathbf{r}_j(t)]) >} \tag{5}$$

Now, assuming that the particles do not interact, so the velocities and positions of different particles are not correlated, then the cross terms with $i \neq j$ vanish, so

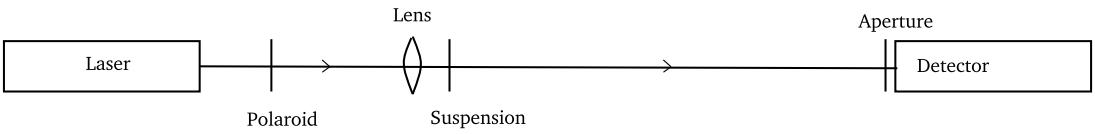

Figure 1: *Experimental setup. The laser and detector were aligned on an optical bench, with a Polaroid to control the intensity reaching the detector; a lens to focus the light onto the specimen - the suspension - and an aperture to ensure that we have a 'point' detector, so that the autocorrelation will be valid.*

the denominator in Equation 5 simplifies to N which cancels with a similar term in the numerator. We can simplify Equation 5 further, without loss of generality by taking only the x-component of position and velocity, and $\mathbf{K}$ to be in the x-direction. The equation then becomes:

$$g^{(1)}(\mathbf{K},\tau) =< \exp(-iK[x(t+\tau)-x(t)]) > \tag{6}$$

where $x(t+\tau)-x(t) = \int_0^\tau v(t)dt$. Since the collisions between the fluid molecules and the particles causes the velocity to fluctuate rapidly, it can be taken as a uniformly distributed random variable with small characteristic fluctuation time, so that for τ much larger than this time, Equation 6 becomes:

$$g^{(1)}(\tau) = \exp(-D_0K^2\tau)$$

Substituting this into Equation 2:

$$g^{(2)}(\tau) = 1+\exp(-2D_0K^2\tau) \tag{7}$$

where D_0 is the diffusion constant, which is given by Equation 1[Pusey].

3 Preliminaries

3.1 Equipment

Before setting out to measure the intensity autocorrelation function of Brownian motion scattered laser light, we conducted experiments to ascertained the limits of our equipment. This involved investigating first the characteristics of the light detector, and then that of the analogue-to-digital converter through which we sent our data to a PC to perform the autocorrelation.

All the experiments used a setup similar to that depicted in Figure 1. Investigating the light detector, as described in Appendix A, we found that the light detector saturates at 5V, but that it stopped behaving in a linear fashion after 3V. Therefore to get accurate data, we must keep the intensity low enough that these voltages are not reached, to be reasonably sure that the intensity is proportional to our voltage signal. Since the autocorrelation function is a difference measure, the absolute value of intensity is not important, merely that the voltage-intensity relation is linear, so that we can be sure the voltage autocorrelation that we calculate closely matches the intensity autocorrelation.

The analogue-to-digital converter (ADC) we used has a frequency bandwidth, or maximum sampling rate, of $15kHz$, so we should expect aliasing for signals with frequency of above $7.5kHz$ by Nyquist's criterion. Software supplied with the ADC allows us to control the sampling rate from the PC. In addition to this, the ADC also has two modes: a real-time mode where the computer accepts data from the ADC as it receives them; and a fast-block mode where the ADC stores the collected data internally and then returns all the data after then end of run.

For both methods, we found that the sampling interval was not constant but varied around the specified interval. In addition the 'real-time' mode returned the wrong times for each samples. That is, if the sampling interval was $1ms$, the ADC would return 10 voltage values and assign them all a time of $10ms$, instead of $1ms$, $2ms$, $3ms$, etc. This may be due to the Windows XP operating system which does not allow a software application direct access to the parallel port where the ADC is connected, for security reasons. This means that the software logging application can only access the parallel port to read the data when the operating system (OS) allows it - every $10ms$ apparently. So the software receives batches of samples from the ADC every time the OS allows it, and assigns them all the same time, which it obtains from the PC's clock.

On the other hand, the fast-block method does not have this problem. However, due to the limited memory on the ADC itself, the fast-block method is limited in the amount of data it can take - and hence the length of time over which it can sample, or the resolution (sampling rate) at which it can sample.

The autocorrelation of the sampled data is done via a simple program in Mathcad. This program also calculates the power spectral density via a fast Fourier transform. This calculated autocorrelation does not introduce more errors, but is only as accurate as the sampled data. Therefore the major source of errors comes from the non-linearity of the light detector at high intensity, and from the ADC. To minimise these, we should ensure that the intensity of light on the detector is below the linear limit, and that the sampling rate of the ADC is much higher than the coherence time of the moving speckle pattern.

3.2 Speckle Patterns

Equation 2 in Section 2, where the intensity correlation function was related to the amplitude correlation function, only holds for Gaussian light. This means that the probability of finding the resultant amplitude of the light in the range A to $A+dA$ is proportional to $AdA\exp(-A^2/A_0^2)$, where A_0 is a constant. Thus we should expect the intensity probability to be proportional to $\exp(-I/I_0)$.

We expect the laser light scattered off particles moving with Brownian motion to be Gaussian, because each scattering particle is independent of each other, so that their total contribution to the amplitude at any point would follow a random walk in an amplitude-phase diagram. Thus for a large number of scatterers, by the central limit theorem, we should expect the amplitude to follow a Gaussian distribution.

We tested this using a ground-glass slide mounted on a motor, rotating at 2 r.p.m., placed between the Polaroid and the detector, and measured the intensity of the light. Because we want to measure the intensity at a single point, as the speckle pattern produced by the moving ground glass varied over time, rather than that over an area, we need a 'point detector'. In practical terms, it is adequate for the detector to be small enough to detect only a single speckle at a time. Thus we want to restrict the detector aperture to the size of a single speckle. However, a smaller aperture lets in less light, so we would need to amplify the signal more, and so introduce more errors. Therefore, we need to find a compromise betweent the need for a 'point' detector and signal strength.

Since the speckles are simply 2D Fraunhofer fringes, their size is given by:

$$d = \frac{\lambda}{\alpha} \tag{8}$$

where α is the angular size of the laser light at the ground glass specimen, as seen from the detector. We use a lens between the Polaroid and ground-glass slide, with the slide at the focus of the lens, to fix the size of the source, and then varied the distance, l, between the slide and detector to vary α, since $\alpha = \tan(s/l)$ where s is the size of the light source at the slide. Using this method we found a configuration that gave a speckles size at the detector of about 1mm, and hence can use the 1mm diameter aperture on the detector.

Using this setup we measured the intensity as a function of time, as the ground glass rotated. A histogram of this measurement would show the intensity probablity which we expect to be an exponential decay. This is seen in Figure 2.

An autocorrelation function was also calculated from the data, and is shown in Figure 3, with a Gaussian fit to the data shown in green. Theory predicts that a chaotic, Gaussian light source can have either a Gaussian or a Lorentzian intensity correlation function. It will be Lorentzian if no Doppler broadening oc-

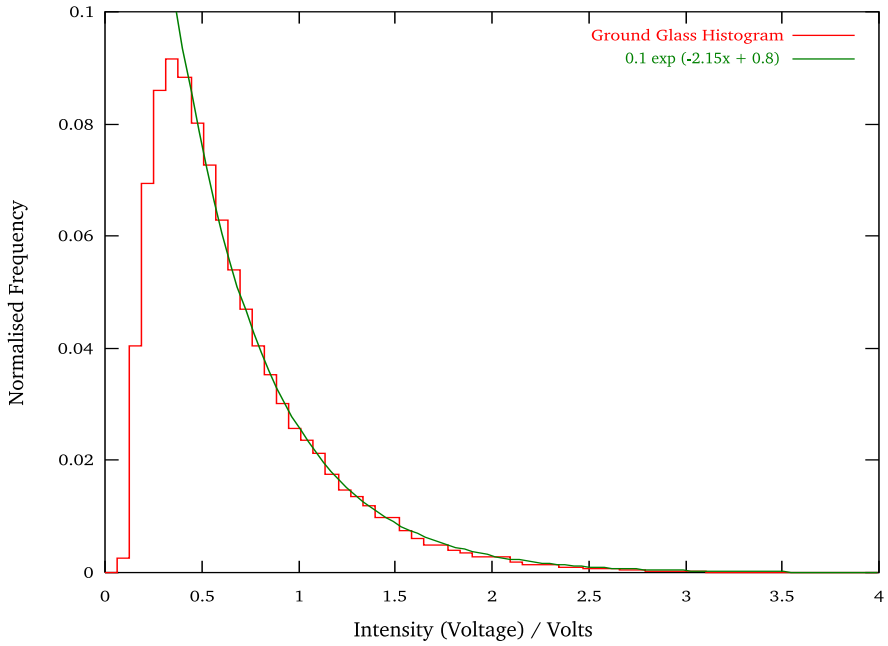

Figure 2: *Histogram of $I(t)$, which shows the probability $p(I)$ of finding an intensity I between I and $I+dI$. This shows that scattered laser light is indeed Gaussian, as it behaves as $p(I) \propto \exp(-I/I_0)$. The exponential decay does not quite start at zero intensity because of background ambient light.*

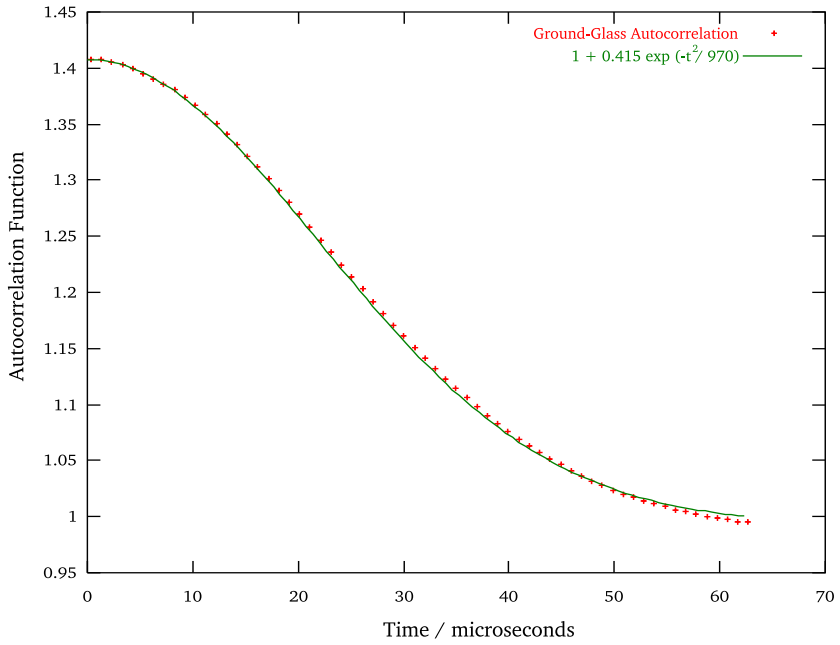

Figure 3: *Autocorrelation function for a rotating ground glass slide, moving at 2 r.p.m. The solid green line indicates a Guassian fit to the data.*

curs. In our case, however, the ground glass is relatively coarse, not very uniform, and moves through a large distance, so the scattering centres move with different speeds, creating a broadened source. Theory predicts in this case that the intensity autocorrelation function is [Loudon]:

$$g^{(2)} = 1 + \exp\left[-\pi\left(\frac{\tau}{\tau_c}\right)^2\right] \tag{9}$$

where τ_c is the coherence time. From the fit to the data, the coherence time is $3 \pm 0.1ms$. We expected that τ_c would be related to the speed of the ground glass slide and the beam diameter at the slide, however, we found that with a speed of $4.2mms^{-1}$ (as the laser illuminated a point about 20mm from the centre of rotation, and the slide moved at $2r.p.m$, and a laser dot of diameter $\approx 0.1mm$, we get a time of $\approx 25ms$, an order of magnitude larger than what we found.

The diameter of the laser dot is only an estimate since we used a lens to focus the laser beam onto the ground glass, making length measurements difficult. In addition, the speed of the speckles moving across the detector maybe different to the speed of the ground glass slide, and this speed should have a greater bearing on the coherence time.

In addition, the autocorrelation function did not start at $g^{(2)} = 2$ as expected by theory, because of ambient light. That is, this background light effectively added noise to the system, and hence reduced the coherence of the detected signal, so that the initial autocorrelation is less than expected.

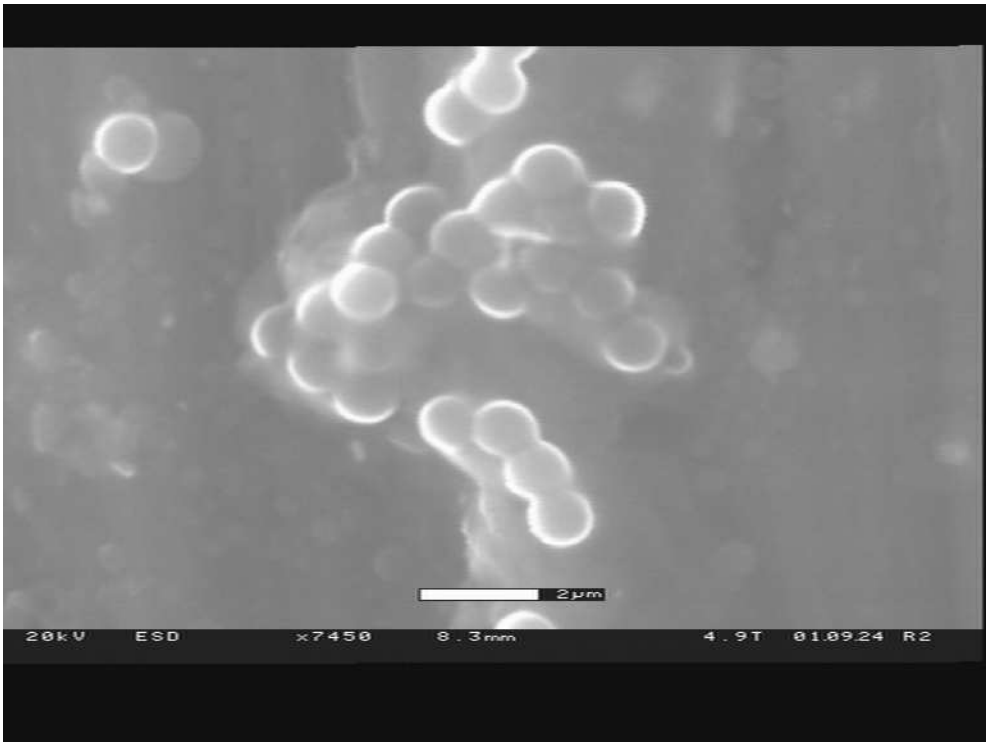

Figure 4: *Environmental Scanning Electron Micrograph of the latex spheres that we used in suspension.*

3.3 Latex Spheres

To measure the size of the latex spheres in the suspension, we used an environmental scanning electron microscope. In this instrument, the sample is placed within a humidity controlled environment. As the humidity is increased by adjusting the pressure and temperature of the sample, water droplets condenses on and forms a film on top of the sample. Electrons are then directed onto the sample, and hence ionises the water film. Other electrons incident on the ionised film get scattered and are detected forming a picture of the sample, such as that in Figure 4. From this micrograph we found that the radius of the latex spheres is $0.52 \pm 0.04 \mu m$. We can now substitute this into the equation for the diffusion constant (Equation 1), with a viscosity appropriate for water at $293K$, to find Boltzmann's constant.

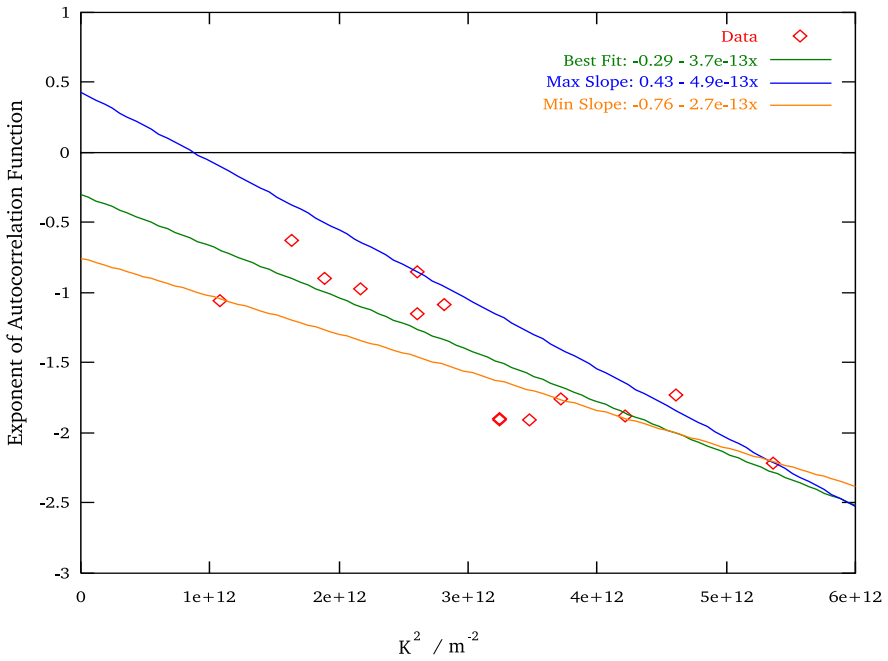

Figure 5: *A plot of the exponent of the autocorrelation function against the square of the wave vector. The gradient gives us the diffusion constant, and in turn Boltzmann's constant.*

4 Brownian Motion

Finally, we turn to the investigation of the Brownian motion of latex spheres in suspension. We will use the setup shown in Figure 1 to measure the intensity correlation function of laser light scattered off the suspension, and to find Boltzmann's constant from this measurement, as described in Section 2.

Equation 7 shows that the autocorrelation depends on **K** the scattering wave vector, which in turns depends on θ the scattering angle. Therefore, to get as accurate an estimate for Boltzmann's constant as possible, we will measure $g^{(2)}(\tau)$ for a range of θ. By fitting a straight line curve to the equation:

$$\ln(g^{(2)}(\tau) - 1) = -2DK^2\tau$$

we can find the gradient, $2DK^2$, which is the exponent in the autocorrelation function. The exponents for different scattering angle is then plotted in Figure 5, along with lines of best fit. This gives an estimate for Boltzmann's constant of $1.26 \pm 0.14 \times 10^{-23} JK^{-1}$. This value for k_B agrees with our expectations, but it should be noted that the error of about 10% is quite large for this technique. When used to estimate the size of the particles in suspension, I.F.S. can give results to within 1 or 2% [Pusey]. The reason for our large error here may be due to our light detector, which has no photomultiplier, and uses electronics amplification, which may introduce error into the measurements.

5 Conclusion

Despite the rather large error in our estimate of Boltzmann's constant, it is still within 2σ of the accepted value. This shows that I.F.S. can be used to accurately estimate various parameters of a suspension of particles, using a more sophisticated setup. In addition, our experiments confirm the theoretical predictions about the statistical nature of chaotic light - that is, it behaves according to Gaussian statistics. We also show that a cheap analogue-to-digital converter / PC combination can give results comparable to that of much more expensive, dedicated analogue electronics, such as a purpose-built autocorrelator, for simple applications.

Nonetheless, we have not really touched some of the deeper physics of I.F.S., as we have only considered the simplest case, where we have only non-interacting particles. Interactions would be of great interests to fields such as biophysics which uses I.F.S. to study proteins, and other complex molecules. These interactions could be studied using the latex spheres that we have, as we observe in the scanning electron microscope that they tend to stick to each other when they get close. This occurs due to ionised water film formed on the spheres attracting each other.

Therefore, future experiments could consider these interactions, by using a suspension with a higher density of latex spheres so that the Coulomb potential between the spheres has a greater effect. We can also improved the light detector, with a photon counter, and photomultiplier instead of just a signal amplifier, and use greater ambient light shielding to reduce noise.

References

[Pusey] P.N. Pusey *The Study of Brownian Motion by Intensity Fluctuation Spectroscopy* Phil. Trans. R. Soc. Lond. A **293**, 429-439 (1979).

[Loudon] R. Loudon *The Quantum Theory of Light, 3rd Edition,* p.111, Oxford University Press (2000).

Appendix

A Characteristics of the Light Detector

To investigate this an optical bench similar to Figure 1 was setup with only a Polaroid film between the laser and detector. The Polaroid could be rotated to polarise the laser light in different directions and hence vary the intensity falling on the detector. Since the laser light would already be plane polarised at the centre of the beam, we found the $\cos^2\theta$ dependency of the intensity of the beam with the angle of the Polaroid off the (up-down) polarisation of the laser, predicted by Malus' Law. However, this occurred only for low voltages as shown in Figure 6. The measured voltage falls away from the expected curve around 3V. A digital multimeter connected in series to the detector was used to measure the voltage output of the detector. The high errors at high intensity is due to fluctuating voltages that the detector produced, probably due to it being at the limit of its detection range.

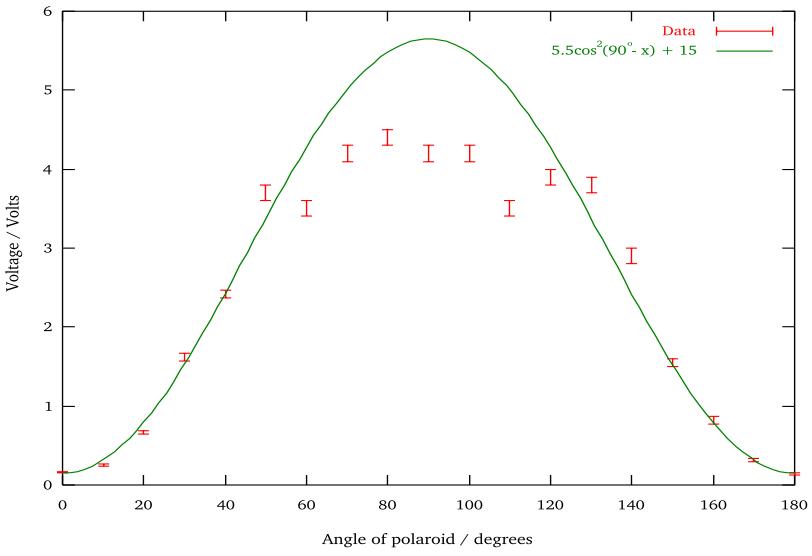

Figure 6: *A plot of the voltage output of the light detector with the angle of the Polaroid. The solid line indicates a Malus' Law (*$\cos^2\theta$ *fit to the data. This fit fails at high voltage as the detector stops being linear, and eventually saturates.*