

Exploration of Percolation through Simulation and Viscometer Experiment

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Abstract

Percolation is a widely applicable, real life phenomenon based on a well known mathematical model for random systems. Our aim was to explore certain properties of percolation, especially phase transitions - a transition of thermodynamic system's state of matter to another - through a 2D simulation and an experiment using pectin and Ca^{2+} solution. After using the simulation to discover our results and other properties of percolation, a viscometer was built to measure viscosity of pectin and Ca^{2+} solution at various Ca^{2+} concentrations, and to ultimately observe the critical point at which a phase transition from liquid to gel occurs in the solution as Ca^{2+} concentration increases. After sample measurements, results supported our hypothesis, viscosity increased as Ca^{2+} concentration increased, also showing a jump at certain values of Ca^{2+} concentration, indicating the range at which the critical point at which phase transition occurs is.

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I. INTRODUCTION

Percolation theory describes the behavior of clusters in a random graph. Applications of percolation in science, however, include epidemic spreading, surface roughening, and flow of the water through porous media. Some of its most significant properties include order parameter, a means of measuring how much order or disorder there is, and phase transition. For our purposes we have focused more on exploring the phase transitive properties of the theory, and the point at which that transition occurs is known as the critical point. A theoretical example of this would be when clusters in a grid reach a spanning cluster - a cluster that reaches all four of its boundaries. The order parameter would be the probability of having a spanning cluster in this case.

To better understand the theoretical aspect of percolation a simulation of this example on a 2D grid was made and used to determine the order parameter and critical probability, because for any other real life application, an order parameter is extremely difficult to find (it is defined as 0 when it is disordered and different from 0 when ordered, formula 2). The 2D simulation first makes an empty grid, then uses the random number generator to occupy sites at a certain probability. It then goes to each area of the grid. If the site is occupied, it labels the site with a number, then checks for any other occupied site up, down, left and right to itself. If there is, then the original site will be labeled the same number as any of its neighbors, forming clusters with unique labels. Afterwards it finally checks whether or not any formed cluster touches all four boundaries of the grid. The critical probability, then, is the probability at which spanning clusters start to emerge, and is also the point of phase transition. The simulation is also able to perform various statistical calculations on clusters, as well to determine the order parameter, a measure of the degree of order in a phase transition system, using the given formula [formula 1].

In our real life experiment, however, pectin and Ca^{2+} solution will be used to observe this phase transition behavior, making the experiment interesting as phase transitions are usually observed in varying temperature, not concentration. Although viscosity (defined as friction among molecules in a particular fluid) is not an order parameter and therefore the point at which phase transition occurs is not a critical probability, a phase transition can still be observed.

Pectin and calcium ions form clusters similar to how clusters were formed randomly in our 2D simulation [image a]. Positively charged calcium ions connect to negatively charged ends of pectin molecules and therefore bridge one pectin molecule to another. Therefore, the number of bonds will increase as Ca^{2+} concentration increases, meaning more friction among molecules, and ultimately higher viscosity. At a certain critical Ca^{2+} concentration, there will be a liquid to gel phase transition, nearly identical to the critical probability in the 2D simulation, which is the point at which a spanning cluster is most likely to emerge. Wolfram Mathematica simulation was then used to graph the solution of the differential equation by amplitude (formula 3). This differential equation represents any forced oscillatory behavior, including the crystal that will act as our viscometer. According to the simulation, the constant b for friction in the differential equation varies proportionally to width (graph a and graph b). Because we knew that the b (friction constant) varies proportionally to viscosity due to the definition of viscosity itself, we could measure relative viscosities depending on the given width of graph. The graph that the oscilloscope gives, however, is time to voltage, but because this graph is a well known Lorentzian curve, we could use pre-derived properties of the curve such as the fact that the width

at half its amplitude is inversely proportional to the amplitude, and that its amplitude is inversely proportional to b like that of the Wolfram simulation. Therefore relative viscosity for various Ca^{2+} concentrations can now be measured and graphed for comparison, and ultimately used to find the critical Ca^{2+} concentration for phase transition.

$$p_{\infty} = \frac{\text{no. of sites in a spanning cluster}}{\text{no. of occupied sites}}$$

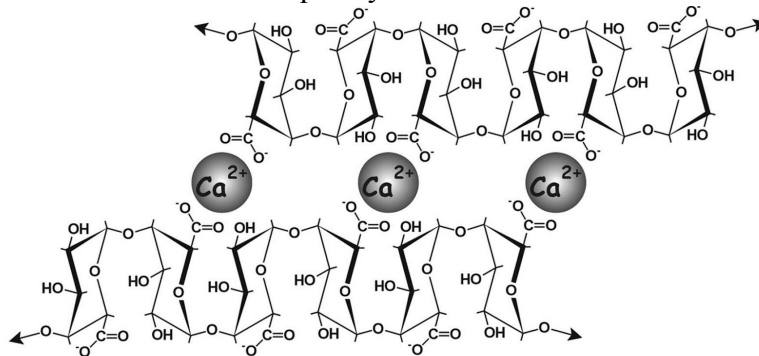
< formula 1. The formula for calculating the order parameter. The results were averaged over 1000 iterations. p_{∞} is a probability of having a spanning cluster >

$$p_{\infty} = C \cdot (p - p_c)^{\beta}$$

< formula 2. Formula for the critical behaviour of the order parameter, where p_{∞} is probability of having a spanning cluster, C is a constant, p probability of occupying a site, p_c critical probability for percolation, and β is a critical exponent >

$$\ddot{x} = -\omega_0^2 x - B\dot{x} + f_0 \cos(\omega t)$$

< formula 3. ω_0^2 is natural frequency of oscillator (quartz crystal), B is friction in medium, ω is frequency of force >



< image a. COO^- and Ca^{2+} ions forming bridges >

II. MATERIALS AND METHODS

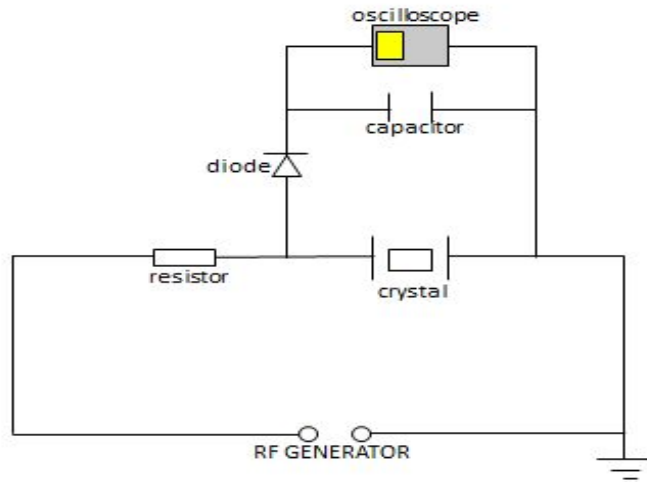
- Circuit (viscometer)
- Machinery
- Sample preparation

- Measurement and washing procedure

Quartz crystal with resonance frequency of 8 MHz was obtained and then soldered with a diode, capacitor, and resistor (image b) to form a circuit. The RF generator powered the circuit, and with the oscilloscope we observed the resonance curve of the crystal. The oscilloscope measured values for peak to peak voltage (amplitude) and width, which is the breadth of the curve at half of the graph's amplitude. Amplitude and width were then recorded and averaged 1280 times for noise reduction to be achieved. The amplitude, however, was more reliable in that it was more noise resistant, so the inverse property of amplitude and width was used to calculate width from amplitude. The width was then a representation of b (friction) coefficient as the graph of the differential equation (based on the oscillatory behavior of the crystal) had previously known properties that stated so. Because it is known that b is proportional to viscosity (viscosity is in fact defined as friction among molecules in a particular fluid), relative viscosity can now be measured and graphed from width measured by the oscilloscope.

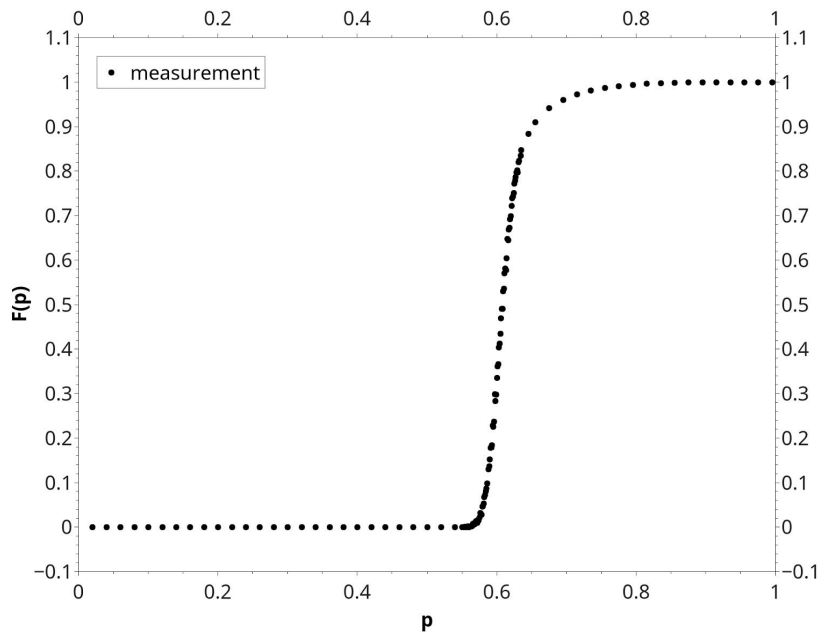
In the very beginning of the experiment, viscosities for water, air and pectin were measured to see if there was an appropriate difference in viscosity (graph d). Then, the measurements explained above were repeated for many samples of varying Ca^{2+} concentrations, which was represented as a ratio of $R = \frac{2N(\text{Ca}^{2+})}{N(\text{COOH}^-)}$, number of Ca^{2+} to the number of COOH^- , the binding site for Ca^{2+} in pectin, therefore representing the percentage of Ca^{2+} bonds in the solution. After calculation for mass of CaCl_2 in 125 ml of H_2O were made based on the fact that 1.1g of pectin were to be in 125 ml, both CaCl_2 and pectin were measured on the electronic balance, which was accurate to the fifth decimal place of a gram. If the actual mass was off by more than 10^{-5} , the R value was recalculated based on the real mass. Each mass of CaCl_2 was then dissolved in 5ml of H_2O , and pectin was dissolved in 125 ml of H_2O and kept to at least 80°C so the solution will stay homogeneous when put into the sample. The final sample then consisted of 0.2 ml of $\text{CaCl}_2 + 5$ ml of H_2O solution, and 5ml of pectin + 125 ml of H_2O solution, to adjust to the original ratio of CaCl_2 and pectin for R . Final samples were put in the oven at approximately 80°C for 10 minutes so all samples reach the same temperature at which the solution is completely liquid, in the oven and cool down at the same rate. This was done due to the hysteresis of the samples.

When measurements were made with cooled, final samples, first the amplitude and width of graph on the oscilloscope were measured and averaged as a standard of comparison. After values for each sample were measured, the crystal was washed as clean as possible using ethanol, H_2O , and paper towel until the values were as similar to those when in air, as possible.



<image b. electrical circuit of viscometer>

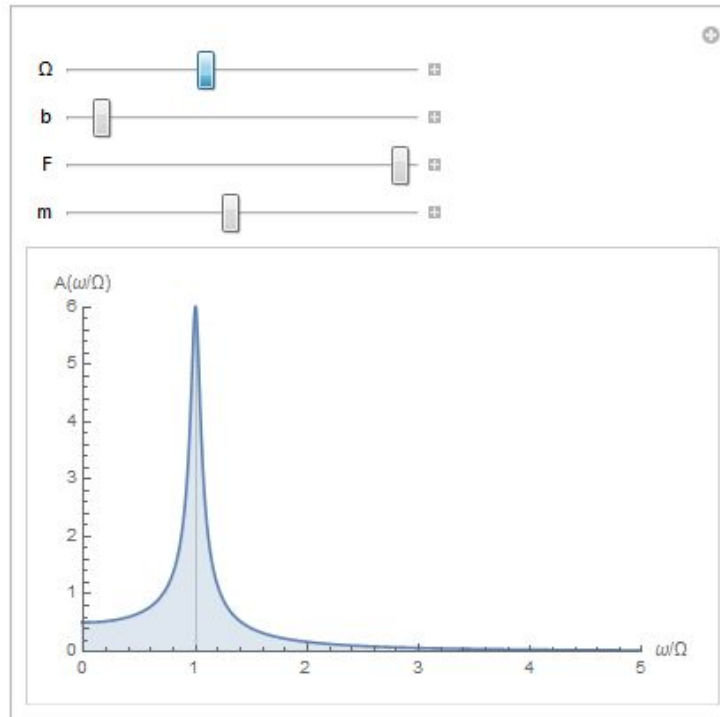
III. RESULTS



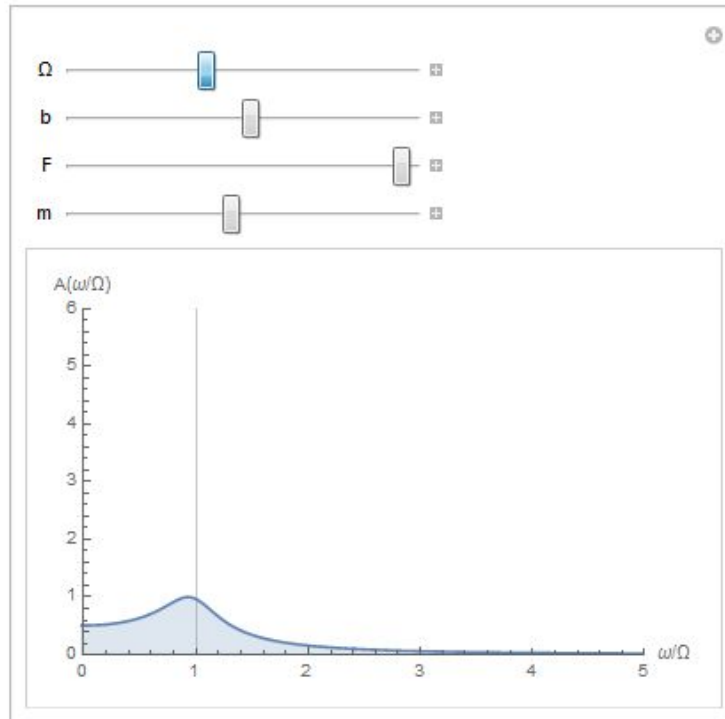
<graph a. Plot of probability of having a spanning cluster to probability. Critical probability can be seen on the graph to be close to 0.6>

Graph d shows the decreasing trend for voltage amplitude as the viscosity of the known fluids and materials increase. When graphed R (Ca^{2+} concentration ratio) to Viscosity for values of R for which we sampled, a generally increasing trend is shown in the viscosity as the R value increases. There is also a jump in values from $R = 0.01$ and $R = 0.1$, and a less variation in viscosity in the values of R greater than $R = 0.1$.

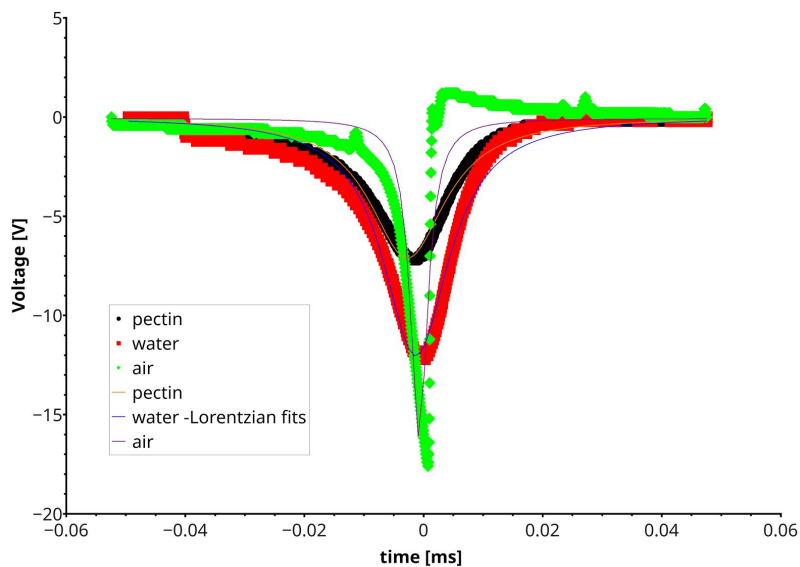
IV. CONCLUSION



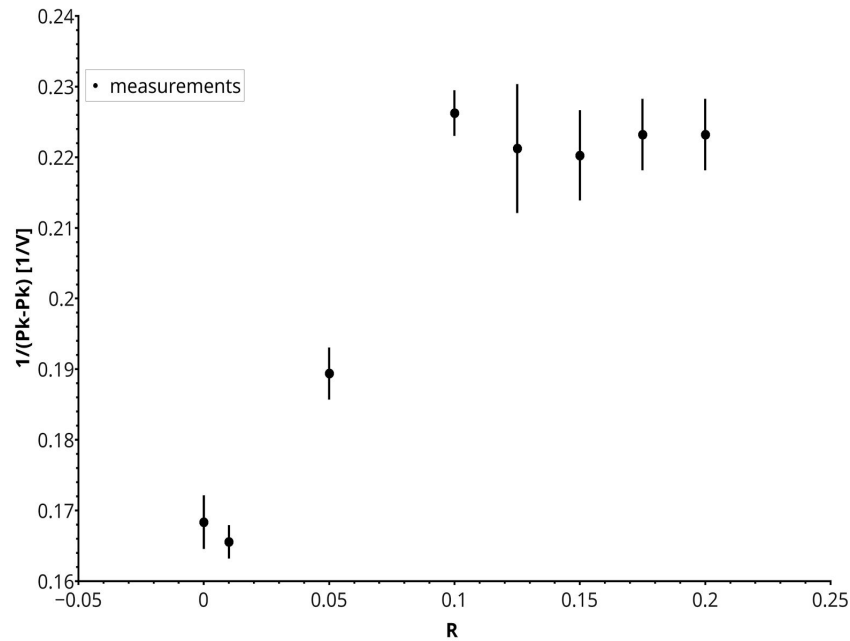
<graph b. Wolfram Mathematica program of solution for differential equation. Amplitude varies depending on b. low b (friction) >



<graph c. Wolfram Mathematica program of solution for differential equation. Amplitude varies depending on b. high b (friction) >



<graph d. Plot of voltage to time on oscilloscope, varying in amplitude depending on viscosity>



<graph e. Plot of viscosity of different Ca^{2+} concentrations, represented by R>

After the viscosities for pre-known materials such as air, water and pectin showed the appropriate trend, verifying the fact that the viscometer works properly, sample measurements were made. The viscosities for the samples also supported our initial prediction - that there will be a jump in viscosity at the critical Ca^{2+} concentration when the phase transition from liquid to gel in the pectin and Ca^{2+} solution will occur. There were, however, not enough values of viscosities between $R = 0.01$ and $R = 0.1$ to show the value of the critical concentration needed for phase transition. Therefore, it can only be concluded that the critical value is between $R = 0.01$ and $R = 0.1$. Perhaps that having more values of R and their corresponding viscosities might have shown the trend better. The fact that there was a jump in the graph, and that we were able to narrow down the value of the critical Ca^{2+} concentration conveys that there is a percolative property - phase transition - in pectin and Ca^{2+} solution.

Possible improvements include having a temperature control that could eliminate possible temperature variations. Therefore, minor deviations on graph might be caused by scale and temperature instability we faced during our measurements. Latter is very important due to dependence of viscosity on temperature.

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