

Answers to exam questions Fys 4460

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June 14, 2014

1 Molecular dynamics

1.1 Molecular dynamics algorithms

Lennard-Jones potential: The interatomic force field is computed from the LJ-potential.

$$U(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (1)$$

The force field is then computed from

$$F_i(t + \Delta t) = -\nabla_i U_i(r, t + \Delta t) \quad (2)$$

From $N2L$ we then get

$$\frac{d^2x}{dt^2} = 24 \left[2r'^{-12} - r'^{-6} \right] \frac{r'}{r'^2} \quad (3)$$

where r' now is dimensionless.

To integrate the equation of motion we used the velocity Verlet algorithm. This is a simple and numerical stable algorithm. It is time reversible and provides energy conservation. The steps are as follows:

$$\begin{aligned} v_i(t + \Delta t/2) &= v_i(t) + \frac{F_i(t)}{2m} \Delta t \\ r_i(t + \Delta t) &= r_i(t) + v_i(t + \Delta t/2) \Delta t \\ F_i(t + \Delta t) &= -\nabla_i U_i(r, t + \Delta t) \\ V_i(t + \Delta t) &= v_i(t + \Delta t/2) + \frac{F_i(t + \Delta t)}{2m} \Delta t \end{aligned}$$

In our code the force calculations were the most time consuming. The number of force terms was $\frac{1}{2}N(N - 1)$ for each time-step, which gives a workload scaling $\propto N^2$. We improved this by neglecting the force terms for particles that are far apart. The LJ-interaction is short ranged and can be neglected for distances over $r \approx 3\sigma$. To exploit this we divide the system

into N_{cells} of size r_{cut} . In each cell we keep a linked list of all the atoms in that cell. An atom will only interact with atoms in the neighboring cells.

Periodic boundary conditions: Because we are interested in atoms in bulk we implemented periodic boundary conditions. In that way we avoided complex boundary conditions to other materials or argon in other states. Due to our periodic boundary conditions we need to take care of the fact that when an atom is at a boundary, let's say $x = 0$. It needs to interact with atoms at the $x = L_x/4$ end of the box. This is called minimum image convention. So we checked if the distance $r_{i,j}$ between the two atoms i and j is larger or smaller than a half box length and then adding or subtracting a box size L_c .

Initialization:

Placing of atoms:

Velocity distribution: At equilibrium temperature T , the velocities of the atoms are given by the Boltzmann distribution. This means that the different components of the velocities are normally distributed with average zero and standard deviation $\sqrt{k_B T/m}$. When using the random number generator provided by C++ we get uniformly distributed random numbers. To get normally distributed random numbers we used the Box-Muller method. After performing this transform the standard deviation is 1. But this is corrected by multiplying with a constant, in our case the standard deviation of a Boltzmann dist. $\sqrt{k_B T/m}$.

Efficiency improvements: The code can be parallelized. The fraction of the code which is most time-consuming is the force calculations. Now that we have divided into boxes we can give different nodes different areas of the total box to compute the forces.

1.2 Molecular dynamics in the micro-canonical ensemble

Discuss initialization and initialization effects: When initializing the system we want it to start out with a temperature T . This temperature then decides the standard deviation of the initial velocities. We draw random numbers from C++ random number generator. These random numbers needed to be normally distributed. This was done by the Box-Muller method, which converts uniform drawn numbers to normally distributed numbers. We did this because in nature you would see velocities distributed in that manner. One effect of this velocity initialization is that the system only has kinetic energy in the beginning, so we have to wait for the system to equilibrate with some of the energy kinetic and some potential.

Temperature measurements and fluctuations: The temperature is measured through the kinetic energy. We calculate the dimensionless temperature and arrive at

$$T = 2/3 E_k / N$$

In the micro-canonical ensemble the energy is constant. The temperature is allowed to fluctuate. But since it is so closely related to the energy, we will only get small fluctuations around the mean, as for the kinetic energy.

Comment on use of thermostats for initialization: When using thermostats we were able to tune the system to a temperature that we wanted. This was done by first equilibrating

the system then turning on the thermostat. Then we had to wait until the system reached equilibrium for that new temperature. We used two different thermostats, the Berendsen and Andersen thermostat. These works as follows;

The thermostats we are using work by rescaling the velocities of all atoms by multiplying them with a factor γ . The Berendsen thermostat uses

$$\gamma = \sqrt{1 + \frac{\Delta t}{\tau} \left(\frac{T_{bath}}{T} - 1 \right)}, \quad (4)$$

with τ as the relaxation time tuning, coupled to the heat bath.

The Andersen thermostat simulates hard collisions between atoms inside the system and in the heat bath. Atoms which collide will gain a new normally distributed velocity with standard deviation $\sqrt{k_B T_{bath}/m}$. For all atoms, a random number uniformly distributed in the interval $[0, 1]$ is generated. If this number is less than $\Delta t/\tau$, the atom is assigned a new velocity. In this case τ is treated as a collision time, and should have about the same value as τ in the Berendsen thermostat [?]. The Andersen thermostat is very useful when equilibrating systems, but disturbs the dynamics of e.g. lattice vibrations.

2 Molecular dynamics in the micro-canonical ensemble

2.1 Temperature and pressure measurements

The temperature was measured as above. There are several ways of measuring the pressure P for a many atom system. The method used here is derived from the virial equation ¹ for the pressure. In a volume V with particle density $\rho = N/V$, the average pressure is

$$P = \rho K_B T + \frac{1}{3V} \sum_{i < j} \vec{F}_{i,j} \cdot \vec{r}_{i,j}, \quad (5)$$

where the sum runs over all interacting particle pairs. Note that this expression depends on the ensemble - and is valid for the micro-canonical ensemble only.

To find the pressure we needed to write equation 5 on reduced units form. We use the conversion factors

$$T = T' T_0 = T' \frac{\epsilon}{k_B},$$

$$V = V' V_0 = V' L_0^3,$$

where $L_0 = \sigma$ and $F_0 = \frac{\epsilon}{k_B}$.

$$P = P' P_0 = P' \frac{F_0}{L_0^2} = P' \frac{\epsilon}{\sigma^2} / \sigma^2,$$

¹ The virial theorem relates the average of kinetic energy over time with that of the total potential energy. The word virial derives from vis the Latin word for energy or force.

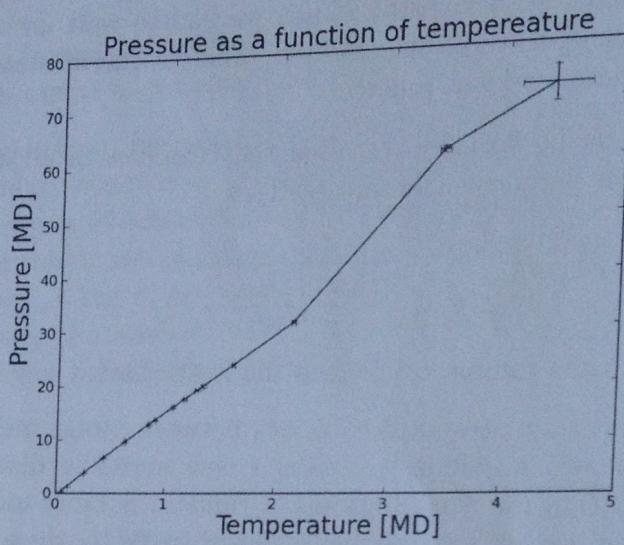


Figure 1: Pressure as the function of temperature T . $N_c = 10$, $dt = 0.01$ and number of atoms = 4000.

and our expression for the temperature

$$T' = \frac{2}{3} E_k / N.$$

Equation 5 can then be written

$$P' P_0 = \frac{N}{V' V_0} T' T'_0 \frac{\epsilon}{k_B} + \frac{1}{3V' V_0} \sum_{i < j} f_{i,j} \cdot r_{i,j} \quad (6)$$

Substituting the expressions above into 6 we get

$$P' = \frac{1}{3V'} (2E_k + \sum_{i < j} f_{i,j} \cdot r_{i,j}) \quad (7)$$

which is the pressure equation in MD units.

We wanted to measure the pressure as a function of temperature of our system.

Pressure P is defined as $P = F/m^2$, when we calculate the pressure in our experiment, there are no enclosed areas, where we can measure the pressure. The pressure we calculate is more of a density measure of the system. As we would expect the pressure to decrease if the distance between the atoms increased, from equation 5. Because the force between the atoms decrease with distance.

The theoretical expectations would be that the pressure depended linearly on the temperature. This we can see from the ideal gas law, and the first expression in equation 5. We observe that our graph in the figure 1 is not linear. For temperatures around $T = 2.2 - 3.5$, the pressure gradient increases more than for lower and higher temperatures. What we see here is a phase transition. If we had sampled for temperatures closer to this area we would have seen the change even better.

2.2 Challenges

The challenges were among others that we had to reach equilibrium for each of the temperatures we computed the pressure for. This was a time-consuming process.

2.3 Applications

The applications can be to see if the system behaves as if it was in bulk. By comparing a bulk result for the pressure and a result from a nanopore. To see if the phase changes and so on happens at the same temperature.

3 Measuring the diffusion constant in molecular dynamics simulation

3.1 How to measure the diffusion constant in molecular dynamics simulations

What we measured was the self-diffusion of an atom. We give each atom a label and measure its position as a function of time.

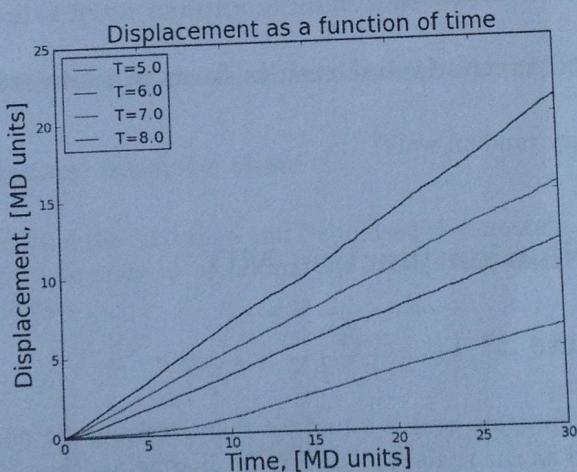


Figure 2: Mean displacement of atoms, time-step $dt = 0.005$, $T_{max} = 30$, system size $N_c = 10$ and 4000 atoms.

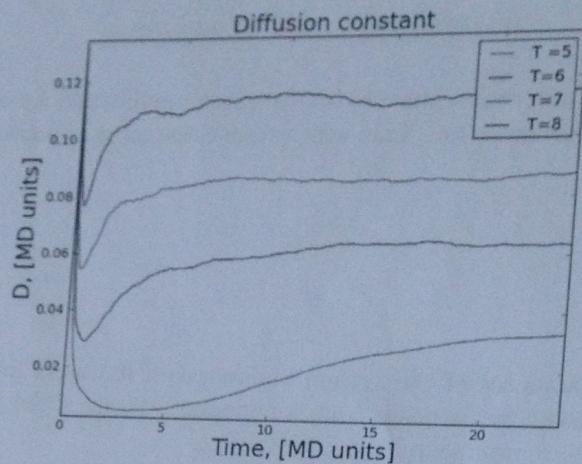


Figure 3: Diffusion constant for different temperatures in the liquid state of argon. Time-step $dt = 0.005$, $T_{max} = 30$, system size $N_c = 10$ and 4000 atoms.

The linear relationship can be described by the equation $\langle r^2(t) \rangle = 6Dt$, when $t \rightarrow \infty$. This result is similar to the behavior of a random walker in three dimensions [?], which is a good approximation to the motion of an atom in a fluid. The equation for the diffusion constant D can then be written $D = \frac{\langle r^2(t) \rangle}{6t}$. From this equation we find diffusion constants for the system we modeled, as seen in table ???. We notice that the lowest temperature in this table is close to 500K, and from graph 1 we assume this temperature to be in the liquid phase of argon. But argon is in gas phase in the atmosphere, which is around 300K, the explanation is then to look at the pressure, which for our system is very large.

3.2 Limitations and challenges

3.3 Compare with methods and results from random walk modeling Plot of random ordinary random walk?

4 Radial distribution function MD

4.1 How to measure it?

The radial distribution function $g(r)$ is a tool for characterizing the microscopic structure of a fluid. It is interpreted as the radial probability for finding another atom a distance r from an arbitrary atom, or equivalently, the atomic density in a spherical shell of radius r around an atom. It is common to normalize it by dividing with the average particle density, so that $\lim_{r \rightarrow \infty} g(r) = 1$.

The easiest way to divide the distance interval into bins, loop over all pairs of particles and count how many distances belong in each bin.

4.2 What does it tell?

It can tell us about the state of the system we are observing. If the system is a perfect crystall you will get narrow spikes at repeating lengths r . When you then increase the temperature, there will be a higher degree of disorder. Some of the atoms move out of their original bins, and the spikes start to diffuse a little outward. They get smoother.

4.3 What challenges will you face?

The challenges with the radial distribution function is that you have to count atoms and put them in right bins and do this for each atom?

4.4 Compare measurments of radial distribution function to measurments of the probability density of random walks

5 Thermostats in molecular dynamics simulations

The system we have been simulating without thermostats is called a micro-canonical system. This is because we assume the energy to be constant. And we use this to equilibrate our system. There will be some energy fluctuations but these are negliable. If we want to simulate the canonical ensemble we must apply a heat bath. The energy is then allowd to fluctuate, but the temperature is now held constant.

5.1 How get results from canonical ensemble

To get results from a canonical ensemble, we need to hold the temperature constant.

5.2 Two thermostats, describe them

This is done by introducing the Andersen and Berendsen thermostats. These two thermostats work by rescaling the velocities of all atoms by multiplying them with a factor γ . The Berendsen thermostat uses

$$\gamma = \sqrt{1 + \frac{\Delta t}{\tau} \left(\frac{T_{bath}}{T} - 1 \right)}$$

with τ as a relaxation time, tuning the coupling to the heat bath.

The Andersen thermostat simulates hard collisions between atoms inside the system and in the heath bath. Atoms which collide will gain a new normally distributed velocity with standard deviation $\sqrt{k_B T_{bath}/m}$. For all atoms, a random number uniformly distributed in

the interval $[0, 1]$ is generated. If this number is less than $\Delta t/\tau$, the atom is assigned a new velocity. In this case τ is treated as a collision time, and should have about the same value as τ in the Berendsen thermostat [?]. The Andersen thermostat is very useful when equilibrating systems, but disturbs the dynamics of e.g. lattice vibrations.

5.3 How can you use such a thermostat for rapid initialization of a micro-canonical simulation

We can start our system with different temperatures. We did three different temperatures, and turned on the thermostats. With a heat bath temperature $T_{bath} = 1.8$ in dimensionless temperature. The number of time-steps from the thermostats where turned on until the system was in equilibrium was a bit short. These two simple models will therefore not preserve the dynamics of the system as good as other models. Like the Nose-Hoover thermostat.

5.4 Advanced Molecular dynamics

6 Generating a nanoporous material

6.1 Prepare a nanoporous matrix with a given porosity

To create a material with a given porosity we can remove a certain amount of atoms from the matrix. What we did was to randomly place a e.g 20 spheres around in the system. Each sphere has a random generated radius. It was important to follow the minimum image convention for these spheres. If the sphere was at the edge of the system we had to reflect it through the other side. We said that if the atom was inside the sphere it was in the matrix. CHECK HOW WE IMPLEMENTED THE PERIODIC BOUNDARY CONDITIONS We also created a cylinder this was done by checking if an atom position was - the center of cylinder was smaller than a given radius. Then the atom was in the cylinder and we gave it a new velocity, keeping all the other atoms outside at a zero velocity.

6.2 Structure and dynamics of fluids in such a material?

Characherizing the structure of such a material: From Darcy's law $U = \frac{k}{\mu}(\Delta P - \rho g)$ one can find the permeability k of a system. But then you have to find it as a function of the porosity an easy task. HOW IS IT EXACTLY DONE, CHECK NOTES.

The dynamics of a fluid in such a material: We measured the diffusion $\langle r^2 \rangle$ for a low density fluid in the spherical system. From this we could find the diffusion constant D given by $6Dt$, from thermodynamics in three dimensions. This is a self diffusion. For the cylindrical system we measured the flow.

7 Diffusion in a nano-porous material

How did we measure the diffusion constant for a low density fluid in a nanoporous system?

Again we used the relation

$$\langle r^2 \rangle = 6Dt$$

We expect the diffusion from a bulk material to a system with nanopores to change. This is due to the larger surface area of the pores. The atoms are not allowed to move as far away as before, and they can end up being trapped. When the pores get small enough, the surface forces are dominant and the molecules never escape from the force field of the surface, even at the center of the pore. From measurements in bulk material we increased the temperature and saw an increase in mean square displacement and an increase in the value of the diffusion constant.

8 Flow in a nano-porous material

How to induce flow in a nano-porous material: We induced flow in the material by introducing an external force, $F = F_x$ acting on each atom - similar to gravity. In our object oriented code we just say, atom.Force += [0], because we want it to work in the x-direction.

How can you check your model? We created a nano-porous cylinder, in which we induced a flow of atoms. By measuring the velocity profile $u(r)$ we found could compare to an analytical solution. In the continuum model you will get a parabolic solution. But here you assume no-slip boundary conditions (the velocity is zero at the edge of the cylinder). From our experiment we saw that the velocity was not zero at the boundaries. This is due to forces between the wall and molecules, becomes important on small length scales.

How we implemented the $u(r)$ function: Created bins and counted the number of atoms in that bin and averaged their velocities.

How can you measure the viscosity and permeability:

9 Percolation

10 Algorithms for percolation systems

How to create: We create a matrix of random numbers. If a random number on this matrix is smaller than a chosen p , we say that we have a site. In this way clusters will start to grow when we raise this p -value until we reach a threshold. Then we have a percolating cluster from one end to another.

How to visualize and analyze the systems:

How to find spanning clusters and measure the percolation probability:

We find the spanning cluster by labeling each cluster. Then each site which is a part of a cluster gets a nametag which is this cluster's number. We then want to check for percolation in the y-direction. We check the topmost row and bottom for the same cluster number. This will typically give you the zero cluster also. So we check the vector for clusters besides this one, and pick the largest one to be the spanning cluster.

Measure the percolation probability:

The percolation probability Π tells us about the probability for percolation at a specific p . The percolation probability Π tells us about the probability for percolation at a specific p . In one-dimension the probability for a site to be taken is $\Pi(p, L) = p^L$ so if we have an infinite cluster the probability is trivial.

$$\Pi(p, \infty) = 0 \text{ if } p < 1 \text{ and } \Pi(p, \infty) = 1 \text{ if } p = 1$$

Numerically we find the probability by looping over different system sizes and vary the p -values doing this for multiple samples gives us a probability p for there to have been a percolation cluster.

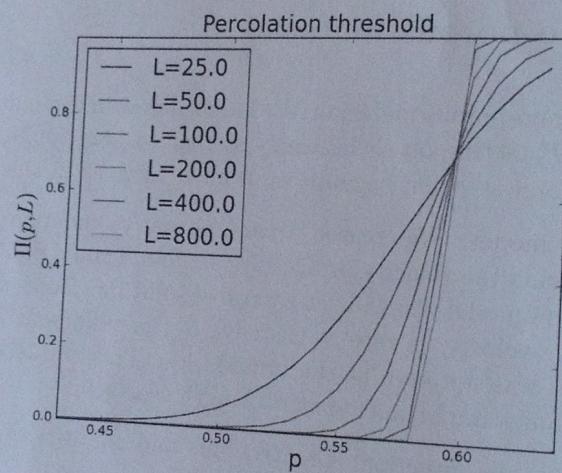


Figure 4: Percolation threshold

11 Percolation on small lattices

Discuss the percolation problem on a 2×2 lattice: In two dimensions we have the configurations:

We have 16 possible configurations. We can find $P(p, L)$ and $\Pi(p, L)$ analytical for a 2×2 system.

The first one is defined as $P(p, L) = \frac{\text{area}}{L^d}$ and is called the density of the spanning cluster. Prob that a site belongs to the spanning cluster. In 2D it is given by

$$P(p, L=2) = p^4 + 3p^3(1-p) + 2p^2(1-p)^2$$

and for the other quantity

$$\Pi(p, L=2) = p^4 + 4p^3(1-p) + 4p^2(1-p)^2$$

Have see previous section for measuring Π . $P(p, L)$ is measured by counting the sites in the spanning cluster and dividing by the system size. My simulations, see plots

12 Cluster number density in 1-d percolation

Define the cluster number density and show how it can be measured:

Cluster number density is the distribution of clusters of various sizes. So if we want to know the probability for a cluster of size s we multiply with $n(s, p)$. It is defined as $n(s, p)$.

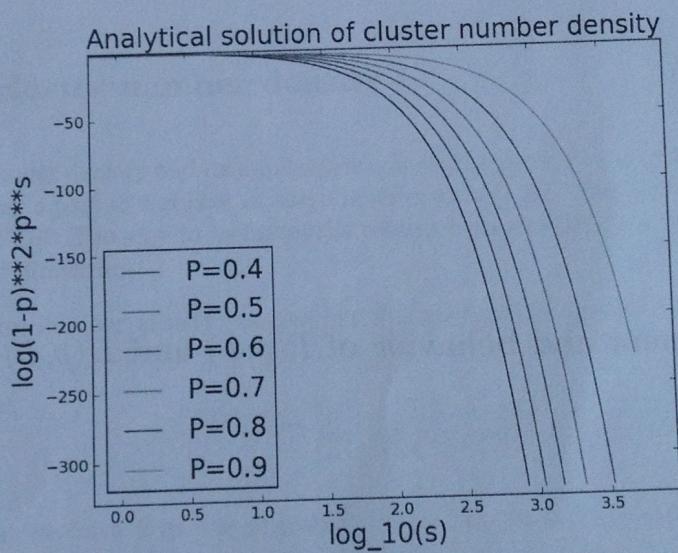


Figure 5: A plot of $n(s, p)$ as a function of s for various values of p for a one-dimensional percolation system. Shows that the cut off increases as a function of s .

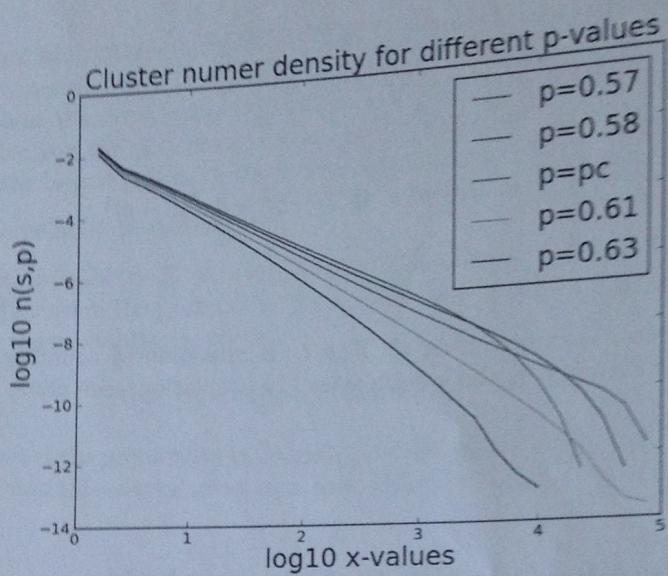


Figure 6: A plot of $n(s, p)$ for various values of p for a two-dimensional percolation system. Total number of samples for each p -value is 10000.

13 Measurement and behavior of $P(p, L)$ and $\Pi(p, L)$

See figure 4 for the behaviour of Π and figure 7

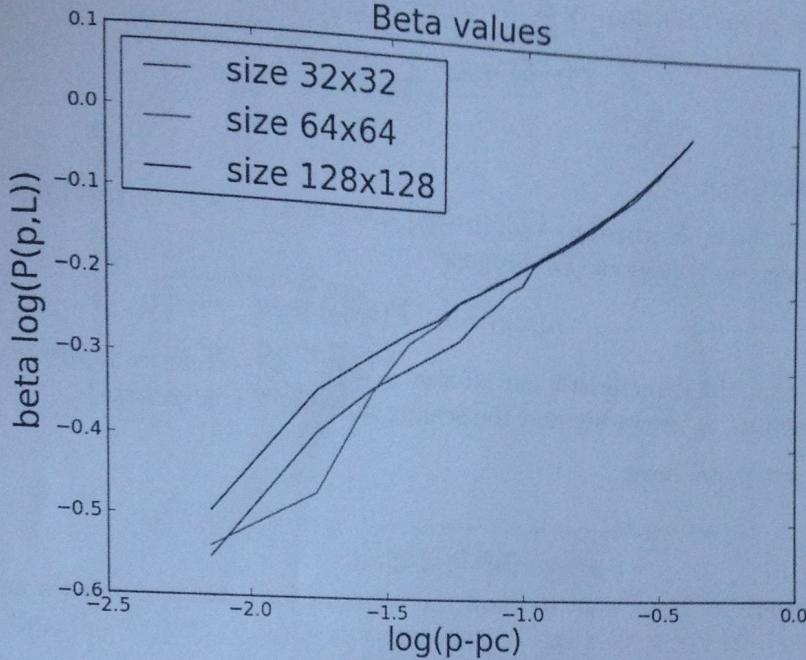


Figure 7: $\log_{10} P(p, L) \sim \beta \log_{10}(p - p_c)$, the slope then gives us a value for β .

What do we observe from these figures? Our $\beta = 0.33$. We find that the probability for a given site to belong to the percolation cluster increases with increasing p -values. This is natural since the percolation cluster also increases.

14 The cluster number density

The cluster number density and its applications: If we choose a site in the lattice the probability of this site being a part of a cluster of size s is given as $sn(s, p)$. The cluster number density is therefore a PDF. The way to estimate the cluster number density is $n(s, p) = \frac{N_s}{L^d}$. This is independent of dimension.

From the cluster number density one can find the average cluster size defined as

$$\langle S(p) \rangle = \sum_s s \left(\frac{sn(s, p)}{\sum_s sn(s, p)} \right) = \sum_s s p(s)$$

And in general we have that the probability for a site to be set must be the sum of the probability to be at the infinite spanning cluster and to belong at a finite cluster.

$$p = P(p, L) + \sum_s sn(s, p)$$

This can be used to find the density of the spanning cluster

$$P(p, L) = p - \sum_s s n(s, p)$$

Scaling theory for CND:

We want to check the limit where $p \rightarrow p_c$, $|p - p_c| \ll 1$ and $s \gg 1$. In this limit s_ξ marks a cross over between two behaviors. We propose:

$$n(s, p) = s^{-\tau} F(s/s_\xi)$$

where we know that the characteristic cut off size $s_\xi = |p - p_c|^{-1/\sigma}$. From figure 6 we see that when we approach p_c , s_ξ grows big and the scaling function F is a constant.

So at the limit $p = p_c$ we have

$$n(s, p_c) = s^{-\tau}$$

And we can compute τ . If we want to know the behavior for lower p-values we use:

$$n(s, p) = s^{-\tau} F(s/s_\xi)$$

$$s^\tau n(s, p) = F(s/(p - p_c)^{-1/\sigma})$$

$$s^\tau n(s, p) = F(s(p - p_c)^{1/\sigma})$$

Since we now know the τ value we can estimate σ by using a data-collapse plot, letting the two graphs fall on top of each other 9

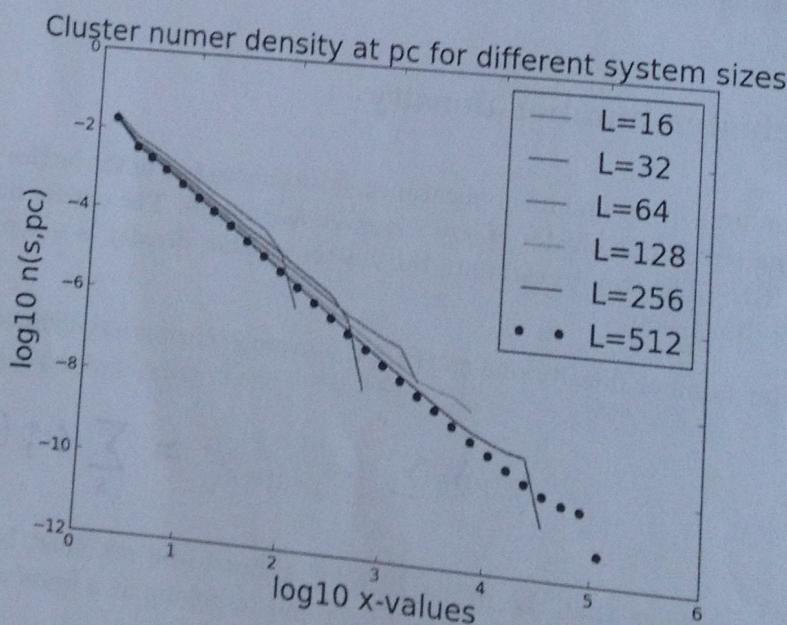


Figure 8: A plot of $n(s, p_c)$ for various values of L for a two-dimensional percolation system. Number of samples is 2000.

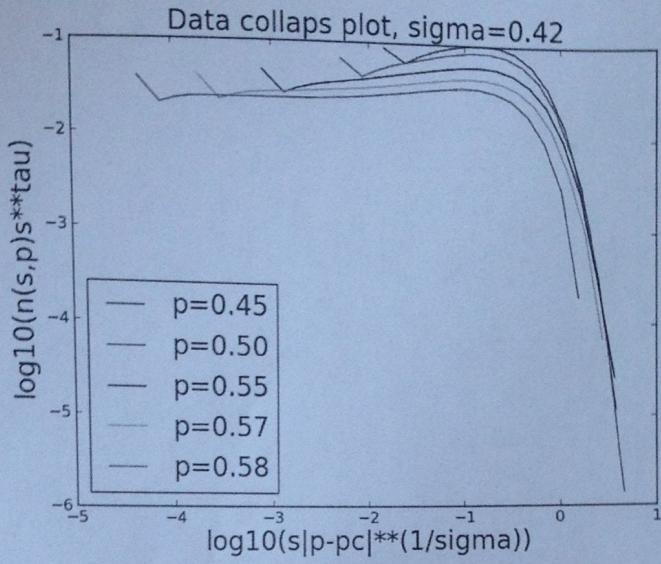


Figure 9: Data collapse plot, computing the value of sigma for $\tau = 1.86$. Number of samples per p -value is 10000. All p -values are below p_c . The different σ values tested where $\sigma = [0.37, 0.38, 0.395, 0.41, 0.42]$

15 Finite size scaling of $\Pi(p,L)$

In 4 we have the behavior of $\Pi(p,L)$. We observe that for large system sizes the probability for percolation is almost a step-function at $p = p_c$. While for the smaller clusters we have a certain probability for percolation at lower p -values.

How do we use this to find the scaling exponent ν and the percolation threshold p_c ? We define $p_{\Pi=x}$ so that

$$\Pi(p_{\Pi=x}) = x$$

Which means that we want to find the probability p at a certain threshold value Π . So from figure 4 we can choose two threshold values on each side of p_c and interpolate to find the x -values (p -values). This is then done for all the cluster sizes, and we find $p_{\Pi=x}$ as a function of L . According to scaling theory we then have

$$p_{x_1} - p_{x_2} = L^{-1/\nu}$$

And we can use a logarithmic plot to find a value for ν . We got $\nu = 1.15$ and the correct value is $4/3$. This we can use to find a value for p_c .

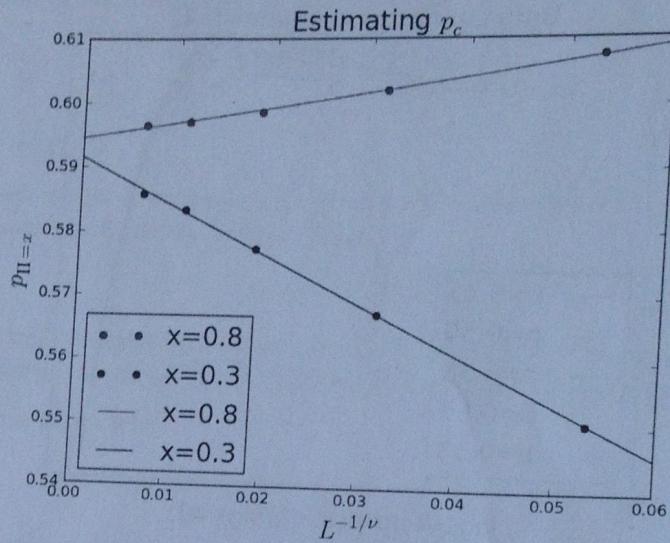


Figure 10: Estimating p_c probability in the range $0.35 - 0.63$ with a step $dp = 0.01$. Number of samples for the different L was $N - \text{samples} = 10.000$. We then got a p_c value in the range between 0.59448 and 0.59156

16 Subsets of the spanning cluster

One subset of the spanning cluster is the singly connected bonds. This is a site with the property that if it is removed, the spanning cluster will no longer be spanning. We propose a scaling like

$$M_{SC} \propto L^{D_{SC}}$$

This is valid for other subsets as the backbone and dangling ends. In general we have $D_{subset} \leq D_{spanningcluster}$.