

FYS4460 - DISORDERED SYSTEMS AND PERCOLATION
SPRING 2016

Exam preparations

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Molecular Dynamics

1. Molecular-dynamics algorithms

Discuss the algorithms for molecular-dynamics modeling: Potentials, Integration, cut-off, boundary conditions, initialization, efficiency improvements.

- Lennard-Jones potential is a reasonable potential to model Argon, but may be less desirable modeling complex molecules.
- Velocity verlet algorithm is a very good choice when simulating MD systems because REASONS. There is no reason not to use this algorithm.
- Periodic boundary conditions allow us to better simulate bulk atoms.
- Initialization of the system is typically done by placing the particles in a lattice. For argon we used an FCC lattice, which is the configuration it obtains at 0K. It is built up by placing unit cells as shown in figure concurrently in space. The initial velocities may be given as one pleases, but one has to be aware that the initial temperature is proportional to the square of the initial velocity.
- Efficiency improvements include cell lists and neighbor lists. We devide the system into cells with a certain size. For instance lets assume the cell length to be $1/8$ of the system length (assuming cubical system). This would result in $5 \times 5 \times 5 = 125$ cells. Each cell contains a cell list of all atoms within this cell. We then say that each atom is only to interact with atoms in the 26 surrounding cells of that it is in, and the one it is in off course. We also define a cut-off range which additionally reduces the number of interactions. This approximation is fine as long as the cut-off radius is larger than ≈ 2.5 . Also these weak interactions which we neglect are quite evenly distributed around the atom of concern, so their cumulative force is very small. All atoms within this cut-off range of an atom is stored in the neighbor list, so that each element contains the pointer to every neighboring atom. This drastically reduces the number of interactions calculated, and the CPU time of our program is no longer proportional to N^2 , but only to $N!$

2. Molecular-dynamics in the micro-canonical ensemble

Discuss initialization and initialization effects. Temperature measurements and fluctuations. Comment on use of thermostats for initialization.

- In this project we initialized the system by setting up all atoms in unit cells of the FCC lattice. This is the configuration that solid state argon will have at low temperatures. We used the unit cell to build up the lattice.

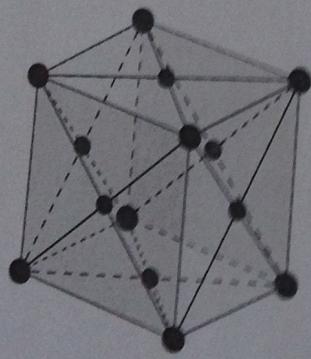


Figure 1: FCC lattice structure

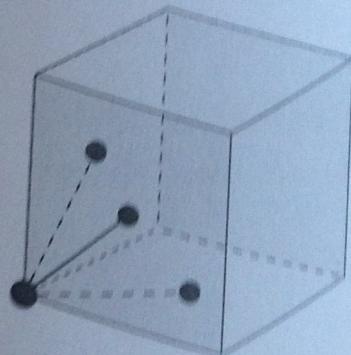


Figure 2: FCC unit cell

- By setting $T = 1$ and simply run a simulation without any thermalization or equilibration time, we collected data like the energy distribution and the evolution of temperature in the system. These results are shown in figure 3 and 4.

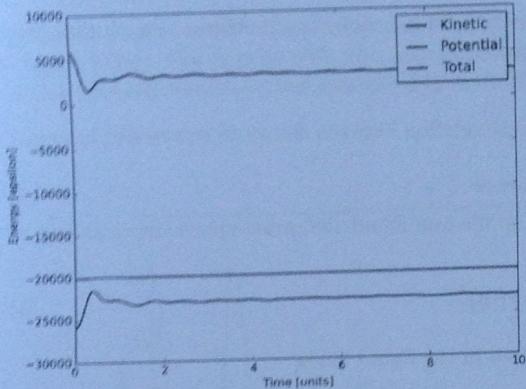


Figure 3: Energy distribution for a simulation without thermostats or equilibrationn.

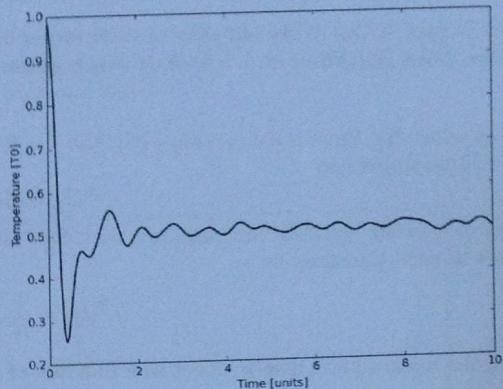


Figure 4: Time evolution of the systems temperature, for a simulation without thermostats or equilibrationn.

- We notice that the energy seems to be conserved, but that there is a shift in the energy distribution; A lot of kinetic energy is converted to potential energy. This is also reflected in the temperature plot. The temperature is related to the kinetic energy through

$$\langle E_k \rangle = \frac{3}{2} N k_B T \quad (1)$$

where we assume the system to be in equilibrium. From figure 4 We see that the temperature basically halves! As does the kinetic energy.

- The reason for this is that the FCC lattice configuration is the configuration the hold the least potential energy. The system starts out in a potential minimum. Thus, as we allow the particles to move, their kinetic energy converts into potential energy, and on average the kinetic energy is halved.
- One may avoid this "problem" of having the temperature halve, by using a thermostat. In this project we have implemented the **Brendsen** thermostat and the **Andersen** thermostat. These are methods to keep the temperature constant, but by doing so we alter the conservation of energy! Usually we are not interested in the energy of the system. If we for instance wish to simulate a system at a specific temperature, one could us a thermostat, and then equilibrate the system, letting it stabilize, before turning of the thermostat and actually start the simulation.

3. Molecular-dynamics in the micro-canonical ensemble

How to measure macroscopic quantities such as temperature and pressure from a molecular-dynamics simulation. What challenges do you expect? What can it be used for?

To measure the temperature we used the equipartition theorem for noble gas

$$\langle E_k \rangle = \frac{3}{2} N k_B T, \quad (2)$$

which relates the temperature to the average kinetic energy at *thermal equilibrium*.

The method we used to measure pressure was derived from the viral equation for the pressure. It can be shown that in a Volume V with particle density $\rho = N/V$, the average pressure is

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

However, this is only valid for the micro-canonical ensemble.

Notice that the pressure is dependent on temperature, so in order to measure pressure we must first measure temperature. Our measurement of the temperature is however only valid at thermal equilibrium, which can be difficult to define.

4. Measuring the diffusion constant in molecular-dynamics simulation

4.1. How to measure the diffusion constant in molecular dynamics simulations – limitations and challenges

Compare with methods and results from random walk modeling.

In the appendix, there is a direct copy of [1] on the derivation of the relation between the mean square displacement and the diffusion process

$$\langle r^2(t) \rangle = 6Dt \text{ when } t \rightarrow \infty.$$

In order to measure the diffusion constant, we stored all positions to file and found the mean square displacement of all atoms at each time step as

$$\langle r^2(t) \rangle = \frac{1}{N} \sum_{i=1}^N (\vec{r}(t) - \vec{r}(0))^2. \quad (6)$$

Plotting the mean square displacement as a function of time, resulted in the figure below.

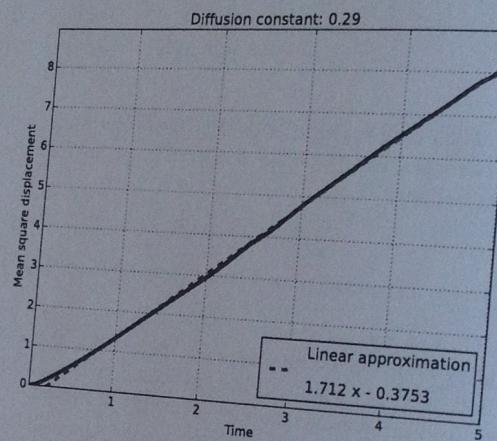


Figure 5: Mean square displacement as a function of time in a single cylindrical pore.

The diffusion constant is then found as the slope of this curve divided by 6.

In the case of random walk modeling, we may argue that the probability P_i of the walker being at site i at time $t + dt$ can be expressed as

$$P_i(t + dt) = P_i(t) + \sum_j [\sigma_{j,i} P_j(t) - \sigma_{i,j} P_i(t)] dt, \quad (6)$$

where $\sigma_{j,i}$ is the transition probability that the walker will move from site j to site i . As $dt \rightarrow 0$ this becomes a differential equation

$$\frac{\partial P_i(t)}{\partial t} = \sum_j [\sigma_{j,i} P_j(t) - \sigma_{i,j} P_i(t)]. \quad (7)$$

If the walker may only move to a neighboring site, using the nearest neighbor convention, during a timestep and assuming that all moves are equally probable $\sigma = 1/Z$, where Z is the number of neighbors, this simplifies to

$$\frac{\partial P_i}{\partial t} = \frac{1}{Z} (P_{i-1} - 2P_i + P_{i+1}) \quad (8)$$

In one dimension. We may recognize the last factor of the right hand side as the numerical gradient.

$$\frac{\partial P_i(t)}{\partial t} = D \nabla^2 P(t), \quad (9)$$

where $D = \partial t^2/Z$. Including more dimensions will not change this result, but the gradient will be more extensive. We recognize equation (9) as the diffusion equation, having the solution

$$P(\mathbf{r}, t) = \frac{1}{(2\pi Dt)^{d/2}} e^{-r^2/2Dt} \quad (10)$$

which we have found the moments of in the lecture notes, with the result

$$\langle r^2 \rangle = Dt \quad (11)$$

5. Measuring the radial distribution function in molecular dynamics simulations

How can you measure the radial distribution function in molecular dynamics simulations. What does it tell? What challenges will you face? Compare the measurement of the radial distribution function to the measurement of the probability densities for a random walk.

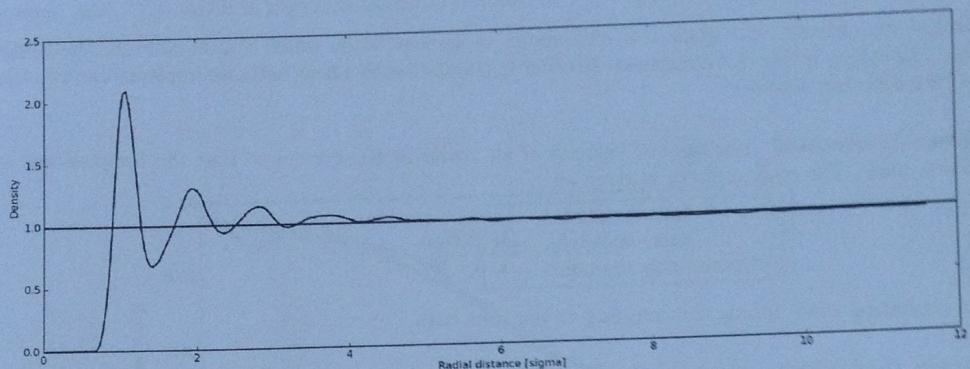


Figure 6: Radial distribution function of argon in a solid state. The density is normalized so that the value 1 is the total density of the system, N/V . Also the data has been smoothed to show the main features more clearly.

This figure shows that there are no atoms that are closer than some value ≈ 0.7 , and that the distribution of atoms vary with radial distance. The reason for this can be explained by the structure of the solid. The solid will have the same structure as a perfect crystal, but with some movement about each lattice site. This is in agreement with the measurement of the probability distribution of a random walker (10), however, it might have moved some. The most probable place a particle may be is where it was initially. A 2d representation of the FCC lattice can be shown in figure 7 and figure 8 show where we expect the peaks to be.

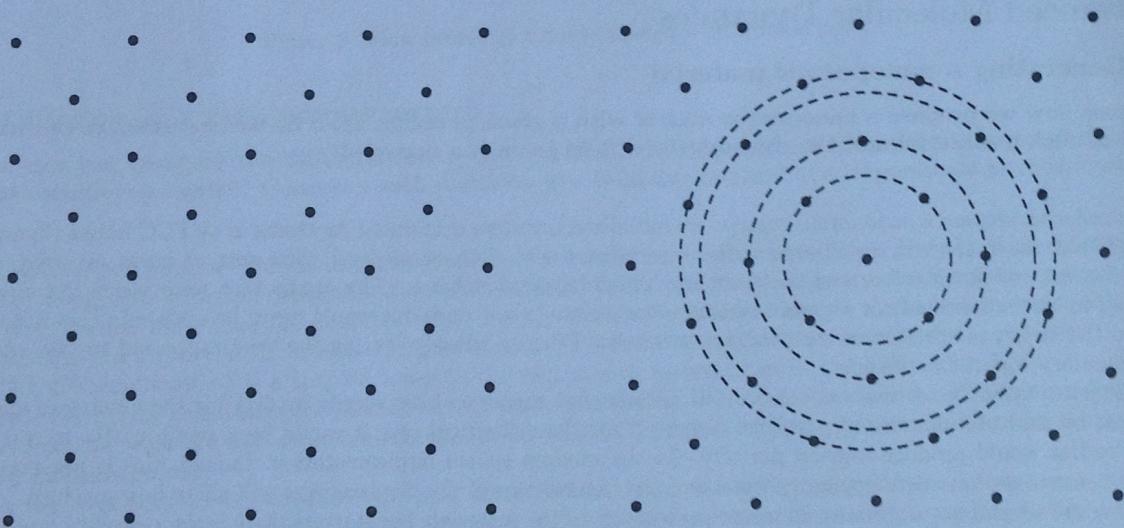


Figure 7: Projection of FCC lattice onto a plane.

Figure 8: Projection of FCC lattice onto a plane, with circles illustrating peaks in the radial density distribution.

For a perfect crystal we would expect the peaks to be vertical lines, with spacing exactly as shown in figure 8. This spacing will depend on the lattice constant/size of the unit cell.

6. Thermostats in molecular-dynamics simulations

Discuss the micro-canonical vs the canonical ensemble in molecular-dynamics simulations: How can we obtain results from a canonical ensemble? Introduce two thermostats, and describe their behavior qualitatively. How can you use such a thermostat for rapid initialization of a micro-canonical simulation?

The canonical ensemble: the system is surrounded by a heat bath, which will equilibrate the system to this temperature. The energy is thus not conserved. In order to simulate such a heat bath, we implemented two thermostats, which have very different behavior.

The Berendsen thermostat rescales the velocity of all atoms in the system so that the temperature approaches that of the heat bath. The scaling factor is given as

$$\gamma = \sqrt{1 + \frac{\Delta t}{\tau} \left(\frac{T_{bath}}{T} - 1 \right)}, \quad (12)$$

where τ is a relaxation time, tuning the coupling 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 uniformly distributed number in the interval $[0, 1]$ is generated. If this number is less than Δt , 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 the τ in the Berendsen thermostat. The Andersen thermostat is very useful when equilibrating systems, but disturbs the dynamics of e.g. lattice vibrations.

The micro-canonical ensemble conserve energy, and the system is thermally isolated. Here we no not need to use these thermostats, but the because of the way we have initialized the system, we might want to use the thermostats to equilibrate the system to the desired temperature we require, before turning them off and do the simulation. See section 2 for more detail.

Advanced Molecular Dynamics

7. Generating a nanoporous material

Discuss how we prepare a nanoporous matrix with a given porosity. How do we characterize the structure of such a material and the dynamics of a fluid in such a material?

In order to prepare a nanoporous matrix, we initialized a system containing Ar atoms in an FCC lattice (figure 1). We allowed the system to equilibrate with a thermostat and then decided on what sort of pores we want. We implemented one single tube, and one from randomly displaced spheres. The atoms that were inside the area we decided to be the solid matrix was set to be non-moving, and their positions would never be updated. This was easy, due to the object orientation of the program structure. When randomly placing the spheres we had to take care of the boundary conditions though.

The porosity of the system was not decided initially, but measured later simply by dividing the number of moving particles by the total number of particles. However, for the cylindrical case it would be a small matter to compute which radius would produce a given porosity. In the random sphere implementation, though, this is not possible, simply because we have overlapping spheres, and the randomness of the displacement will affect how much so.

There are several ways of characterizing the structure of the material. For starters there is the **porosity**, measured as described above. Secondly we may measure the **permeability**, which is a measure of the ability of a porous material to allow fluids to pass through it. In order to measure the permeability, though, we have to induce a flow through the material. This was achieved by applying a constant force on all moving particles. Using Darcy's law,

$$U = \frac{k}{\mu} (\nabla P - \rho g), \quad (13)$$

where U is total flux, k the permeability, μ viscosity, P pressure, ρ mass density, and g the gravitational acceleration

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 $\rho g = Nm/V$ is a constant quantity. Noticing that F induce an acceleration, $a = F/m$, which we may consider "our" g , we can rewrite (13) as

$$k = -\frac{U\mu}{nF}, \quad (14)$$

where $n = N/V$ is a number density. For some reason we could exclude the pressure gradient.

To characterize the dynamics of the fluid we measured the **flow profile**. In our project we did this only for a single cylindrical pore. The result is shown in figure 9. We can use our result to estimate the viscosity, μ , through

$$u(r) = \frac{\Delta P}{L} \frac{1}{4\mu} (a^2 - r^2). \quad (15)$$

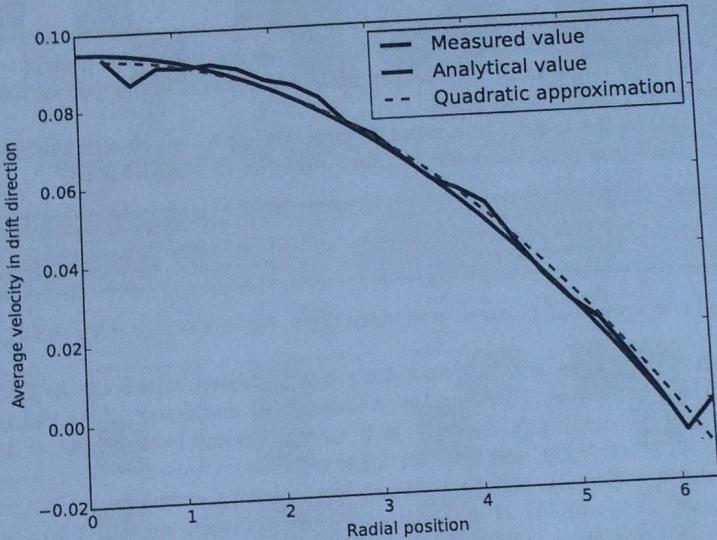


Figure 9: Flow profile of a fluid through a cylindrical pore.

8. Diffusion in a nano-porous material

How can you measure the diffusion constant for a low-density fluid in a nanoporous system? Discuss what results you expect. Compare with diffusion in a bulk liquid and in a larger-scale porous medium.

I believe that we measured the diffusion constant in the same manner as in project 1. Namely using equation (5). What I would have expected depends a lot on the system at hand. Had the pore been a single sphere, an atom could not move further away than the diameter. Had the pore been a cylindrical tube, it would be constraint to motion primarily in one dimension. In any case I would expect the diffusion constant to increase with the porosity.

The diffusion constant is a tiny bit lower in the nanoporous system than in the bulk. This is due to the solid matrix interrupting or blocking the path of the particles. The smaller the pores, the lower the diffusion constant. The forces from the walls are also short ranged, though, about 3σ . Thus, having large pores, will not make a big change on the diffusion process.

In the large-scale porous medium, we have three different behaviors of the diffusion for $p < p_c$, $p > p_c$ and a behavior before the walker may notice that it is on a finite or infinite cluster. If we drop a random walker onto a arbitrary filled site, measure the mean square displacement and repeat this process taking the average, we expect $\langle r^2 \rangle$ to converge to some constant value for $p < p_c$. This will only happen after a transient time t_0 , because the walker doesn't know that it is on a finite cluster yet. If $p > p_c$ we get that $\langle r^2 \rangle = D(p)t$, where when $p = 1$, we have the relation in (11). For other $p_c < p < 1$ we have

$$D(p) \propto \sigma(p) \propto (p - p_c)^\mu \quad (16)$$

which is proportional to the conductivity and density.

9. Flow in a nano-porous material

Discuss how to induce flow in a nano-porous material. How can you check your model, calculate fluid viscosity and measure the permeability? What challenges do you expect?

See section 7.

Percolation

10. Algorithms for percolation systems

How do we generate a percolation system for simulations? How to analyze and visualize the systems? How to find spanning clusters and measure the percolation probability?

To make a percolation system for simulations we chose a system size L and a solid fraction $p \in [0, 1]$, and made a matrix of random uniformly distributed numbers from 0 to 1. Then we compared this matrix to the solid fraction and set all elements less than p to 1 and larger to 0. This binary matrix is a model of our porous material. Filled elements are considered as pores, and empty elements as solids.

We relabel all the filled sites in the matrix to a number representing which cluster this site belongs to, using the nearest neighbor convention. This was done using the `bwlabel` function in MATLAB as

```
1 z = rand(L,L); % Random matrix
2 m = z < p; % Binary matrix containing pores and solids
3 [lw,num] = bwlabel(m,4); % Matrix where all sites of the same cluster have the same value
```

From this point we could find the sizes of all clusters, and store their size in a vector with their group index as position in the vector.

We could check for spanning clusters using the bounding box approach, which checks if the maximum length in either dimension is equal to the system size. This could as well be done, and faster, using the `intersect` and `union` approach; using the `lw` matrix and check if any cluster is in both the top and bottom row, or leftmost and rightmost column. The latter proved to be much faster, specially for large systems.

The percolation probability, $\Pi(p, L)$, can be measured by creating a system as in the code snippet above, and check for spanning clusters as described. If we have a spanning cluster, we add 1 to the count of percolating realizations. We do this N times, and lastly we say that $\Pi \approx \text{counts}/N$.

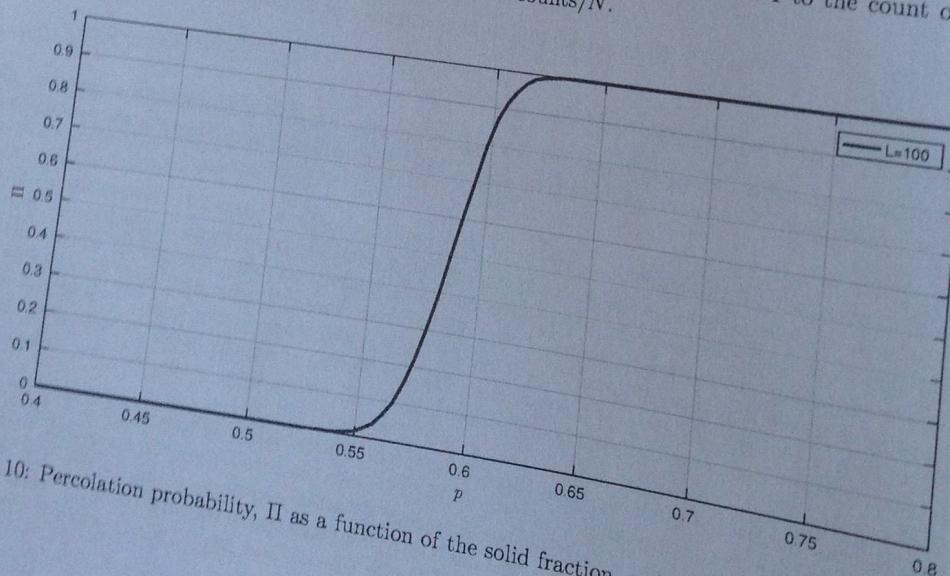
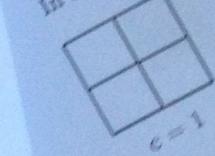


Figure 10: Percolation probability, Π as a function of the solid fraction, p , for a system of size 100×100 .

11. Percolation on a 2×2 system



$c = 1$



11. Percolation on small lattices

Discuss the percolation problem on a 2×2 lattice. Sketch $P(p, L)$ and $\Pi(p, L)$ for small L . Relate to your simulations. How do you calculate these quantities and how do you measure them in simulations?

In a 2×2 system we have very few possible configurations.

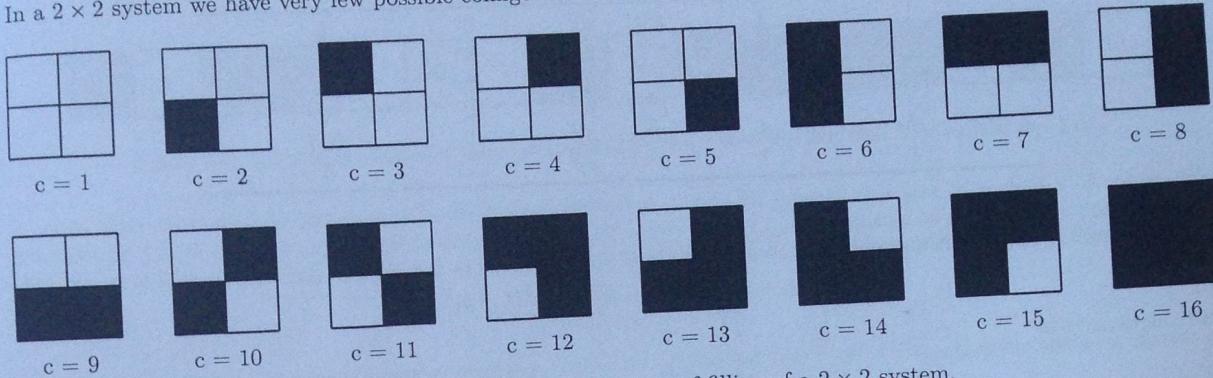


Figure 11: All possible configurations of filling of a 2×2 system.

However in two dimensions, if we define percolation as having a spanning cluster in either direction, it becomes advantageous to group the configurations who are rotational symmetric.

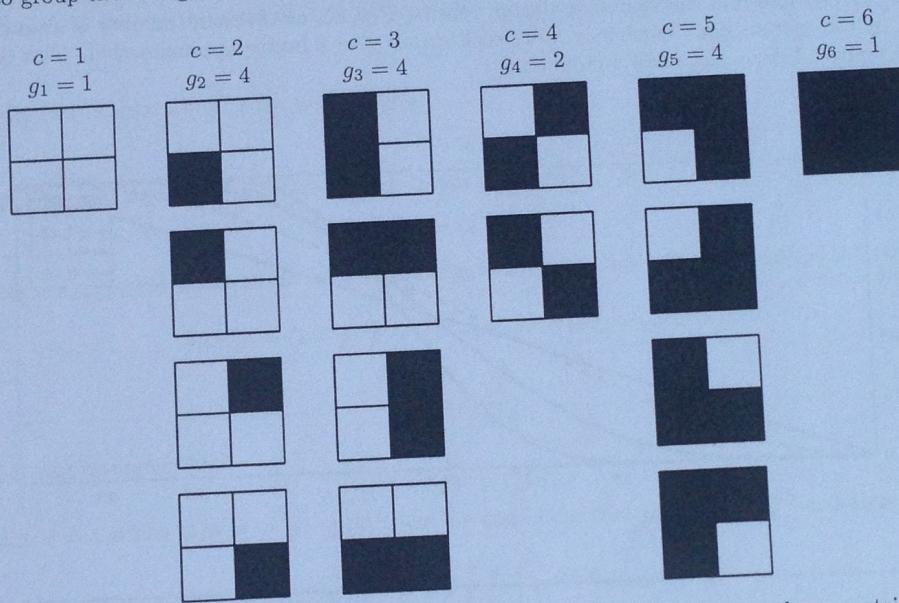


Figure 12: All possible configurations of filling of a 2×2 system, grouped by rotational symmetric configurations, c . The degeneracy of a group is g .

We have the degeneracy and probability of each configuration listed in table 1, with their corresponding degeneracy, We have the degeneracy and probability of each configuration listed in table 1, with their corresponding degeneracy, probability of the configuration, probability of percolation, and the density of the spanning cluster, if any. The probability of percolation is trivially 1 or zero for each configuration. The desity, however is computed as

$$P(p, L) = \frac{M(p, L)}{L^d}, \quad (17)$$

where $M(p, L)$ is the mass of the spanning cluster.

Table 1: Configurations, c , of the 2×2 system with degeneracy g_c , probability of this configuration $\text{Prob}(c)$, the probability of percolation given this configuration, $\Pi(p, L|c)$, and the density of the spanning cluster given this configuration, $P(c)$.

| c | g_c | $\text{Prob}(c)$ | $\Pi(p, L c)$ | $P(c)$ |
|-----|-------|------------------|---------------|--------|
| 1 | 1 | $p^0(1-p)^4$ | 0 | 0 |
| 2 | 4 | $p^1(1-p)^3$ | 0 | 0 |
| 3 | 4 | $p^2(1-p)^2$ | 1 | 2/4 |
| 4 | 2 | $p^2(1-p)^2$ | 0 | 0 |
| 5 | 4 | $p^3(1-p)^1$ | 1 | 3/4 |
| 6 | 1 | $p^4(1-p)^0$ | 1 | 1 |

Thus for the 2×2 system the probability of percolation is

$$\Pi(p, L=2) = 4p^2(1-p)^2 + 4p^3(1-p)^1 + p^4 \quad (18)$$

and the density is

$$P(p, L=2) = 2p^2(1-p)^2 + 3p^3(1-p)^1 + p^4. \quad (19)$$

In general, for an $L \times L$ system we will have 2^{L^2} different configurations. This increases rapidly with L . Thus this method is not suited for large systems. Just a 3×3 system has 516 different configurations! We can, however, measure P and Π by averaging the results from series of realizations. For each, we check if there is percolation as described in section 10. If so, we can also find the spanning cluster density, $P(p, L)$, as the mass/number of sites of the spanning cluster, divided by the system size. Obviously more realizations give a better approximation. This is produced the results shown in figure 13, for some small system sizes.

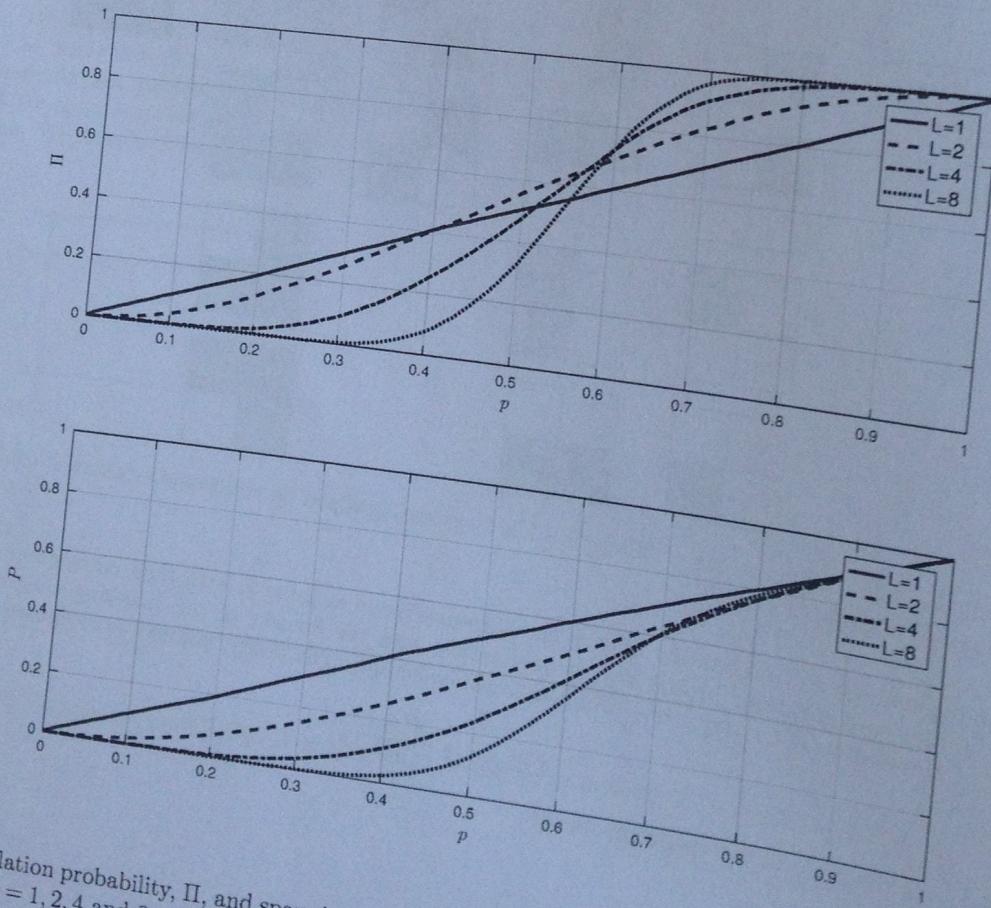


Figure 13: Percolation probability, Π , and spanning cluster density, P , as a function of solid fraction, p . Here for small systems of size $L = 1, 2, 4$ and 8 .

12. Cluster number density in 1-d percolation

Define the cluster number density for 1-d percolation, and show how it can be measured. Discuss the behavior when $p \rightarrow p_c$. How does it relate to your simulations in two-dimensional systems?

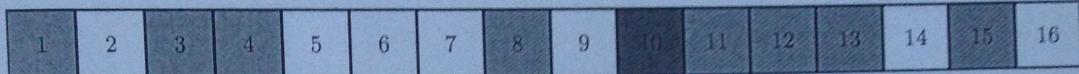


Figure 14: A configuration of a one dimensional system, with system size $L = 16$ and $p < p_c$.

The cluster number density $n(s, p)$ is the probability for a site to be a particular site in a cluster of size s . For example, in 1d, $n(s, p)$ is the probability for a site to be the left-most site in a cluster of size s . This probability is then the probability of being in a cluster of size s divided by the number of sites in this cluster, s . Thus we have

$$n(s, p) = \frac{P(s)}{s}, \quad (20)$$

since all the sites in the cluster are just as probable. Now, the probability for a site to be a specific site in a cluster of size s can be expressed mathematically as the product of the following factors:

The probability of the site to be present:

$$p \quad (21)$$

Probability of the $s - 1$ sites to the right of it to be present:

$$p^{s-1} \quad (22)$$

Probability of the two "surrounding" sites to be empty:

$$(1 - p)^2 \quad (23)$$

The product of these give the cluster number density in one dimension.

$$n(s, p) = (1 - p)^2 p^s \quad (24)$$

This quantity is approximately constant for a wide range of s values, but falls off rapidly at a certain characteristic value s_ξ .

$$n(s, p) = (1 - p)^2 p^s = (1 - p)^2 e^{s \ln p} = (1 - p)^2 e^{-s/s_\xi} \quad (25)$$

where

$$s_\xi = -\frac{1}{\ln p}. \quad (26)$$

As $p \rightarrow p_c = 1$ it can be shown that

$$s_\xi = |p - p_c|^{-1/\sigma}. \quad (27)$$

In one dimension $\sigma = 1$ which give $s_\xi = |p - p_c|^{-1}$, and we can claim that $(1 - p)^2 \simeq s_\xi^{-2}$ and thus

$$n(s, p) = s_\xi^{-2} e^{-s/s_\xi} = s^{-2} \left(\frac{s}{s_\xi} \right)^2 e^{-s/s_\xi} = s^{-2} F \left(\frac{s}{s_\xi} \right) \quad (28)$$

We notice that 0comaprison1d2dperc has the same form as the general result for cluster number density namely

$$n(s, p) = s^{-\tau} F \left(\frac{s}{s_\xi} \right). \quad (29)$$

This is a general result in percolation systems, the only difference lying in σ and τ which varies with dimensionality; 1 and 2 in 1D and 0.4 and 2.05 in 2D. As we see from equation (26) and (27) the characteristic length $s_\xi \rightarrow \infty$ as $p \rightarrow p_c$. Thus at $p = p_c = 1$ we can find clusters of all sizes in the infinite one dimensional system. In a finite system, however, we are limited to clusters less or equal to the system size. Of course, as $p \rightarrow 1$ the cluster sizes increase.

In order to measure the cluster number density, we approximate

$$\overline{P(s)} = \frac{s N_s}{L^d}, \quad (30)$$

where N_s is the number of clusters of size s , L is the system size and d is the dimensionality. Inserting this into equation (20) we're left with

$$\overline{n(s, p)} = \frac{N_s}{L^d}. \quad (31)$$

13. Correlation length in 1-d percolation

Define the correlation length ξ for 1-d percolation. Discuss its behavior when $p \rightarrow p_c$. How is it related to cluster geometry and your results for two-dimensional percolation?

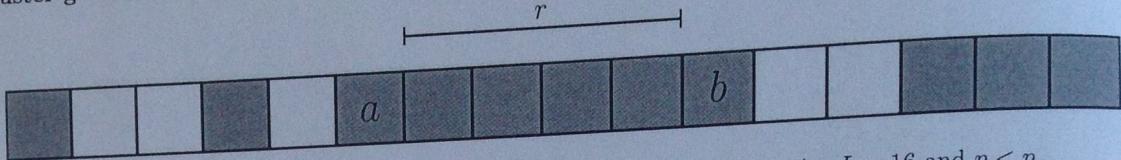


Figure 15: A configuration of a one dimensional system, with system size $L = 16$ and $p < p_c$.

The correlation function $g(r)$ describes the conditional probability that two sites a and b , which both are occupied and are separated by a distance r belong to the same cluster. In order for a and b to belong to the same cluster, all the intermediate sites, r , must be filled. Thus the correlation function is

$$g(r) = p^r = e^{r \ln p} = e^{-r/\xi} \quad (32)$$

where

$$\xi = -\frac{1}{\ln p} \quad (33)$$

is called the correlation length, and diverges as $p \rightarrow p_c = 1$. How it diverges can be found from a Taylor expansion

$$\ln p \xrightarrow{p \rightarrow 1} \ln 1 + \frac{1}{1}(p-1) = -(1-p). \quad (34)$$

We may now express the correlation length as

$$\xi = \xi_0(p_c - p)^{-\nu} \quad (35)$$

where $\nu = 1$ in 1D. In general systems we have

$$\xi = \xi_0|p - p_c|^{-\nu}, \quad (36)$$

where ν is dependent on dimensionality. The omitted terms in the expansion are less important since their contribution approaches zero with order.

In two dimensions we cannot compute the correlation length analytically. It can be measured, but this is computationally expensive. We did not measure it directly in this project. We did, however, measure s_ξ , which is the corresponding cluster mass.

14. Cluster size in 1-d percolation

Introduce the characteristic cluster size for the 1-d percolation problem, and discuss their behavior when $p \rightarrow p_c$. Relate to your simulations on two-dimensional percolation.

We introduced the characteristic cluster size s_ξ in section 12, as the cluster size at which the cluster number density started decreasing rapidly. Its value was defined in equation (26) and (27). The intermediate step between the two is the simple Taylor expansion of $\ln p$ shown in (34). In two dimensions we also got this rapid drop in cluster number density, as shown in figure 16.

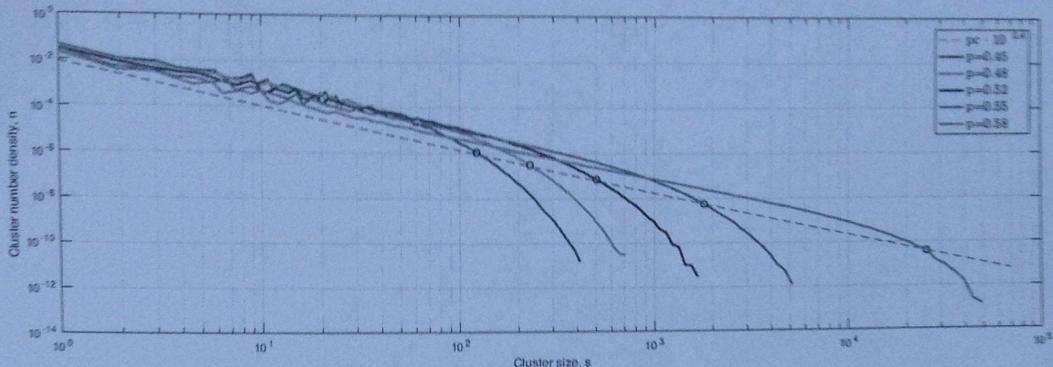


Figure 16: Cluster number density for some p -values below p_c . A line parallel to the p_c -line is added a factor $10^{-0.5}$ below, and the intersection of this curve indicates the stored value of s_ξ . In this simulation the system was of size $L = 512$, and averaged by 1000 samples.

We see clearly that each curve has one behavior when $s/s_\xi < 1$ and another where $s/s_\xi > 1$.

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

Discuss the behavior of $P(p, L)$ and $\Pi(p, L)$ in a system with a finite system size L . How do you measure these quantities?

A system is percolating when there is a connecting path from one side to the opposite. In the infinitely large system, this occurs only when $p \geq p_c$. However, in a finite system it is possible to observe percolation at any $p > 0$. When estimating the value of p_c we do a series of realizations for several values of p , and try to statistically express the probability of percolation for these values of p . This quantity is denoted $\Pi(p, L)$. It is measured as described in section 10. For small L the percolation probability is a gentle function as illustrated in figure 13. As L increases, the percolation probability function become steeper, as shown in figure 17. As $L \rightarrow \infty$, $\Pi(p, L)$ approaches a step function at $p = p_c \simeq 0.59275$.

Given that we have percolation the probability of picking a site in the spanning cluster, when randomly picking any site, is given as the *density*. It is defined as in equation 17. It is measured in a similar manner as the percolation probability, but instead of just counting the number of realizations that produced percolation, we add the mass of the spanning cluster into a cumulative mass variable, find the average of the masses by dividing by the number of realizations and finally dividing by the system size. The mass of each cluster can be obtained by using the *Area* property on the labeled matrix as `regionprops(1w, 'Area')`. Since there is a probability of percolation for any $p > 0$ in the finite system, the density is non-zero for all $p > 0$ as well. Figure 13 shows $P(p, L)$ for some small values of L . As $L \rightarrow \infty$, $\Pi(p < p_c, L) \rightarrow 0$ and there is a rapid change in behavior at $p = p_c$.

A simple algorithm for measuring the percolation probability and the density is shown below.

```

1 N = 10;
2 L = 100;
3 p = (0.4:0.01:1.0);
4 nx = length(p);
5 Ni = zeros(nx,1);
6 Mi = zeros(nx,1);
7
8 for i = 1:N
9     z = rand(L,L);
10
11    for ip = 1:nx
12        m = z < p(ip);
13        [lw,num] = bwlabel(m,4);
14        s = regionprops(lw, 'Area');
15        area = cat(1,s.Area);
16
17        jx = find(bbox(:,3)==L);
18        jy = find(bbox(:,4)==L);
19        j = union(jx,jy);
20
21        if length(j)>0 % Percolation
22            Ni(ip) = Ni(ip) + 1;
23            for jj = 1:length(j)
24                Mi(ip) = Mi(ip) + area(j(jj));
25            end
26        end
27    end
28 end
29
30
31 Pi = Ni/N;
32 P = Mi/(N*L*L);

```

So, $\Pi(p, L)$ describes the probability for there to be a spanning cluster, but we can characterize this specific cluster by its size, $M S$, or by its density, $P(p, L) = M S / L d$, which also corresponds to the probability for a site to belong to the spanning cluster. We can measure $P(p, L)$ by counting the mass, M_i of the spanning cluster as a function of p_i for various values of p_i . We can find the mass of the spanning cluster by finding a cluster that spans the system (there may be more than one) as we have explained above for $\Pi(p, L)$, and then measuring the number of sites in the cluster using the Area property of `regionprops(lw, 'Area')`. We will then loop over all samples and we will sum all the areas found for each value of p_i , and then divide by the total volume of the system considering also the total number of realizations. The resulting plot of $P(p, L)$ is shown at the bottom of fig. XX.b. We see that $P(p, L)$ changes rapidly around $p = p_c$ and then it grows slowly – approximately linearly – as $p \rightarrow 1$. We can understand this linear behavior: When p is near 1 all the setsites are connected and part of the spanning cluster. The density of the spanning cluster is therefore proportional to p in this limit.

16. The cluster number density

Introduce the cluster number density and its applications: Definition, measurement, scaling and data-collapse.

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

Discuss the behavior of $\Pi(p, L)$ in a system with a finite system size L . How can we use this to find the scaling exponent ν , and the percolation threshold, p_c ?

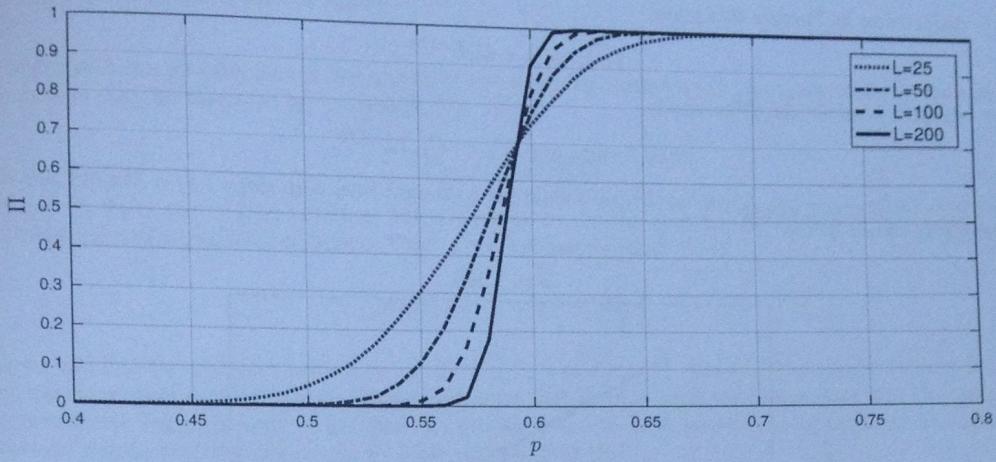


Figure 17: Percolation probability $\Pi(p, L)$ as a function of solid fraction, p , for several system sizes, L .

In two dimensions, the percolation probability, $\Pi(p, L)$, will look like a step function in the infinite system. However, in a finite system it is not. Take a look at the figure 17. We see that $\Pi(p, L)$ becomes steeper and the interval where $\Pi \in (0, 1)$ gets slimmer. Also notice that the function approaches a step function as $L \rightarrow \infty$. For small L , see the top plot in figure 13.

From figure 17 we may argue that $\Pi(p, L)$ has two different behaviors; one far from p_c and another close to p_c . We express this as

$$\Pi(p, L) = \phi(p - p_c) + F\left(\frac{L}{\xi}\right). \quad (37)$$

We assume that $\phi(p - p_c)$ is zero close to p_c . We also know that $\Pi(p, L)$ does not diverge as $L \rightarrow \infty$. Inserting equation 36 in the denominator we have

$$\Pi(p, L) = F\left(\frac{L}{|p - p_c|^{-\nu}}\right) = F(L|p - p_c|^\nu) = F\left(\left[L^{1/\nu}|p - p_c|\right]^\nu\right) = \tilde{F}\left[|p - p_c|L^{1/\nu}\right] \quad (38)$$

where $\tilde{F}(u) = F(u^\nu)$.

One way to determine the value of ν is to create a plot of datacollapse from this equation. The value of ν that makes the curves fall onto each other, is then the optimal value.

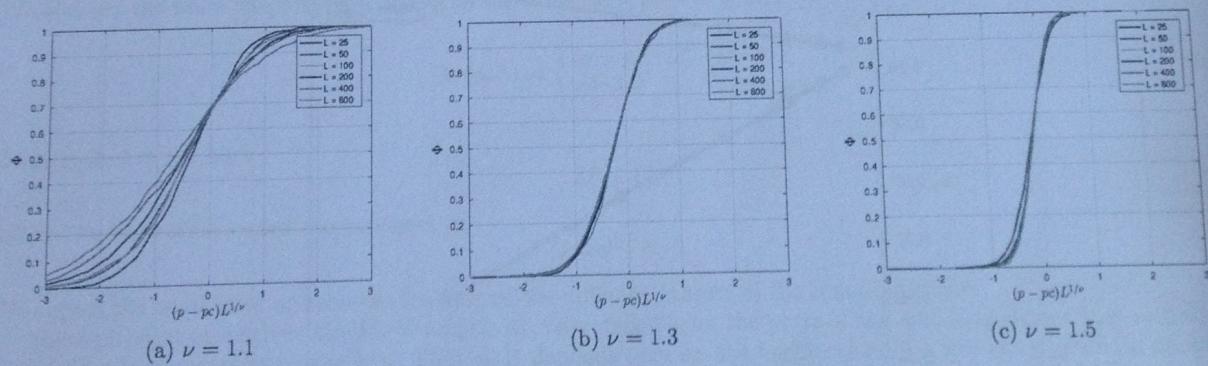


Figure 18: Datacollapse of $\tilde{F}[|p - p_c|L^{1/\nu}]$ plotted as $\Pi(p, L)$ vs $(p - p_c)L^{1/\nu}$, for three values of ν .

However, as you can see, this method is not very exact in this case. Luckily we have another method. Lets define $p_{\Pi=x}$ as the solid fraction which results in percolation probability $\Pi(p_{\Pi=x}, L) = x$, and notice that since

$$x = \Pi(p_{\Pi=x}, L) = \tilde{F}\left(|p_{\Pi=x} - p_c|L^{1/\nu}\right), \quad (39)$$

we can use the inverse function to show that

$$|p_{\Pi=x} - p_c|L^{1/\nu} = \tilde{F}^{-1}(x) = C_x, \quad (40)$$

which only depends on x . Further this gives

$$p_{\Pi=x} = p_c + C_x L^{-1/\nu}, \quad (41)$$

If we have two such p values the difference is

$$p_{\Pi=x_1} - p_{\Pi=x_2} = (C_{x_1} - C_{x_2}) L^{-1/\nu}. \quad (42)$$

Thus, if we plot $\log(p_{\Pi=x_1} - p_{\Pi=x_2})$ vs $\log(L)$, we should get a straight line, with slope $-1/\nu$. We did this in project 3, with the result shown below.

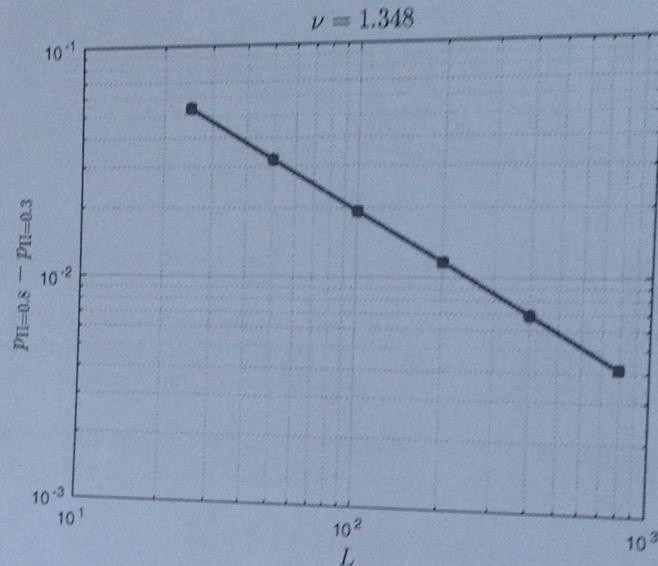


Figure 19: $p_{\Pi=0.8} - p_{\Pi=0.3}$ vs L in logarithmic scales.

This can in turn be used to find the value of the percolation threshold, p_c , by using equation (41). Plotting the measured $p_{\Pi=x}$ vs $L^{-1/\nu}$, the value of p_c should be the point it crosses the y-axis. The slope should be C_x , though this isn't much of interest to us. The result is shown below.

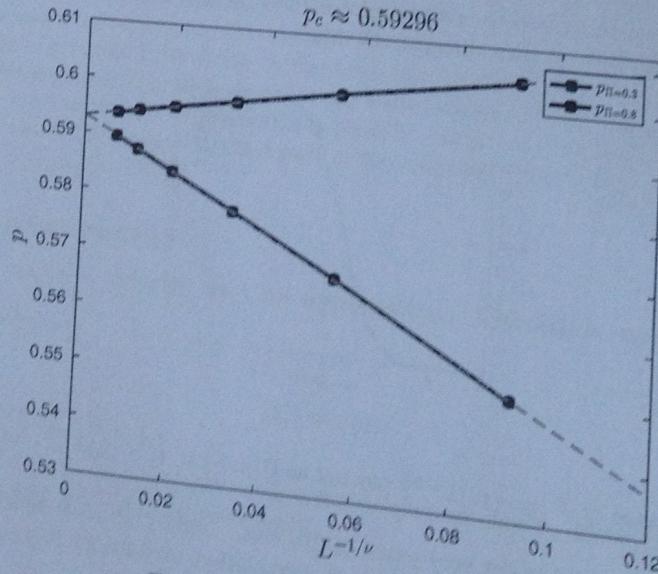


Figure 20: $p_{\Pi=0.8}$ and $p_{\Pi=0.3}$ vs L .

18. Subsets of the spanning cluster

Introduce and discuss the scaling of subsets of the spanning cluster. How can we measure the singly-

(41) connected bonds, and how does it scale?

Let's begin with the introduction of the scaling of the spanning cluster itself. We know that the spanning cluster of a finite system may be described by its density, $P(p, L)$ as

$$P(p, L) = \frac{M(p, L)}{L^d} \quad (43)$$

Our approach to finite size scaling problems will always be to assume that the finite size enters through a scaling function modifying the asymptotic behavior. That is, we will assume that

$$P(p, L) = (p - p_c)^\beta X\left(\frac{L}{\xi}\right) \quad (44)$$

for which we will find two different behaviors, i.e. for $L/\xi \gg 1$ or $L/\xi \ll 1$. For the first case, $L/\xi \gg 1$, we expect to reproduce the same state as when $p = p_c$. Thus we demand that $X(u)$ is constant in this case. For the latter case, i.e. when the correlation length is much larger than the system size, $\xi \gg L$, we expect the behavior to be independent of the correlation length, but only depend on L . That is, we expect that

$$P(p, L) = (p - p_c)^\beta X\left(\frac{L}{\xi}\right) = \xi^{-\beta/\nu} \left(\frac{L}{\xi}\right) = Y(L) \quad (45)$$

where we have used

$$\xi = |p - p_c|^{-\nu} \quad (46)$$

In order to get rid of the factor $\xi^{-\beta/\nu}$ in front of the function, we require that the function $X(u)$ has a similar power-law behavior in the limit of small u , so that the ξ in front of X and the ξ inside the X cancel each other. We achieve this by setting

$$x(u) \propto u^{-\beta/\nu} \quad (47)$$

We have therefore found that the scaling function X has the form

$$X(u) = \begin{cases} \text{constant} & , u \gg 1 \\ u^{-\beta/\nu} & , u \ll 1 \end{cases} \quad (48)$$

We may now recover the density expression as

$$P(p, L) = \begin{cases} (p - p_c)^\beta & , L \ll \xi \\ L^{-\beta/\nu} & , L \gg \xi \end{cases} \quad (49)$$

We also get the finite size scaling behavior of the mass $M(p, L) = P(p, L)L^d$

$$M(p, L) = \begin{cases} (p - p_c)^\beta L^d & , L \ll \xi \\ L^{d-\beta/\nu} & , L \gg \xi \end{cases} \quad (50)$$

Thus as $p \rightarrow p_c$ we have

$$M \propto L^D \quad (51)$$

Where we have abbreviated the exponent as

$$D = d - \beta/\nu. \quad (52)$$

We expect the same kind of behavior for each of the different subsets of the spanning cluster.

We expect the same kind of behavior for each of the different subsets of the spanning cluster. Some physical properties, like the conductivity, only depends on the parts of the spanning cluster that contribute to the flow from one side to another. That is, it depends only on the backbone and it will not depend on dangling ends (part of the cluster that are blind alleys). Each of these parts is typically referenced as a subset of the spanning cluster. We propose that these subsets of the spanning cluster must also obey similar scaling relations as the entire spanning cluster (51). That is

$$M_{SC} \propto L^{D_{SC}} \quad M_{BB} \propto L^{D_{BB}} \quad M_{DE} \propto L^{D_{DE}}, \quad (53)$$

where we use the acronyms BB for backbone, DE for dangling ends and SC for singly connected bonds; and their exponents correspond to each of their fractal dimensions. Since all of them are subsets of the spanning cluster, we know that all the exponents must be smaller than D . Also we know that the minimum mass a spanning cluster can

have is if all sites are singly connected sites. Furthermore I seem to recall that the dangling ends grow faster than the backbone, so we have the relations:

$$M_{SC} \leq M_{BB} \leq M_{DE} \leq M, \quad (54)$$

which imply that

$$D_{SC} \leq D_{BB} \leq D_{DE} \leq D, \quad (55)$$

In order to measure the singly connected bonds, we use so called self-avoiding walkers (SAW). One that always turn left, sticking to the left boundary of the cluster, and one that always turn right. All sites where these walkers paths intersect is a singly connected site.

19. Random walks / Flow in a disordered system

Either: Discuss the scaling theory for the distance $r^2(t)$ of a random walker dropped at a random occupied site on either (1) the percolation system or (2) the spanning cluster. (You can choose which case to discuss). Relate the results to diffusion in a bulk fluid and in a nanoporous system. Or: How do you measure the conductivity of the spanning cluster? Discuss the scaling theory for the conductivity $\sigma(p, L)$ when $p > p_c$. Relate the results to permeability in a nanoporous system.

the dangling ends grow faster than the

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these walkers

(54)

(55)

Appendix

Diffusion constant

Let's first look at diffusion in one dimension, and define $w(x, t)$ to be the probability of finding a given number of particles in an interval of length dx in $x \in [x, x + dx]$ at a time t . From experiments there are strong indications that the flux of particles $j(x, t)$ is proportional to the gradient of $w(x, t)$

$$j(x, t) = -D \frac{\partial w(x, t)}{\partial x}, \quad (56)$$

where D [length²] is a diffusion constant. Since the number of particles is conserved, we have the continuity equation

$$\frac{\partial j(x, t)}{\partial x} = -\frac{\partial w(x, t)}{\partial t}, \quad (57)$$

which leads to

$$\frac{\partial w(x, t)}{\partial t} = D \frac{\partial^2 w(x, t)}{\partial x^2}. \quad (58)$$

With the probability distribution function $w(x, t)dx$ we can evaluate expectation values such as the mean distance

$$\langle x(t) \rangle = \int_{-\infty}^{\infty} x w(x, t) dx, \quad (59)$$

or

$$\langle x^2(t) \rangle = \int_{-\infty}^{\infty} x^2 w(x, t) dx, \quad (60)$$

which allows for the computation of the variance $\sigma^2 = \langle x^2(t) \rangle - \langle x(t) \rangle^2$. Note as well that these expectation values are time-dependent. The normalization condition

$$\int_{-\infty}^{\infty} w(x, t) dx = 1 \quad (61)$$

imposes significant constraints on $w(x, t)$. We have

$$w(x = \pm\infty, t) = 0 \quad \frac{\partial^n w(x, t)}{\partial x^n} \Big|_{x=\pm\infty} = 0, \quad (62)$$

implying that when we study the time-derivative $\partial \langle x(t) \rangle / \partial t$, we obtain after integration by parts and using Eq. (58).

$$\frac{\partial \langle x \rangle}{\partial t} = \int_{-\infty}^{\infty} x \frac{\partial w(x, t)}{\partial t} dx = D \int_{-\infty}^{\infty} x \frac{\partial^2 w(x, t)}{\partial x^2} dx, \quad (63)$$

leading to

$$\frac{\partial \langle x \rangle}{\partial t} = D x \frac{\partial w(x, t)}{\partial x} \Big|_{x=\pm\infty} - D \int_{-\infty}^{\infty} \frac{\partial w(x, t)}{\partial x} dx. \quad (64)$$

The result is

$$\frac{\partial \langle x \rangle}{\partial t} = 0. \quad (65)$$

This means in turn that $\langle x \rangle$ is independent of time. If we choose the initial position $x(t = 0) = 0$, the average displacement $\langle x \rangle = 0$. If we link this discussion to a random walk in one dimension with equal probability of jumping to the left or right and with an initial position $x = 0$, then our probability distribution remains centered around $\langle x \rangle = 0$ as function of time.

The variance is not necessarily 0. Consider first

$$\frac{\partial \langle x^2 \rangle}{\partial t} = D x^2 \frac{\partial w(x, t)}{\partial x} \Big|_{x=\pm\infty} - 2D \int_{-\infty}^{\infty} x \frac{\partial w(x, t)}{\partial x} dx, \quad (66)$$

where we have performed an integration by parts as we did for $\frac{\partial \langle x \rangle}{\partial t}$. Integration by parts results in

$$\frac{\partial \langle x^2 \rangle}{\partial t} = -D x w(x, t) \Big|_{x=\pm\infty} + 2D \int_{-\infty}^{\infty} w(x, t) dx = 2D, \quad (67)$$

leading to

$$\langle x^2 \rangle = 2Dt, \quad (68)$$

and the variance as

$$\langle x^2 \rangle - \langle x \rangle^2 = 2Dt. \quad (69)$$

The root mean square displacement after a time t is then

$$\sqrt{\langle x^2 \rangle - \langle x \rangle^2} = \sqrt{2Dt}. \quad (70)$$

In three dimensions our starting point, equation (56), would look like

$$j(x, y, z, t) = -D \left(\frac{\partial w(x, y, z, t)}{\partial x} + \frac{\partial w(x, y, z, t)}{\partial y} + \frac{\partial w(x, y, z, t)}{\partial z} \right) \quad (71)$$

And our root mean square displacement after a time t would be

$$\sqrt{\langle x^2 \rangle - \langle x \rangle^2} = \sqrt{6Dt}. \quad (72)$$