1 Introduction

Percolation is a standard model for disordered systems. Its applications range from transport in amorphous and porous media and composites to the properties of branched polymers, gels and complex ionic conductors. Because of universality the results do not depend on the specific model, and general scaling laws can be deduced. In this chapter we give a short introduction to percolation theory and describe one application to composites. We start with the structural properties of site percolation clusters and their substructures and report on other percolation systems after that. Then we turn to the dynamical properties of percolation clusters and discuss the way the laws of diffusion and conduction are modified on random fractal structures. Finally, we review a particular application of the percolation concept, transport in heterogeneous ionic conductors.

2 The (Site-)Percolation Model

Percolation represents the basic model for a structurally disordered system (for recent reviews see [1,2], for applications see [3]). Let us consider a square lattice, where each site is occupied randomly with probability \( p \) or is empty with probability \( 1 - p \) (see Fig. 1). Occupied and empty sites may stand for very different physical properties. For illustration, let us assume that the occupied sites are electrical conductors, the empty sites represent insulators, and that electrical current can only flow between nearest-neighbour conductor sites.

At low concentration \( p \), the conductor sites are either isolated or form small clusters of nearest-neighbour sites. Two conductor sites belong to the same cluster if they are connected by a path of nearest-neighbour conductor sites, and a current can flow between them. At low \( p \) values, the mixture is an insulator, since no conducting path connecting opposite edges of our lattice exists. At large \( p \) values on the other hand many conducting paths between opposite edges exist, where electrical current can flow, and the mixture is a conductor. At some concentration in between, therefore, a threshold concentration \( p_c \) must exist where for the first time electrical current can percolate from one edge to the other. Below \( p_c \) we have an insulator, above \( p_c \) we have a conductor. The threshold concentration is called the percolation threshold, or, since it separates two different phases, the critical concentration.
Fig. 1. Site percolation on the square lattice: The small circles represent the occupied sites for three different concentrations: \( p = 0.2, 0.59, \) and \( 0.80 \). Nearest-neighbour cluster sites are connected by lines representing the bonds. Filled circles are used for finite clusters, while open circles mark the large \textit{infinite} cluster.

If the occupied sites are superconductors and the empty sites are conductors, \( p_c \) separates a normal-conducting phase below \( p_c \) from a superconducting phase above \( p_c \). Another example is a mixture of ferromagnets and paramagnets, where the system changes at \( p_c \) from a paramagnet to a ferromagnet.

In contrast to the more common thermal phase transitions, where the transition between two phases occurs at a critical temperature, the \textit{percolation transition} described here is a \textit{geometrical phase transition}, which is characterized by the geometric features of large clusters in the neighbourhood of \( p_c \). At low values of \( p \) only small clusters of occupied sites exist. When the concentration \( p \) is increased the average size of the clusters increases. At the critical concentration \( p_c \) a large cluster appears which connects opposite edges of the lattice. We call this cluster the \textit{infinite} cluster, since its size diverges in the thermodynamic limit. When \( p \) is increased further the density of the infinite cluster increases, since more and more sites become part of the infinite cluster, and the average size of the \textit{finite} clusters, which do not belong to the infinite cluster, decreases. At \( p = 1 \), trivially, all sites belong to the infinite cluster.

The critical concentration depends on the details of the lattice and increases, for fixed dimension \( d \) of the lattice, with decreasing coordination number \( z \) of the lattice: For the triangular lattice, \( z = 6 \) and \( p_c = 1/2 \), for the square lattice, \( z = 4 \) and \( p_c \cong 0.592746 \), and for the honeycomb lattice, \( z = 3 \) and \( p_c \cong 0.6962 \). For fixed \( z \), \( p_c \) decreases if the dimension \( d \) is enhanced. In both the triangular lattice and the simple cubic lattice we have \( z = 6 \), but \( p_c \) for the simple cubic lattice is considerably smaller, \( p_c \cong 0.3116 \).

The percolation transition is characterized by the geometrical properties of the clusters near \( p_c \) [1,2]. The probability \( P_\infty \) that a site belongs to the infinite cluster is zero below \( p_c \) and increases above \( p_c \) as

\[
P_\infty \sim (p - p_c)^\beta.
\]  

\( (1) \)
Table 1. Critical exponents and fractal dimensions for percolation in two and three dimensions. The numerical values are taken from [1].

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Exp.</th>
<th>$d = 2$</th>
<th>$d = 3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Order parameter</td>
<td>$P_\infty(p) \sim (p - p_c)^\beta$</td>
<td>$\beta$</td>
<td>$5/36$</td>
</tr>
<tr>
<td>Correlation length</td>
<td>$\xi(p) \sim</td>
<td>p - p_c</td>
<td>^{-\nu}$</td>
</tr>
<tr>
<td>Cluster mass</td>
<td>$M(r) \sim r^{d_f}$</td>
<td>$d_f$</td>
<td>$91/48$</td>
</tr>
<tr>
<td>Backbone mass</td>
<td>$M_B(r) \sim r^{d_B}$</td>
<td>$d_B$</td>
<td>$1.62 \pm 0.02$</td>
</tr>
<tr>
<td>Chemical Path</td>
<td>$l(r) \sim r_{\min}$</td>
<td>$d_{\min}$</td>
<td>$1.13 \pm 0.004$</td>
</tr>
<tr>
<td>Random Walk</td>
<td>$\langle r^2(t) \rangle \sim t^{2/d_w}$</td>
<td>$d_w$</td>
<td>$2.871 \pm 0.001$</td>
</tr>
<tr>
<td>Conductivity</td>
<td>$\sigma_{\infty}(p) \sim (p_c - p)^\mu$</td>
<td>$\mu$</td>
<td>$1.30 \pm 0.002$</td>
</tr>
<tr>
<td>Superconductivity</td>
<td>$\sigma_S(p) \sim (p - p_c)^{-\delta}$</td>
<td>$\delta$</td>
<td>$1.30 \pm 0.002$</td>
</tr>
</tbody>
</table>

This behaviour is illustrated in Fig. 2. The linear size of the finite clusters, below and above $p_c$, is characterized by the correlation length $\xi$. The correlation length is defined as the mean distance between two sites on the same finite cluster and represents the characteristic length scale in percolation. When $p$ approaches $p_c$, $\xi$ increases as

$$\xi \sim |p - p_c|^{-\nu},$$

with the same exponent $\nu$ below and above the threshold (see also Fig. 2). While $p_c$ depends explicitly on the type of the lattice, the critical exponents $\beta$ and $\nu$ are universal and depend only on the dimension $d$ of the lattice, but not on the type of the lattice. The values of the critical exponents are given in Tab. 1 for two and three dimensions.

![Fig. 2. Schematic diagram of the probability $P_\infty$ (Eq. (1), bold line) and the correlation length $\xi$ (Eq. (2), thin line) versus the concentration $p$ of occupied sites.](image)

3 The Fractal Structure of Percolation Clusters near $p_c$

Near $p_c$, on length scales smaller than $\xi$ both the infinite cluster and the finite clusters are self-similar, i.e., if we cut a small part out of a large cluster, magnify it to the
Fig. 3. Four successive magnifications of the incipient infinite cluster that forms at the percolation threshold on the square lattice. Three of the panels are magnifications of the center squares marked by black lines. In the figure that you see, however, the labels of the four panels have been removed and the panels have been scrambled. Attempt to put them back into sequence by eye – it is extremely difficult if the system is at the percolation threshold ($p = p_c$). An educational game is to time how long it takes each player to detect by eye which of the 24 possible orderings is the correct one that arranges the four panels in increasing order of magnification.

original cluster size and compare it with the original, we cannot tell the difference: Both look the same. This feature is illustrated in Fig. 3, where a large cluster at $p_c$ is shown in four different magnifications. We leave it to the reader to find out what is the original and what are the magnifications.

We have learnt in chapter 18 that – as a consequence of the (non-trivial) self-similarity – the cluster is characterized by a ”fractal” dimension, which is smaller
than the dimension $d$ of the embedding lattice. The mean mass of the cluster within a circle of radius $r$ increases with $r$ as

$$M(r) \sim r^{d_f}, \quad r \ll \xi,$$

with the fractal dimension $d_f$. The numerical values of $d_f$ can be found in Tab. 1. Above $p_c$, on length scales larger than $\xi$ the infinite cluster can be regarded as an homogeneous system which is composed of many cells of size $\xi$. Mathematically, this can be summarized as

$$M(r) \sim \begin{cases} \xi d_f, & \text{if } r \ll \xi, \\ \xi d, & \text{if } r \gg \xi. \end{cases}$$

Fig. 4 shows a part of the infinite cluster above $p_c$ ($p = 1.003 p_c$) on different length scales. At large length scales ($r \gg \xi$, upper left) the cluster appears homogeneous, while on lower length scales ($r \ll \xi$, lower pictures) the cluster is self-similar.

The fractal dimension $d_f$ can be related to $\beta$ and $\nu$ in the following way: Above $p_c$, the mass $M_\infty$ of the infinite cluster in a large lattice of size $L^d$ is proportional to $L^d P_\infty$. On the other hand, this mass is also proportional to the number of unit cells of size $\xi$, $(L/\xi)^d$, multiplied by the mass of each cell which is proportional to $\xi^{d_f}$. This yields (with Eqs. (1) and (2))

$$M_\infty \sim L^d P_\infty \sim L^d (p - p_c)^\beta \sim (L/\xi)^d \xi^{d_f} \sim L^d (p - p_c)^{\nu d - \nu d_f},$$

and hence, comparing the exponents of $(p - p_c)$,

$$d_f = d - \frac{\beta}{\nu}.$$
Fig. 4. The same as Fig. 4 except that now the system is slightly (0.3 %) above the percolation threshold and the panels are not scrambled. The upper left picture shows the original and the other pictures are magnifications of the center squares marked by black lines. The correlation length $\xi$ is approximately equal to the linear size of the third (lower left) picture. When comparing the two lower pictures, the self-similarity at small length scales below $\xi$ is easy to recognize.

A further important substructure of the cluster is the external perimeter (which is also called the hull). The hull consists of those sites of the cluster which are adjacent to empty sites and are connected with infinity via empty sites. It is an important model for random fractal interfaces. In two dimensions, the hull has the fractal dimension $d_h = 7/4$, while its mass seems to be proportional to the mass of the cluster in $d = 3$, i.e. $d_h = d_f$. In contrast to the hull, the total perimeter also includes the holes in the cluster.
Further Percolation Systems

So far we have considered site percolation, where the sites of a lattice have been occupied randomly. When the sites are all occupied, but the bonds between the sites are randomly occupied with probability $q$, we speak of bond percolation (see Fig. 5a). Two occupied bonds belong to the same cluster if they are connected by a path of occupied bonds, and the critical concentration $q_c$ of bonds ($q_c = 1/2$ in the square lattice and $q_c \approx 0.2488$ in the simple cubic lattice) separates a phase of finite clusters of bonds from a phase with an infinite cluster [1,2].

If sites are occupied with probability $p$ and bonds are occupied with probability $q$, we speak of site–bond percolation. Two occupied sites belong to the same cluster if they are connected by a path of nearest-neighbour occupied sites with occupied bonds in between. For $q = 1$, site–bond percolation reduces to site percolation, for $p = 1$ it reduces to bond percolation. In general, both parameters characterize the state of the system. Accordingly, a critical line in $p$-$q$ space separates both phases, which for $p = 1$ and $q = 1$ takes the values of the critical bond and site concentrations, respectively.

Perhaps the most common example of bond percolation in physics is a random resistor network, where the metallic wires in a regular network are cut randomly with probability $1 - q$. Here $q_c$ separates a conductive phase at large $q$ from an insulating phase at low $q$. A possible application of bond percolation in chemistry is the polymerization process, where small branching molecules can form large molecules by activating more and more bonds between them. If the activation probability $q$ is above the critical concentration, a network of chemical bonds spanning the whole system can be formed, while below $q_c$ only macromolecules of finite size can be generated. This process is called a sol-gel transition. An example of this gelation process is the boiling of an egg, which at room temperature is liquid and upon heating becomes a more solid-like gel. Site–bond percolation can be relevant for gelation in dilute media.
The most natural example of percolation is *continuum percolation*, where the positions of the two components of a random mixture are not restricted to the discrete sites of a regular lattice. As a simple example, consider a sheet of conductive material, with circular holes punched randomly in it (see Fig. 5b). The relevant quantity now is the fraction $p$ of remaining conductive material. Compared with site and bond percolation, the critical concentration is further decreased: $p_c \approx 0.312$ for $d = 2$, when all circles have the same radius. This picture can easily be generalized to three dimensions, where spherical voids are generated randomly in a cube, and $p_c \approx 0.034$. Due to its similarity to Swiss cheese, this model of continuous percolation is called the Swiss cheese model. Similar models, where also the size of the spheres can vary, are used to describe sandstone and other porous materials.

It is important that close to the percolation threshold all these different percolation systems are characterized by the same critical exponents $\beta$, $\nu$, and $d_f$ given in Tab. 1. The exponents are universal and depend neither on the structural details of the lattice (e.g., square or triangular) nor on the type of percolation (site, bond, or continuum), but only on the dimension $d$ of the lattice.

![Random walk on a square lattice. The lattice constant $a = 1$ is equal to the jump length of the random walker. Sixteen steps of the walk are shown.](image)

\section{Diffusion on Regular Lattices}

After we have discussed the structural properties of percolation systems close to the percolation threshold, we will now focus on the *dynamical* properties of percolation systems, where to each site or bond a physical property such as conductivity is assigned. We show that due to the fractal nature of the percolation clusters near $p_c$, the physical laws of dynamics are changed essentially and become *anomalous*.

At first, we consider regular lattices. The diffusion process is commonly modelled by a simple random walk (see e.g., chapters 17 and 18), which advances one step of length $a$ in one time unit. Each step brings the random walker to a randomly chosen nearest-neighbour site on a given $d$-dimensional lattice. Assume that the
walker starts at time \( t = 0 \) at the origin of the lattice. After \( t \) time steps, the actual position is described by the vector (see Fig. 6)

\[
\mathbf{r}(t) = a \sum_{\tau=1}^{t} \mathbf{e}_\tau,
\]

(7)

where \( \mathbf{e}_\tau \) denotes the unit vector pointing in the direction of the jump at the \( \tau \)th time step.

The mean distance the random walker has travelled after \( t \) time steps is described by the root mean square displacement

\[
\langle r^2(t) \rangle = a^2 \sum_{\tau, \tau' = 1}^{t} \langle \mathbf{e}_\tau \cdot \mathbf{e}_{\tau'} \rangle = a^2 t + \sum_{\tau \neq \tau'} \langle \mathbf{e}_\tau \cdot \mathbf{e}_{\tau'} \rangle.
\]

(8)

Since jumps at different steps \( \tau \) and \( \tau' \) are uncorrelated, we have \( \langle \mathbf{e}_\tau \cdot \mathbf{e}_{\tau'} \rangle = \delta_{\tau \tau'} \), and we obtain the Einstein relation

\[
\langle r^2(t) \rangle = a^2 t,
\]

(9)

which is equivalent to Fick’s first law (see chapter 10). Note that Eq. (9) is independent of the dimension \( d \) of the lattice.

In the general case, when the lengths of the steps of the random walker may vary, Eq. (9) is modified into

\[
\langle r^2(t) \rangle = 2d D t,
\]

(10)

where \( D \) is the diffusion coefficient. The diffusion coefficient is (approximately) related to the dc conductivity \( \sigma_{dc} \) by the Nernst-Einstein equation,

\[
\sigma_{dc} = n(e^2/k_B T) D,
\]

(11)

where \( n \) is the density and \( e \) the charge of the diffusing particles.

A more complete description of the diffusion process is possible with the probability density \( P(r, t) \), which is the probability of finding the walker after \( t \) time steps at a site within distance \( r \) from its starting point. The mean square displacement can be obtained from \( P(r, t) \) via \( \langle r^2(t) \rangle = \int dr r^2 P(r, t) \). For \( t \gg r \), \( P(r, t) \) is described by a Gaussian: \( P(r, t) \approx \frac{1}{\sqrt{2\pi D t}} e^{-r^2/2Dt} \). This “normal” probability density – commonly referred to as the propagator (see chapters 10, 18, and 23) – characterizes the diffusion on regular lattices. Next we consider disordered structures.

6 Diffusion on Percolation Clusters

We start with the infinite percolation cluster at the critical concentration \( p_c \). The cluster has loops and dangling ends, and both substructures slow down the motion of a random walker. Due to self-similarity, loops and dangling ends occur on all
length scales, and therefore the motion of the random walker is slowed down on all length scales. The time the walker needs to travel a distance $R$ is no longer, as in regular systems, proportional to $R^2$, but scales as $t \sim R^{d_w}$, where $d_w > 2$ is the fractal dimension of the random walk [1,2]. For the mean square displacement this yields immediately

$$\langle r^2(t) \rangle \sim t^{2/d_w}. \quad (12)$$

The fractal dimension $d_w$ is approximately equal to $3d_f/2$ [4]; the results of numerical simulations can be found in Tab. 1. For continuum percolation (Swiss cheese model) in $d = 3$, $d_w$ is enhanced: $d_w \cong 4.2$ [5]. Diffusion processes described by Eq. (12) are generally referred to as anomalous diffusion (cf. chapter 10).

The probability density $\langle P(r, t) \rangle_N$, averaged over $N$ percolation clusters, is not so easy to calculate. Analytical expressions for $\langle P(r, t) \rangle_N$ that fully describe the data obtained from numerical simulations can be derived. The derivation is beyond the scope of this book and we refer the interested reader to [1,6].

![Fig. 7. Schematic diagram of the (usual) dc conductivity $\sigma_{dc}$ (Eq. (15), bold line) and the conductivity $\sigma_S$ for a conductor-superconductor percolation network (Eq. (20), thin line for $p < p_c$) versus the concentration $p$ of occupied sites. The cluster capacitance $C$ is proportional to $\sigma_S$ for $p < p_c$ and diverges with the same exponent for $p > p_c$ (see Eq. (25)).](image)

Comparatively simple, however, is the scaling behaviour of $\langle P(0, t) \rangle$, that denotes the probability of being, after $t$ time steps, at the site where the random walker started. Since for very large times each site has the same probability of being visited, the probability of being at the origin is proportional to the inverse of the number of distinct sites $S(t)$ the random walker visited. Since $S(t)$ increases with $R(t) \equiv \langle r^2(t) \rangle^{1/2}$ as $S(t) \sim R(t)^{d_f}$, we have

$$\langle P(0, t) \rangle \sim R(t)^{-d_f} \sim t^{-d_f/d_w} \quad (13)$$

(see also chapter 18). Above $p_c$, fractal structures occur only within the correlation length $\xi(p)$ from Eq. (2). Thus the anomalous diffusion law, Eq. (12), occurs only below the corresponding crossover time $t_\xi \sim R(t_\xi)^{d_w} \sim \xi^{d_w}$, which decreases proportional to $(p-p_c)^{-d_w}$, if $p$ is further increased. Above $t_\xi$, on large time scales, the random walker explores large length scales where the cluster is homogeneous, and $\langle r^2(t) \rangle$ follows Fick’s law (Eqs. (9) or (10)) increasing linearly with time $t$. Thus,

$$\langle r^2(t) \rangle = \begin{cases} t^{2/d_w}, & \text{if } t \ll t_\xi, \\ t, & \text{if } t \gg t_\xi. \end{cases} \quad (14)$$
7 Conductivity of Percolation Clusters

The diffusion coefficient is related to the dc conductivity $\sigma_{dc}$ by the Nernst-Einstein equation, Eq. (11). Below $p_c$, there is no current between opposite edges of the system, and $\sigma_{dc} = 0$. Above $p_c$, $\sigma_{dc}$ increases by a power law (see Fig. 7 for illustration),

$$\sigma_{dc} \sim (p - p_c)^{\mu},$$ (15)

where the critical exponent $\mu$ is (semi)-universal. For percolation on a lattice, $\mu$ depends only on $d$; the numerical results are contained in Tab. 1. For continuum percolation (Swiss cheese model) in $d = 3$, however, $\mu$ is enhanced: $\mu \cong 2.38$.

Combining Eqs. (11) and (15), we can obtain the behaviour of the diffusion coefficient $D$ as a function of $p - p_c$. Since only the particles on the infinite cluster contribute to the dc conductivity, we have (from Eq. (1)) $n \sim P_{\infty} \sim (p - p_c)^{\beta}$ in Eq. (11). This yields

$$D \sim (p - p_c)^{\mu - \beta}.$$ (16)

Next we use scaling arguments to relate the exponent $\mu$ to $d_w$. Equations (16) and (10) imply that above $t_\xi$, the mean square displacement $\langle r^2(t) \rangle$ behaves as

$$\langle r^2(t) \rangle \sim (p - p_c)^{\mu - \beta} t, \quad t > t_\xi.$$ (17)

On the other hand we know that for times below $t_\xi$ on distances $r < t_\xi^{1/d_w}$,

$$\langle r^2(t) \rangle \sim t^{2/d_w}, \quad t < t_\xi.$$ (18)

By definition, for $t = t_\xi$, we have $\langle r^2(t) \rangle \sim \xi^2$. Substituting this into Eqs. (17) and (18) and equating both relations we obtain immediately $(p - p_c)^{\mu - \beta} t_\xi \sim t_\xi^{2/d_w}$. Using $t_\xi \sim \xi^{d_w} \sim (p - p_c)^{-\beta d_w}$ (from Eq. (2)) we get the relation between $\mu$ and $d_w$,

$$d_w = 2 + (\mu - \beta)/\nu.$$ (19)

8 Further Electrical Properties

In the last section we have already seen that the dc conductivity in the conductor-insulator system is zero below $p_c$ and increases with a power law above $p_c$. If we consider, instead, the corresponding superconductor-conductor system, the conductivity is infinite above $p_c$ and diverges with a power law when approaching $p_c$ from below (see Fig. 7),

$$\sigma_s \sim (p_c - p)^{-s}.$$ (20)

The numerical results for $s$ can be found in Tab. 1.

Next, for generalizing this result and for obtaining further electric properties, let us assume that each bond in the network represents (with probability $p$) a circuit
conductivity
complex conductivity tends to
characteristic time scale in this short-circuit model. Splitting the complex function
mined by the asymptotic behaviour of Eq. (21) by a complex scaling function
with the same exponent
and
For satisfying these conditions, we must require that
the capacitance of the whole system:

\[ \sigma(\omega) = \sigma_A(\sigma_A/\sigma_B)^{-u}, \tag{21} \]

where the exponent
\[ u = \mu/(\mu + s) \tag{22} \]
is related to the exponents \( \mu \) and \( s \) from above, \( u = 0.5 \) in \( d = 2 \) and \( u \approx 0.71 \) in \( d = 3 \) (see Tab. 1).

For extending this result to the critical regime below and above \( p_c \), we multiply Eq. (21) by a complex scaling function \( S(z) \) that depends on \( z = |p - p_c|(\sigma_A/\sigma_B)^\Phi \) and can be different above and below \( p_c \) [9,10],

\[ \sigma(\omega) = \sigma_A(\sigma_A/\sigma_B)^{-u} \cdot S[p - p_c|(\sigma_A/\sigma_B)^\Phi]. \tag{23} \]
The exponent \( \Phi \) as well as the asymptotic behaviour of the scaling function is determined by the asymptotic behaviour of \( \sigma(\omega) \) in the limit \( \omega \to 0 \) and \( \sigma_A/\sigma_B \to \infty \).

In the following, let us concentrate on the conductor-capacitor limit, where
\( \sigma_A = \sigma_A^0 \) and \( \sigma_B = -i\omega C_B \). Then the complex scaling variable \( z \) is proportional to \( |p - p_c|[\sigma_A^0/( -i\omega C_B)]^\Phi \sim (\tau \omega)^{-\Phi} \), and \( \tau = |p - p_c|^{-1/\Phi} C_B/\sigma_A^0 \) defines the characteristic time scale in this short-circuit model. Splitting the complex function \((-i)^u S(z)\) into its real part \( S_1 \) and imaginary part \( S_2 \), we obtain for the complex conductivity

\[ \sigma(\omega) = \sigma_A^0(C_B/\sigma_A^0)^u \cdot \omega^u \cdot [S_1(\tau \omega)] + i S_2(\tau \omega)], \tag{24} \]

where \( S_1 \) and \( S_2 \) are real functions.

According to standard electrodynamics, in the limit of \( \omega \to 0 \) the real part of the complex conductivity tends to \( \sigma_{dc} \), while the imaginary part becomes \( -\omega C \), with \( C \) the capacitance of the whole system:

\[ \sigma(\omega) \to \begin{cases} \sigma_{dc} - i\omega C, & \text{if } p > p_c, \\
-\omega C, & \text{if } p < p_c \end{cases} \quad (\omega \to 0). \tag{25} \]

For satisfying these conditions, we must require that \( S_1(\tau \omega) \sim (\tau \omega)^{-u} \) above \( p_c \) and \( S_2(\tau \omega) \sim (\tau \omega)^{1-u} \) below and above \( p_c \). The first condition determines, together with Eqs. (15) and (22), the scaling exponent \( \Phi, \Phi = 1/(\mu + s) \). The second condition yields the new relation for the capacitance [1,9,10],

\[ C \sim S_2(\tau \omega) \sim |p - p_c|^{(u-1)/\Phi} = |p - p_c|^{-s}, \tag{26} \]

with the same exponent \( s \) below and above \( p_c \) (see Fig. 7). The divergency of \( C \) at \( p_c \) has a simple physical interpretation: each pair of neighboured clusters forms a
Diffusion and Conduction in Percolation Systems

The effective surface increases when $p_c$ is approached and tends to infinity at $p_c$. Accordingly, the effective capacitance $C$ of the system also diverges. Next, we discuss a (non-trivial) application of the percolation concept, the ionic transport in heterogeneous ionic conductors.

9 Application of the Percolation Concept: Heterogeneous Ionic Conductors

9.1 Interfacial Percolation and the Liang-Effect

Fig. 8. Illustration of the three-component percolation model for dispersed ionic conductors, for different concentrations $p$ of the insulating material. The insulator is represented by the grey area, the ionic conductor by the white area. The bonds can be highly conducting bonds ($A$ bonds, bold lines), normal conducting bonds ($B$ bonds, thin lines), or insulating ($C$ bonds, dashed lines). (a) $p < p_c^B$, (b) $p = p_c^B$, (c) $p = p_c^C$, and (d) $p > p_c^C$ (redrawn after [15]).

Let us now turn to percolation models that describe electrical transport in specific composite materials. A substantial amount of research has concentrated on "dispersed ionic conductors" after the discovery by Liang [11] that insulating fine particles with sizes of the order of 1 µm, dispersed in a conductive medium (e. g. Al₂O₃ in LiI), can lead to a conductivity enhancement [12]. This effect has been found to arise from the formation of a defective, highly conducting layer following the boundaries between the conducting and the insulating phase [13]. Effectively, the system thus contains three phases. Theoretical studies therefore have focused on suitable three-component impedance network models.

Figure 8 shows a two-dimensional illustration of such composites in a discretized model [14,15]. In its simplest version this model is constructed by randomly selecting a fraction $p$ of elementary squares on a square lattice, which represent the insulating phase, while the remaining squares are the conducting phase. The distribution of both phases leads to a correlated bond percolation model with three types of bonds and associated bond conductances $\sigma_\alpha$; $\alpha = A, B, C$; as defined in Fig. 8. For example, bonds in the boundary between conducting and insulating phases correspond to the highly conducting component ($A$ bonds). The analogous construction for three dimensions is obvious. Finite-frequency effects are readily included, when we allow bond conductances to be complex [16]. For simplicity, we may assume
the ideal behaviour $\sigma_\alpha = \sigma_\alpha^0 - i\omega C_\alpha$, as in the previous section, but more general forms can be chosen when necessary. Clearly, the experimental situation described above requires that $\sigma_\alpha^0/\sigma_\beta^0 = \tau \gg 1$; $\sigma_\beta^0 = 0$. Thereby it is natural to assume that $\sigma_\alpha^0$ and $\sigma_\beta^0$ are thermally activated, such that their ratio $\tau \propto \exp(-\Delta E/k_B T)$ increases with decreasing temperature.

A remarkable feature of this model is the existence of two threshold concentrations. At $p = p_c'$, interface percolation (i.e., percolation of $A$ bonds) sets in, whereas at $p = p_c'' = 1 - p_c'$ (normally not accessible by experiment) the system undergoes a conductor-insulator transition. In two dimensions we have $p_c' = 0.41$, while in $d = 3, p_c = 0.097$, corresponding to the threshold for second-neighbour ($d = 2$) and third-neighbour ($d = 3$) site percolation on a $d$-dimensional lattice, respectively. At zero frequency, the total conductivity can be obtained from Monte Carlo simulation [14,15].

Figure 9 shows results for $d = 3$ and three different temperatures (corresponding to $\tau = 10, 30$ and 100). Good agreement with the experimental curves [17] is achieved, which show a broad maximum in the conductivity as a function of $p$ in the range between the two thresholds. Changing $\tau$ (by varying the temperature) offers the possibility to interpret the measured activation energies as a function of $p$ [18] and, in principle, also to detect the critical transport behaviour associated with interface percolation. In the vicinity of $p_c''$ it seems interesting in addition to study critical ac effects. For examples, at $p_c''$ the effective capacitance develops a peak, whose height should scale with $\tau$ as $C_{\text{eff}} \sim \tau^{-u}$, where $u = \mu/(\mu + s)$, see Eqs. (21,22). Ac-properties in the whole range of $p$-values have been calculated by renormalization group techniques [16].
Several extensions of this model are conceivable. In the case of dc transport \((\omega = 0)\), the variation of the total conductivity with the size of dispersed particles has been calculated and successfully compared with experiments \([19–21]\). In particular, it was found that as the particle size decreases while the thickness of the highly conducting interfacial layer is fixed, the maximum in the total conductivity as a function of the insulator concentration \(p\) shifts to smaller values of \(p\). The observation of conductivity maxima at very low volume fractions \((\approx 10\%)\) in certain composite electrolytes, however, was interpreted recently by a grain boundary mechanism within the bulk of the electrolyte phase \([22]\).

Related work also emphasized aspects of continuum percolation in dispersed ionic conductors \([20]\), which, depending on the geometrical conditions, can lead to dynamical critical properties differing from lattice percolation (see e.g. Sec. 7).

![Graph](image)

**Fig. 10.** Plot of the dc conductivities of the micro- and nanocrystalline composites vs insulator volume fraction \(p\) at \(T = 433\) K. The conductivity of the nanocrystalline samples (open circles) shows an enhancement up to a maximum at \(p \approx 0.7\) \((\approx 0.5)\), while the conductivity of the microcrystalline composites (full circles) decreases monotonically. The lines show the dc conductivities obtained from the continuum percolation model discussed in the text (after \([26]\)).

### 9.2 Composite Micro- and Nanocrystalline Conductors

In the foregoing subsection, we have discussed dispersed ionic conductors that were prepared by melting the ionic conductor and adding the insulator (mainly \(\text{Al}_2\text{O}_3\)) to it. Next we consider diphase micro- and nanocrystalline materials, which were prepared by mixing the two different powders and pressing them together to a pellet. This way, in contrast to the classic dispersed ionic conductors discussed above, the grain size of both ionic conductor and insulator can be varied over several orders of magnitude. For reviews on nanocrystalline materials, see e.g. \([23–25]\).
Very recently, the ionic conductivity of micro- and nanocrystalline $(1-x)\text{Li}_2\text{O} : x\text{B}_2\text{O}_3$ composites, for different content $x$ of insulator $\text{B}_2\text{O}_3$, has been studied by Indris et al. [26]. In the nanocrystalline samples, with an average grain size of about 20 nm, the dc conductivity increases with increasing content of $\text{B}_2\text{O}_3$ up to a maximum at $x \approx 0.5$. Above 0.92, the dc conductivity vanishes.

In contrast, in the microcrystalline samples (grain size about 10 $\mu$m), the dc conductivity decreases monotonically when $x$ is increased and seems to vanish above $x \approx 0.55$ (see Fig. 10). The activation energy remains almost constant in both cases, $E_{\text{act}} \approx 1$ eV, for all $x$ values.

To explain these surprising experimental observations, Indris et al. assumed that (as for the classical dispersed ionic conductors) (i) $\text{B}_2\text{O}_3$ acts as an insulator for the lithium ions, (ii) the mobility of the Li ions along the diphase boundaries between ionic conductor and $\text{B}_2\text{O}_3$ is larger than in the bulk lithium oxide, and (iii) that the thickness $\lambda$ of this highly conducting interface is independent of the grain size.

For a quantitative treatment one has to note that the insulator content $x$ is related to the volume fraction $\phi$ (considered in percolation theory) by $p = \alpha x / (\alpha x - x + 1)$, where $\alpha = V_{\text{mol}}(\text{B}_2\text{O}_3) / V_{\text{mol}}(\text{Li}_2\text{O}) \approx 1.9065$ is the ratio between the mole volumes. Accordingly, the experimental results suggest the existence of two different percolation thresholds for the conduction paths, $p_c \approx 0.7$ for the microcrystalline samples and $p_c \approx 0.96$ for nanocrystalline ones, above which the dc conductivity of the composite vanishes.

These different thresholds can be understood by simple geometrical arguments. In the case of micro-crystalline samples, the highly conducting region at the interface between $\text{B}_2\text{O}_3$ and $\text{Li}_2\text{O}$ grains does not play a role since its width is negligible compared to the grain sizes, and conducting paths can open up only when two $\text{Li}_2\text{O}$ grains get in direct contact to each other. Qualitatively, we can expect a percolating conducting path when the $\text{Li}_2\text{O}$ concentration gets larger than 0.3 (i.e., $p = 0.7$), which is between the percolation threshold of spheres in a three dimensional continuum percolation model and the percolation threshold of sites in the simple cubic lattice.

In the case of nanocrystalline samples, however, the width of the highly conducting interface becomes comparable to the grain sizes. In this case, the highly conducting region can act as a bridge between two $\text{Li}_2\text{O}$ grains not in direct contact to each other, opening up additional paths for Li ions. A percolating conducting path can be disrupted only at much higher concentrations of $\text{B}_2\text{O}_3$ than for micrometer sized grains. Again, the value suggested by the experiment is in the expected regime.

To describe the actual dependence of the dc conductivity of $\text{Li}_2\text{O} : \text{B}_2\text{O}_3$ composites, $\sigma_{\text{dc}}(p)$, on the insulator concentration $p$, Indris et al. employed a continuum percolation model similar to that studied earlier for dispersed ionic conductors [20]. In this model, the size of dispersed particles is considered explicitly and the conductivity is estimated by means of the effective medium approximation (EMA), yielding an analytical expression for $\sigma_{\text{dc}}(p)$. Denoting by $P_0(p)$, $P_1(p)$, and $P_2(p)$, the con-
centrations of the insulator, the highly conducting diphase boundaries and the ionic conductor, respectively. \( \sigma_{dc}(p) \) is given within EMA by

\[
\sigma_{dc}(p) = \sigma_B^0 \frac{1}{z-2} \left\{ -A + [A^2 + 2\tau(z - 2 - zP_B)]^{1/2} \right\},
\]

where \( A = \tau(1 - zP_A/2) + (1 - zP_B/2) \), \( z \) is a parameter determining the percolation threshold \( p_c \) at which \( \sigma_{dc} = 0 \), and \( \tau = \sigma_A^0 / \sigma_B^0 \) is (as before) the enhancement factor, defined as the ratio between the conductivities of the highly conducting interface and of pure Li₂O, respectively. For details of the treatment, we refer to [20,26]. The concentrations of the three components are given by \( P_0(p) = p \), \( P_B(p) = (1 - p)^{\eta^3} \) and \( P_A(p) = 1 - p - P_B(p) \), with

\[
\eta = \frac{R + \lambda}{R},
\]

where \( R \) is the radius of the particles (\( R \approx 10 \) nm for the nanoparticles and \( R \approx 5 \) \( \mu \)m for the microparticles) and \( \lambda \) between 1 and 2 nm.

According to Eq. (27), the percolation threshold for the disruption of conducting paths, \( p_c \), is given by \( p_c = (z - 2)/z \). Thus, from our previous discussion, we expect that for nanocrystalline samples, \( p_c \approx 0.96 \), obtaining \( z_{nano} = 59 \), while in the microcrystalline case \( p_c \approx 0.7 \) and \( z_{poly} = 7 \). The remaining parameters, except the interface conductivity \( \sigma_A^0 \), can be easily estimated from the measurements. The theoretical results, obtained for a reasonable fit of \( \sigma_A^0 \), are displayed in Fig. 10 as straight thin lines. The agreement is quantitatively good in view of the simplicity of the model employed.

Both nanocrystalline and microcrystalline materials have been described within the same model. The striking difference between both is the parameter \( \eta \); \( \eta - 1 \) describes the thickness of the interface in relation to the grain size. For \( \eta \) close to one, the blocking effect of the large insulating grains dominates, and the dc conductivity decreases monotonically, while for smaller grain sizes a similar behaviour as in the classic dispersed ionic conductors occurs.

### 10 Conclusion

In this chapter we gave a short introduction to the standard model for disordered systems, the percolation model. Percolation clusters at the critical concentration are self-similar on all length scales and their structure as well as several substructures can be described with the concept of fractal dimensions. Because the clusters have loops and dangling ends on all length scales diffusion processes on these structures are slowed down and become anomalous. Diffusion is related to electrical conductivity via the Nernst-Einstein relation, and thus the scaling behaviour of the dc conductivity can be deduced from it. Other scaling arguments give the dependence of the capacity on the concentration of conducting sites, and show that the capacity diverges at the percolation threshold. In the last section, we reviewed experimental results and numerical simulations for ionic conduction in heterogeneous ionic conductors.
Notation

- \( C \) capacitance
- \( D \) diffusion coefficient
- \( M \) cluster mass
- \( p, q \) concentration of occupied sites, resp. bonds
- \( p_c, q_c \) critical concentrations (percolation thresholds)
- \( P_\infty \) concentration of sites from infinite cluster
- \( P(r,t) \) probability density of random walk
- \( r, l \) Euclidean and topological (chemical) distance
- \( R(t) \equiv \left\langle r^2(t) \right\rangle^{1/2} \) root mean square displacement of random walk
- \( \xi \) correlation length
- \( \sigma_{dc} \) dc conductivity
- \( \sigma_S \) conductivity in conductor-superconductor system

References