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Rigid–floppy percolation threshold

I Avramov

Institute of Physical Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

E-mail: avramov@ipc.bas.bg

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Abstract

The mathematical limits for the percolation of rigid and floppy clusters throughout continuous networks are considered. Results are compared to the previous prediction of Thorpe based on the assumption that the threshold condition is the equality of degrees of freedom and the number of constraints. It is demonstrated that, in two-dimensional systems, the thresholds values predicted here and in the Thorpe model are relatively close. Our investigation demonstrates that, in 3D, there is a range of strong bond concentrations in which both floppy and rigid clusters percolate simultaneously. Depending on the particular property, either the rigid or the floppy cluster plays the key role. This explains the existence of solid electrolytes. They are solid because of the percolating rigid skeleton and at the same time have high conductivity controlled by the floppy cluster that also percolates.

1. Introduction

A realistic description of the structure of disordered systems is often obtained in the frameworks of models of continuous random networks. A fruitful idea how to treat the transition from floppy to rigid networks was introduced by Thorpe [1, 2] and Phillips [3, 4]. Each node of the network can have Z bonds. However, a part of them are broken (or dangling). The role of each node depends on the number of dangling bonds. Up to now there is no mathematical prediction of the percolation threshold. Instead, the idea of Thorpe and Phillips [1–4] is used. According to this, which we call here the 'physical' idea, the threshold appears when the number of degrees of freedom of building units of the network becomes equal to the number of constraints imposed on it. The length of each bond imposes $1/2$ constraint per node. Therefore a node with Z non-dangling bonds has $Z/2$ length constraints. Also the fixed angles between the bonds belonging to the same node impose constraints. If a node has Z bonds the number of angular constraints is $2Z - 3$. The degrees of freedom of a node are equal to the dimension Δ of the space. Since every constraint disables one degree of freedom, all degrees of freedom are disabled [1–4] when the number of non-dangling bonds satisfies the equation $\Delta = Z/2 + 2Z - 3$. In this way the threshold condition for three-dimensional space becomes $Z = 2.4$. This is a 'physical' approach to the otherwise pure mathematical problem of a special kind of percolation. The aim of the present paper is to develop a mathematical approach and to compare our results with that of the physical model.

2. The model

We consider a Δ-dimensional network with coordination number Z. A given part $0 \leqslant f \leqslant 1$ of the bonds is strong while a fraction $1 - f$ of the bonds are dangling. When the concentration of the non-dangling bonds exceeds the threshold value of f_{rigid} a 'rigid' cluster percolates throughout the network. To determine f_{rigid} we consider the concentration Q_n of lattice nodes with n 'non-broken' bonds. This is given by the binomial distribution function, specifying that the number of times, n, an event occurs in Z independent trials is given according to

$$Q_n = \frac{Z!}{n!(Z-n)!}(1-f)^{Z-n} f^n. \tag{1}$$

If the number, n, of non-dangling bonds of a given node exceeds a given critical value M, (i.e. if $n \geqslant M$) this node is 'rigid'; otherwise it is 'floppy'. To simplify the problem, in the following we assume that the value of M is always equal to the dimensionality of the space Δ. The concentration $Q(\Delta)$ of all 'rigid' nodes is given by the following sum:

$$Q(\Delta) = \sum_{n=M}^{Z} \frac{Z!}{n!(Z-n)!}(1-f)^{Z-n} f^n. \tag{2}$$

The 'rigid' clusters will percolate if their concentration exceeds the bond percolation threshold P_c, i.e. if

$$Q(\Delta) \geqslant P_c. \tag{3}$$

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Table 1. Rigid and floppy threshold limits in dependence on the coordination number Z.

Δ	Z	P_c	f_{floppy}	f_{rigid}	N_{rigid}	N_{floppy}
2	4	0.5	0.614	0.614	2.457	2.457
3	4	0.375	0.54	0.685	2.74	2.16
3	6	0.25	0.297	0.553	3.319	1.783
3	8	0.1875	0.193	0.47	3.76	1.546
3	12	0.125	0.105	0.367	4.402	1.265

There are (see, for instance, [5]) a number of estimations of P_c. Here we use the formula

$$P_c = \frac{d}{(\Delta - 1)Z}. \quad (4)$$

The critical value of f_{rigid} is obtained by combining equations (2)–(4):

$$\sum_{n=\Delta}^{Z} \frac{Z!}{n!(Z-n)!}(1 - f_{rigid})^{Z-n} f_{rigid}^{n} = \frac{\Delta}{(\Delta - 1)Z}. \quad (5)$$

A tetragonal network, $Z = 4$, that spreads in three-dimensional space, $\Delta = 3$, is a good example for silicate glass-forming melts. In this particular case equation (5) transforms to: $4(1 - f_{rigid}) f_{rigid}^3 + f_{rigid}^4 = 0.5$ or $f_{rigid} = 0.685$. Since the condition that the node is floppy is $n < \Delta$ the critical fraction of bonds f_{floppy} below which the floppy cluster percolates throughout the system is given by an expression that is quite similar to equation (5), with only different limits of summation:

$$\sum_{n=0}^{\Delta-1} \frac{Z!}{n!(Z-n)!}(1 - f_{floppy})^{Z-n} f_{floppy}^{n} = \frac{\Delta}{(\Delta - 1)Z}. \quad (6)$$

In two-dimensional systems $f_{floppy} = f_{rigid}$. Therefore, there is a sharp transition from the floppy to rigid state. The values of f_{floppy} and f_{rigid}, together with the P_c value, are summarized in table 1 in dependence on the coordination number Z and on the space dimension Δ. The columns labeled $N_{rigid} = Zf_{rigid}$ and $N_{floppy} = Zf_{floppy}$ give the threshold values of the average number N of bonds per node for the percolation of rigid (respectively floppy) clusters. For $Z = 4$ and $\Delta = 2$ the critical value of $N = 2.457$ is close to the value of 2.4 predicted by the degrees of freedom model [1–4].

3. Results and discussion

A remarkable result is that the regions in which rigid clusters and floppy clusters percolate are overlapping. In other words, there is a range of f values at which both rigid and floppy clusters can percolate simultaneously. Although the range of overlapping increases with coordination number Z, the 2.4 limit obtained by the 'physical' approach remains close to the average value as illustrated in figure 1. The overlapping effect could be the reason why some material properties are well explained by the rigidity model while other properties of the same materials behave in a different manner. One and the same structure could behave as rigid with respect to some properties and floppy with respect to other properties. The mechanical properties depend very much on whether a rigid skeleton percolates throughout the system. Therefore we expect that stiffness, Young's modulus, velocity of sound propagation, etc, depend on the possibility of a rigid cluster to percolate. On the other hand, for ion conductivity, as well as for nucleation and crystallization processes, the percolation of a floppy cluster is most important. This can explain the existence of solid electrolytes. They are formed in the overlapping region where materials behave like solids, due to percolation of the rigid cluster, but can conduct due to the simultaneous percolation of the floppy cluster.

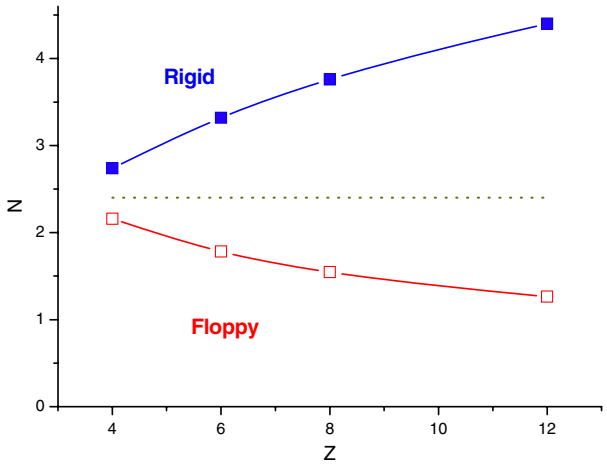

Figure 1. Dependence of the critical bond number N on coordination number Z: solid points are for the limits of the floppy cluster (above this range only rigid clusters percolate); open points are the limits of the rigid cluster (below this limit only floppy clusters percolate).
(This figure is in colour only in the electronic version)

A similar approach could be applied to describe the properties of the oil fields. They are rigid because the pumice-like stones create a rigid skeleton and at the same time the oil can flow through.

Oxide glasses are typical representatives of systems that could be described by the rigid networks model. Silicate glasses create 3D networks of tetrahedral Si connected with oxygen bridges. The coordination number $Z = 4$ explains why the floppy/rigid transition is observed in a relatively narrow region near 2.4. The network rigidity depends on the number of covalent bridges between the network formers. Therefore, the concentration of network formers determines the composition limits of the appearance of solid electrolytes. As seen from figure 1 the way to widen the range of the possible appearance of solid electrolytes is by increasing the coordination number.

It is remarkable that more than one cluster can percolate simultaneously in high dimensional spaces. This could give a background to consider, in future, the dimensionality of the space of social contacts. In countries governed by non-democratic regimes only one party spreads nationwide. The situation with religions is similar. This means that the imposed restrictions make the space of social contacts two-dimensional. The number of parties that percolate throughout the country increases when restrictive rules are removed. Thus, the space of contacts in a democratic society becomes three- or higher-dimensional.

4. Conclusions

It was demonstrated that, for three-dimensional systems, there are two separate thresholds one for rigid clusters and another for the floppy one. There is a range where rigid and floppy clusters can percolate simultaneously. The average number of bonds in the middle of the overlapping region is close to the Thorpe and Phillips limit of 2.4.

Acknowledgments

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