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Finite size scaling in grain boundary wetting

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Experimental studies of grain boundary invasion by a wetting fluid give clear evidence for a size dependence. In order to get a better numerical insight into grain boundary (GB) wetting as a percolation process, we have investigated size effects during gallium penetration into quasi-2D zinc polycrystalline strips of various width and during water penetration into 3D cylindrical NaCl polycrystals. Both systems are likely to be good objects for studying percolation effects because of a random distribution of wettable GB's. Computer simulation on the square lattice, with a "wetting" probability $p = 0.60$ close to the number of experimental points (several dozens), shows a striking resemblance between both sets of data. Making more runs (about 10^5) demonstrates consistency of our model with an earlier reported work by Marrink and Knackstedt describing finite size effects in elongated lattices. Using their approach, an excellent agreement can be obtained between the experimental and simulated data, as well as between the latter and theoretical predictions.

1. Introduction

The degree of interconnectivity of a liquid phase inside an internally wetted solid is fundamental for understanding rheological, mechanical, transport and other properties of the material. The percolation theory has been developed to analyze such kind of systems, where connectedness of a given component determines the bulk behaviour. Possible applications of this theory for describing grain boundary (GB) wetting were previously discussed [1–3] and the importance of taking into account finite size effects was outlined. Study of such effects is motivated not only by the need for generalizing each given laboratory result by extrapolating it to any size, but also by the possibility of directly obtaining fundamental percolation parameters (threshold, critical exponents) from 2D data and extending them to more work-consuming 3D cases.

The simplest "home-made" tutorial model for demonstrating size-dependent 2D site percolation on the square lattice can be created by randomly putting black pixels on a computer display (with any image-making software) and letting anothers paint to spread over them, for example with the Bucket tool. If we create a sufficiently dense population of black pixels on a large field, the paint will spread from one border to another, but if we split the field into narrow strips, the paint will stop after running a shorter or longer distance along a strip, obviously as a result of cutting away some sinuous spreading paths (see pictures in [3]). It should be underlined that even such a rudimentary computer experiment requires the random positioning of percolation elements (pixels): it risks to fail if any kind of correlation is present.

Polycrystalline materials brought into contact with a liquid able to penetrate along GB's happen to behave similarly. There are couples solid/liquid, such as NaCl/water, where size effects are really dramatic: intergranular invasion path either extends over miles (in rock salt deposits), or vanishes within a distance range typical for laboratory specimens. A similar difference in GB invasion distance on the samples having various width has been qualitatively observed in Zn/Ga [3].

In general, GB wetting is known to be sensitive to a great number of factors, and discriminating finite size effects among many others requires their quantitative description and comparing to percolation models and/or theoretical predictions, without neglecting the requirement of randomness. In this work, we have made such an attempt using Zn/Ga and NaCl/water because GB wetting in these systems was extensively studied earlier [4, 5].

2. Experimental

2.1. Misorientation dependence of GB wetting in Zn/Ga and NaCl/water

The objective of the first set of experiments has been to try to link the GB wettability to a parameter whose random or non-random distribution can be easily verified.

We have investigated GB wetting of zinc by liquid gallium as a function of GB misorientation angle θ [6].

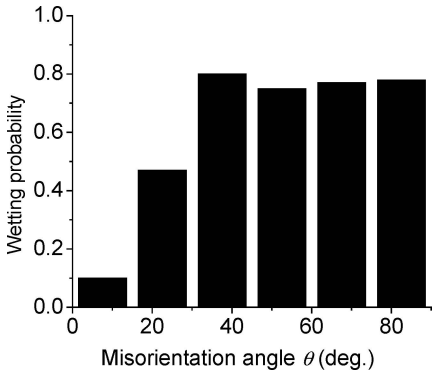


Figure 1 Probability of GB wetting in Zn with Ga as a function of misorientation angle θ.

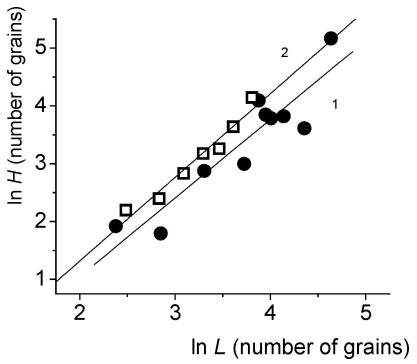


Figure 3 Length of penetration H of Ga into GB's of Zn in strips of various width L (rings) and 2D computer simulation results (squares) for "wetting" on the square lattice.

Pure zinc (99.95%) needles were cold rolled and cut into specimens of $30 \times 5 \times 0.6$ mm^3. The grain structure was stabilized by a 30 h annealing at 350°C. The final average grain size was about 40 μm. After electrochemical polishing, grain orientations were determined by electron back-scattering diffraction (EBSD), and no preferential orientation was observed. Specimens were wetted along the perimeter with liquid gallium (99.99%) previously saturated with zinc, and held at 40°C during 72 h. GB misorientation maps were compared to SEM maps of Ga distribution at GB's which were categorized as being either wet or dry.

GB wetting probability is clearly seen to monotonously increase with increasing θ (Fig. 1), so that 80% of GB's can be predicted to be wet if they fall into the range of misorientation angles between 30 and 90°.

Misorientation dependence of NaCl intergranular wetting with water (more exactly, with brine) has been studied on coarse-grained (300 μm) NaCl polycrystals. Specimens $20 \times 30 \times 5$ mm^3 were prepared by hot pressing of single crystals at 650°C and annealing at 500°C during 6 h. Grain orientation was determined with a triaxial goniometric device by catching light beams reflected from {100} faces of surface epitaxial microcrystals. All the wetted GB's are clearly visible on optical micrographs.

Here again, GB wetting probability grows monotonously with θ, attaining 80% for $\theta > 40°$ (Fig. 2).

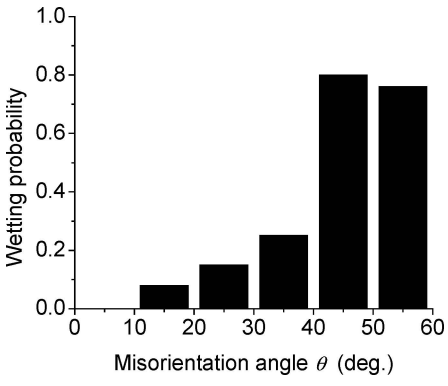


Figure 2 Probability of NaCl GB wetting with water as a function of misorientation angle θ.

2.2. Experimental study of finite size effects in GB wetting

We have measured the ultimate length H of intergranular invasion of liquid gallium into thin zinc foil strips as a function of their width L. Zinc rectangular specimens were prepared basically as for EBSD study, but were of 60 μm in thickness and had average grain size of 85 ± 8 μm. No residual stresses were detected by X-ray diffraction. A gallium droplet of a mass by far exceeding the amount necessary for wetting all the GB's was spread along the narrow side of rectangles and the samples were held at 40°C during several days and then frozen in liquid nitrogen. Usually, no further advance of gallium front was seen after 48 h. Gallium was detected by SEM technique at about 60 to 65% of all GB's behind the wetting front, and practically no gallium was revealed on grain surfaces far from GB's.

Another set of experiments was made on zinc of technical purity with grain size of about 300 μm. Gallium front position was determined by observing microcracking in the Ga-wetted part of specimen while progressively indenting it from the side opposite to the Ga source. No statistically significant difference was found between both sets of results, so the combined data for 127 samples are presented in Fig. 3.

Water penetration into NaCl was studied on cylindrical polycrystals of 4.5 mm in diameter and 10 cm in height. Specimens were prepared by hot extrusion of single crystals at 430°C and recrystallized at 600°C until obtaining average grain size of 300 to 350 μm. Saturated aqueous solution labeled with LiCl was put on the butt of specimens. Water content determined by atomic absorption was found to decrease with increasing distance from the source (Fig. 4). No water was detected beyond the distance of ~300 grain layers.

Electrical conductivity of NaCl polycrystals near to the water source was found to be of $(5.2 \pm 0.9) \times 10^5$ Ohm$^{-1} \cdot$ m^{-1}.

3. Computer simulation: method and results

Computer simulation of GB wetting has been performed as site percolation on the square lattice with open boundary conditions (the degree of geometrical adequacy to a quasi-2D GB network was discussed

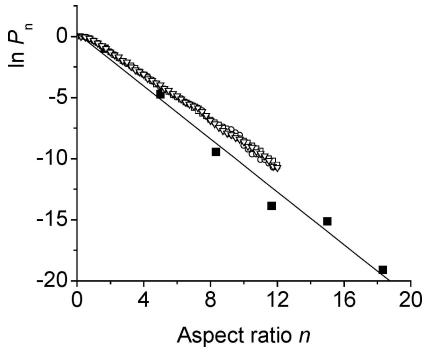


Figure 4 GB wetting probability of NaCl polycrystals (squares) and computed probability of 2D percolation (triangles and rings) as a function of aspect ratio n.

earlier [1]). Wettable elements were designed as 1, the non-wettable ones as 0, and both were distributed with respective frequencies of p and $1 - p$ using a randomizer. Foil samples of a width L have been modeled by matrixes containing L columns and a sufficiently large number of rows. "Invasion wetting" consisted in transforming all the "1" elements into "2" in the first row, followed by the same transformation, but only among the "1" points touching one another along the rows and columns. Invasion length H was found as the number of the last row containing a "2" point.

Computer experiments with deliberately limited sampling comparable to the number of physical experimental points (several dozens) show a striking resemblance between both sets of data (Fig. 3). In order to interpret the results on the basis of percolation parameters (such as percolation threshold and critical exponents), we extended the simulation to a total of $\sim 10^5$ computer experiments over a range of widths from 3 to 20 and p from 0.6 to 0.85.

4. Analysis and discussion

4.1. Significance of θ-correlation

The mechanism involving interface energy decrease as wetting driving force has been validated for both system studied [4, 5]. However, no direct evidence was available which would certify the random character of GB energy distribution, crucial for applying percolation models. Strictly speaking, many unpredictable correlation effects (such as stresses arising near the front of intruding liquid which could locally affect the wetting probability, etc.) can never be excluded. Therefore only a "quasi-random" character of GB energy distribution can be controlled.

An indirect way for linking GB wetting and energy is studying geometrical characteristics of wetted and dry GB's. A good correlation for the couple Fe-30%Mn-10%Cu/liquid Cu has been found by Wynblatt and Nakashima [7]. They have proposed a GB energy model as a function of five macroscopic degrees of freedom (DoF's) leading to correct predictions for 80% of GB's. On the contrary, plotting GB wettability vs only one DoF (misorientation angle) has been reported to give poor correlation: low wettability is observed both at small and large misorientation angles, in accordance with the Read-Shockley model and a large fraction of $\Sigma 3$(twin) boundaries, respectively.

A better correlation with a single DoF is observed in Zn/Ga and NaCl/water (Figs 1 and 2). This may indicate that, in these systems, the special GB's do not affect appreciably the correlation (for the chosen width of histogram bins). Thus, the θ value is informative with a reliability of 80%, and the random character of wettable GB's distribution in these systems can be inferred from the random θ distribution (absence of texture) which can be easily controlled.

4.2. Extraction of percolation parameters from simulation results and experimental data

Using simulation results averaged over many thousands of computer experiments (standard error being of 10^{-4}) and plotting $\ln H$ ($\ln L$) shows a progressive slope increase with increasing p. Search of H for the preset p and L values is equivalent to the search of an effective percolation threshold $\langle p_c^{(n)}(L)\rangle (n = H/L$ is aspect ratio) on an elongated lattice of the preset size $L \times nL$, provided that median rather than mean values of H are taken. Due to size effects, $\langle p_c^{(n)}(L)\rangle$ differs from the well known value of the true percolation threshold for an infinite lattice $\langle p_c(\infty)\rangle$.

Interpretation of the relationship between $\langle p_c^{(n)}(L)\rangle$, n and L requires a detailed analysis of current knowledge in the field, because of lack of generally accepted theoretical schemes. We have found the best fit for our data on the basis of the scheme proposed by Marrink and Knackstedt [8]. From their work it may be inferred that a scaling law should exist linking the above parameters:

$$\left\langle p_c^{(n)}(L)\right\rangle - \langle p_c(\infty)\rangle = L^{-\frac{1}{\nu}}\left[C_1 + C_2(\ln n)^{\frac{1}{\nu}}\right] \quad (1)$$

where C_1 and C_2 are constants and ν is the critical scaling exponent of percolation correlation length ($\nu = 4/3$ and $\nu \cong 0.88$ in two and three dimensions). Thus the percolation threshold of a lattice that is elongated in one direction is shifted towards higher values and scales both with n and with L.

We find indeed that plotting $(\ln n)^{1/\nu}$ vs. $\langle p_c^{(n)}(L)\rangle$ gives straight lines converging to the point $\langle p_c^{(n)}(L)\rangle \cong 0.59$ (Fig. 5) which is close to the percolation threshold $\langle p_c(\infty)\rangle = 0.592746$ for the site problem in square lattice used in our simulation. More exactly, we should obtain slightly varying points situated between $\langle p_c^{(n=1)}(L)\rangle = \langle p_c(\infty)\rangle + 0.11C_1$ and $\langle p_c^{(n=1)}(L)\rangle = \langle p_c(\infty)\rangle + 0.35C_1$, but this difference does not exceed the limits of accuracy. In other words, analyzing experimental data, we may afford neglecting the shift in percolation threshold due to finite size of a square $L \times L$ or cubic $L \times L \times L$ sample which is small as compared to elongated shape effects for $n \gg 1$.

Another evidence for the consistency of our simulated data with Equation 1 is given by the slope of the straight lines in Fig. 5 which should vary linearly with $L^{-1/\nu}$: in Fig. 6 we see that it really does.

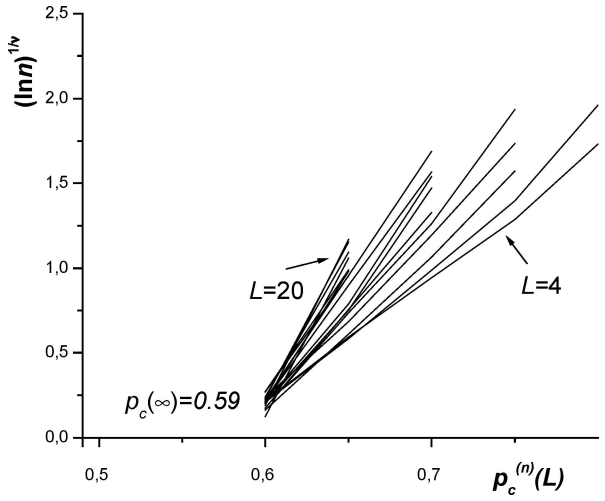


Figure 5 Simulation results for effective percolation threshold on 2D lattice for strips with various width L and aspect ratio n.

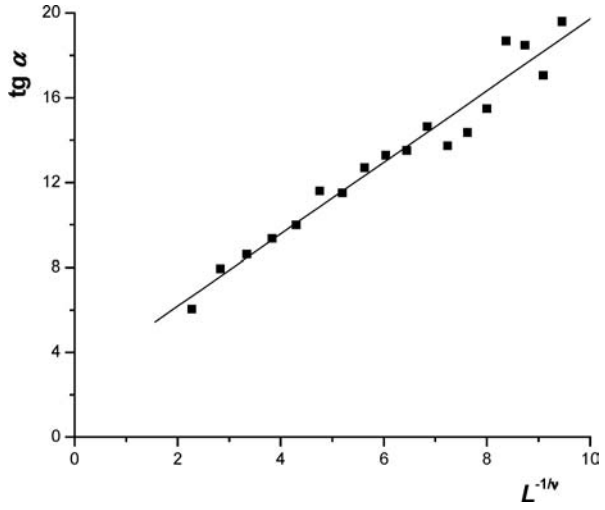


Figure 6 Slope of lines of Fig. 5 for strips with various width L.

Although Equation 1 matches perfectly well the simulation technique we chose, which in its turn seems to fit the experimental data for quasi-2D polycrystals, its use is possible only for $n > 1$, i.e., for percolation in a specified direction along the elongated axis. An alternative approach had been proposed in the paper by Monetti and Albano [9] which is analyzed in [8]. Both approximations show the same L-dependent scaling but a different n-dependent scaling for $n > 8$. For small aspect ratios, even for $n < 1$, we obtain:

$$H^{-1/\nu} - L^{-1/\nu} + p_c^{(n)}(L) = p_c(\infty) \qquad (2)$$

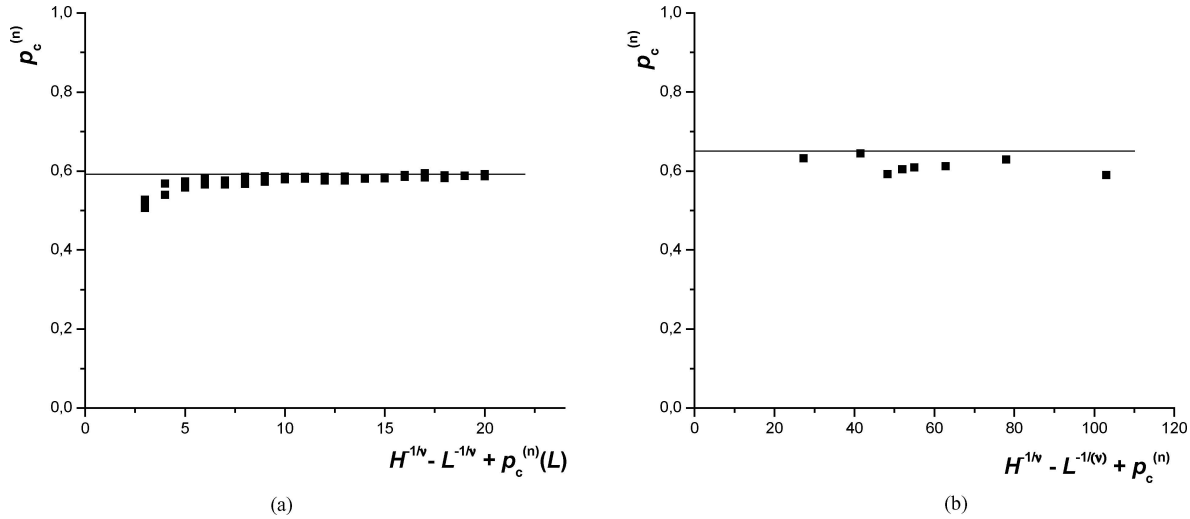
Fig. 7a shows that plotting the computed data of Fig. 5 according to Equation 2 really brings the points together onto the horizontal line drawn at the site percolation threshold for the square lattice $p_c(\infty) = 0.59275$.

Plotting the experimental data in the same way (Fig. 7b) also gives a good agreement with the line drawn at the bond percolation threshold for the honeycomb lattice $p_c(\infty) = 0.65271$. As far as we know, this is the first reported direct fit of a percolation parameter to physical GB wetting data.

4.3. Analysis of 3D experimental data

We have tried to use the percolation approach for explaining two features of GB wetting in 3D NaCl polycrystals: electrical conductivity and progressive water amount decrease along the wetting path.

The ratio of conductivity of wet NaCl polycrystals to brine bulk conductivity is $\sim 2 \times 10^{-6}$. The fraction of cross section occupied with water layers present at $\sim$30% of GB's accounts for a ratio of $\geq 2 \times 10^{-4}$, for a grain size of $\sim$300 μm and water layer thickness of $\geq$0.1 μm reported in [10]. The difference of about 2 orders of magnitude is difficult to understand, unless we have recourse to percolation concepts of conductivity. Indeed, above the threshold most of the mass of the infinite network belongs to dead ends, not to the backbone which is responsible for the electrical current. Not too far from p_c, the conductivity is approximately proportional to $(p - p_c)^{\mu}$, where $\mu = 2$ (in 3D objects) is the conductivity critical exponent [11]. Percolation threshold for GB wetting in 3D polycrystals was theoretically estimated as $\sim$0.2 [1], which gives the lacking 2 orders of magnitude, if we take $p - p_c \cong 0.1$ in wet NaCl.



(a) (b)

Figure 7 True penetration threshold in square (a, simulation results) and honeycomb (b, experiment on Zn/Ga) obtained by combining strip dimensions and wetting probability.

The gradual decrease of water amount at NaCl GB's (Fig. 4) can be interpreted as decrease of percolation density typical for elongated lattices. The probability P_n that the elongated lattice of an aspect ratio n percolates at $p > p_c$ is essentially an exponential decay with n [8]. It should be emphasized that this gradient of density can hardly be observed in a single physical or computed specimen, but is a result of statistical averaging which gives a good linearity ln P_n vs. n, the correlation coefficient growing very rapidly with the number of specimens. Marrink and Knackstedt [8] propose a simple general relationship which they claim to be valid for values of p much larger than p_c and for large values of n. This expression can be written as:

$$\ln P_n / \ln P(L) = 2n - 1 \qquad (3)$$

where $P(L)$ is the probability of percolation of a square $L \times L$ or cubic $L \times L \times L$ sample. Fig. 4 demonstrates the accuracy of Equation 3 even for not too large values of $p - p_c$ and n. Thus the above approximation may be expected to be a promising tool for studying finite size effects in GB wetting both on 2D and 3D elongated samples by analyzing distribution of a wetting liquid along the elongated axis.

The first attempt to interpret the results of the physical experiment made on $NaCl/H_2O$ seems to have been successful: the experimental data expressed in units of Equation 3 fit quite well the computed plots (Fig. 4). However, such an excellent agreement is likely to be rather fortuitous because of the extreme sensitiveness of the slope to the accuracy of measuring $P(L)$ (the scatter becomes infinite as $P(L) \rightarrow 1$). In order to gain further insight on the subject, the study is under progress.

5. Conclusions

In spite of apparently obvious adaptability of the percolation theory for describing GB wetting, there are many hidden factors which may lead to erroneous estimates. Therefore, any direct evidence demonstrating the consistency between experimental data and theoretical predictions is not trivial. One of ways to verify such an agreement is studying finite size effects in physical systems and checking whether they can be accounted for with the known percolation constants. The present work shows that, at least in two systems Zn/Ga and $NaCl/H_2O$, the answer is positive. The main conclusions, as applied to these couples, can be summarized as follows: (1) a 80% correlation exists between GB wettability and misorientation angle which suggests a random character of the former; (2) $H(L)$ dependence (H is depth of GB Ga invasion into quasi-2D Zn strips of a width L) fits computer simulation, and both can be characterized using the known values for percolation parameters; (3) electrical conductivity of wet NaCl polycrystals is in agreement with the topology of the infinite percolation cluster; (4) decrease of water content along GB invasion path into NaCl cylindrical samples is consistent with a percolation model.

References

1. V. TRASKINE, Z. SKVORTSOVA and L. PRIESTER, in "High Temperature Capillarity-97," edited by N. Eustathopoulos and N. Sobczak (Foundry Research Institute, Cracow, Poland, 1998) p. 339.
2. V. TRASKINE, P. PROTSENKO, Z. SKVORTSOVA and P. VOLOVITCH, *Colloids Surf. A: Physicochem. Engng. Asp.* **166** (2000) 261.
3. V. TRASKINE, P. VOLOVITCH, P. PROTSENKO, *et al.*, *Trans. JWRI* **30** (2001) 21.
4. A. PERTSOV, L. POGOSYAN, B. SUMM and YU. GORYUNOV, *Kolloidnyi Zhurnal* **36** (1974) 699 (in Russian).
5. V. TRASKINE, Z. SKVORTSOVA, V. KUKSHEV, *et al.*, *ibid.* **44** (1982) 62 (in Russian).
6. P. VOLOVITCH, V. TRASKINE, T. BAUDIN and L. BARRALLIER, *Interf. Sci.* **10** 303 (2002).
7. P. WYNBLATT and M. TAKASHIMA, *ibid.* **9** (2001) 265.
8. S. J. MARRINK and M. A. KNACKSTEDT, *Physical Rev.* **62** (2000) 3205.
9. R. A. MONETTI and E. V. ALBANO, *Z. Phys. B: Condensed Matter.* **82** (1991) 129.
10. V. TRASKINE and Z. SKVORTSOVA, *Kolloidnyi Zhurnal* **59** (1997) 827 (in Russian).
11. D. STAUFFER, "Introduction to Percolation Theory" (Taylor and Francis, London and Philadelphia, 1985) p. 87.

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