Wetting of rough walls[1]

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ABSTRACT

Quenched geometric disorder of a wall delimiting a spectator phase can have dramatic effects on the nature of critical wetting transitions. We consider self–affine walls in $2D$ with roughness exponent ζ_W. Transfer matrix results for directed interfacial models with short–range interactions suggest that wetting turns first–order as soon as ζ_W exceeds ζ_0, the anisotropy index of interface fluctuations in the bulk. Discontinuous interface depinning is best signalled by a peculiar two-peak structure in the statistical distributions of wall–interface contacts obtained by sampling over disorder. On the other hand, for $\zeta_W < \zeta_0$ wetting remains continuous, most plausibly in the same universality class as with flat walls. This occurs both with ordered ($\zeta_0 = 1/2$), and with bond–disordered ($\zeta_0 = 2/3$) bulk. A precise location of the thresholds at $\zeta_W = \zeta_0$ can be argued on the basis of an analysis of different terms in the interfacial free energy. This analysis elucidates the peculiar role played by the intrinsic interfacial roughness and suggests extensions of the results to $3D$ and to long–range substrate forces.

KEY WORDS: bulk disorder; geometrical surface disorder; statistical physics; wetting transitions.

1. INTRODUCTION

Wetting phenomena occurring when an interface between two coexisting phases unbinds from an attractive substrate (spectator phase) have been intensively studied in the last two decades and are rather well understood by now [1]. The wetting transition takes place with both long–range, and short–range substrate forces, and can be either continuous, or first–order. In recent years also systems in which coexistence takes place in a quenched random bulk have been extensively studied [2–5]. In the case of short–range substrate forces, with which we mostly deal in this paper, first–order wetting never occurs in $2D$. Indeed, bulk disorder, for example, can only modify the universality class of critical wetting transitions, but not, in general, their continuous, second–order character.

A relatively much less studied disorder is that associated with the wall delimiting the substrate [2]. One can distinguish between two types of wall disorder: chemical surface disorder, pertaining to some inhomogeneity in the strength of interactions exerted by a smooth substrate, and geometrical surface disorder, determined by wall roughness alone. In this report we concentrate exclusively on geometrical surface disorder and discuss its effects on critical wetting transitions, when it occurs both alone, and in the presence of bulk disorder.

From a theoretical point of view, cases of wall roughness characterized by some scaling are of special interest. An example is self–affine roughness, in which transverse displacements of the wall profile have an average width, $w_X \propto X^{\zeta_W}$ $(0 < \zeta_W < 1)$, where X is the longitudinal sample length. Indeed, also the roughness displayed by interfaces in the bulk is known to be self–affine below criticality, no matter whether their fluctuations are controlled by temperature or by disorder [2]. So, a direct competition between the roughness of the wall and that of the interface can be anticipated when wetting occurs. With ordered bulk in d dimensions the roughness, or anisotropy exponent of the interface is $\zeta_0(d) = (3-d)/2$, for $1 \leq d \leq 3$, and $\zeta_0 = 0$ for $d > 3$ [6]. For random bonds $\zeta_0(2) = 2/3$ holds exatly [7], while, e.g., $\zeta_0(3) \sim 0.41$ [6].

Substrates with self–affine roughness can also be studied experimentally, and adsorption phenomena have been already observed on them [8]. Indeed, the first studies of the consequences of this roughness, especially for complete wetting, were also motivated by the controversial interpretation of such experiments [9]. However, it was not until very recently that the peculiar effects of roughness on critical wetting discussed below were predicted and started to be elucidated [10].

In this report we review recent progress and present new results on the effects of self–affine roughness on the nature of wetting transitions in a variety of situations. The main body of our results is for short–range forces and is obtained by transfer matrix methods on $2D$ lattices. However, on the basis of our numerical analysis in $2D$, we are able to draw a more general scenario, which, although on more conjectural basis, includes cases in $3D$ and even with long–range interactions.

This article is organized as follows. In the next section we introduce our interfacial model in $2D$ and briefly present the main transfer matrix results in the case of ordered and disordered bulks. The third section is devoted to conclusions and to a more general discussion of the mechanism by which roughness can turn critical wetting into first–order. Here some natural extensions of our results to cases not accessible by a numerical analysis are also proposed.

2. MODELS AND RESULTS IN $2D$

We want to describe the interface between plus and minus phases of a $2D$ Ising ferromagnet ($T < T_c$), either pure, or with random nearest neighbor couplings. The phases are enforced by fixed spin boundary conditions on opposite sides of the sample. One of the (flat) boundaries attracts the interface because, e.g., the nearest neighbor couplings with the spins fixed at the border are weakened by a fixed energy δ with respect to the bulk ones. This amounts to a short–range attraction effect. It is well known that to the purpose of describing wetting phenomena one can disregard the possibility of bubbles in the two phases and of overhangs of the interface [1,2]. This leads to describe the interface as a directed

path on the dual lattice [11]. Each step has an associated energy $2J_b = 2\epsilon_b$, where J_b is the exchange energy of the broken bond in the spin problem. If taken at the border (wall), the step has a lower energy $2(J_b - \delta)$. The interfacial free energy of the interface is then

$$F_X = \ln Z_X = \ln \left[\sum_P \exp(-E_P/T) \right] \tag{1}$$

where the sum is over all allowed directed paths, P, from the origin to points of abscissa X, and

$$E_P = \sum_{b \in P} \epsilon_b - \sum_{b \in W \cap P} \epsilon_W . \tag{2}$$

Here $\epsilon_W = 2\delta$ and W indicates the path running on the wall. Of course, no P can trespass W. We study the effects of rough W. Let us indicate by x the longitudinal coordinate and by y the transverse one. A random self–affine wall will have $y = y_W(x)$ satisfying

$$\left[\overline{(y_W(x_1) - y_W(x_2))^2} \right]^{1/2} \sim |y_W(x_1) - y_W(x_2)|^{\zeta_W} \tag{3}$$

for large $|x_2 - x_1|$. Here the overbar indicates quenched average over a given distribution of possible wall profiles. By proper algorithms we are able to generate samples of profiles satisfying eq.(3) with preassigned ζ_W [10]. Fig. 1 illustrates the situation with a rough wall, in a case when wall and paths are directed along $(1, 1)$. Other schemes used in our calculations were with W and interfaces along $(1, 0)$ [10].

For a given configuration of the wall, and of the energies ϵ_b, in case of random bulk, the partition function Z_X can be obtained by transfer matrix methods. If we indicate by $Z_x(y)$ the restricted partition of paths ending at (x, y) ($x \geq y \geq y_W(x)$, of course), in a case like in Fig. 1 we can write

$$Z_{x+1}(y) = Z_x(y+1) \exp(-E_{b_1}/T) + Z_x(y-1) \exp(-E_{b_2}/T) \tag{4}$$

where $E_b = \epsilon_b - \epsilon_W$ or $E_b = \epsilon_b$, according to whether the bond b does, or does not belong to W. In eq.(4), b_1 and b_2 refer to the upper left and lower left neighbors of $(x+1, y)$, respectively; the terms corresponding to either b_1, or b_2 will not appear in case y is at one of

its bounds. When discussing situations with random bonds in the bulk, our choice for the probability distribution of ϵ_b was simply a uniform one in the interval $0 < \epsilon_b < 1$.

We made extensive calculations of quantities like $n(X) = (1/X)\,[\partial ln(Z_X)/\partial ln(\epsilon_W/T)]$, for X up to 150000. The quenched averages $\overline{n}(X)$ over wall, and, where applicable, bulk disorder, involved samples from a minimum of 50, to a maximum of 10^6 realizations. Careful extrapolations gave estimates of the fraction of interface steps on W, $\overline{N}(\epsilon_W/T) = lim_{X\to\infty}\overline{n}(X)$. We make explicit only the dependence on ϵ_W/T, because this is for us the parameter driving the wetting transition. In the $T = 0$ cases, which are relevant in the presence of bulk disorder, wetting is induced by varying the ratio of ϵ_W to some reference energy, rather than T; below, to simplify notations, we generally indicate by ϵ_W dimensionless energies.

As ϵ_W approaches from above a critical value, ϵ_c, we always observe that $\overline{N}$ becomes zero, within our accuracy, and stays such for all $\epsilon_W < \epsilon_c$. Of course, ϵ_c depends also on ζ_W and always increases with increasing ζ_W, provided other parameters are kept fixed. Thus, rougher walls have more difficulty in pinning the interface.

The nature of the wetting transition occurring at ϵ_c can be revealed by the way in which $\overline{N}$ approaches zero. Indeed, with both ordered and random bulks we verified that, for sufficiently low ζ_W ($\zeta_W \lesssim 1/2$ and $\zeta_W \lesssim 2/3$, in the ordered and disordered cases, respectively), $\overline{N}$ approaches zero as a power of $\Delta\epsilon = \epsilon_W - \epsilon_c$, i.e. $\overline{N} \sim \Delta\epsilon^{\psi}$ (Fig.2). For ordered bulk we found $\psi = 1.01 \pm 0.02$ in a rather wide range of roughnesses ($\zeta_W \lesssim 2/5$), while for random bonds $\psi = 2.0 \pm 0.1$ and $\psi = 2.1 \pm 0.1$ were estimated for $\zeta_W = 1/2$ and $\zeta_W = 0.557$, respectively. Such results suggest that, as long as ζ_W is not too large, the wetting transitions are continuous and, moreover, remain in the respective flat wall universality classes. Indeed, with flat wall in $2D$, $\psi = 1$ with ordered bulk [11], and $\psi = 2$ with bond disorder [4] are both exact results.

In the region of high ζ_W the plots of $\overline{N}$ vs. ϵ_W show a steep jump to zero at $\epsilon_W = \epsilon_c$ (Fig.2). It is not possible to fit well this approach to zero as a power law. This holds both with and without bulk disorder: the only difference is in the respective ζ_W thresholds beyond

which the new behavior starts. A steep drop is suggestive of a first–order transition. Clear numerical evidence of this first–order can be obtained by plotting hystograms of $n(X)$, as obtained in our samples over disorder at different values of X and ϵ_W (Fig.3). For values of ζ_W below threshold the hystograms always show only a single peak, whose support shifts gradually to zero as ϵ_W approaches ϵ_c. This is consistent with a second–order wetting transition. On the contrary, if ζ_W is above threshold, the hystograms show a double peak structure for ϵ_W close to ϵ_c. One of the peaks is at zero, while the other remains always at nonzero n. In this case the mechanism by which $\overline{N}$ approaches zero is a rapid depletion of the peak at nonzero n in favor of that at $n = 0$. This depletion occurs in narrrower and narrower ϵ_W intervals, as X increases. The two–peak structure reveals clearly a discontinuity, which can only be compatible with first–order wetting.

A sharp determination of the threshold ζ_W-s for first–order wetting is not easy, numerically. The evidence collected, and considerations made below, indicate $\zeta_W = 1/2$ and $\zeta_W = 2/3$ as the plausible thresholds, in the cases of ordered and bond–disordered bulks, respectively.

A study of interface depinnings occurring on hierarchical diamond lattices can give some extra qualitative insight into the transition to first–order wetting. Paths on these lattices are often used to mimic directed polymers or $2D$–interfaces. In the same context one can study depinning from random rough attractive walls. The results have very high numerical accuracy and support the changes from continuous to discontinuous wetting at the expected thresholds [10,12].

3. DISCUSSION AND GENERALIZATIONS

The results illustrated above are limited to $2D$ Euclidean lattices. In spite of such limitation, they are quite remarkable and definitely challenge us to gain a better theoretical understanding of the role of geometrical surface disorder in interfacial phenomena.

With short–range forces, first–order wetting is not expected in $2D$, as a rule. Indeed, so far, discontinuous depinning could only be obtained with special, extreme setups, like an

attractive defect line in the bulk competing with the (flat) wall [13], or a bulk disorder fully correlated longitudinally [14]. According to eq.(3), in our models only surface disorder is longitudinally (power–law) correlated. This physically plausible and more subtle correlation is sufficient to induce the tricritical phenomenon described above. Here geometric surface disorder seems also to act somehow opposite to its chemical counterpart. Indeed, chemical disorder on the wall has been found to turn back continuous the first–order depinning observed with attractive bulk defect [15].

A qualitative understanding of the thresholds at $\zeta_W = 1/2$ or $2/3$ can be gained by referring to the concept of entropic, or bulk–disorder induced repulsion [5,6]. A repulsive potential is experienced by an interface with roughness ζ_0, when it is bound at an average distance $\overline{y}$ from a substrate. Scaling arguments and, in $2D$, a random walk necklage–like description of the interface, lead to a repulsive wall–interface potential $\propto \overline{y}^{-\tau(\zeta_0)}$, with $\tau(\zeta) = 2(1-\zeta)/\zeta$, at large $\overline{y}$ [6]. In continuum descriptions based on interface Hamiltonians, this potential originates from a stiffness term proportional to the gradient squared of the interfacial profile in the free energy density. With short–range forces the stiffness term is the longest range contribution to the free energy (or energy, at $T = 0$) of the bound interface.

Qualitative arguments [16] suggest that the above repulsion potential should persist with unaltered long $\overline{y}$ behavior as long as $\zeta_W < \zeta_0$. For $\zeta_W > \zeta_0$, on the contrary, we expect a behavior $\propto \overline{y}^{-\tau(\zeta_W)}$, because the bound interface must follow the wall geometry at large distances, and intrinsic fluctuations become irrelevant. In the case of ordered bulk, this change of repulsion potential has been also derived on the basis of renormalization group methods when the substrate exerts long–range van der Waals forces with potential $V(\overline{y}) = u/\overline{y}^{\sigma-1} + v/\overline{y}^{\sigma}$ on the interface [9]. We expect a similar change to occur in more general situations. Consistently with our numerical results, as long as $\zeta_W < \zeta_0$, it is conceivable that nature and universality class of critical wetting transitions do not change, upon varying ζ_W. This, at least, if only short–range substrate forces are acting. Indeed, the long–range wall repulsion is not altered with respect to the flat case, and there is no reason to expect drastic changes in the balance of effects determining the transition. When $\zeta_W > \zeta_0$, on the

other hand, a drastic increment of the large-$\overline{y}$ positive free energy barrier is determined by roughness ($\tau(\zeta_W) < \tau(\zeta_0)$). With such a barrier increment, while other conditions remain essentially unchanged, it is not surprising that the transition to $\overline{y} = \infty$, which takes place through a continuous tunneling in the flat case, becomes discontinuous. Of course, further work is needed to support this mechanism. Functional renormalization group techniques seem particularly promising, especially for the case of ordered bulk.

The idea that, as soon as $\zeta_W > \zeta_0$, the long–range wall repulsion becomes stronger turning depinning discontinuous, leads us to conjecture similar changes also in $3D$. With an ordered $3D$ bulk, $\zeta_0 = 0$. This means that entropic repulsion decays exponentially in $\overline{y}$ [6]. Thus, as soon as $\zeta_W > 0$, a long–range free energy barrier builds up and first–order wetting is expected, if no long–range substrate forces are acting. A similar threshold should fall at $\zeta_W = \zeta_0 \sim 0.41$ with a $3D$ bond–disordered bulk.

Finally, let us come to the long–range substrate potential V mentioned above. With flat wall, critical wetting is known to fall into three possible regimes, each one corresponding to a distinct universality class. For $\zeta_0 < 2/(\sigma+2)$, $2/(\sigma+2) < \zeta_0 < 2/(\sigma+1)$, and $\zeta_0 > 2/(\sigma+1)$ one has, respectively, the mean field (MF), the weak fluctuation (WFL), and the strong fluctuation (SFL) regimes [5,6]. The exponent σ enters in the asymptotic behavior of V. Since the regimes with flat wall are determined by the relative importance of the terms in V and the stiffness repulsion $\propto \overline{y}^{-\tau(\zeta_0)}$, in the formulas for ψ and other exponents, ζ_W should always replace ζ_0, as soon as $\zeta_W > \zeta_0$ [9]. Indeed, the stiffness repulsion is controlled by $\tau(\zeta_W)$, rather than $\tau(\zeta_0)$, at large $\overline{y}$. One can then foresee that, e.g., a wall roughness $\zeta_W > \zeta_0$ converts a MF ($\zeta_0 < 2/(\sigma+2)$) into a WFL, or a SFL regime, depending on which interval ζ_W falls into. The case $\zeta_0 > 2/(\sigma+1)$, which already implies SFL regime with flat wall, is particularly relevant for us. Indeed, in this case $\zeta_W > \zeta_0$ implies that the roughness controlled stiffness repulsion becomes the most long–range contribution to the free energy, and it is plausible that the associated barrier effect drives the transition first–order [16].

Our results lead to the general conclusion that, as soon as $\zeta_W > \zeta_0$, critical wetting transitions become first–order, no matter whether the intrinsic fluctuations of the interface

are controlled by temperature or by disorder [17]. In the case of long–range forces the conclusion is limited to critical wetting in the SFL regime. We expect similar results to hold also for other types of randomness or inhomogeneity in the bulk. An interesting example are interfaces in quasi–crystals [18].

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FIGURE CAPTIONS

Fig. 1 Wall delimiting the substrate (shaded region) and interface configuration (1 wall-interface contact).

Fig. 2 Results for $T = 0$ with random bonds. For two of the curves $\zeta_W < 2/3$, for the others $\zeta_W > 2/3$. The inset shows a power law fit for $\zeta_W = 1/2$.

Fig. 3 Hystograms of $n(X)$ for $\epsilon_W \gtrsim \epsilon_c$ and $\zeta_W = \ln(6)/\ln(8)$.

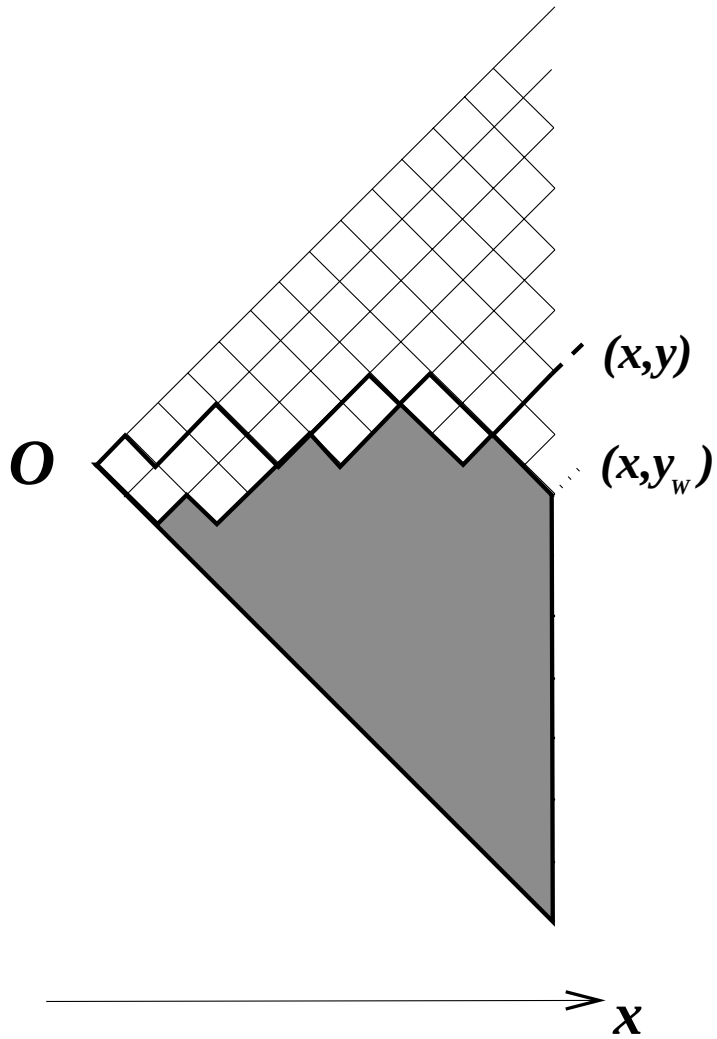

Fig. 1

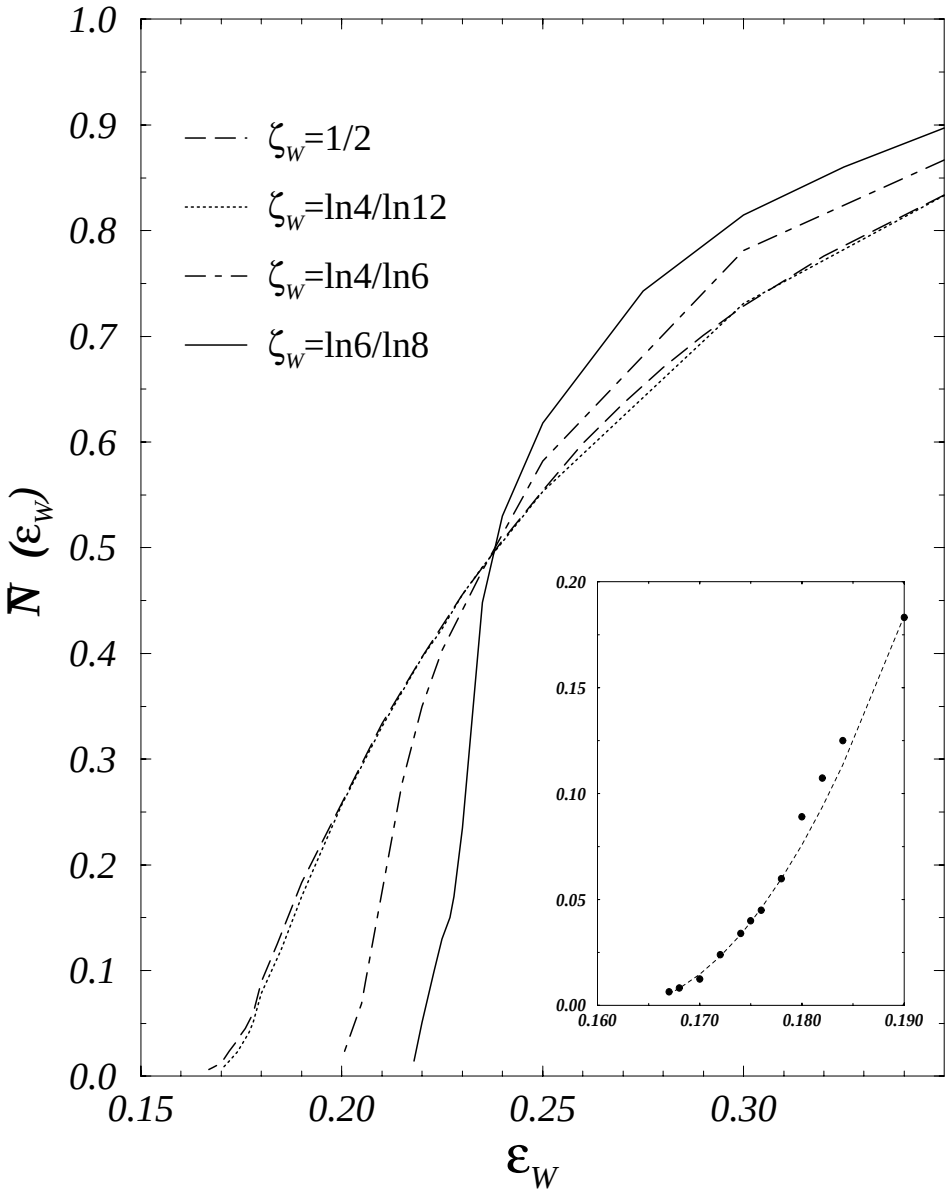
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0.15
0.20
0.25
0.30
ζ_W=1/2
ζ_W=ln4/ln12
ζ_W=ln4/ln6
ζ_W=ln6/ln8
$\bar{N}$ (ε_W)
ε_W
0.20
0.15
0.10
0.05
0.00
0.160
0.170
0.180
0.190

Fig. 2

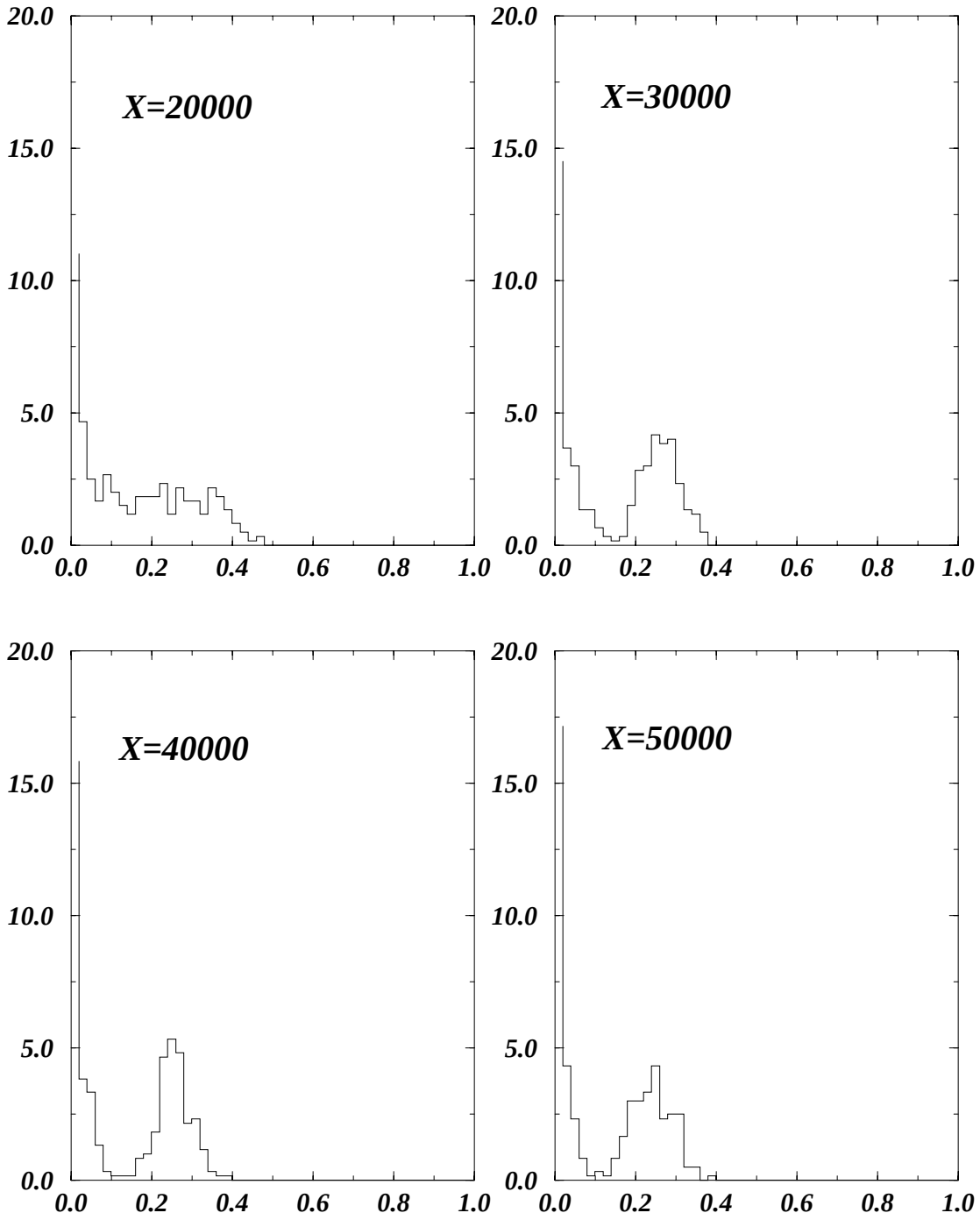

Fig. 3