Influence of the geometry of a rough substrate on wetting

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The wall tension of a rough wall is considered within a semi-infinite planar Ising model. Using Monte Carlo simulation techniques, we have studied the influence of the geometry of a rough surface on the wall tension. Different geometries are examined in detail, ranging from elementary deformation of the flat surface, including pores, to more realistic substrates generated randomly with a given roughness. We give evidence that complex geometries lead to wall tensions that are bounded by those associated with two simple well-characterized substrates, protrusion and pits. [S1063-651X(97)13009-4]

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I. INTRODUCTION

The wetting of solid substrates by a liquid is a phenomenon of primary importance in many fields of science and technology. Applications can be found in biology, agriculture, food technology, the paper industry, and more. The wettability of a solid substrate by a sessile drop is governed by Young's classical equation

$$\tau_{AB}\cos\theta=\tau_{AW}-\tau_{BW}\equiv\Delta\tau, \tag{1}$$

where θ is the contact angle between the drop (B) and the solid surface (W), τ_{ij} represents the interfacial tension along the interface between phases i and j ($i,j=A,B,W$), and A refers to the fluid phase surrounding the sessile drop. The associated wettability of the substrate W is conditioned by its wall tension ($\Delta\tau$). One should realize, however, that Young's equation was established for large drops of liquid on top of smooth, chemically homogeneous substrates. Such ideal surfaces never appear in nature; chemical heterogeneities together with finite sized surface roughness occur in all realistic solid surfaces, and should be taken into account when analyzing their wettability.

Recently [1], we employed Monte Carlo simulations in a wetting study of a two-dimensional chemically heterogeneous solid surface. Results exhibited the validity of Cassie's law [2], as well as the independence of wall wettability with respect to the geometry of the heterogeneities. Here, we are interested in the effect of substrate surface roughness on its wetting characteristics, including the importance of microscopic features of the surface as well as other parameters (e.g., temperature).

According to Wenzel [3], such a substrate can be characterized by its roughness, $r\equiv|W|/|W_0|$, where $|W|$ is the substrate's surface area and $|W_0|$ is the surface area of projection of W onto the tangent plane. Sixty years ago, Wenzel [3] suggested that the substrate roughness should affect its wettability according to

$$\Delta\tau(r)\simeq r\Delta\tau(1) \tag{2}$$

for small enough roughness values r, where $r=1$ represents a perfectly flat surface.

Although this equation was originally derived based on experimental observations, a recent rigorous analysis of a three-dimensional lattice (Ising) model [4] has proved Eq. (2) to be correct at very low temperatures and small r values. Interestingly, it is easy to show that different geometrical structures of a substrate surface can yield the same r value. For example, a surface decorated by several raised features (hills) will exhibit the same r value as a substrate supporting depressions (holes) of similar size and density as those of the hills. In this study, we investigate substrate roughness as well as the geometry of roughness, and their combined effect on the wall tension $\Delta\tau$; we consider hereafter the two-dimensional ($d=2$) Ising model where $\Delta\tau$ is exactly computable for a chemically homogeneous, smooth wall. The paper is organized as follows. Section II is devoted to the presentation of the model. The results are then given in Sec. III. Concluding remarks end the paper.

II. MODEL

This model is defined on the lattice $Z\times Z$, with a plot of an integer valued step function representing the rough wall. Each lattice point (i_1,i_2) is associated with a spin variable σ_i, which may take on one of two possible values, $+1$ or -1. Let $\Lambda_L=[-L,L]\times[-L,L]$ be a finite square in $Z\times Z$ and let us fix the value of the spins outside Λ_L to be $\overline{\sigma}$. The rough wall is introduced as follows. Consider the step function $I_L:R\rightarrow[-L,L]$ defined as

$$I_L(x)=\sum_{i=-L}^{L}(c_i+1/2)\mathbb{1}_{[i-\frac{1}{2},i+\frac{1}{2})}(x), \tag{3}$$

where $c_i\in Z\cap[-L,L-1]$ and

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$$\mathbb{1}_A(x)=\begin{cases}1 & \text{if } x\in A\\ 0 & \text{if } x\in A^c.\end{cases}$$

The plot of $I_L(x)$ versus x for $x\in[-L,L]$ physically outlines the rough wall. Let $W_L=\{(i_1,i_2)\in\Lambda_L : i_2\leqslant I_L(i_1)\}$. We assume that $\sigma_i=+1$ for all $i\in W_L$. Inside the interior (bulk), spins σ_i are coupled with a nearest neighbor coupling constant $J>0$, while the spins at the boundary between the bulk and the substrate W_L are coupled with coupling constant h. The Hamiltonian $H_\Lambda(\sigma|\overline{\sigma})$ of the model is formally given by

$$H_\Lambda(\sigma|\overline{\sigma})=-J\sum_{\substack{\langle ij\rangle\\ i\in\Lambda\setminus W, j\in\Lambda\setminus W}}\sigma_i\sigma_j-J\sum_{\substack{\langle ij\rangle\\ i\in\Lambda\setminus W, j\in\Lambda^c\setminus W}}\sigma_i\overline{\sigma_j}-h\sum_{\substack{\langle ij\rangle\\ i\in\Lambda\setminus W, j\in W}}\sigma_i,$$

where $\langle ij\rangle$ denotes nearest neighbor pair, Λ^c is the complement of the set Λ, and $\overline{\sigma}$ is the chosen configuration of spins outside Λ. We will consider two types of boundary conditions (BC), the $+$BC and $-$BC defined as $\sigma_i=+1$ for all $i\in\Lambda^c$, and $\sigma_i=-1$ for all $i\in\Lambda^c$, respectively. In addition, the Hamiltonians with these boundary conditions are denoted by $H_\Lambda(\cdot|+)$ and $H_\Lambda(\cdot|-)$, respectively. Finally, for a given inverse temperature value β, we define $\mathcal{Z}^+(\Lambda,\beta)$ and $\mathcal{Z}^-(\Lambda,\beta)$ to be the partition functions associated with these Hamiltonians. The wettability of the substrate at a given inverse temperature β, can defined in a similar way as for the smooth wall,

$$\beta\Delta\tau=\lim_{L\to\infty}-\frac{1}{2L+1}\ln\frac{\mathcal{Z}^+(\Lambda_L,\beta)}{\mathcal{Z}^-(\Lambda_L,\beta)},\tag{4}$$

which can be simplified to the following useful expression [1]:

$$\Delta\tau=\lim_{L\to\infty}\frac{1}{\beta(2L+1)}\ln\left\langle\exp\left(-2\beta h\sum_{i\in\partial W}\sigma_i\right)\right\rangle_{\mu_L},\tag{5}$$

where ∂W includes all the spins in the bulk at the boundary between the bulk and the substrate W_L, and the average $\langle\rangle_{\mu+L}$ has to be taken with respect to the measure

$$\mu_L(\{\sigma\})=\frac{\exp[-\beta H_{\Lambda_L}(\sigma|+)]}{\mathcal{Z}^+(\Lambda_L,\beta)}.\tag{6}$$

This thermal average can be (and is) determined using Monte Carlo techniques, as already used in our previous study [1]. Results presented hereafter are obtained by applying Monte Carlo techniques, based on Metropolis dynamics [5], to the two-dimensional Ising model. Starting from a randomly selected initial configuration, our results (obtained for a 64×64 and/or 256×256 lattice) were shown to reach equilibrium well within 5000 Monte Carlo (MC) time steps [1]. All the results presented in this work were obtained by averaging 50 statistically independent Monte Carlo simulations, each consisting of a time average between 6000 and 12 000 time steps. This technique allows a numerical determination of $\Delta\tau(1)$ within 3% of the analytically determined value.

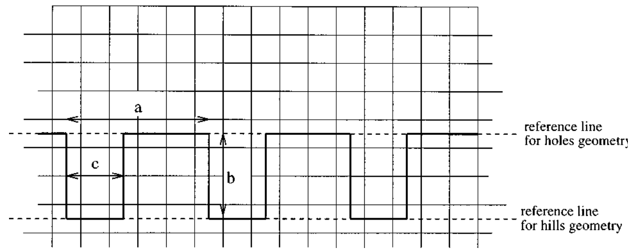

FIG. 1. Description of holes and hills geometry.

III. RESULTS

Using this technique, we have studied the wall tension $\Delta\tau$ for rough substrates. These rough substrates were constructed as periodic square-wave perturbations of the smooth case, see Fig. 1.

As already proved [4], it is known that for low enough temperatures, Wenzel's law, Eq. (2), should hold. To illustrate this behavior, we have studied $\Delta\tau(r)$ for different temperatures as a function of the roughness r of the substrate, using the substrates shown in Fig. 1. The perturbations appear with a wavelength a and a peak-to-peak distance b. It is then straightforward to show that

$$r=1+2b/a.\tag{7}$$

For these kinds of substrates, as can be seen in Fig. 2, Wenzel's law only holds for low enough temperatures. For increasing temperature, the roughness of the substrate becomes effectively less and less important, $\Delta\tau(r)$ thus approaches $\Delta\tau(1)$.

More precisely, there is a temperature-dependent correction $\Delta\tau(r)\simeq rf(\beta,\mathcal{G})\Delta\tau(1)$, where, for any fixed geometry

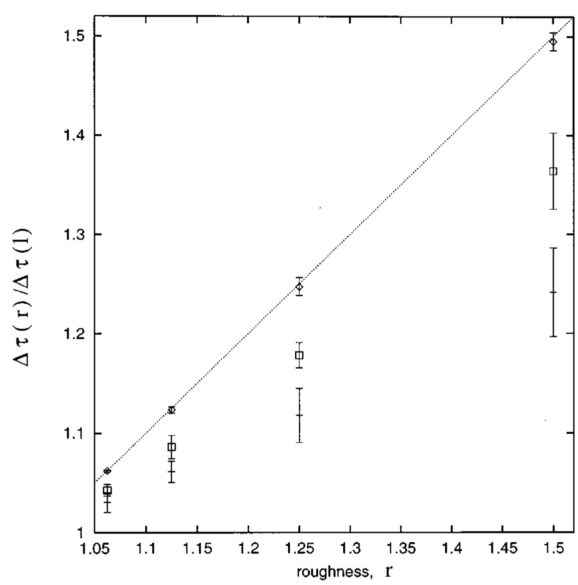

FIG. 2. $\Delta\tau(r)/\Delta\tau(1)$ as a function of roughness r for three different temperatures $Tk_B=0.6$ (diamonds), $Tk_B=1.176$ (squares), and $Tk_B=1.538$ (pluses), for fixed geometry of holes with $c=2$ and $b=2$. The wall binding constant h is 0.2. The dotted line refers to Wenzel's law.

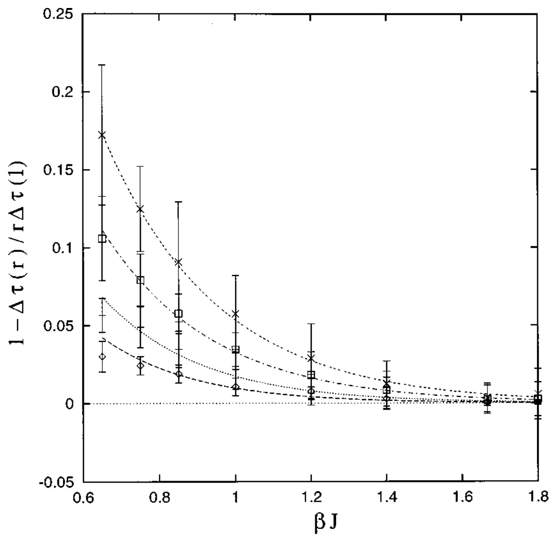

FIG. 3. $1-\Delta\tau(r)/r\Delta\tau(1)$ as a function of βJ for several roughnesses, from top to bottom $r=1.5$, 1.25, 1.125, 1.0625 with $h=0.2$, $J=1$, $b=2$, and $c=2$. The corresponding A's are 0.6551, 0.8776, 1.103, 1.5556 and the B's are 4.2136, 3.9264, 3.5065, 3.3726; the fitted curves are represented in dots.

$\mathcal{G}$, $\lim_{\beta\to\infty} f(\beta,\mathcal{G}) \to) \to 1$, as illustrated by the different cases appearing in Fig. 2. Now, for any geometry, low temperature expansion arguments [4] lead to

$$f(\beta,\mathcal{G}) = 1 + A\exp-(B\beta J), \tag{8}$$

and our results presented in Fig. 3 reveal how good this approximation is over a wide range of temperatures.

Now, for a given roughness r, let us study the role of the geometry of the substrate. Let us first compare $\Delta\tau$ for perturbations consisting of hills with those consisting of holes. As presented in Fig. 4, hills are more favorable toward wetting than holes, which is in agreement with cluster expansion arguments [4] for a small h/J ratio, i.e., a solid-liquid interaction smaller than a liquid-liquid interaction, which is expected within a partial wetting regime [6].

The results given in Fig. 4 are related not only to the small h value (0.1) but also to the rather large value (0.5), which is more than half the critical value of h leading to complete wetting ($h_c = 0.828\,68\ldots$). These results confirm that the way we prepare a substrate of a given roughness is very important: adsorbing molecules on top of a flat substrate should enhance wetting more than desorbing molecules from the top of a flat substrate. This effect seems to be important since here at least it is of the order of 10% to 20% of the flat wall tension. To find parameters of the surface geometry that are important for wetting, let us choose the description of geometry in terms of holes and let us now study, for a given roughness r, the effect of the opening of the holes (pores) on wetting. We present in Fig. 5 the wall tension $\Delta\tau(r)$ for a given roughness, $r=1.25$, as a function of the opening c in lattice units.

As can be seen, the wall tension increases with c up to a certain plateau appearing for $c \geqslant c_T$. This effect certainly has to be related to the finiteness of the correlation length. Moreover, the value of c_T, which characterizes the appearance of the plateau, should also depend on he temperature in the

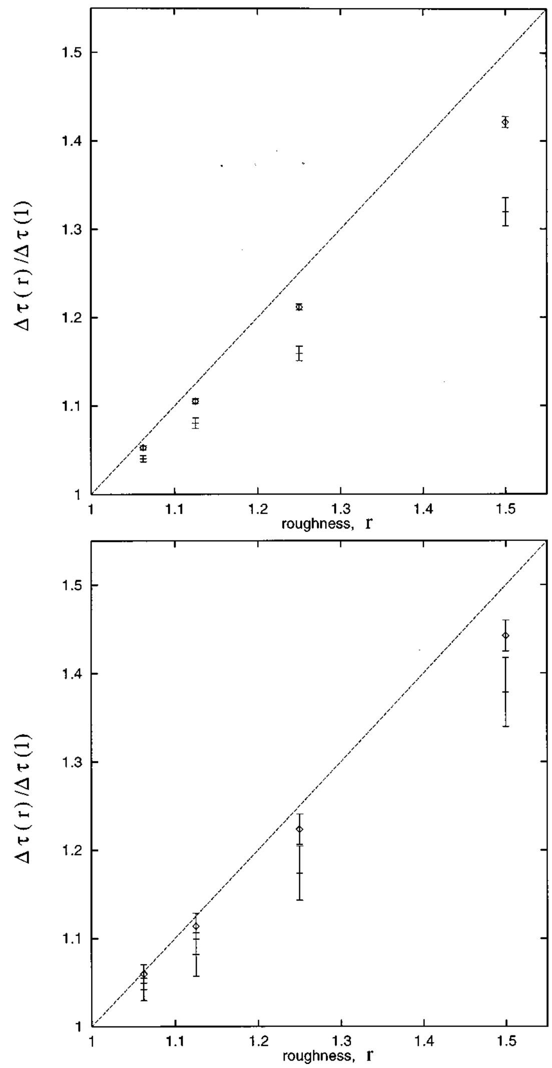

FIG. 4. $\Delta\tau(r)/\Delta\tau(1)$ as a function of roughness r for $Tk_B = 1.333$ and $b=2$. Diamonds on the figure are related to hills of size 2 $(a-c=2)$ and pluses to holes of size 2 $(c=2)$. Data plotted in (a) are obtained for $h=0.1$ while in (b) for $h=0.5$.

same way as the correlation length. It means that the dependence of $\Delta\tau(r)$ on c becomes less important for a low enough temperature, as presented in Fig. 2. The effect of the depth of the holes is also considered in Fig. 6, again for $r=1.25$, where we plot $\Delta\tau(r)$ as a function of the opening c for three different depths $b=2$, 4, and 5.

Obviously here, the depth b seems to play a minor role in comparison to the opening c. We do not plot the associated error bars in the figure, since they overlap almost completely. Up to now, we have been dealing with a rather oversimplified type of substrate. In order to consider more realistic situations let us then consider a random geometry for the substrate built in the following way. Consider a strip of height H and let the surface of the substrate be described by a step function that is the realization of a random walk with reflecting boundary conditions, moving in this strip with a probability of jump of size i ($|i| < H/2$) distributed as

$$P\{i\} = M\exp(-m|i|), \tag{9}$$

where m is some fixed constant and M is the normalizing

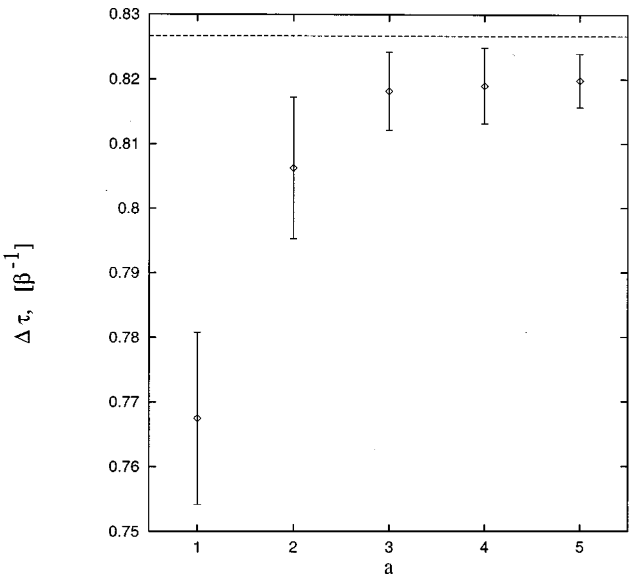

FIG. 5. $\Delta\tau$ as a function of the opening of the holes c for $Tk_B=1$ with given roughness $r=1.25$, $h=0.333$, $b=4$ for a 128×128 lattice. The dashed line describes the value predicted by Wenzel's law.

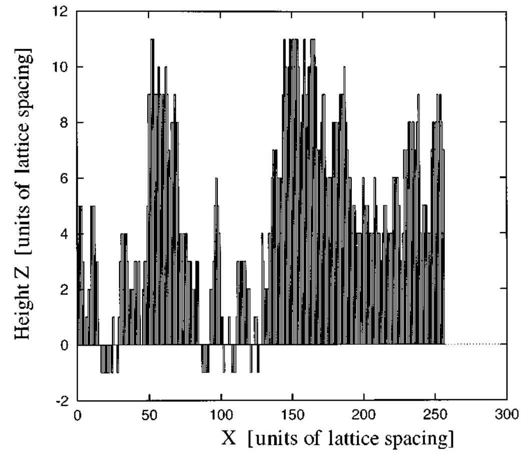

FIG. 7. A typical substrate with $m=1$ and $r=2.015$.

constant. A typical substrate generated by this procedure is given in Fig. 7 for a given roughness $r=2.015$.

Using this procedure, we compute the associated wall tension $\Delta\tau$ for 100 independent realizations of the substrate. Changing the constant m, we may construct several substrates with different average roughness. On the basis of typical AFM-STM surface measurements [7], we restrict ourselves to average roughness r between 1 and 2. Results for four different values of the average roughness, 1.25, 1.5, 1.75, and 2.0, are given in Fig. 8.

Such a complex geometry can be described by a combination of different depths and opening holes. These results show, however, surprisingly that the holes of the opening 1 curve and the simple hill of opening 1 seem to give some upper and lower bounds for the wall tension of a complex

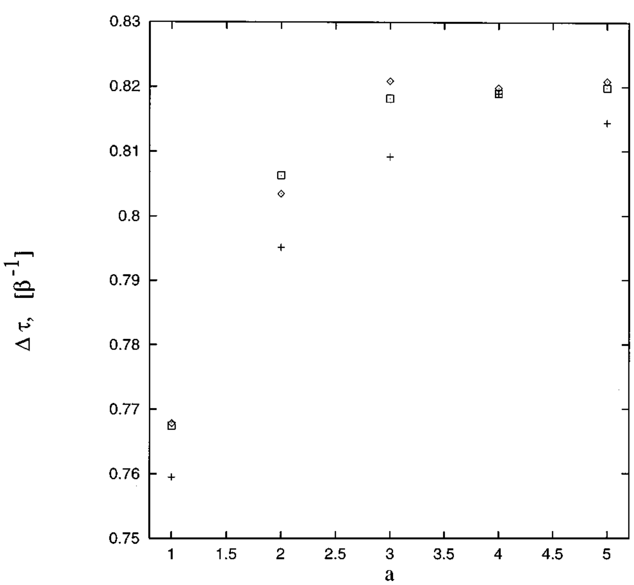

FIG. 6. $\Delta\tau$ as a function of the opening c of the holes for different hole depths $b=2$ (crosses), $b=4$ (squares), and $b=5$ (diamonds) for temperature $Tk_B=1$ and $h=1/3$ and given roughness $r=1.25$.

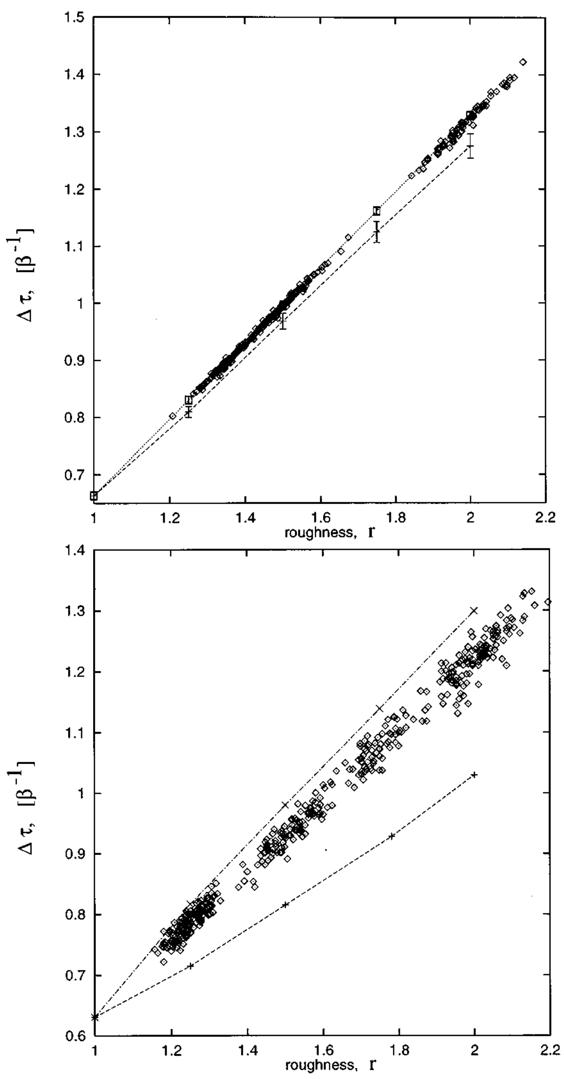

FIG. 8. $\Delta\tau(r)$ as a function of roughness for holes of depth $b=1$ and opening $c=1$ geometry (pluses), hills of depth 1 and opening 1 geometry (crosses) and random geometry (diamonds) for temperature $Tk_B=0.6$ (a) and for $Tk_B=1.4$ (b) with $h=1/3$.

substrate. The fact that the difference between the upper and lower bounds increases with temperature is in agreement with Wenzel's idea that geometry plays no role at low enough temperature, as observed in Fig. 8. This property is quite remarkable since it would lead, if it could be generalized in three dimensions, to a very powerful way to characterize surface wetting properties.

IV. CONCLUDING REMARKS

To summarize, we have thus studied the wall tension $\Delta\tau$ of the two-dimensional Ising model of a rough substrate. It appears that for high temperature, Wenzel's law should be corrected by some thermal factor

$$\Delta\tau(r) \simeq r f(\beta,\mathcal{G}) \Delta\tau(1).$$

We give here evidence that the geometry of the wall surfaces may be usefully characterized to study its effects on wetting. By considering different geometries, for a given roughness r, we observe significantly different effects when considering hills versus holes on top of the flat substrate. The effect of the thickness of the rough region as well as its porosity are also examined. More complex geometries are also studied and can be approached by the hill and hole cases. That these effects are not limited to the two-dimensional Ising model remains an open question.

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