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Competing bulk and surface fields in d = 2 Ising films near bulk criticality: effects of fluctuations*

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Abstract. The two-dimensional Ising films $L \times \infty$ with bulk H and surface H_1 fields of opposite sign are studied above and close to bulk criticality by the density matrix renormalization group method. This technique, applied recently to $d = 2$ Ising films, allows for very accurate results for the adsorption Γ as a function of the reduced deviation from the critical temperature τ. For strong H_1 three distinct classes of shapes of $\Gamma(\tau)$, determined by the value of the parameter $\tau_H \sim (|H|L)^{1/(\Delta-\nu)}$, where L is the width of the film, are found in agreement with earlier predictions [A. Maciołek, A. Ciach, R. Evans, J. Chem. Phys. **108**, 9765 (1998)]. For strong and for weak bulk fields $\Gamma(\tau)$ is a monotonic function, increasing for strong H and decreasing for weak H, in agreement with scaling analysis and earlier mean-field results. For H between these extreme cases $\Gamma(\tau)$ assumes a maximum for $\tau \sim \tau_H$ and for $\tau < \tau_H$ a depletion occurs, as in recent experiments for critical adsorption in porous materials. For a limited range of H a qualitatively new behavior of $\Gamma(\tau)$ is found. In addition to a maximum, a minimum of $\Gamma(\tau)$ for $\tau \sim L^{-1/\nu} < \tau_H$ appears, which in the mean-field analysis was absent.

PACS. 05.50+q Lattice theory and statistics; Ising problems – 05.70.Jk Critical point phenomena

1 Introduction

The statistical physics of fluids confined in narrow pores or capillaries is a subject that currently attracts much research effort [1]. Interest in this area stems from the need to understand the rich variety of phenomena observed experimentally for fluids adsorbed in real porous solids as Vycor or silica gels and the "fundamental" issues of how finite-size and substrate-fluid forces affect bulk properties. Separating "single pore" effects from those associated with the complex network of interconnected pores characteristic of a real porous solid is a major challenge for theory and experiment. In this work we focus on a problem of current interest that concerns a phenomenon of critical adsorption in porous media and is inspired by recent experiments [2].

The phenomenon of critical adsorption occurs when a simple fluid, binary liquid mixture, ferromagnet, or another system in a single-phase region is brought to its bulk critical point in the presence of an attracting external wall or another distinct physical interface. For example, as the critical temperature T_c is approached along a critical isochore the amount of adsorbed fluid, or the relative adsorption in the case of binary liquid mixtures, or the excess magnetisation for (Ising) magnets diverges as $\tau \equiv (T - T_c)/T_c \to 0$. Theory [3–5] attributes these divergences to a substrate-system interaction causing a perturbation of the relevant Order Parameter (OP) over a distance from the wall of the order of ξ_b, the bulk correlation length. Thus, for situations away from bulk criticality the OP profile differs from its bulk value (fixed by the properties of the reservoir far from the substrate) over microscopic distances and the amount adsorbed is finite. On the other hand, close to criticality, where $\xi_b \sim \mid \tau \mid^{-\nu}$ (ν is the critical exponent), the influence of the wall extends to macroscopic distances and the amount adsorbed can be a diverging quantity. Near criticality, ξ_b is the controlling length scale and one expects that as $T \to T_c$ the OP profile should be described in terms of universal scaling function as proposed by Fisher and de Gennes [3]

$$m(r) = \tau^{\beta} \mathcal{M}_{si}\Big(\frac{r}{\xi_b}, y\Big), \tag{1}$$

where the subscript "si" stresses that we are dealing with a semi-infinite system. The adsorption (coverage) Γ has in the semi-infinite system the form

$$\Gamma \equiv \int_0^{\infty} m(r) dr = \tau^{\beta} \xi_b \mathcal{G}_{si}(y). \tag{2}$$

r is the distance measured normal to the substrate, located at $r = 0$. For the magnetic case $m(r)$ is the magnetisation profile, β is the critical exponent describing

* Dedicated to J. Zittartz on the occasion of his 60th birthday

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the vanishing of the bulk (OP) magnetisation and Γ is the (excess) magnetisation. These formulae refer to $\tau > 0$ and the situation where the bulk magnetic field $H = 0$. $\mathcal{M}_{si}$ and $\mathcal{G}_{si}$ are universal scaling functions and $y = \tau^{-\nu} H_1^{\nu/\Delta_1}$ is the scaling variable describing coupling to the surface magnetic field H_1. $y \sim \xi_b/l_1$ is the ratio of the two length scales ξ_b and $l_1 \propto H_1^{-\nu/\Delta_1}$, where Δ_1 is the surface gap exponent [6].

Within the general context of surface critical phenomena [6] critical adsorption corresponds to the $H_1 \neq 0$ fixed point so that as $\tau \to 0$, $y \to \infty$. In this limit $\mathcal{G}_{si}(y)$ is asymptoticaly constant and, from (2), Γ takes on the asymptotic form (for $\tau \to 0$ and for any non-zero value of H_1)

$$\Gamma \sim \tau^{\beta-\nu}. \tag{3}$$

Recent experiments by Thommes *et al.* [2] designed to test above prediction for SF_6 on a colloidal graphite adsorbent found that as T was lowered on a near critical isochore Γ first increased (as predicted) but then decreased very rapidly, taking on negative values for $T - T_c < 1\,\mathrm{K}$. Microgravity experiments by the same group confirmed these results and lead them to study adsorption of SF_6 in a mesoporous glass CPG-10, which comprises a rigid interconnected system of mesoporous with a nominal pore diameter of 31 nm. Γ showed a very similar temperature dependence and they attributed this critical depletion to finite-size effects [2] but the precise origin of such a dramatic variation of Γ was unclear.

Only very recently in the work by Maciołek *et al.* [7] it was argued that critical depletion is a general phenomenon associated with a fluid in a *single* idealized pore and resulting from a competition between positive adsorption (the walls or surface fields favor the dense liquid phase) and negative adsorption associated with the bulk-like field which favors the dilute gas phase. Such a bulk-like field is present when the bulk reservoir is not exactly at the critical density, because then the chemical potential for the pore becomes uncritical. In the vicinity of the bulk critical point even very slight difference between the actual and the critical values of the chemical potential may lead to the pronounced differences in the density due to the large compressibility $\kappa_T \sim \tau^{-\gamma}$. For the subcritical values of the chemical potential in the pore there is a competition between the bulk and the surface critical behavior. Sufficiently close to T_c the bulk effects may take over, because $\gamma > |\beta - \nu|$ and the critical depletion would result. This explanation proposed first in reference [7] was supported by the critical scaling analysis and the mean-field (MF) calculation for a lattice gas confined between two identical planar walls.

MF results, however, are not sufficient to capture the true criticality of the system. The MF approximation ignores the effects of fluctuations which may be particularly pronounced when the bulk correlation length is comparable to the pore size. In the presence of fluctuations the behavior of the OP profiles and the adsorption Γ as a function of temperature may be qualitatively different from the MF predictions. On the other hand, scaling analysis, although generally valid, does not provide the actual forms of the scaling functions.

In this paper we study the effects of fluctuations in the same simplest model of confined fluid as in reference [7], namely the lattice gas (Ising model) subject to identical surface fields located at the two walls. Our first goal is to test whether the predictions of reference [7] persist when the critical fluctuations are taken into account. Secondly, we investigate whether in the case of a critical film the fluctuations may lead to a qualitatively different behavior of the OP profiles and the adsorption, especially in the temperature interval corresponding to $\xi_b \sim L$, where the effects of fluctuations should be particularly pronounced. Such relevant qualitative differences in physical quantities related to effects of fluctuations were discovered recently in reference [8]. It was found that contrary to the MF predictions in the critical region the OP profiles near the weakly adsorbing wall were nonmonotonic functions of the distance from the wall.

We study the lower critical dimension $d = 2$. The case of two-dimensional systems is the ultimate test of the validity of the MF predictions, since we know that in this low dimension, fluctuations are particularly strong. The effects of fluctuations on the adsorption Γ in the two-dimensional Ising model of a pore was studied only in case of zero bulk field H by exact transfer-matrix calculations [7]. However, for the interesting case of competing bulk and surface fields, the exact solution of the two-dimensional Ising film does not exist and to go beyond the mean-field approach one has to employ the approximate methods. We propose here the density matrix renormalization group (DMRG) method, introduced first by White [9] for quantum systems. The method is very accurate and has been successfully applied for two-dimensional classical systems by Nishino [10] for the construction of effective transfer matrices of large systems. In principle the DMRG method is equivalent for $d = 2$ classical systems to the transfer matrix method. The role of the renormalization is only to construct a transfer matrix of a large strip by series of iterations. At low temperatures in order to renormalize the transfer matrix we have to use its two eigenvectors related to both phases (substantially different here). By this we overcome the problem of metastability [11]. The method works equally well for vanishing as well as nonvanishing bulk fields. Recently this method was applied for studying the wetting phenomena in Ising films [12].

The paper is organized as follows. In Section 2 the recent theory for the critical adsorption phenomenon for simple fluids confined in a single, idealized slit-like pore is summarized. The special attention is paid to the case of competing bulk and surface fields. In Section 3 the DMRG method is briefly reviewed and the results of the calculations for two-dimensional Ising films are presented. Summary and conclusions end the paper.

2 Background

We consider a confined system belonging to the Ising universality class, that is: a simple fluid, a binary mixture or a magnet, close to the bulk criticality. We will use the magnetic language, but our considerations apply to the simple fluid or to the binary mixture as well, with the usual correspondence between magnetization and a difference between the density or concentration and their critical values respectively, and between the magnetic field and the deviations of chemical potential or chemical potential difference and their values at critical density or concentration, respectively [7].

We concentrate on supercritical phenomena, hence we assume for the reduced temperature $\tau \equiv (T - T_c)/T_c$ and for the dimensionless field H, measured in units of the coupling constant, the following conditions:

$$0 < \tau \ll 1 \tag{4}$$

$$|H| \ll 1. \tag{5}$$

In terms of the bulk correlation length ξ_b the proximity to the critical point means that $\xi_b \gg a$ where a is a microscopic distance (size of molecules). Typically, the fluid interacts with the confining walls. We thus assume that there is a surface field H_1 associated with the walls and that this field is short-ranged. Finally, we assume that the considered system is confined between two parallel walls (slit geometry) separated by a mesoscopic distance L. Such conditions correspond, for example, to a supercritical fluid confined in a single pore of a typical porous material, for example vulcan glass.

For a slit the order-parameter (OP) profile $m(r)$ and the adsorption (coverage), defined as in equation (2) but with the upper limit of integration equal to L, should have, according to the finite-size scaling, the following forms (up to the nonuniversal metric factors):

$$m(r) = \tau^{\beta} \mathcal{M}\left(\frac{r}{L}; x, y, z\right) \tag{6}$$

and

$$\Gamma = \tau^{\beta} L \mathcal{G}(x, y, z), \tag{7}$$

where $\mathcal{M}$ and $\mathcal{G}$ are scaling functions,

$$x = |H|^{\nu/\Delta} \tau^{-\nu}, \tag{8}$$

$$y = H_1^{\nu/\Delta_1} \tau^{-\nu} \tag{9}$$

and

$$z = L\tau^{\nu}. \tag{10}$$

All the exponents have their standard meaning [6]. Usually, instead of x and y one considers $x^{\Delta/\nu}$ and $y^{\Delta_1/\nu}$ as scaling variables. With our choice, x and y are proportional to the ratio between the bulk correlation length and the lengths related to the bulk and the surface fields respectively.

In the sequel we will concentrate on the case of strongly adsorbing walls. Strictly speaking, we will assume $y \gg 1$, or equivalently $\tau \ll H_1^{1/\Delta_1}$, where H_1 is, as H, measured in units of the coupling constant. For fixed H_1 this condition is always satisfied sufficiently close to criticality. In the case of semi-infinite system the strong-field limit is therefore referred to as the *normal* [13] transition. In this case, for sufficiently large y, the scaling functions $\mathcal{M}$ and $\mathcal{G}$ assume their asymptotic forms for $y \to \infty$, $\mathcal{M}_0(\frac{r}{L}; x, z)$ and $\mathcal{G}_0(x, z)$ respectively.

For a given slit of a size L and a given sample specified by H, the OP profile and the Γ depend on τ through the dependence of the scaling functions on x and z. This dependence, in general, can be determined by exact or approximate calculations for various model systems. Some features of $m(r)$ and $\Gamma(\tau)$, however, can be deduced on general grounds. First of all, for a given slit of a size L, we can distinguish two asymptotic temperature intervals within the critical region: $\tau \ll L^{-1/\nu}$ and $L^{-1/\nu} \ll \tau \ll 1$, corresponding to $\xi_b \gg L$ and $\xi_b \ll L$. In the first case the system behaves as at the critical isochore. For temperatures so close to criticality, increasing the correlation length, already much larger than the size of the system has little effect on the OP and the adsorption is limited rather by the size of the system. In the second case, $\xi_b \ll L$, the inner part of the slit is not affected by the walls and behaves as the bulk, whereas near the surfaces the semi-infinite like behaviour occurs. In the crossover region $\xi_b \sim L/2$ the fluctuations play particularly important role, unless H is strong enough to suppress them. A reduced temperature τ_0, corresponding to

$$\xi_b(\tau_0) = L/2 \tag{11}$$

is a "mirror image" of the critical temperature for the capillary condensation [1], in the sense that the extent of correlations reaches the size of the system in both cases, above and below T_c.

Let us analyze the different temperature intervals for a given slit in more detail

- $\tau \ll \tau_0 \sim L^{-1/\nu}$
  As already noted, if the correlation length ξ_b is much larger than the size of the pore, then the adsorption is rather determined by the size of the pore, and only very weakly depends on τ, *i.e.* for $\tau \ll \tau_0 \sim L^{-1/\nu}$ a saturation of the adsorption is expected. Therefore the behavior *at* the critical point should approximately hold. According to scaling [13], the OP profile has at criticality the shape:

  $$m(r) = r^{-\beta/\nu} \mathcal{M}_c(r/L; xz) \tag{12}$$

  where $\mathcal{M}_c$ is a scaling function, and $xz = H^{\nu/\Delta} L$ is a scaling variable appropriate at $T = T_c$. The adsorption has thus the form

  $$\Gamma \sim L^{(\nu-\beta)/\nu} \mathcal{G}_c(xz), \tag{13}$$

where

$$\mathcal{G}_c(xz) = \int_0^1 d\zeta \zeta^{-\beta/\nu} \mathcal{M}_c(\zeta, xz). \tag{14}$$

In the case of $H = 0$, *i.e.* $x = 0$, the behavior of Γ is given by (13) with $\mathcal{G}_c(xz)$ replaced by a constant, $\mathcal{G}_c(0)$, and $\Gamma \sim L^{(\nu-\beta)/\nu}$.

For $H \neq 0$, at the critical isotherm we have $m \sim H^{1/\delta}$ in the bulk. For sufficiently strong H (compared to H_1) similar dependence of Γ on H is expected, hence Γ should behave as

$$\Gamma \sim \mathrm{sgn}(H)|H|^{1/\delta} L. \tag{15}$$

Consistency between the above dependence on H and the scaling prediction (13) gives the behavior of $\mathcal{G}_c(xz)$ for $xz \to \infty$ as:

$$\mathcal{G}_c \sim (xz)^{\beta/\nu}. \tag{16}$$

In the above we make use of the scaling relation [6] $\Delta/\delta = \beta$.

For $x = 0$ ($H = 0$) the relation (13) was confirmed in exact calculations in the Ising model [7] and in reference [14] in case of Widom approximation with rational values of critical indices. For $x \neq 0$ ($H \neq 0$), Γ was calculated only within the MF approximation, and (15) was confirmed for strong H with $\delta = 3$, which is the MF value of δ [7].

The value at which $\Gamma(\tau)$ saturates for $\tau \ll L^{-1/\nu}$ strongly depends on H and H_1. It ranges from a positive value for $H = 0$, of order of $\Gamma \sim L^{(\nu-\beta)/\nu}\mathcal{G}_c(0)$, then, for $H < 0$ decreases for increasing $|H|$, becomes negative, and for strong $H < 0$ behaves according to (15).

- $L^{-1/\nu} \sim \tau_0 \ll \tau \ll 1$

When the size of the pore is mesoscopic, the inner part of it behaves as the bulk fluid near criticality, as long as the bulk correlation length, although much larger than the size of molecules, is much smaller than the width of the pore. In this case the walls have very little effect on the properties of the fluid in the central part of the slit. The magnetization in this "core part" then only very weakly depends on the position, and behaves as

$$m_b = H\chi = \mathcal{A}H\tau^{-\gamma} \qquad L^{-1/\nu} \ll \tau \ll 1 \tag{17}$$

where $\mathcal{A} = O(1)$ is a constant amplitude and χ is the susceptibility.

Near the walls, on the other hand, the fluid behaves as in the semi-infinite, nearly critical system subjected to the surface field H_1, if the other wall is much further away than the extent of correlations. When the near-surface region is not disturbed by the other wall, the OP profile should have almost the same form as in the semi-infinite case at normal transition, namely

$$m(r) = \tau^{\beta}\mathcal{M}_{si}\left(\frac{r}{\xi_b}; x, z\right), \tag{18}$$

where $\mathcal{M}_{si}(\frac{r}{\xi_b}; x, z)$ decays exponentially for $\left(\frac{r}{\xi_b}\right) \gg 1$.

From the above considerations we can approximate the value of adsorption by

$$\Gamma \sim 2\tau^{\beta}\xi_b\mathcal{G}_{si} + \mathcal{A}H\tau^{-\gamma}L, \tag{19}$$

where $\mathcal{G}_{si} = \int_0^\infty d\zeta \mathcal{M}_0(\zeta) = O(1)$ and the contribution from the two walls is taken into account.

A particularly interesting situation occurs when the surface and the bulk fields favour different phases, say $H_1 > 0$ and $H < 0$, and the bulk and the surface contributions to Γ compete. As $\xi_b \sim \tau^{-\nu}$ and $\gamma > \nu - \beta$, for not too weak H, the bulk term exceeds the surface term for sufficiently small τ, and the Fisher-de Gennes (FdeG) form is no longer valid.

In order to analyze the influence of H on the shape of $\Gamma(\tau)$, we rewrite (19) with the help of the exponent relation [6] $\gamma = \Delta - \beta$ as

$$\Gamma(\tau) = \tau^{\beta-\nu}\left[\mathcal{G} - \left(\frac{\tau}{\tau_H}\right)^{\nu-\Delta}\right], \tag{20}$$

where $\mathcal{G} = O(1)$ and

$$\tau_H = (\mathcal{A}|H|L)^{1/(\Delta-\nu)} \tag{21}$$

is a crucial parameter, which allows to distinguish various kinds of systems, with qualitatively different shapes of $\Gamma(\tau)$. The different ranges of τ_H are approximately: (1) $\tau_H > 1$ (strong-field limit), (2) $L^{-1/\nu} \sim \tau_0 < \tau_H < 1$ (crossover case) and (3) $\tau_H < \tau_0 \sim L^{-1/\nu}$ (weak–field limit).

1. $\tau_H > 1$

   In this case $\tau/\tau_H \ll 1$ in the whole critical region. Thus, the second term in (20) dominates, since it is a small number taken to a negative power. Hence the adsorption is negative *i.e.* in fact *desorption* takes place despite the adsorbing walls. For $\tau_H \gg 1$ the adsorption assumes for $L^{-1/\nu} \ll \tau \ll 1$ the asymptotic form

   $$\Gamma(\tau) \sim -|H|L\tau^{-\gamma}. \tag{22}$$

   The consistency of the above form with the finite-size scaling was verified in reference [7]. The MF calculations for Γ also confirm (22) for strong H, with $\gamma = 1$ in MF. However, L must be sufficiently large so that the condition $\tau \gg L^{-1/\nu}$ can be satisfied within the region of validity of the asymptotic behavior $\chi \sim \tau^{-\gamma}$, which occurs only asymptotically, for sufficiently small τ.

2. $L^{-1/\nu} \sim \tau_0 < \tau_H < 1$

   For a given slit this condition corresponds to weaker H, *i.e.* to more critical bulk system. When $\tau \gg L^{-1/\nu}$ is increased, the second term in (20) dominates as long as $\tau < \tau_H$, as argued previously, and $\Gamma(\tau)$ increases. For $\tau \sim \tau_H$ the maximum of $\Gamma(\tau)$ is expected. Finally for $\tau \gg \tau_H$ the constant term in (20) dominates over the second term,

in which a large number is taken to a negative power. For such temperatures the usual Fisher-de Gennes form of adsorption, $\Gamma \sim \tau^{\beta-\nu}$ is expected.

3. $\tau_H < \tau_0 \sim L^{-1/\nu}$
   In this case the first term in (20) dominates in the whole region of validity of this approximation, hence in this region the adsorption has the FdeG form.

We can summarize the conclusions of the above analysis and the results of the MF (in case of $H < 0$) and exact (in case of $H = 0$) calculations [7]. The behavior of the adsorption $\Gamma(\tau)$ is qualitatively different in the three cases determined for a given pore by the strength of H for $H < 0$.

- Strong bulk field
  In the case of strong $H < 0$ the adsorption is a monotonically increasing function of τ, which has a negative value at $\tau = 0$, very weakly depends on τ for $\tau < L^{-1/\nu}$, and increases for growing τ, according to the power law (22) if τ_H and L are sufficiently large.
- Intermediate bulk field
  The adsorption is weakly negative and constant for $\tau \ll L^{-1/\nu}$, next it increases and reaches a maximum for $\tau \sim \tau_H$, and for $\tau > \tau_H$ decreases, assuming the FdeG form.
- Weak and vanishing bulk field
  The positive and almost constant adsorption for $\tau \ll L^{-1/\nu}$ monotonically decreases for larger reduced temperatures, and for sufficiently large τ Γ follows the FdeG law.

In the crossover region between temperatures $\tau \ll L^{-1/\nu}$ and $\tau \gg L^{-1/\nu}$, *i.e.* in the region where the extent of correlations is comparable to the size of the system, the fluctuations play a major role. Their effect on $\Gamma(\tau)$ has not been studied yet. From general grounds we can only conclude that strong H suppresses the fluctuations and the qualitative behavior of $\Gamma(\tau)$ should be correctly described by the MF calculations (the quantitative form is of course different due to different values of critical exponents). For weak H, however, the system should be particularly susceptible to fluctuations, and the form of $\Gamma(\tau)$ can sensitively depend on H, particularly in the temperature range $\tau \sim L^{-1/\nu}$. In this temperature interval the form of $\Gamma(\tau)$ can be qualitatively different in presence of fluctuations from the MF predictions.

3 Results for two-dimensional Ising films

In this section we present the results of DMRG calculations for the two-dimensional ($d = 2$) Ising film defined on the square lattice $L \times M, M \to \infty$. The lattice consists of L columns at spacing $a \equiv 1$, so that the width of the strip is $La = L$. At each site, labeled i, j, ..., there is an Ising spin variable taking the value $\sigma_i = \pm 1$. We assume only nearest-neighbor interactions of strength J and

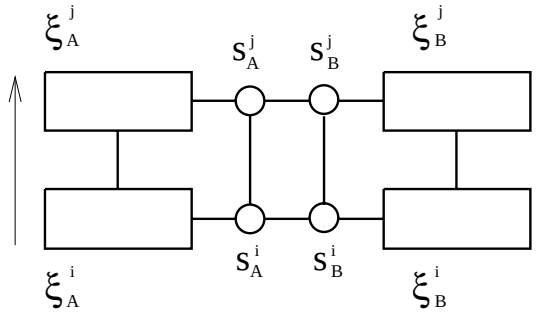

Fig. 1. Schematic view of a transfer matrix element of a strip of width L generated by the DMRG. ξ and s label block and spin variables respectively, with $\xi = 1, 2 \ldots m$ and $s = \pm 1$. The total dimension of the matrix is $4m^2 \times 4m^2$. The arrow denotes the transfer direction.

a Hamiltonian of the form:

$$\mathcal{H} = -J\Big[\sum_{\langle i,j\rangle}\sigma_i\sigma_j - H\sum_i \sigma_i - H_1\sum_i^{(1)}\sigma_i - H_L\sum_i^{(L)}\sigma_i\Big], \tag{23}$$

where the first sum runs over all nearest-neighbour pairs of sites while the last two sums run, respectively over the first and the L-th column. H is the bulk magnetic field and H_1 and H_L are the surface fields corresponding to a direct, short range ("contact") interaction between the walls and the spins in the film. H, H_1 and H_L are all dimensionless fields, measured in units of J. We assume that both surface fields lead to preferential adsorption of the positively magnetized bulk phase on the inner surfaces of the pore (*i.e.* $H_1 = H_L > 0$). The pore has finite width La but we will take the limit $M \to \infty$.

The analysis of this model has been based on the density matrix renormalization group approach originally introduced by White to study the ground state properties of quantum spin chains [9]. Exploiting the relation between a d-dimensional quantum system and a $d+1$-classical system, Nishino extended the DMRG to study equilibrium properties of two-dimensional classical lattices [10]. Although the name DMRG is widely used, the method has only some analogies with the traditional renormalization technique [15].

In the DMRG calculation for classical systems one starts from a transfer matrix of a small system that can be solved exactly. With the help of the information about the thermodynamics of the system [10], one generates the *effective* transfer matrix of a larger system. The strip width grows at each DMRG iteration and the spin space is truncated to keep the dimensionality of the effective transfer matrix controlled.

Figure 1 shows schematically an element of the effective transfer matrix generated by the DMRG algorithm. The matrix consists of block and spin variables. A block describes approximately a collection of spins. The block states are labeled by a variable ξ which can take $m \ll 2^L$ possible values. Keeping m larger one obtains more accurate numerical results. In the present case we found that

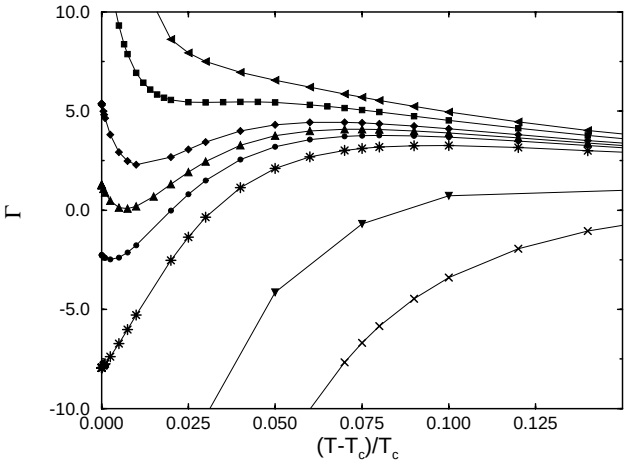

Fig. 2. Adsorption Γ as a function of the deviation from the bulk critical temperature τ calculated by the DMRG method for the $d = 2$ Ising film of width $L = 96$ and surface fields $H_1 = H_L = 0.8$ and various bulk fields: (triangles left) $H = -0.002$; (squares) $H = -0.0022$; (diamonds) $H = -0.0024$; (triangles up) $H = -0.0025$; (circles) $H = -0.0026$; (stars) $H = -0.0028$; (triangles) $H = -0.004$; (crosses) $H = -0.006$.

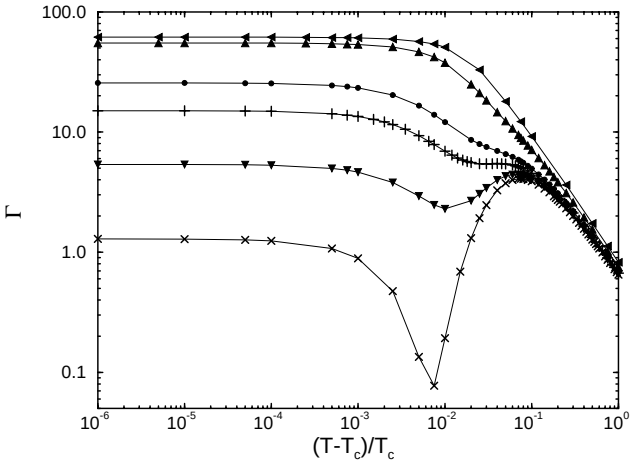

Fig. 3. Log-log plot of the adsorption Γ for the same system as in Figure 2 but for weak and intermediate bulk fields: (triangles left) $H = -10^{-7}$; (triangles up) $H = -10^{-3}$; (circles) $H = -0.002$; (pluses) $H = -0.0022$; (triangles) $H = -0.0024$; (crosses) $H = -0.0025$ exposing the behavior near T_c and in the crossover region for τ around $\tau_0 \sim 0.001$. For $\tau = (T - T_c)/T_c \leq 10^{-4}$ Γ is almost constant.

for the strip $L = 96$ a value of states kept $m = 40$ is sufficient to guarantee a very high accuracy of our magnetization profiles [12]. In our calculation we have used the finite-system version of DMRG algorithm designed to accurately study finite size systems [16]. For more details see references [17–19].

The leading eigenvalue λ_L of the effective transfer matrix T_L

$$T_L|v_L\rangle = \lambda_L|v_L\rangle, \tag{24}$$

gives the free energy per spin as

$$f_L = -\frac{1}{L}\ln\lambda_L. \tag{25}$$

If the dominant eigenvector $|v_L\rangle$ is normalized, the squares of its elements $v_L^2(i)$ are equal to the probabilities of finding a row in a state i. That provides us the average quantities as, *e.g.* the magnetization at l site:

$$\langle m_l\rangle = \sum_{i=1}^{4m^2} v_L^2(i)s_l(i), \tag{26}$$

where $s_l(i) = \pm 1$ is the value of spin in the $i-th$ state.

Calculations are done for the film of width $L = 96$ with fixed surface fields $H_1 = H_L = 0.8$ and various magnetic bulk fields H. For the $d = 2$ Ising model there exist analytical expressions for both ξ_b and χ, so the amplitudes of ξ_b and χ defined by $\xi_b = \mathcal{A}_b\tau^{-\nu}$ and $\chi = \mathcal{A}\tau^{-\gamma}$ (see Eq. (17)) are known: $\mathcal{A}_b \approx 0.56$, $\mathcal{A} \approx 0.963$ [20]. The value of critical exponents used in our derivations are the following $\nu = 1$, $\Delta = 15/8$ and $\gamma = 7/4$. Hence the crossover temperature, defined by the equation (11), for our system is $\tau_0 = 0.011$, and the dependence of τ_H on H is given by $\tau_H = (94.33H)^{8/7}$. Note the important difference between τ_0 in this case and in the MF approach with the width of the slit equal to 400 [7]. In the latter case $\tau_0 \sim 10^{-5}$. Although $L \sim 10^2$ in both cases, τ_0 is three orders of magnitude larger in the case of the $d = 2$ Ising slit. Therefore the region $1 \ll \xi_b \ll L$, *i.e.* $L^{-1/\nu} \ll \tau \ll 1$ is in our case $10^{-2} \ll \tau \ll 1$, *i.e.* it is significantly narrower than in the MF approach considered in reference [7]. From the classification summarized in the Section 2 and from the explicit form of τ_H given above, we find that the strong and the weak field regions correspond to $|H| > 10^{-2}$ and to $|H| < 2 \times 10^{-4}$ respectively.

To meet the scaling analysis and MF predictions we take H ranging from very small values $H = -10^{-7}$ up to $H = -0.8$. The results of these calculations for the adsorption $\Gamma \equiv \sum_{l=1}^{L} m_l$ as a function of the reduced deviation from the critical temperature τ are presented in Figures 2, 3 and 4. Various curves in these figures correspond to various bulk magnetic fields H between -10^{-7} and -0.1. The general feature shared by all the plots of $\Gamma(\tau)$ is the saturation which starts for $\tau \sim 10^{-3}$. This perfectly agrees with the expectation of saturation taking place for $\tau \ll \tau_0 \approx 10^{-2}$. Our results thus agree with the general predictions and the earlier results obtained within the MF approximation [7]. For larger τ the shape of $\Gamma(\tau)$ strongly depends on H, as expected.

For the weakest bulk fields $H = -10^{-7}, -10^{-3}$ the behavior of $\Gamma(\tau)$ is similar to the case of vanishing bulk field [7] (see Fig. 3). Γ is positive for all values of τ. It first increases monotonically as T decreases and in the temperature range corresponding to τ between 0.2 and 0.8, $\log\Gamma$ *versus* $\log\tau$ is approximately linear with a slope equal to $-7/8$, which agrees with the Fisher-de Gennes result $\Gamma \sim \tau^{\beta-\nu}$, since $\beta = 1/8$ and $\nu = 1$ for the $d = 2$ Ising model. On reducing T further the adsorption

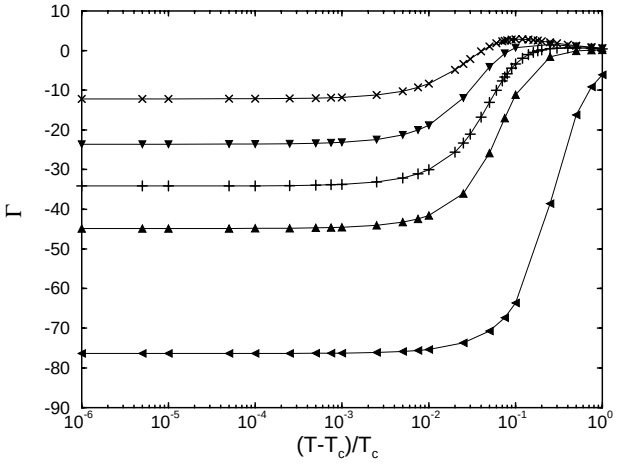

Fig. 4. Semilog plot of the adsorption $\Gamma(\tau)$ for the same system as in Figure 2 for (a) "intermediate" bulk field (crosses) $H = -0.003$ and (b) "strong" bulk fields (triangles) $H = -0.004$; (pluses) $H = -0.006$; (triangles up) $H = -0.01$; (triangles left) $H = -0.1$. As for the "weak" and "intermediate" bulk fields of Figure 3 the adsorption is almost constant for $\tau = (T - T_c)/T_c \leq 10^{-4}$, however unlike in Figure 3 it takes on a negative value.

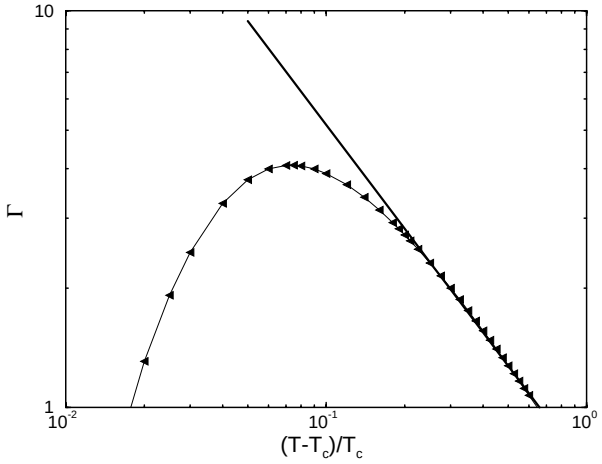

Fig. 5. Log-log plot of the function $\Gamma(\tau)$ calculated for the same system as in Figures 2–4 with the bulk field $H = -0.0025$ to show the Fisher-de Gennes power law behavior for $\tau \gg \tau_H$. The straight line has a slope $-7/8$ (see text).

continues to increase but the curve deviates from the Fisher-de Gennes power law behavior. There is also an inflextion point on the Γ curve which for $H = -10^{-7}$ is located at approximately the same T/T_c as for $H = 0$, *i.e.* $T/T_c \sim 1.01286$. For $H = -10^3$ it is shifted towards $\tau = 0$. Eventually Γ saturates for $\tau < 10^{-3}$. In the MF calculations of reference [7] for $H_1 = 0.1$ and $L = 400$ such a small bulk field as $H = -10^{-7}$ was strong enough to cause the critical depletion. However, contrary to the $d = 2$ Ising film, $\tau_H > \tau_0$ in that case, *i.e.* $|H| = 10^{-7}$ was not in the weak field region, as in our case, but rather in the intermediate field range.

For the bulk fields equal to and stronger than -4×10^{-3} the adsorption is negative for all $\tau < 1$ (see Fig. 4). Γ decreases monotonically on approaching T_c and for $\tau < 10^{-3}$ it saturates. This is the behavior typical for the "strong field" regime (we estimated that the strong field region corresponds to $|H| > 10^{-2}$). However, the predicted power law asymptotic form of Γ (22) is not found in the expected range of $L^{-1/\nu} \sim 10^{-2} \ll \tau \ll 1$. The width of the film ($L = 96$) might not be large enough to assure that τ simultaneously satisfies the above condition and lies within the region of validity of the approximation (20).

In the case of intermediate bulk fields, for the fields between -10^{-3} and -4×10^{-3} (τ_H between 0.07 and 0.3) a very peculiar behavior of the adsorption as a function of temperature can be seen in Figures 2, 3. This is qualitatively new behavior, not found in the MF approximation of reference [7]. It is characterized by dramatic changes of the shape of the function $\Gamma(\tau)$ which take place in very narrow range of values of H. For $\tau > \tau_H$ $\Gamma(\tau)$ assumes the FdeG form but then ceases to be a monotonically decreasing function – on approaching T_c the maximum and then the minimum gradually develop as the value of the bulk magnetic field is lowered ($|H|$ increases). The locations of the maximum and the minimum change with H. The maximum shifts slightly towards higher values of τ. This behavior is consistent with the prediction of Section 2 for the case of intermediate bulk fields, which says that Γ should reach its maximum for $\tau \sim \tau_H$, since τ_H is an increasing function of $|H|$.

The minimum shifts towards smaller values of τ and becomes deeper as $|H|$ is increased. At the same time the value at which Γ saturates, which for $H = -0.0022$ and $H = -0.0024$ is greater than the value of Γ at the maximum, quickly decreases with growing $|H|$, so that the minimum disappears for $H = -0.003$. For this value of H the shape of $\Gamma(\tau)$ becomes similar to the MF result for the intermediate bulk field regime, *i.e.* the adsorption is negative and constant for $\tau \ll L^{-1/\nu} \approx 0.01$, next it increases and reaches maximum for $\tau \sim 10^{-1}$, which is of the same order of magnitude as $\tau_H \approx 0.24$, and for $\tau > \tau_H$ decreases, assuming the FdeG form (see Fig. 5).

As expected, this new behavior occurs in the crossover region between temperatures $\tau \ll L^{1/\nu} \approx 0.01$ and $\tau \gg L^{1/\nu} \approx 0.01$, *i.e.* when the bulk correlation length is comparable to the system size and can be explained as the effect of the strong fluctuations. The bulk field $H = -0.003$ is strong enough to suppress these fluctuations and the behavior of $\Gamma(\tau)$ is qualitatively correctly described by the MF calculations. For weaker H, however, the depletion tendency of Γ is changed by the fluctuations and the minimum results for $\tau \approx 0.01$ or smaller, corresponding to $\xi_b \sim L/2$. For higher values of $|H|$, $\xi_b \sim L/2$ is achieved for lower value of τ since the bulk field suppresses fluctuations, and hence the minimum of $\Gamma(\tau)$ should shift towards T_c which is observed.

In Figure 6 the value of the magnetization at the middle of the pore is sketched as a function of temperature for $H = -0.0025$ in the vicinity of the minimum of $\Gamma(\tau)$. The log scale for temperature is used to expose

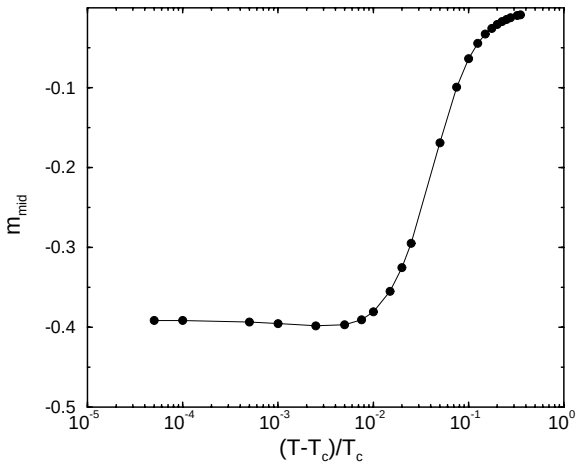

Fig. 6. The value of the magnetization in the middle ($l = 48$) of the $d = 2$ Ising film of width $L = 96$, surface fields $H_1 = H_L = 0.8$ and bulk field $H = -0.0025$ calculated by the DMRG method and plotted on the logarithmic deviation from the critical temperature τ scale.

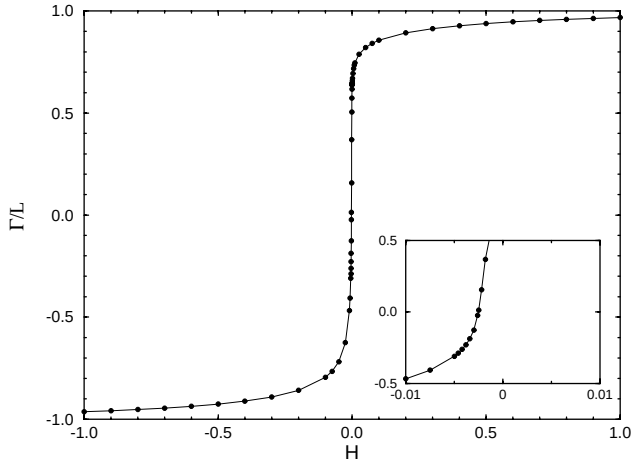

Fig. 7. Plot of Γ/L as a function of the bulk field H calculated by the DMRG method for the $d = 2$ Ising film of width $L = 96$ and surface fields $H_1 = H_L = 0.8$ for the bulk critical temperature T_c. In the insert the vicinity of the origin of the plot is blown up.

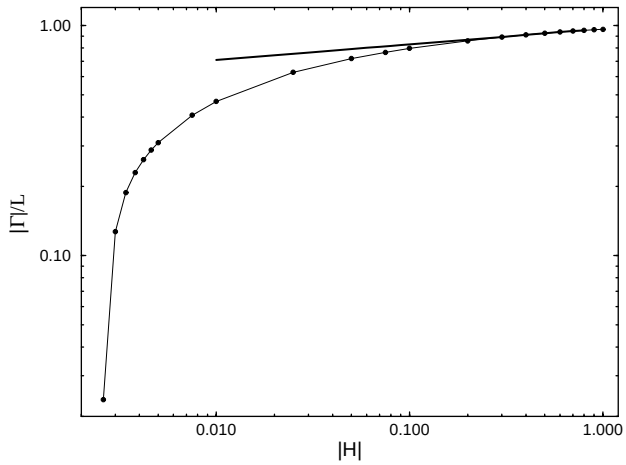

Fig. 8. The same result as in Figure 7 but now plotted on the log-log scale for the absolute value of Γ/L as a function of the absolute value of the bulk magnetic field H. The straight line has slope equal to 1/15 (see text).

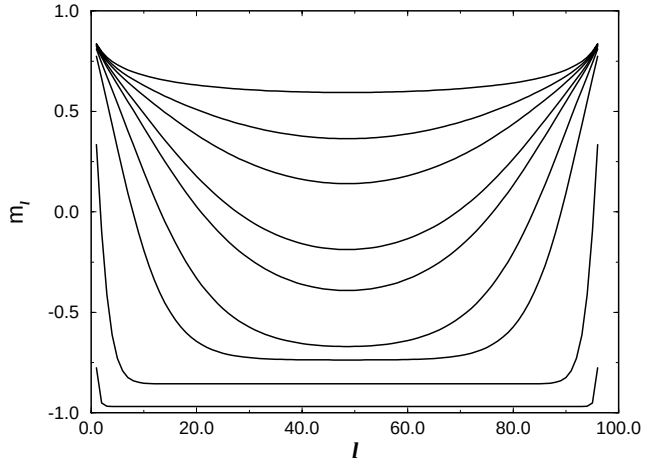

Fig. 9. Selection of the critical magnetization profiles calculated by the DMRG method for the $d = 2$ Ising film of width $L = 96$ and surface fields $H_1/J = H_L/J = 0.8$ for various bulk fields: the most upper profile corresponds to $H = -10^{-7}$, then subsequently to the bottom profile: $H = -0.0014, -0.0018, -0.0022, -0.0025, -0.0042, -0.01, -0.1, -1$.

the behavior near T_c. Due to the presence of the negative bulk magnetic field m_{mid} decreases as T_c is approached ($m_b \sim |H|\tau^{-\gamma}$) but around $\tau \sim \tau_0$, for which $\mathcal{A}_{\xi_b}\tau^{-\nu} = 112 > L = 96$, the critical fluctuations take over. The walls start to "feel" each other strongly, their influence extends over the whole pore and as a result the magnetization inside the pore has a minimum for $\tau \sim 0.005$. For still lower value of τ m_{mid} saturates.

Figures 7 and 8 show the behavior of the adsorption Γ at the critical temperature. Figure 7 plots Γ/L against H for H between -1 and $+1$. The shape of this function has a familiar "step-like" form which, due to the presence of positive surface fields is shifted towards negative values of H (see insert), *i.e.* Γ takes on the zero value for $H \sim -0.00255$. Figure 8 shows the log-log plot of $|\Gamma|/L$ *versus* $|H|$. The straight line has a slope 1/15 so that the predicted behavior $\Gamma \sim |H|^{1/\delta}$ (Eq. (15)) with $\delta = 15$ in the $d = 2$ Ising model is obeyed in the range of $|H|$ between 0.3 and 0.9.

The sequence of the critical magnetization profiles for various bulk magnetic fields ranging between -10^{-7} and -1 is shown in Figure 9. The critical profiles are flat inside the pore only for such extremely weak bulk fields as -10^{-7} or much stronger, *i.e.* $H \leq -0.01$. In the intermediate range of H the bulk and surface fields compete and the profiles are much more curved.

4 Summary

We studied $d = 2$ Ising strips ($L \times \infty$) with competing bulk and surface fields near the bulk criticality using the DMRG method [12], which allows for obtaining very accurate results [6]. Physically our system describes for example a single idealized pore with attractive walls, containing a nearly critical fluid in contact with a bulk reservoir. In this example of our system the bulk-like field is related to the difference between the chemical potential and its critical value.

Our results in general confirm the recent theory of the critical adsorption in a confined system in the case of competing bulk and surface fields [7]. We have shown that the behavior of the adsorption Γ as a function of the reduced temperature τ strongly depends on the strength of the bulk field H for $\tau > L^{-1/\nu}$, whereas for $\tau \ll L^{-1/\nu}$ Γ saturates at positive or negative value determined by H and H_1.

We verified that three distinct field ranges occur, with qualitatively different shapes of $\Gamma(\tau)$. The different field intervals are, as previously found, determined by the value of the parameter $\tau_H = (\mathcal{A}|H|L)^{1/(\Delta-\nu)}$ ($\mathcal{A}$ is the amplitude related to susceptibility) and we confirm that the strong-field region is approximately given by $\tau_H > 1$, whereas the weak field region by $\tau_H < \tau_0 \sim L^{-1/\nu}$. Thus the strong- and the weak-field intervals are larger then the approximate estimation. The conditions for the strong and the weak field intervals are derived on the basis of an approximate formula, thus rather the order of magnitude, not the actual value of the field can be predicted. The numerical values of H obtained in the calculations slightly differ from the estimated values (the strong field region corresponds to -4×10^{-3} not to -10^{-2} and the weak field region to 10^{-3} not to 2×10^{-4}). In both these regions our results qualitatively agree with the earlier MF results.

In the intermediate field range the form of $\Gamma(\tau)$ agrees with the MF results only in a limited range of sufficiently strong H. For $|H|$ between 10^{-3} and 3×10^{-3} (τ_H between 0.07 and 0.24) we observe *qualitatively new* behavior. In addition to the maximum of Γ present in the intermediate field region for $\tau \sim \tau_H$, a *minimum* appears for $\tau \sim \tau_0$, and only for smaller $\tau \ll \tau_0$ the saturation takes place, as expected. The peculiar behavior of $\Gamma(\tau)$, not observed within the MF occurs for $\tau \sim \tau_0$, where the extent of fluctuations reaches the size of the system and the competition between the effect of adsorbing walls and susceptibility of the core part favouring the dilute phase is particularly strong. Sufficiently close to the critical point the adsorbing effects of the walls appear to dominate, but only for a limited range of H. We do not find simple general arguments which would determine the range of H for which the minimum of $\Gamma(\tau \sim \tau_0)$ occurs. We should stress that the general analysis presented in Section 2 did not concern this temperature region.

The reduced temperature $\tau_0 \sim L^{-1/\nu}$ is very special in a confined geometry. Not only the $\Gamma(\tau)$, but also the solvation force assumes extremum near τ_0 [21]. This special meaning of τ_0 may be related to the rounding of critical point in a confined geometry. As we have shown, near the critical point the adsorption is analytic function of τ at $\tau = 0$, it is rather a very smooth, almost constant function for $\tau < L^{-1/\nu}$. If we consider the extent of correlations and compare it with the size of the system, then the temperature interval $\Big((-\tau_0+1)T_c, T_c(1+\tau_0)\Big)$ corresponds to the correlation extending over the whole sample. The lower boundary of the above interval is of the order of the critical temperature for the capillary condensation. The upper boundary is also special in the sense that physical quantities attain extrema or have inflection points for τ close to τ_0.

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