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Metastability in an SOS model of wetting

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Abstract. Using the transfer-matrix technique and Monte Carlo simulations we examine a one-dimensional SOS model of wetting with unequal attracting potentials at the boundaries. At low temperatures the model has a metastable state with the interface pinned to the boundary of weaker potential. Monte Carlo simulations suggest that the lifetime of this metastable state diverges exponentially with the system size. Above a certain temperature this state becomes unstable and diffusion drives the interface to the boundary of a stronger potential. The transfer matrix of this model contains information about the equilibrium state (the largest eigenvalue) as well as the metastable state (the second largest eigenvalue). Gaps between these two largest eigenvalues and the continuous band close at distinct temperatures. The behaviour of our model is also described in terms of introduced constrained free energy.

1. Introduction

Despite intensive studies over recent decades, metastability still constitutes a challenging problem in statistical mechanics. Even the very existence of metastable states is a highly nontrivial issue. It is believed that in the thermodynamic limit and in short-range interacting systems such states eventually decay although their lifetime τ might be very long. Only in certain long-range interacting systems are such states known to have an infinite lifetime [1]. One of the main objectives in studying metastable systems is to infer their quasistationary properties from suitably generalized principles of equilibrium statistical mechanics. In this context an important result of Langer states that for a certain class of models the nucleation rate is proportional to the imaginary part of the free energy of the metastable state, which is obtained by analytic continuation of the equilibrium free energy [2]. Moreover, Newman and Schulman [3] suggested that some information on metastable states and their decay can be obtained from the spectrum of the transfer matrix. Probably the most thorough confirmation of these (not rigorous) results was obtained for certain lattice systems and in particular for the Ising model (for a recent discussion of metastability and an extensive list of references see [4]). However, as we have already mentioned, in these short-range interacting models metastability is only a quantitative effect. Moreover, to study metastability in the Ising model we have to include a magnetic field or introduce specific boundary conditions, which precludes a rigorous analysis and considerably hampers numerical approaches even for static properties. It would be desirable to find some other short-range interacting models of metastability, which would be easier to analyse and in which metastability would be a qualitative effect, i.e. the lifetime of the metastable state would be infinite (in the thermodynamic limit) for a certain range of parameters.

In this paper we show that a certain one-dimensional (1D) SOS model possesses a metastable state. With respect to the static properties, the model is quite simple and its

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thermodynamic quantities, such as free energy and internal energy, can be determined exactly even in the metastable states. These quantities are actually obtained from the largest and second largest eigenvalues of the transfer matrix of the model. Moreover, in this model at a certain temperature T_{M} the metastable state loses its (meta)stability and at higher temperatures diffusion, relatively quickly, drives the interface into the stable (equilibrium) state. Thus, the transition at T_{M} is a kind of dynamical phase transition. We also introduce the constrained free energy which is actually the free energy with the interface fixed at the boundaries. Numerical evidence is presented that such free energy not always converges to the ordinary free energy (obtained, for example from the largest eigenvalue of the transfer matrix) but might converge to the free energy of metastable states. The fact that the bulk free energy depends on the boundary conditions is in our opinion quite surprising.

This paper is organized as follows. In section 2 we introduce the model and examine the spectrum of its transfer matrix. Results of Monte Carlo simulations are presented in section 3. In section 4 we describe our model in terms of constrained free energy. Conclusions and possibilities of extensions of our research are described in section 5.

2. Model and its transfer matrix

Let us consider a 1D SOS model described by the Hamiltonian:

$$H = J\sum_{i=1}^{N_\parallel}|h_i - h_{i+1}| + v_1\sum_{i=1}^{N_\parallel}\delta_{h_i,0} + v_2\sum_{i=1}^{N_\parallel}\delta_{h_i,N_\perp} \tag{2.1}$$

where $\{h_i\}$ are discrete height variables $h_i = 0, 1, \ldots, N_\perp$ and the boundary potentials v_1, v_2 are negative. In the following we put $J = 1$ and $v_1 > v_2$. The horizontal and vertical sizes are denoted as $N_\parallel$ and $N_\perp$, respectively.

Similar models, namely with only one boundary potential have already been studied in the context of wetting phenomena [5]. In such a case at low temperature the interface described by the Hamiltonian (2.1) is localized at the attracting boundary and only above a certain critical temperature T_{w} does it delocalize. Thermodynamic properties of the model (2.1) with only one attracting potential can be easily obtained using the transfer-matrix technique. For example, assuming that only the $h = 0$ potential is present and the limit $N_\perp \to \infty$ is taken, the largest eigenvalue λ_1 of the transfer matrix

$$T_{h,h'} = \mathrm{e}^{-\beta(|h-h'|+v_1\delta_{h,0})} \tag{2.2}$$

can be easily found assuming that its eigenvector has the form $\psi_1(h) = \mathrm{e}^{-\mu h}$ for $h > 0$ and $\psi_1(0)$ is determined separately. One obtains [5]:

$$\lambda_1 = \frac{(\mathrm{e}^{-\beta v_1} - 1)(1 - \mathrm{e}^{-2\beta})}{1 - \mathrm{e}^{\beta v_1} - \mathrm{e}^{-2\beta}} \tag{2.3}$$

where $\beta = \frac{1}{k_{\mathrm{B}}T}$ and k_{B} is the Boltzmann constant which in the following is put to unity. The parameter μ might be regarded as an inverse of one of the characteristic lengths of the system [5]. From the eigenvalue λ_1 one can easily obtain free energy $f = -\beta^{-1}\ln\lambda_1$ and internal energy $u = -\frac{\partial}{\partial\beta}\ln\lambda_1$. Assuming an eigenvector of oscillatory form, one can also determine other eigenvalues of the transfer matrix (2.2) which constitute a continuous band of extended states. The largest eigenvalue of this band is given by the following expression:

$$\lambda_{\mathrm{extended}} = \frac{1 + \mathrm{e}^{-\beta}}{1 - \mathrm{e}^{-\beta}}. \tag{2.4}$$

The extended states describe the free interface (let us note that (2.4) does not depend on v_1). The wetting temperature in this model is given as a solution of the following equation [5]:

$$e^{-v_1/T_{w_1}} = (1 - e^{-1/T_{w_1}})^{-1}. \tag{2.5}$$

A version of model (2.1), where neighbouring heights differ at most by unity (RSOS), with $v_1 = v_2$ has been studied several years ago by Privman and Švrakić [6] in the context of equilibrium finite-size scaling. However, these authors did not examine the case of $v_1 \neq v_2$ where the model has a metastable state and which in our opinion is worth further examination.

The static free energies of model (2.1) can be obtained from the eigenvalues corresponding to the two bound states of the transfer matrix:

$$T_{h,h'} = e^{-\beta(|h-h'|+v_1\delta_{h,0}+v_2\delta_{h,N_\perp})}. \tag{2.6}$$

The form of these eigenvectors can be easily found in the limit $N_\perp \to \infty$. In this limit the bound state $\psi_1(h) = e^{-\mu h}$ does not 'feel' the potential v_2 at the opposite boundary and thus this is also a bound state for the transfer matrix (2.6) with the corresponding eigenvalue λ_1 the same as in (2.3). However, in the same way one can argue that the bound state localized at the opposite boundary $h = N_\perp$ and having the form $\psi_2(h) = e^{-\mu'(N_\perp - h)}$ does not 'feel' the potential v_1 and thus this is also an eigenvector of (2.6). The eigenvalue λ_2 corresponding to $\psi_2(h)$ is given by (2.3) with v_1 replaced by v_2.

To confirm our predictions concerning the spectrum of (2.6) we diagonalized this matrix numerically. Since the dimension of (2.6) increases linearly with $N_\perp$, we could perform accurate diagonalization even for $N_\perp \sim 1000$. We found that indeed for increasing $N_\perp$ the largest and second largest eigenvalues rapidly converge to (2.3) with potentials v_2 and v_1, respectively. With our choice of potentials ($v_1 > v_2$) only the first eigenvector corresponds to the equilibrium state (the interface pinned to the $h = 0$ line) while the second one corresponds to the metastable state (the interface pinned to the $h = N$ line). In figure 1 we present the three largest eigenvalues for $v_1 = -2$ and $v_2 = -3$ as functions of temperature. Numerical diagonalization has been performed for $N_\perp = 500$. One can easily see that gaps between these eigenvalues close at distinct temperatures which we denote by T_{w1} and T_{w2} ($T_{w1} < T_{w2}$). Moreover, our numerical results show that these temperatures are very close to the wetting temperatures (2.5) which for our choice of potentials are equal to $T_{w1} = 2.078\,087\ldots$ and $T_{w2} = 2.616\,123\ldots$, respectively.

It is interesting to consider the limit $v_1 = v_2$. In such a case, in the thermodynamic limit we have $\lambda_1 = \lambda_2$. There is, however, no contradiction with the Frobenius theorem [7] about nondegeneracy of the largest eigenvalue of the positive matrix because for $N_\perp \to \infty$ almost all elements of the transfer matrix vanish. For every finite $N_\perp$ two largest eigenvalue λ_1 and λ_2 are, of course, nondegenerate even for $v_1 = v_2$. Let us also note that in this case in the thermodynamic limit we have spontaneous symmetry breaking for $T < T_{w1} = T_{w2}$.

For comparison with Monte Carlo data, in figure 2 we also present the internal energies of both bound states and extended state as calculated from the derivatives of λ_1, λ_2 and $\lambda_{\text{extended}}$.

3. Monte Carlo simulations

To examine the dynamical properties of our model, we resorted to standard Monte Carlo simulations [8]. In each time step the interface at a randomly chosen site can increase or decrease its height by unity or it can remain at the same height. When the move increases the

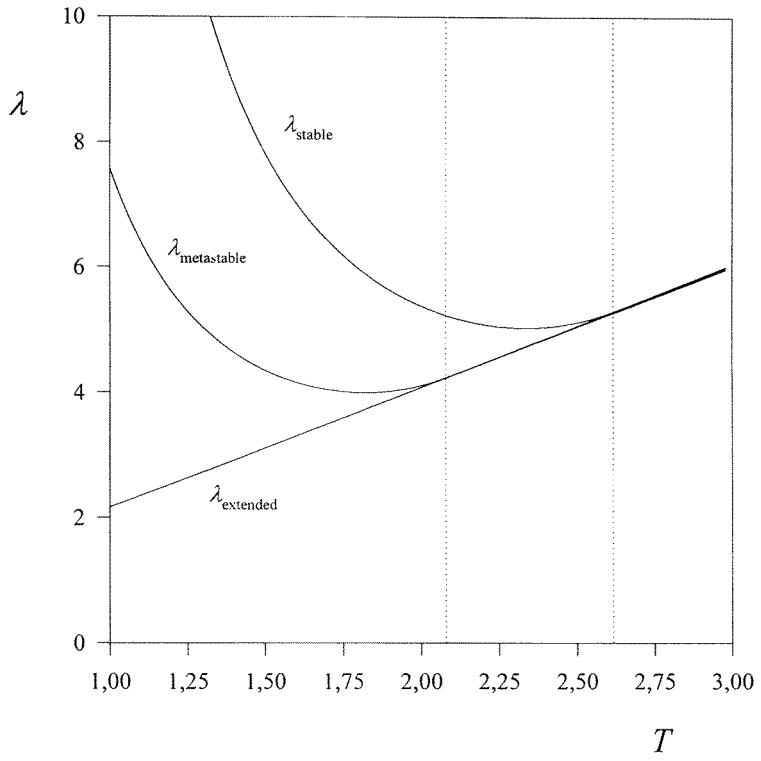

Figure 1. The three largest eigenvalues of transfer matrix (2.6) as functions of temperature. Vertical dotted lines indicate the wetting temperatures $T_{w1} = 2.078\,087\ldots$ and $T_{w2} = 2.616\,123\ldots$. Within the resolution of our figure the exact expressions given by (2.3) and (2.4) are indistinguishable from our numerical results.

total energy by ΔE, then it is accepted with the probability $p = e^{-\beta\Delta E}$. Initially the interface is placed at a metastable boundary, i.e. at $h = 0$. We present results for $N_\perp = N_\parallel = N$ but our simulations show that for other aspect ratio qualitatively similar results are obtained. However, it is possible that when the thermodynamic limit is approached in another way (e.g. $N_\perp, N_\parallel \to \infty$ with $N_\perp/N_\parallel \to 0$) our results, especially those concerning the dynamical properties, would be considerably modified. The importance of the way of taking the thermodynamic limit was already emphasized by Nijmeijer [9] who studied equilibrium properties of a continuous version of model (2.1) with $v_1 = v_2$.

A typical Monte Carlo run which shows internal energy as a function of temperature for $N = 60$ and 200 000 Monte Carlo steps for each data point is shown in figure 2. As expected, at low temperatures the system remains in the metastable state and at higher temperature it jumps to the equilibrium state. This jump happens very close to T_{w1} and we believe that in this model this is also the temperature T_M of the dynamical transition where a metastable state dramatically loses its stability. Let us recall that at this temperature, according to figure 1, the gap between the second and third eigenvalue closes.

To confirm that indeed at $T = T_{w1}$ the qualitative change in the properties of the metastable state takes place, we measured the average lifetime of metastable state τ defined as a time needed to reach the state with certain threshold internal energy u_t. For $T = 1.5, 1.8$ we chose $u_t = -2$ while for $T = T_{w_1}$ and $T = 2.3$ we chose $u_t = -1$ and $u_t = -0.1$,

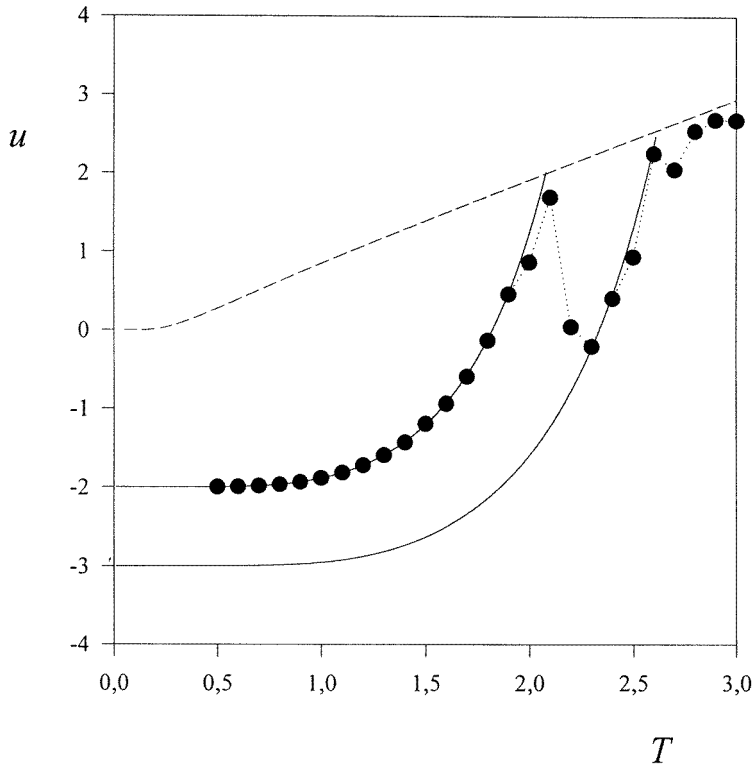

Figure 2. The internal energy calculated from the eigenvalues of the two bound states of the transfer matrix (2.6) (——) and the internal energy of the extended state (– – –) for $v_1 = -3$ and $v_2 = -2$. Full circles show the results from the Monte Carlo simulations.

respectively. Justification for this somewhat arbitrary definition is that, as we noted, once the system reaches this energy, further evolution towards the equilibrium state is very fast. For $T = T_{w_1}$ and $T = 2.3$ we also had to measure the location of the interface to ensure that reaching the threshold energy the system is really close to the boundary with the stronger potential (i.e. is close to the equilibrium state).

Our results for several temperatures are shown on a logarithmic scale in figure 3. One can see that, indeed, there are two regimes with different size dependence of τ. For $T < T_{w1}$ the lifetime τ rapidly increases with the system size N. An increasing slope suggests that asymptotically the power-law increase $\tau \sim N^a$ is rather unlikely. Using the least square method we fitted our data to the function $\tau = ab^{N^\omega}$ and we noted that for increasing N the exponent ω is close to unity. Thus, in this temperature range the characteristic time τ probably increases exponentially $\tau \sim b^N$. Such a rapid increase of τ implies that the metastable state is very stable. Let us notice that the exponential divergence of τ is an indication of broken ergodicity [10]. Usually, however, the breakdown of ergodicity decomposes the system into components of equal free energy. This is, for example, the case in the Ising model, where below the critical temperature each of the two ferromagnetic phases have the same free energy. This is clearly not the case in our SOS model.

For $T \geqslant T_{w1}$ we observe different size dependences of τ. Namely, our results show that in this temperature range we have $\tau \sim N^3$. Although τ also diverges in the thermodynamic limit, this divergence does not indicate metastability. Indeed, we checked that simulating

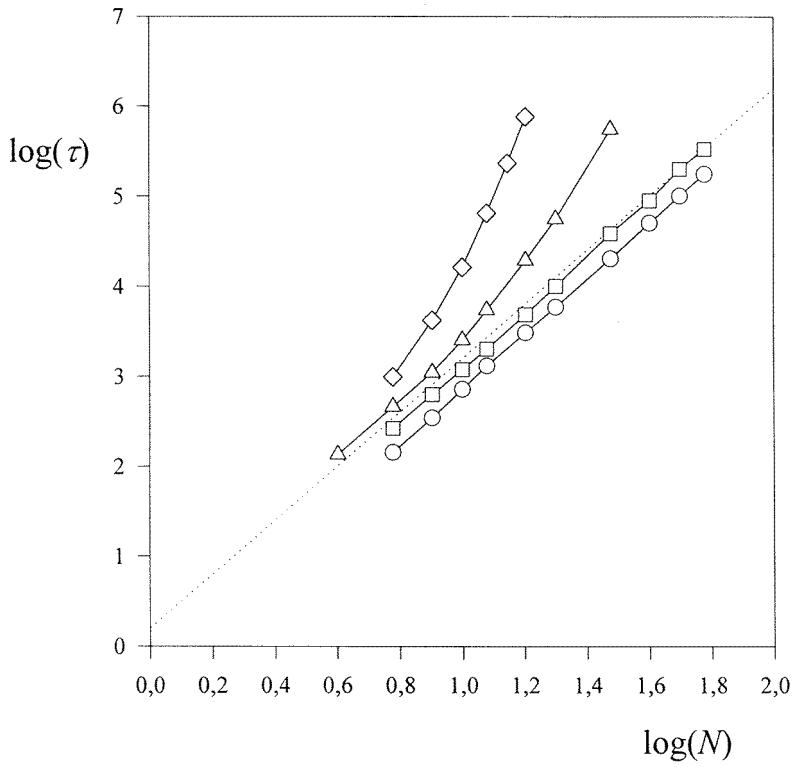

Figure 3. Size dependence of the lifetime τ in the logarithmic scale for $T = 1.5$ (◇), $T = 1.8$ (△), $T = T_{w1} \sim 2.078\,087$ (□) and $T = 2.3$ (○). The dotted curve has a slope corresponding to $\tau \sim N^3$. Each point represents an average over 10 000 runs and only some results for largest system size are obtained averaging over 1000 runs.

the system with $v_1 = -3$ and $v_2 = 0$, i.e. with no attracting potential at the boundary where the interface is placed initially, we have also the same size dependence $\tau \sim N^3$, which is thus related with the purely diffusive spreading of an interface.

It would be desirable to understand the simple relation $\tau \sim N^3$ at least qualitatively. It seems to us that in this temperature range the diffusion of our interface is related with diffusion of polymers. Indeed, there is numerical evidence supported by some scaling arguments [11] that the characteristic time needed for the polymer to diffuse the distance of its own size N increases as N^3 in agreement with our observations. Analytical arguments supporting such a behaviour are best explained using the so-called Rouse model [12]. In this model, which is basically a Gaussian model of a polymer, one can show [13] that the effective diffusion constant of a polymer decreases as $1/N$ where N is the number of monomers. On the other hand, the average square spread during the time t in the diffusion process increases like Dt where D is the diffusion constant. Combining this result with the Rouse model prediction $D \sim 1/N$ we easily arrive at $\tau \sim N^3$.

To close this section let us compare metastability in our model with the Ising model. In the latter model metastability appears when, for example the positively magnetized system (below a critical temperature) is immersed in the negative magnetic field. Subsequent evolution to the equilibrium, negatively magnetized phase proceeds through saddle-point configurations which are droplets of negative spins. In model (2.1) the 'bulk' field is the

boundary potential at the opposite end of the system. Thus, to reach the equilibrium state the system has to proceed through spike-like configurations (stretching from one boundary to another). The energy of these saddle-point configurations is, however, much higher (grows linearly with N) and this is the basic reason why the metastable state in model (2.1) is so stable.

4. Constrained free energy

In this section we describe the behaviour of our model in terms of constrained free energy $f(m)$ which is defined as follows

$$\mathrm{e}^{-\beta N_{\|} f(m)} = \sum_{\{h_i\}}{}' \mathrm{e}^{-\beta H} \qquad 0 \leqslant m \leqslant 1 \tag{4.1}$$

where the prime indicates that the summation is performed only over h_i with $i = 2, 3 \ldots N_{\|} - 1$ while h_1 and $h_{N_{\|}}$ are kept fixed and $h_1 = h_{N_{\|}} = mN_{\perp}$=M. For computational purposes we replace the right-hand side of (4.1) with $(T^{N_{\|}})_{MM}$ which is equivalent to (4.1) in the thermodynamic limit; T is the transfer matrix (2.6). Plots of $f(m)$ as a function of m for $N_{\perp} = N_{\|} = 512$ are shown in figure 4 and the size dependence is presented in figure 5.

A surprising result is that the extensive (with $N_{\|}$) quantity $f(m)$, depends on m, i.e. on the boundary conditions. The most interesting feature of $f(m)$ suggested by our numerical

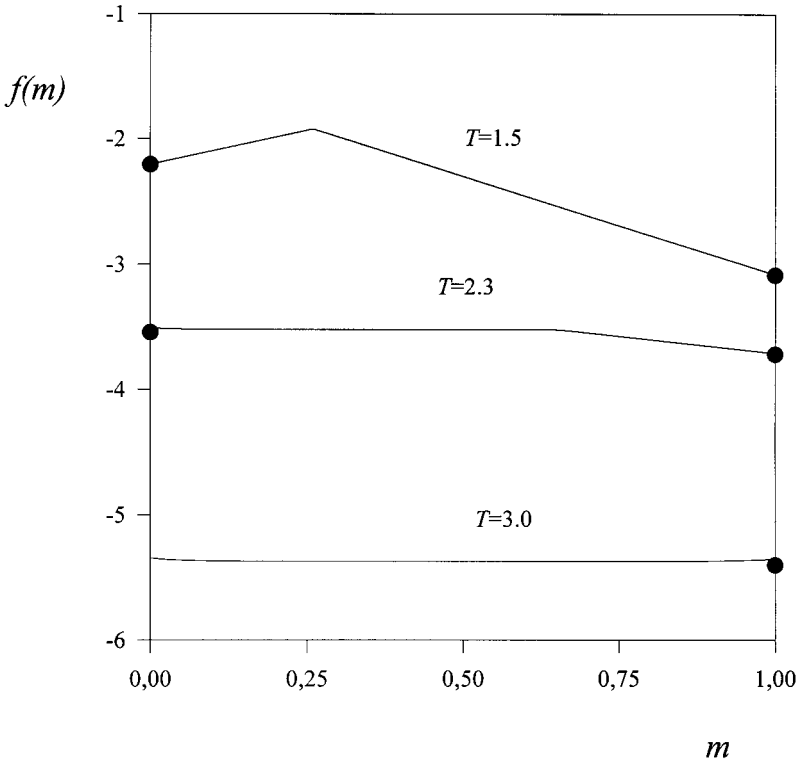

Figure 4. The constrained free energy $f(m)$ as a function of m. Full circles denote free energies as calculated from the spectrum of the transfer matrix (2.6). Numerical calculations were done for $N = 512$ and within the resolution of the figure finite-size effects are negligible.

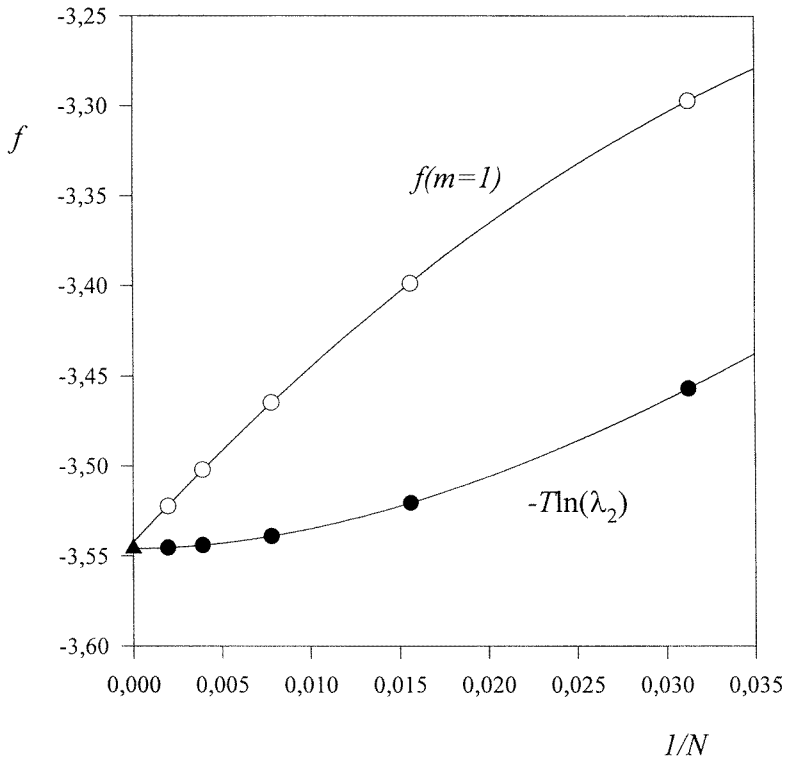

Figure 5. The free energy of extended state for $T = 2.3$ as a function of $1/N$ calculated from the second largest eigenvalue (●) of transfer matrix (2.6) and using (4.1) with $m = 0$ (○). Results of both methods seem to converge to the same value. The triangle on the vertical axis corresponds to the exact free energy of extended state as given (2.4). At this temperature the second and the third eigenvalues are degenerate in the thermodynamic limit (see figure 1).

calculations is that for $T < T_{w_1}$, $f(0)$ equals the free energy of the metastable state. Moreover, for $T_{w_1} < T < T_{w_2}$ and sufficiently small m, $f(m)$ equals the free energy of the extended state. It would be interesting to examine whether in more general cases the boundary-dependent free energy is the indication of metastability. Let us notice that the extended state is also in some sense metastable: the interface placed initially in the position with finite m reaches the equilibrium state after the time which most likely grows like N^3 (provided $T_{w_1} < T < T_{w_2}$).

Finally let us emphasize that the m-dependence of $f(m)$ is a consequence of taking the thermodynamic limit by increasing both sizes $N_\perp$ and $N_\parallel$ simultaneously. This effect would disappear if we took the limit $N_\parallel \to \infty$ first. In such a case the largest eigenvalue of transfer matrix would dominate the sum in (4.1) independently of m.

5. Conclusions

We showed that in a certain range of temperatures a simple 1D SOS model has an exponentially long-lived metastable state. In this model a number of static properties are known exactly or can be calculated very accurately. Such a wealth of results makes this model very useful for testing some other approaches developed in the context of metastable

systems, e.g. Rikvold's constrained transfer matrix technique [4, 14]. The most interesting conclusion which follows from our results is that the metastable state, at least in certain models, can be examined using suitably generalized methods of equilibrium statistical mechanics. Indeed, in our model the free energy of metastable state is encoded in the standard transfer matrix as a second largest eigenvalue. Moreover, as follows from section 4, this quantity can be obtained just by imposing certain boundary conditions. It is, however, not known to us to what extent these results generalize to other systems with metastable state [15].

Is the kind of metastability which we described above restricted to only model (2.1) or might it appear in some other models as well? Some years ago Forgacs *et al* [16] studied a model where there are also two lines of attracting potential but one of them was in the interior of the model. They have shown that for such a model the continuous delocalization of the interface does not take place; instead at a lower temperature there is a discontinuous jump of the interface to the other (interior) line of attracting potential. Their calculations are exact in the sense of equilibrium statistical mechanics but such an approach obviously misses any metastable effects. However, in our opinion, in their model metastability will appear for the same reasons as in our model (2.1). Namely, from our results it follows that for any temperature below the wetting transition, an interface pinned to the boundary by attractive potential remains in this state (in the thermodynamic limit for infinitely long time) even if there is another more stable (equilibrium) state. The last statement applies to the case when both attractive boundaries are spatially separated over the distance N and, in our opinion, this is essential for the (presumably) exponential with N divergence of τ. Such a separation in a slightly different geometry appears in the model examined by Forgacs *et al* and thus we expect that very strong metastable effects are present in their model too. Thus, if our arguments are correct, Forgacs *et al*'s predictions concerning experimental relevance of the distant defects and imperfections in the unbinding transition require serious reconsiderations. Checking that indeed metastability suppresses the first-order transition in the Forgacs *et al*'s model is, however, left for the future.

Acknowledgments

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