

SOLVATION FORCE FOR SYSTEMS IN A SQUARE-LIKE GEOMETRY

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Abstract. The solvation force of a simple fluid confined between four identical walls is studied with different settings of surface fields. Our numerical results, obtained by density-matrix renormalization techniques for a strip-like systems of widths up to 500 lattice constants, provide excellent the bulk free-energy extrapolation. The influence of surface fields setting on the pseudo-coexistence line and on the solvation force is presented.

Introduction

When simple fluids are confined between walls, their properties may differ dramatically from those in bulk [1]. Understanding the influence of confinement on the phase behavior of the fluid is relevant for fluids in porous solids and for experiments performed with nanomachines. In the later case there is a hope that repulsive solvation force acting at the nano-scale would allow engineers to design novel nanodevices [2].

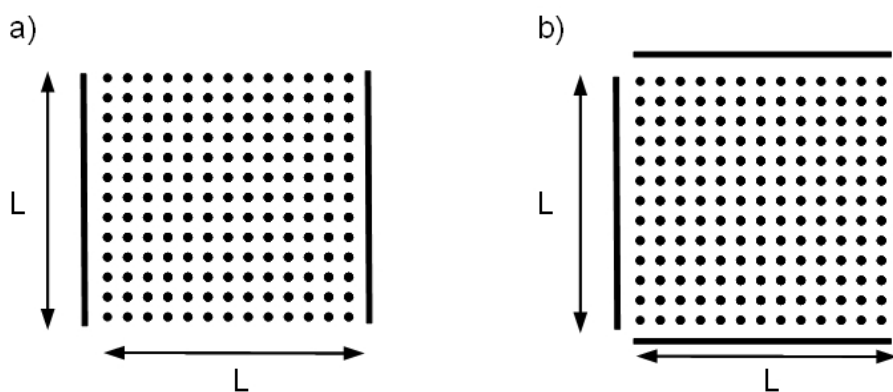


Fig. 1. Two settings of surface fields: a) only on two opposite sides of a square, b) on all sides of a square

When the confining walls attract the atoms of the fluid, the phenomenon of capillary condensation occurs at temperatures T below the bulk critical temperature

T_c whereby the bulk first-order phase transition (the coexistence line) is displaced in the (μ, T) plane: condensation of the gas to liquid occurs at a value of the chemical potential μ smaller than in bulk [3]. On the other hand, fluid mediated interactions between two surfaces appear, usually referred to as the solvation force f_{solv} , that is a generalized force conjugate to the distance between the walls. For temperatures sufficiently far away from the bulk critical temperature T_c , solvation force f_{solv} decays exponentially, but near T_c , f_{solv} becomes long ranged as a result of critical fluctuations, a phenomenon which is known as the critical Casimir effect [4, 5].

The solvation force has been investigated very intensively recently [6], especially when the experiment with a classical binary liquid mixture confirmed its existence [7]. Nevertheless, the understanding of its behavior is far from being complete. One of the issues which has not been investigated is how the properties of the solvation force depends on more complex settings of the surface fields then for a strip-like geometry. That is why, in this article we deal with the system in a square-like geometry with various field settings.

1. Model

Here we exploit the mapping between fluids and the Ising model and study Ising spin systems subject to identical surface fields [8]. The system we consider is an Ising spin system in a square-like geometry $L \times L$ subject to surface fields with the same magnitude h_l . For finite L there are no true thermodynamic singularities and quantities such as the free energy and the magnetization depend smoothly on temperature, surface and bulk fields. Therefore, the magnetization jump on the coexistence line, characteristic for the first-order phase transition, is replaced by a sharp but continuous growth. Therefore, it is more correct to use the name: the pseudo-coexistence line.

Two setting of surface fields are presented in Figure 1. At each site, labeled i, j , there is an Ising spin variable taking the value $s_i = \pm 1$. We assume nearest-neighbor interactions of strength J and the reduced bulk magnetic field h (corresponding to the chemical potential μ). The Hamiltonian for the case with two reduced surface fields is:

$$H = -J \sum_{\langle i,j \rangle} s_i s_j - h \sum_{i=1}^N s_i - h_1 \sum_{i=1}^L (s_{1,i} + s_{L,i}) \quad (1)$$

where the first sum runs over all nearest-neighbor pairs of sites, while the last one over the first and the L -th column. The Hamiltonian for the case with four reduced surface fields has the following form:

$$H = -J \sum_{\langle i,j \rangle} s_i s_j - h \sum_{i=1}^N s_i - h_1 \sum_{i=1}^L (s_{1,i} + s_{L,i}) - h_1 \sum_{i=1}^L (s_{i,1} + s_{i,L}) \quad (2)$$

where last two sums cover all surface sites.

The total free energy per site may be written as:

$$f(L, T, h, h_1) = f_b(T, h) + \frac{2f_w(T, h, h_1)}{L} + \frac{f^*(L, T, h, h_1)}{L} \quad (3)$$

where f_b is the bulk free energy, f_w is the L -independent surface excess free-energy contribution from each surface, and f^* is the finite-size contribution to the free energy [5]. All energies are measured in units of J and the temperature in units of J/k_B . The quantity f^* , which vanishes for $L \rightarrow \infty$, gives rise to the solvation force.

$$f_{solv} = - \left(\frac{\partial f^*}{\partial L} \right)_{T, h, h_1} \quad (4)$$

Our calculations on the square have been done by means of the finite-size transfer matrix method [9].

2. Results

It is well known that the combined effect of identical boundary fields (positive here) and confinement shifts the phase coexistence from the bulk coexistence line ($h = 0$) to a finite value of h (negative here). In order to see how the both settings of surface fields affect this shift, we have studied the square with $L = 11$. To determine the pseudo-coexistence line we have scanned the phase diagram (h, T) at fixed temperature. As one can see, the presence of surface fields on all walls requires the larger (in magnitude) h to compensate positive surface fields ($h_1 = 0.1$) compared to the case with two surface fields.

To calculate the solvation force from Eq. (4), determination of the bulk free energy is necessary. Therefore we have applied the density-matrix renormalization technique, which is doing excellent for the Ising strip-like systems. This method, which is based on the transfer-matrix approach, provides a numerically very efficient iterative truncation algorithm for constructing the effective transfer matrices for strips of fixed width and infinite length [5, 10]. In the present paper, to extrapolate the strip free energies to the bulk free energy the systems of widths up to $L = 500$ lattice constants were studied.

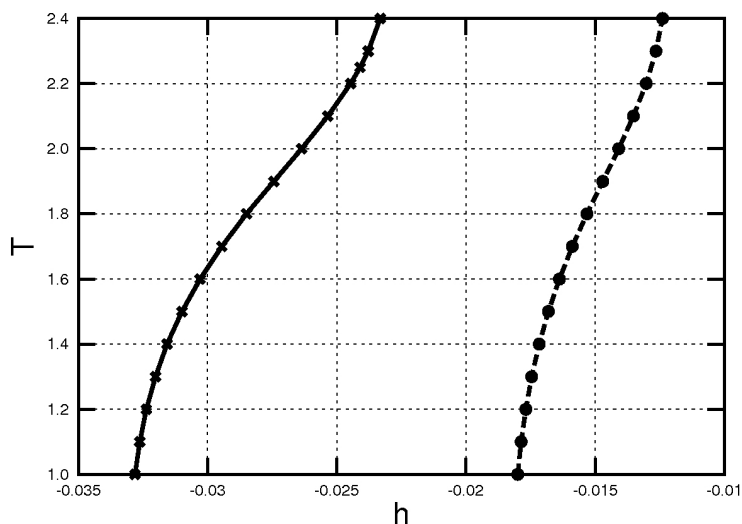


Fig. 2. The pseudo-coexistence curves at the square (11×11) with two (dot symbols) and four surface fields (cross symbols) for $h_1 = 0.1$

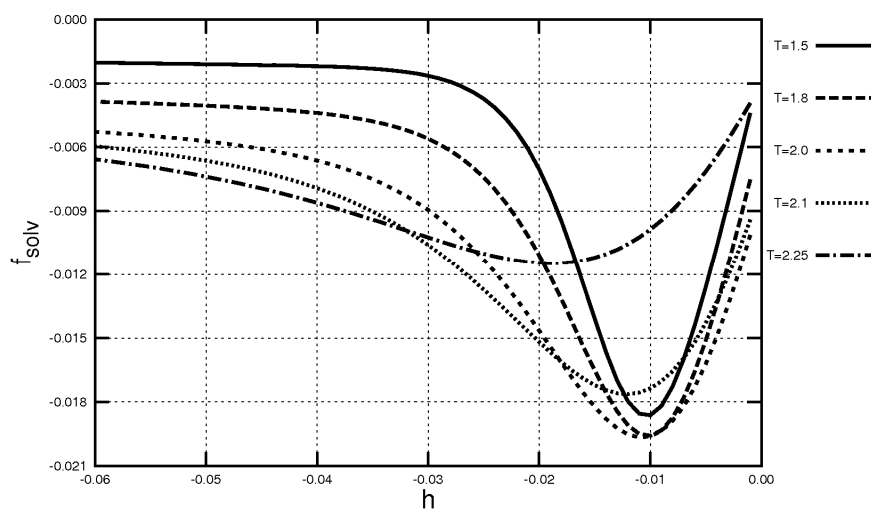


Fig. 3. The solvation force (in units of $k_B T$) at the square (15×15) with two surface fields for $h_1 = 0.1$

The curves presented in Figures 3 and 4 are similar in nature. With the increase of $|h_1|$, the value of the solvation force rapidly decreases, passes through a minimum, and next grows softer, until it reaches almost a constant value. The sign of the solvation force is of particular interest. In our case, when it is always negative, the force is attractive for all temperatures, which leads to the presence of additional pressure.

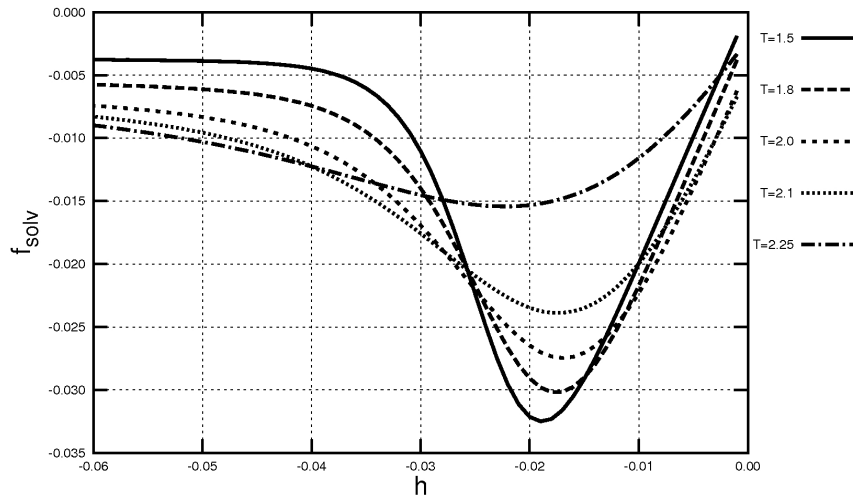


Fig. 4. The solvation force (in units of $k_B T$) at the square (15×15) with four surface fields for $h_1 = 0.1$

It can be assumed that the shape of the f_{solv} curve (in particular the position of its minimum) is associated with the location of the coexistence curve. However, we have considered relatively small systems and the finite-size corrections are significant, so we can hardly draw firm conclusions.

3. Discussion

We have confirmed the importance of surface field settings on the capillary condensation phenomena and on the magnitude of the solvation force. In the case of the four surface fields the increase of solvation force leads to larger values of effective pressure, than for the case with only two surface fields. However, to minimize the influence of the finite-size effects, these computational studies require larger systems.

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