MATEC Web of Conferences **145**, 01009 (2018) https://doi.org/10.1051/matecconf/201814501009
NCTAM 2017

Order parameter profiles in a system with Neumann – Neumann boundary conditions

Vassil M. Vassilev[1,⋆], *Daniel M.* Dantchev[1,⋆⋆], and *Peter A.* Djondjorov[1,⋆⋆⋆]

[1] *Institute of Mechanics, Bulgarian Academy of Sciences, Acad. G. Bonchev St., Bl. 4, 1113 Sofia, Bulgaria.*

Abstract. In this article we consider a critical thermodynamic system with the shape of a thin film confined between two parallel planes. It is assumed that the state of the system at a given temperature and external ordering field is described by order-parameter profiles, which minimize the one-dimensional counterpart of the standard ϕ^4 Ginzburg–Landau Hamiltonian and meet the so-called Neumann – Neumann boundary conditions. We give analytic representation of the extremals of this variational problem in terms of Weierstrass elliptic functions. Then, depending on the temperature and ordering field we determine the minimizers and obtain the phase diagram in the temperature-field plane.

1 Introduction

In the current article we consider one generic mean-field model describing a phase transition in a film in which the surfaces order exactly at the same temperature as the bulk. Mathematically this is described by imposing (Neumann, Neumann) boundary conditions on the order parameter. This type of boundary conditions can be achieved in a magnetic system. They can, in principle, be also accomplished for a fluid, but a very precise arrangement for the surfaces shall be performed so that the wall-fluid interaction exactly matches that one of the interactions inside the fluid system. Let is recall that in the vicinity of the critical temperature T_c of the bulk system, one observes a diversity of surface phase transitions [1, 2] of different kind in which the surface orders before, together, or after ordering in the bulk of the system, which are known as normal (or extraordinary), surface-bulk and ordinary surface phase transitions. Mathematically these surface transitions correspond to different boundary conditions imposed on the order parameter characterizing the system. For a simple fluid or for binary liquid mixtures the wall generically prefers one of the fluid phases or one of the components. In the vicinity of the bulk critical point the last leads to the phenomenon of critical adsorption [3–15]. This can be modelled by considering local surface field h_1 acting solely on the surfaces of the system. When the system undergoes a phase transition in its bulk in the presence of such surface ordering fields one speaks about the "*normal*" transition [16]. It has been shown that it is equivalent, as far as the leading critical behavior is concerned, to the "*extraordinary*" transition [2, 16] which is achieved by enhancing the surface couplings stronger than the bulk couplings. The usual way one mathematically

⋆The authors gratefully acknowledge the financial support via contract DN 02/8 with Bulgarian National Science Fund.
e-mail: vasivas@imbm.bas.bg
⋆⋆e-mail: danieldantchev@gmail.com
⋆⋆⋆e-mail: padjon@imbm.bas.bg

describes these boundary conditions is to require that the order parameter diverges and, thus, one has the so called $(+,+)$ or $(+,-)$ boundary conditions which differ by the equal, or opposite behaviour of the order parameter in vicinity of the borders of the system. There is also a special case of surface enrichment, when the surface orders simultaneously with the bulk. This is normally termed surface-bulk, or special phase transition. One way to achieve it is to enhance the coupling on the surface and very near to it, so that one achieves the delicate balance needed to get the both orderings to become simultaneously. On a mean field level this can be described by imposing Neumann boundary conditions on the boundary. These are the boundary conditions studied in the current article.

2 Statement of the problem

Let us consider an Ising type critical thermochemical system having the shape of a thin film confined between two parallel planes placed at a distance L from one another. Then, within the framework of the Ginzburg–Landau theory of phase transitions, see e.g. [17, 18], the state of the system is described by the minimizers of the one-dimensional counterpart

$$\mathcal{F}\left[\phi;\tau,\eta,L\right] = \int_0^L \mathcal{L}(\phi,\phi')dz, \qquad \mathcal{L}(\phi,\phi') = {\phi'}^2 + \phi^4 + \tau\phi^2 - \eta\,\phi, \tag{1}$$

of the standard ϕ^4 Ginzburg–Landau Hamiltonian in terms of the order parameter $\phi(z)$, $z \in (0, L)$ being the independent variable associated with the position of a layer perpendicular to the bounding planes. Here, the parameters τ and η represent the temperature of the system and the applied ordering field, respectively, and the prime indicates differentiation with respect to the variable z.

Given three real numbers $L > 0$, τ and η, we are interested in the minimizers $\phi = \phi(z)$ of the functional $\mathcal{F}\left[\phi;\tau,\eta,L\right]$, which are:

(i) continuous together with their derivatives up to the second order in the interval $[0, L]$;

(ii) satisfy the so-called Neumann – Neumann boundary conditions

$$\phi'\,(0) = \phi'\,(L) = 0. \tag{2}$$

Actually, (2) are the natural boundary conditions associated with the regarded variational problem, which means that any variation of the order parameter ϕ is allowed at both end points $z = 0$ and $z = L$.

It is clear that each such minimizer should satisfy the corresponding Euler-Lagrange equation, which, on account of expressions (1), reads

$$\phi'' - \phi\left(\tau + 2\,\phi^2\right) + \frac{\eta}{2} = 0. \tag{3}$$

Obviously, the order parameter $\phi_b\,(\tau,\eta,L)$ of the bulk system, which is a constant, with respect to z, solution of equation (3) determined as the real root of the cubic polynomial

$$Q(\phi) = \phi\left(\tau + 2\,\phi^2\right) - \frac{\eta}{2} \tag{4}$$

for which

$$\mathcal{F}\left[\phi_b;\tau,\eta,L\right] = L\left(\phi_b^4 + \tau\phi_b^2 - \eta\,\phi_b\right) \tag{5}$$

attains its minimum, meets the requirements (i) and (ii). Therefore, a minimizer of the regarded functional with the required properties always exists and the question is whether it is ϕ_b or some other (but non-constant) solution $\phi(z)$ of equation (3) such that the conditions (i) and (ii) hold and

$$\mathcal{F}\left[\phi;\tau,\eta,L\right] \le \mathcal{F}\left[\phi_b;\tau,\eta,L\right]. \tag{6}$$

Equation (3) possesses a first integral $\varepsilon(\phi)$ of the form

$$\varepsilon(\phi) = \phi'^2 - \phi^4 - \tau\phi^2 + \eta\,\phi, \tag{7}$$

i.e. $\varepsilon = \varepsilon(\phi)$ is a certain real number on any non-constant sufficiently smooth real-valued solution of equation (3). Thus, the problem we are interested in can be formulated as follows. Given three real numbers $L > 0$, τ and η, find the non-constant real-valued solutions $\phi(z)$ of the equation

$$\left(\frac{d\phi}{dz}\right)^2 = P(\phi), \qquad P(\phi) = \phi^4 + \tau\,\phi^2 - \eta\,\phi + \varepsilon \tag{8}$$

corresponding to certain $\varepsilon \in \mathbb{R}$, which meet the conditions (i), (ii) and (6).

3 Solution of the problem

Let us first express the general solution of equation (8) taking advantage of the fact that the polynomial $P(\phi)$ should have at least one simple real root ρ because of the considered boundary conditions (2). Then

$$\varepsilon = \rho\left(\eta - \rho^3 - \rho\tau\right) \tag{9}$$

as $P(\rho) = 0$, and since the right-hand side of equation (8), that is $P(\phi)$, is a polynomial of fourth degree with respect to the variable ϕ, we can, following [19, pp. 452–455], express each solution of equation (8) in the form

$$\phi(z) = \rho + 3\frac{\eta - 2\rho\left(2\rho^2 + \tau\right)}{6\rho^2 + \tau - 12\wp(z; g_2, g_3)} \tag{10}$$

where $\wp(z; g_2, g_3)$ is the Weierstrass elliptic function with elliptic invariants

$$g_2 = \eta\rho - \rho^4 - \rho^2\tau + \frac{\tau^2}{12}, \qquad g_3 = -\frac{1}{432}\left[27\eta^2 + 72\rho\tau\left(\rho^3 + \rho\tau - \eta\right) + 2\tau^3\right]. \tag{11}$$

Now, taking into account the well known properties of the Weierstrass elliptic functions (see, e.g., [20]), it is evident that each function of form (10) is real-valued provided that $z, \rho, g_2, g_3 \in \mathbb{R}$, just as in the considered case. Consequently

$$\phi'(z) = 36\wp'(z; g_2, g_3)\,\frac{\eta - 2\rho\left(2\rho^2 + \tau\right)}{\left[6\rho^2 + \tau - 12\wp(z; g_2, g_3)\right]^2} \tag{12}$$

and hence, bearing in mind that $\eta - 2\rho\left(2\rho^2 + \tau\right) \neq 0$, since ρ is a simple root of the polynomial $P(\phi)$, $\lim \wp(z; g_2, g_3)|_{z\to 0} = \infty$ and the Weierstrass equation

$$\wp'^2 = 4\wp^3 - g_2\wp - g_3, \tag{13}$$

we see that each function of form (10), which is such that

$$\wp'(L; g_2, g_3) = 0 \tag{14}$$

meets the conditions (i) and (ii).

4 Determination of minimizers and phase diagram

Hereafter we assume $L = 1$ and solve numerically for ρ the transcendental equation (14) for given values of the parameters τ and η. In this way we find the functions of form (10) that satisfy the conditions (i) and (ii). Then, we compare the energy of each such state of the system with the energy corresponding to the constant solution $\phi_b(\tau, \eta, 1)$ and determine the minimizers.

Two minimizers of the functional $\mathcal{F}[\phi; \tau, \eta, 1]$ corresponding to $\tau = -400$ and $\eta = -97.52$ are depicted in Figure 1. They both have energy equal to the energy $\mathcal{F}[\phi_b; \tau, \eta, 1]$ of the "finite" bulk system. As a result of a number of lengthy computations, we have obtained the phase diagram shown in Figure 2.

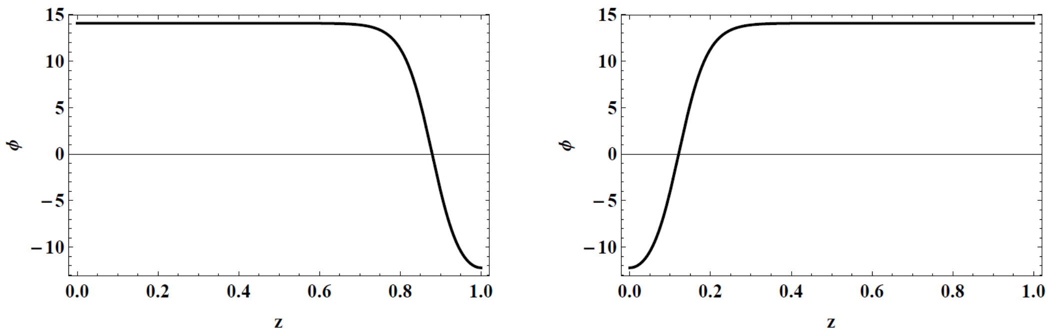

Figure 1. Two minimizers of the functional $\mathcal{F}[\phi; \tau, \eta, 1]$ corresponding to $\tau = -400$, $\eta = -97.52$.

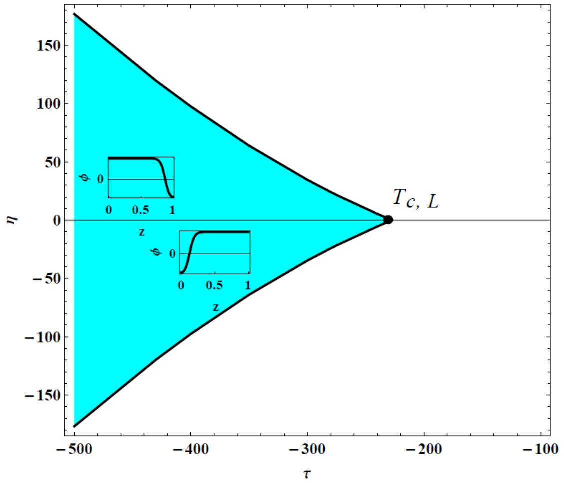

Figure 2. Phase diagram. The blue region in the (τ, η)-plane comprises the values of the parameters τ and η for which there co-exists two non-constant minimizers, while in the white region we find only the constant solution $\phi_b(\tau, \eta, 1)$. All these three types of minimizers co-exists at the border of the foregoing regions indicated by the black thick curves. The point $T_{c,L}$ of coordinates $\tau = -227.556$, $\eta = 0$ marks the critical point of the finite system.

5 Concluding remarks

This is a work in progress, which is focused mainly on the mathematical aspects of the problem. The physics behind this study will be discussed elsewhere. In the current article we have found the general form of the solution, see Eq. (10), of the equation (3) for the order parameter profile of a system with a film geometry subjected to the (Neumann-Neumann) boundary conditions – see Eq. (2). The usual form of the order parameter profile as a function of the orthogonal variable z is shown in Fig. 1. One observes that they are mirror-symmetric with respect to the middle of the system. We have determined the phase diagram of the film system – it is shown in Fig. 2. The two branches of the diagram below the point $T_{c,L}$ are symmetric with respect to the $\eta = 0$ line. For such a system it would be interesting to determine the response functions – the local and the total ones, as well as the force acting between the plates of the system which near $T_{c,L}$ is known as the Casimir force [21–24].

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