

ON THE FINITE-SIZE BEHAVIOR OF ONE BASIC MODEL OF STATISTICAL MECHANICS DESCRIBING SECOND ORDER PHASE TRANSITION

D. DANTCHEV^{1,2,3*}

¹*Institute of Mechanics, Bulgarian Academy of Sciences,
Akad. G. Bonchev St., Block 4, 1113 Sofia, Bulgaria*

²*Max-Planck-Institut für Intelligente Systeme,
Heisenbergstrasse 3, D-70569 Stuttgart, Germany*

³*Institut für Theoretische Physik IV, Universität Stuttgart,
Pfaffenwaldring 57, D-70569 Stuttgart, Germany*

[Received: 30 January 2021. Accepted: 29 March 2021]

ABSTRACT: We present a short review and some new results on the finite-size behavior of finite systems exhibiting second order phase transition. We will be mainly focused on one basic model of statistical mechanics – the Ginzburg-Landau ϕ^4 model under the influence of temperature bath and an external ordering field.

KEY WORDS: statistical mechanics, phase transitions, critical phenomena, finite-size scaling, Casimir effect.

1 INTRODUCTION

The current article is *in memory* to Prof. D. Sci. Jordan Brankov, with whom I had the pleasure to work together at the beginning of my scientific carrier.

In memory OF PROF. D. SCI. JORDAN BRANKOV

I first met Prof. Brankov in 1985 when I joined the Laboratory of Statistical Mechanics and Thermodynamics at the Institute of Mechanics of Bulgarian Academy of Sciences. At that time the Laboratory was headed by him. With him as my supervisor, initially I wrote my Diploma work for the faculty of Physics at the Sofia University. After that, I wrote in a cooperation with him one monograph [1] and more than 10 scientific articles on various topics. It turns so that basically all of them deal, in one way or the other, with the influence of finite size of the system on different its properties. We performed our studies exclusively via treating analytically exactly solvable statistical mechanical models.

*Corresponding author e-mail: daniel@imbm.bas.bg

As it is customary in the corresponding theoretical studies, one considers as *finite* any system that is characterized by *at least one* finite dimension. Let us denote this characteristic finite size by L .

Obviously, any finite system possesses boundary. One expects that near it the behavior of the system differs from that one deep in the bulk of the system. A given constituent in a finite system is influenced by the presence of a boundary, i.e., it “feels” that the system is finite, either (i) through the chain of correlations, or (ii) directly, through interactions with the other constituents of the system, when the interaction decays slow enough with the distance r . The both mechanisms lead to interesting effects. It happens so that with Dr. Brankov we dealt with the case of systems exhibiting a second order phase transition, i.e., possessing a diverging *correlation length*, and governed by *leading long-ranged interactions*, i.e., with the case when the both effects are acting simultaneously on the thermodynamic behavior of the system.

Before going into any details, in order to set properly the stage and to avoid possible misunderstandings, let us make some definitions concerning (i) the correlation length and (ii) the types of interactions.

(i) In statistical mechanics one describes the systems with thermodynamic potentials which are piece-wise analytical functions of, say, the temperature T and the ordering field h . The set of points at which a first derivative with respect to, say, h is discontinuous determines the positions of *first-order phase transitions*; these sets form the phase diagram of the system. They separate the different possible coexisting phases. The point at which a line of first order phase transitions ends is called *critical point*, normally at some $T = T_c$ and $h = 0$. The distance up to which two-point correlations are not negligible is called *correlation length* ξ . In the vicinity of the bulk critical point ($T_c, h = 0$) the bulk correlation length of the order parameter ξ becomes large, and theoretically diverges: $\xi_t^+ \equiv \xi(T \rightarrow T_c^+, h = 0) \simeq \xi_0^+ t t^{-\nu}$, $t = (T - T_c)/T_c$, and $\xi_h \equiv \xi(T = T_c, h \rightarrow 0) \simeq \xi_{0,h} |h/(k_B T_c)|^{-\nu/\Delta}$, where ν and Δ are called *critical exponents* and ξ_0^+ and $\xi_{0,h}$ are the corresponding nonuniversal amplitudes of the correlation length along the t and h axes. One obviously shall expect interesting and important finite-size effects when ξ becomes comparable to the system size. This turns out to be indeed the case - it has been shown that the behavior of the finite system differs in this case essentially from that one of the bulk system, the thermodynamic functions describing its behavior depend on the ratio L/ξ and take scaling forms given by the so-called *finite-size scaling theory* [1–3, 5, 22]. Further information of the phase transitions and related physical and mathematical problems can be found in, say, [1] and the set of articles on the topic cited therein.

(ii) In nature as slow decaying interactions are considered such which decay in a power-law with the distance. They are normally described mathematically as decay-

ing $\propto r^{-(d+\sigma)}$, where d is dimensionality of the system and σ is a parameter governing the rate of the interaction's decay. As examples one can think of Coulomb or van der Waals interactions. We will only have in mind the case $\sigma > 0$, for which the standard thermodynamic potential are well defined. Let us quantify the above terminology. To keep the presentation as simple as possible, let us further consider only models embedded on a d -dimensional hypercubic lattices \mathcal{L} , where $\mathcal{L} = L_1 \times L_2 \times \dots \times L_d$. Let $L_i = N_i a_i, i = 1, \dots, d$, where $N_i \in \mathbb{N}$ is the number of dynamical variables (particles, spins) along direction i , and a_i is the lattice constant along the axis i with \mathbf{e}_i being a unit vector along that axis, i.e., $\mathbf{e}_i \cdot \mathbf{e}_j = \delta_{ij}$. We suppose that the interaction between any two constituents at a distance \mathbf{r} apart is given by $J(\mathbf{r}) \in \mathbb{R}$. Then, if for any $m \in \mathbb{N} < \infty$ one has $\sum_{\mathbf{r} \in \mathcal{L}} r^m |J(\mathbf{r})|^m < \infty$ the corresponding interaction is called a *short-ranged* one. If $\exists m \in \mathbb{N} < \infty : \sum_{\mathbf{r} \in \mathcal{L}} r^m |J(\mathbf{r})|^m = \infty$, $J(\mathbf{r})$ is called *long-ranged* interaction. Then, if $m = 2$ this interaction is called *leading long-ranged* interaction, while if $m > 2$ it is called *sub-leading* long ranged interaction [6]. An example of the latter is the omnipresent van der Waals interaction.

With Dr. Brankov we started our combined scientific endeavor with study of a system governed by a dipole interaction, which is anisotropic and of long-ranged interaction type [7]. This article has been well received by the community and has been used, e.g., for explanation of experimental properties of some nano-systems [8]. It is interesting that we encountered the finite-size scaling theory along a nontraditional path – during studying the limit Gibbs states [9] within the spherical model, applying an ordering field that depends on the number of particles in the system, i.e., using approach similar to the one used for calculation of the quasi-average values of Bogolyubov. It turns out that our strict mathematical approach did agree with the predictions of the finite-size theory for first-order phase transition. This provoked us to embark on the finite-size scaling theory and to obtain serious of results mainly devoted to verification of its predictions. However, we have also succeeded in formulating this theory in terms of limit distribution of dependent random variables [10]. Specifically, we have shown that the finite-size scaling functions of the infinitely coordinated spherical model can be expressed via limit probability distributions of a triangular array of properly normalized block spin variables. The triangular array is defined with the aid of a two-parameter family of Gibbs distributions which approach the critical point together with the increase of the size of the system. This is an very interesting approach to the finite-size scaling theory that interconnects it to the theory of limit distributions of Gibbs mutually dependent random variables. This approach still waits for it further development. It is worthwhile also to mention the explicit result which demonstrated that the finite-size scaling functions do depend on the thermodynamic ensemble [10] in which the system is considered. This result became recently of special interest because it is directly showing the ensemble de-

pendence of the fluctuation induced forces, a hot topic of recent research, see, e.g., Ref. [11].

In the remainder of the current article we pass to the consideration of the finite-size behavior and especially of the Casimir force in one specific very well known in statistical mechanics exactly solvable model - the Ginzburg-Landau Φ^4 model. The Casimir force is an example of a fluctuation induced force which will be of interest for us in the model for the specific case of Dirichlet-Dirichlet boundary conditions.

2 SOME BASIC FACTS ON THE CASIMIR FORCE

As it is well known, a random variable ζ with zero average $\langle \zeta \rangle = 0$ has a nonzero dispersion $\langle \zeta^2 \rangle$, provided this variable is not identically zero. This trivial mathematical fact leads to highly nontrivial physical consequences. Among them is the existence of the so-called Casimir force [12].

In 1948 the Dutch physicist H. B. G. Casimir realized, after a discussion with Niels Bohr, that the zero-point fluctuations of the electromagnetic field in vacuum lead to the remarkable *mechanical effect* of the appearance of a long-ranged *attractive* force between two perfectly conducting uncharged parallel plates at a distance L from each other, and calculated this force. When the force is divided by the cross-sectional area of the plates, for the Casimir pressure he obtained

$$(1) \quad F_{\text{Cas}}^{\parallel}(L) = -\frac{\pi^2}{240} \frac{\hbar c}{L^4} = -1.3 \times 10^{-3} \frac{1}{(L/\mu\text{m})^4} \frac{\text{N}}{\text{m}^2}.$$

We emphasize that in the absence of charges on the plates the mean value of both the electric \mathbf{E} and the magnetic field \mathbf{B} vanishes, i.e.,

$$\langle \mathbf{E} \rangle = 0 \quad \text{and} \quad \langle \mathbf{B} \rangle = 0, \quad \text{but} \quad \langle \mathbf{E}^2 \rangle \neq 0 \quad \text{and} \quad \langle \mathbf{B}^2 \rangle \neq 0,$$

and, therefore, the expectation value of the energy due to the electromagnetic field between the plates, i.e., $\langle \mathcal{H} \rangle$ with

$$\mathcal{H} = \int \left[\frac{1}{2} \varepsilon_0 \mathbf{E}^2(\mathbf{r}) + \frac{1}{2\mu_0} \mathbf{B}^2(\mathbf{r}) \right] d^3\mathbf{r},$$

is nonzero. Here ε_0 and μ_0 are the dielectric permittivity and the magnetic permeability of the free space, respectively. Supposing, as Casimir did, in the simplest case the plates to be ideal conductors, it follows that the component of the electric field parallel to the plates has to be zero, i.e., *Dirichlet* boundary conditions are imposed on that component of the field. The last leads to L -dependence of the energy of the field in-between the plates and, thus in changing the distance L between them a force shall appear acting on them. This phenomenon is known today as the quantum-mechanical

Casimir effect. There is a plethora of articles in the nowadays literature devoted to this effect, and, subsequently, a series of reviews on them, e.g., [13–17].

An inspection of the result shown in Eq. (1) leads to a conclusion that the result is *universal*, in the sense that it depends only on the *fundamental constants*: c - the speed of light in vacuum and the Planck's constant \hbar . The L -dependence of the force can easily be predicted on dimensional grounds: as any force $F_{\text{Cas}}^{\parallel}$ it is $F_{\text{Cas}}^{\parallel} \propto \text{Energy}/\text{Length} \propto E/L$. The energy E is proportional to the cause of the effect, i.e., the energy of the relevant fluctuations. At $T = 0$, these are the quantum fluctuations. Therefore, $E \sim hc/L$. If one normalizes per unite area $A \sim L^2$, the result is $F_{\text{Cas}}^{\parallel} \propto hc/L^4$, which is the Casimir result cited in Eq. (1).

Thirty years after Casimir, in 1978 Fisher and De Gennes [18] have shown that a very similar effect exists in fluids. In that case the fluctuating field is the field of its order parameter. Then the interactions in the system are mediated not by photons, as in the case of the electromagnetic field, but by different type of massless excitations such as critical fluctuations or Goldstone bosons (spin waves). Nowadays one usually terms the corresponding Casimir effect the critical or the thermodynamic Casimir effect [1]. On the critical Casimir effect only two general reviews [1, 19] so far are devoted, one of which is co-authored by Dr. Brankov [1]. The L -dependence of the force again can easily be determined for the general case of a d -dimensional system. Taking into account that the surface then $A \propto L^{d-1}$ and that the energy of the fluctuations $E \propto k_B T$, one concludes that for the thermodynamic Casimir effect near the critical point of the system $F_{\text{Cas}}^{\parallel} \propto k_B T/L^d$. For the ($d = 3$)-dimensional system one can write the force at the critical point $T = T_c$ in the form

$$(2) \quad F_{A,\text{Cas}}^{(\tau)}(T = T_c, L) \simeq 8.1 \times 10^{-3} \frac{\Delta^{(\tau)}(d=3)}{(L/\mu\text{m})^3} \frac{T_c}{T_{\text{room}}} \frac{\text{N}}{\text{m}^2},$$

where $T_{\text{room}} = 20 \text{ }^\circ\text{C}$ (293.15 K). Here $\Delta^{(\tau)}$ is the so-called Casimir amplitude that depends on the bulk and surface *universality classes* of the system and the applied boundary conditions τ . For the most systems and boundary conditions $\Delta^{(\tau)}(d) = \mathcal{O}(1)$. Thus, the both forces, the quantum and the thermodynamic one, can be of the same order of magnitude, i.e., they both can be essential, measurable and obviously significant at or below the micrometer length scale. Let us stress that $\Delta^{(\tau)}(d)$ can be both positive and negative, i.e., $F_{A,\text{Cas}}^{(\tau)}(T, L)$ can be both attractive and repulsive. The accepted terminology terms the negative force as attractive one.

According to the *universality hypothesis*, as formulated by Kadanoff [20] “all (continuous) phase transition problems can be divided into a small number of different classes depending upon the dimensionality of the system and the symmetries of the ordered state. Within each class, all phase transitions have identical behavior in

the critical region, only the names of thermodynamic variables are changed.” All such systems are then part of the same *universality class*. For example, we have the Ising universality class characterized by the breaking of the \mathbb{Z}_2 symmetry of the original effective Hamiltonian for the scalar order parameter, the XY universality class with a two-component order parameter and a disordered phase with $O(2)$ symmetry, and the Heisenberg universality class characterized by a vectorial order parameter with an $O(3)$ symmetry. Any of these bulk universality classes is accompanied with a set of surface universality classes, which depend on what is the behavior of the order parameter near and at a surface(s) of the semi-infinite or finite system. For a film geometry the accumulated till nowadays both experimental and theoretical evidences support the statement that the Casimir force is attractive when the boundary conditions on either plate are the same, or similar, and is repulsive when they essentially differ from each other. For the case of a one-component fluid the last means, e.g., that one of the surfaces adsorbs the liquid phase of the fluid, while the other prefers the vapor phase.

Currently the Casimir effect is a popular subject of research. The Casimir and Casimir-like effects are object of studies in quantum electrodynamics, quantum chromodynamics, cosmology, condensed matter physics, biology and, some elements of it, in nano-technology. The reader interested in that problematic can consult the existing reviews - see the above references to some of these reviews.

In the current article we will study the thermodynamic Casimir effect in a system with $\infty^{d-1} \times L$ film geometry under Dirichlet-Dirichlet boundary conditions. We envisage a system exposed at a temperature T and to an external ordering field h that couples to its order parameter - density, concentration difference, magnetization, etc. We imagine a simple fluid system at its liquid - vapor critical point, a magnet at the phase transition from paramagnetic to ferromagnetic state, or a binary liquid mixture with phases A and B near its consolute temperature point. Let $(T = T_c, h = 0)$ is this bulk critical point in the (T, h) plane. We will consider only the case of an one-dimensional order parameter $\phi \in \mathbb{R}$. The thermodynamic Casimir force $F_{\text{Cas}}(T, h, L)$ in such a system is the *excess pressure*, over the bulk one, acting on the boundaries of the finite system, which is due to the finite size of that system, i.e.,

$$(3) \quad F_{\text{Cas}}(T, h, L) = P_L(T, h) - P_b(T, h).$$

Here P_L is the pressure in the finite system, while P_b is that one in the infinite system. Let us note that the above definition is actually equivalent to another one which is also commonly used [1, 19, 21]

$$(4) \quad F_{\text{Cas}}(T, h, L) \equiv -\frac{\partial \omega_{\text{ex}}(T, h, L)}{\partial L} = -\frac{\partial \omega_L(T, h, L)}{\partial L} - P_b,$$

where $\omega_{\text{ex}} = \omega_L - L\omega_b$ is the excess grand potential per unit area, ω_L is the grand canonical potential of the finite system, again per unit area, and ω_b is the density of the grand potential for the infinite system. The equivalence between the definitions, Eq. (3) and Eq. (4), comes from the observation that $\omega_b = -P_b$, and for the finite system with surface area A and thickness L one has $\omega_L = \lim_{A \rightarrow \infty} \Omega_L/A$, with $-\partial\omega_L(T, h, L)/\partial L = P_L$. When $F_{\text{Cas}}(\tau, h, L) < 0$ the excess pressure will be inward of the system,, thus it corresponds to an *attraction* of the surfaces of the system towards each other, and to a *repulsion*, if $F_{\text{Cas}}(\tau, h, L) > 0$. For such a system positioned near its critical point the finite-size scaling theory [1,3,5,19,22–24] predicts:

- For the Casimir force

$$(5) \quad F_{\text{Cas}}(t, h, L) = L^{-d} X_{\text{Cas}}(x_t, x_h);$$

- For the order parameter profile

$$(6) \quad \phi(z, T, h, L) = a_h L^{-\beta/\nu} X_\phi(z/L, x_t, x_h),$$

where $x_t = a_t t L^{1/\nu}$, $x_h = a_h h L^{\Delta/\nu}$. In Eqs. (5) and (6), β is the critical exponent for the order parameter, d is the dimension of the system, a_t and a_h are nonuniversal metric factors that can be fixed, for a given system, by taking them to be, e.g., $a_t = 1/[\xi_0^+]^{1/\nu}$, and $a_h = 1/[\xi_{0,h}]^{\Delta/\nu}$.

In the next section we are going to consider the Casimir force within the Ginzburg-Landau mean-field model. We have studied in [25] the case of (+, +) boundary conditions, in [26] - the case of (+, -) boundary conditions. Some elements of the behavior of the force under (Neumann, +) boundary conditions have been presented in [27], while recently few basic results for the case of Dirichlet boundary conditions have been exposed in [28]. Here we will present some summary of the results for the Dirichlet-Dirichlet boundary conditions and will extend them.

3 DEFINITION OF THE MODEL AND BASIC EXPRESSION FOR THE CASIMIR FORCE

Within this model the system is characterized by the scalar order parameter $\phi(z|\tau, h, L) \in \mathbb{R}$ given by functions representing minimizers of the standard ϕ^4 Ginzburg-Landau functional

$$(7) \quad \mathcal{F}[\phi; \tau, h, L] = \int_{-L/2}^{L/2} \mathcal{L}(\phi, \phi') dz,$$

where

$$(8) \quad \mathcal{L} \equiv \mathcal{L}(\phi, \phi') = \frac{1}{2}\phi'^2 + \frac{1}{2}\tau\phi^2 + \frac{1}{4}g\phi^4 - h\phi.$$

Here L is the film thickness, $\phi(z|\tau, h, L)$ is the order parameter assumed to depend on the perpendicular position $z \in (-L/2, L/2)$ only, $\tau = (T - T_c)/T_c (\xi_0^+)^{-2}$ is the bare reduced temperature, h is the external ordering field, g is the bare coupling constant, and the primes indicate differentiation with respect to the variable z . It is well known that for the model considered here $\xi_{0,h}/\xi_0^+ = 1/\sqrt{3}$ [29], $\nu = 1/2$ and $\Delta = 3/2$ [1, 30, 31].

In Ref. [25] we have shown that for the model considered here, the pressure in the finite system is

$$(9) \quad P_L(\tau, h) = \frac{1}{2}\phi'^2 - \frac{1}{4}g\phi^4 - \frac{1}{2}\tau\phi^2 + h\phi,$$

while in the bulk system it equals to

$$(10) \quad P_b(\tau, h) = -\frac{1}{4}g\phi_b^4 - \frac{1}{2}\tau\phi_b^2 + h\phi_b.$$

This result *does not* depend on the boundary condition applied on the system. This dependence enters via the dependence of the order parameter $\phi(z|\tau, h, L)$. In the light of the above it is evident that once the order parameter profile ϕ and its bulk value ϕ_b are known in analytic form for given values of the parameters τ and h , then the corresponding Casimir force can be easily determined in an exact manner.

The variable ϕ_b of the order parameter of the bulk system does not depend on the boundary conditions at all. It is determined as the solution the cubic equation

$$-\phi_b [\tau + g\phi_b^2] + h = 0,$$

ϕ_b that minimizes

$$\mathcal{L}_b = \frac{1}{2}\tau\phi_b^2 + \frac{1}{4}g\phi_b^4 - h\phi_b.$$

Let us note that $P_b = -\mathcal{L}_b$, i.e., P_b has its *maximum* over the possible solutions of the cubic equation for ϕ_b .

The order parameter of the finite system ϕ minimizes the functional \mathcal{F} . It is determined by the solutions of the corresponding Euler-Lagrange equation

$$(11) \quad \frac{d}{dz} \frac{\partial \mathcal{L}}{\partial \phi'} - \frac{\partial \mathcal{L}}{\partial \phi} = 0,$$

which, on account of Eq. (8), reads

$$(12) \quad \phi'' - \phi [\tau + g\phi^2] + h = 0.$$

Let us note that multiplying the above equation by ϕ' and integrating over z one obtains P_L in Eq. (9), i.e., P_L is a *first integral* of the system. The behavior of ϕ depends on the boundary conditions. For Dirichlet - Dirichlet boundary conditions:

$$(13) \quad \lim \phi(z)|_{z \rightarrow -L/2} = 0, \quad \text{and} \quad \lim \phi(z)|_{z \rightarrow L/2} = 0.$$

Since the thermodynamic Casimir force is normally presented in terms of the scaling variables

$$(14) \quad l_t \equiv \text{sign}(\tau) L/\xi_t^+ = \text{sign}(\tau) L\sqrt{|\tau|},$$

$$(15) \quad l_h \equiv \text{sign}(h) L/\xi_h = L\sqrt{3}(\sqrt{g}h)^{1/3},$$

in the remainder we are going to use such variables as the basic parameters determining the behavior of the force. In the above we have taken into account that for the model considered here $\xi_{0,h}/\xi_0^+ = 1/\sqrt{3}$, see [29], and $\nu = 1/2$, $\Delta = 3/2$.

In terms of the scaling variables given in equations (14) and (15), the value $P_L(\tau, h)$ of the first integral, see Eq. (9), becomes

$$(16) \quad P_L(\tau, h) = \frac{1}{gL^4} p(l_t, l_h),$$

where $p(l_t, l_h)$ is

$$(17) \quad p(l_t, l_h) = X'^2 - X^4 - \text{sign}(l_t) l_t^2 X^2 + \frac{2}{3\sqrt{6}} l_h^3 X.$$

Here

$$(18) \quad X(\zeta|l_t, l_h) = \sqrt{\frac{g}{2}} L^{\beta/\nu} \phi(z)$$

is the scaling function of the order parameter ϕ , $\beta = 1/2$ and hereafter the prime means differentiation with respect to the variable $\zeta = z/L$, $\zeta \in [-1/2, 1/2]$. Similarly, for the bulk system, see Eq. (10), one has

$$(19) \quad P_b(\tau, h) = \frac{1}{gL^4} p_b(l_t, l_h),$$

where

$$(20) \quad p_b(l_t, l_h) = -X_b^4 - \text{sign}(l_t) l_t^2 X_b^2 + \frac{2}{3\sqrt{6}} l_h^3 X_b.$$

The free energy functional then reads

$$(21) \quad \mathcal{F}[X; l_t, l_h, L] = \frac{1}{gL^4} \int_{-1/2}^{1/2} \mathcal{L}(X, X') d\zeta,$$

where

$$(22) \quad \mathcal{L}(X, X') = X'^2 + X^4 + \text{sign}(l_t) l_t^2 X^2 - \frac{2}{3\sqrt{6}} l_h^3 X.$$

3.1 THE PHASE DIAGRAM

In order to understand the behavior of the system in one thermodynamic model the first question one shall answer is what is the phase diagram of the system - that of the bulk and of the finite one with given boundary conditions.

We start with the phase diagram of the infinite system.

The phase diagram of the infinite system is well known. It is shown on the left side of Fig. 1. At high temperature the system is in disordered phase and when $h \rightarrow 0$ the order parameter $\phi_b \rightarrow 0$. This is no longer true below some temperature T_c , called critical temperature, when $\lim_{h \rightarrow 0^\pm} \phi(T < T_c, h) = \pm m_0(T) \neq 0$. The physical interpretation is the coexistence of two phases - they have the same free

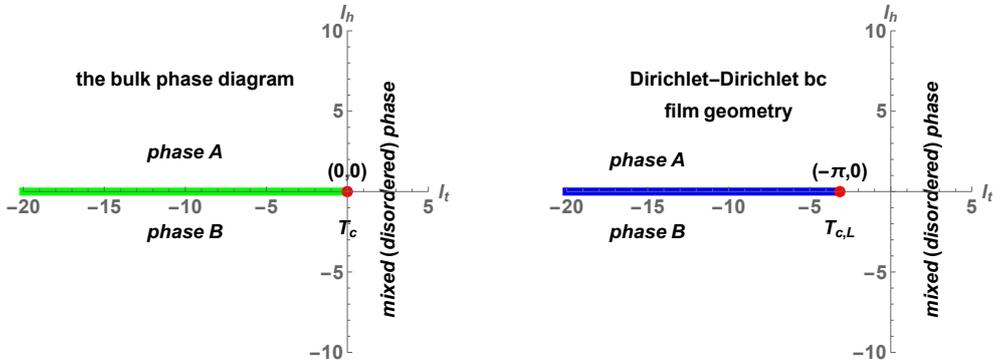


Fig. 1: Phase diagram in the (l_t, l_h) plane of the bulk (left) and of the finite system under Dirichlet-Dirichlet boundary conditions (right). In the bulk system a phase transition of first order happens when crossing the phase coexistence line that is at $l_h = 0$ and spans for $T \in (0, T = T_c)$. At $T = T_c$ the bulk system exhibits a second order phase transition. In the finite system the coexistence line is at $l_h = 0$ and spans for $T \in (0, T = T_{c,L})$. The second order phase transition happens in it at $T = T_{c,L} \equiv (-\pi, 0)$.

energy for $h = 0$ but the “plus” phase with $\phi_b(T, h) > 0$ will prevail, i.e., will have lower free energy, if $h > 0$, and the “negative” one with $\phi_b(T, h) < 0$, when $h < 0$. When crossing the line $\{h = 0, T < T_c\}$ by changing the field h one observes first order phase transitions, while at $\{T = T_c, h = 0\}$ one observes second order phase transition, which basic features we briefly discussed above.

The phase diagram of a system with a film geometry under Dirichlet-Dirichlet boundary conditions is shown on the right side of Fig. 1. When one crosses the line $\{T < T_{c,L}, l_h = 0\}$ by varying the field variable l_h the system possesses a line of first-order phase transitions $\{T < T_{c,L}, l_h = 0\}$ that ends at the critical point $T = T_{c,L}, l_h = 0$. In terms of l_t and l_h the coordinates of the critical point $T_{c,L}$ are $\{l_t = -\pi, l_h = 0\}$. When $T < T_{c,L}$ the stable state with minimum energy is with $\phi(z) > 0$ for $h > 0$, and $\phi(z) < 0$ for $h < 0$. More details can be found in [28].

In what follows we will present results for the behavior of the Casimir force under Dirichlet - Dirichlet boundary conditions.

3.2 ON THE CASIMIR FORCE

In the case of Dirichlet-Dirichlet boundary conditions the corresponding results for the scaling function of the Casimir force for zero field, i.e. for $l_h = 0$, have been derived in [32, 33]. Here we will present only results for the case $h \neq 0$. Some results in that respect have been published in [28].

From Eqs. (16) and (19), for the Casimir force defined in Eq. (3) one obtains

$$(23) \quad F_{\text{Cas}}(\tau, h, L) = \frac{1}{gL^4} X_{\text{Cas}}(l_t, l_h),$$

where its scaling function X_{Cas} is

$$(24) \quad X_{\text{Cas}}(l_t, l_h) = p(l_t, l_h) - p_b(l_t, l_h).$$

Obviously, the scaling function of the Casimir force can be written in the form

$$(25) \quad X_{\text{Cas}}(l_t, l_h) = X_b^4 - X_m^4 + \text{sign}(l_t) l_t^2 (X_b^2 - X_m^2) - \frac{2}{3\sqrt{6}} l_h^3 (X_b - X_m).$$

Here X_m is the value of the scaling function of the order parameter profile at the middle of the system, i.e., $X(1/2|l_t, l_h) = X_m(l_t, l_h)$.

3.2.1 ON THE BEHAVIOR OF THE ORDER PARAMETER PROFILE

Under Dirichlet boundary conditions one has $X = 0$ at $\zeta = -1/2$ and $\zeta = 1/2$. Obviously $X(\zeta)$ is either increasing, or decreasing function of ζ with, due to the symmetry, $X'(1/2) = 0$. Again because of the symmetry it is enough to study

one of these sub-cases, say with $X'_m(\zeta) \geq 0$. Since, furthermore, the physical order parameter profiles *minimizes the free energy*, see Eq. (21), it is clear that $l_h X(\zeta) > 0$, when $l_h > 0$. Next, the problem is symmetric under the *simultaneous* change of the signs of X and l_h . Therefore, it is enough to study the case $l_h \geq 0$ with $X(\zeta) \geq 0$. In this case, from Eq. (17) one obtains

$$(26) \quad \zeta = \int_0^{X(\zeta)} \frac{dX}{\sqrt{X^4 + \text{sign}(l_t) l_t^2 X^2 - \frac{2}{3\sqrt{6}} l_h^3 X + p(l_t, l_h)}}.$$

Expressing $p(l_t, l_h)$ in terms of X_m , one has

$$(27) \quad \frac{1}{2} = \int_0^{X_m} \frac{dX}{\sqrt{(X^4 - X_m^4) + \text{sign}(l_t) l_t^2 (X^2 - X_m^2) - \frac{2}{3\sqrt{6}} l_h^3 (X - X_m)}}.$$

Now we can outline one straightforward procedure for determining the Casimir force. The algorithm is the following. From Eq. (27) one determines X_m as a function of l_t and l_h . Then, from Eq. (26) one determines ζ as a function of X_m . Inverting this dependence, one arrives at the function $X(\zeta)$. If there is more than one solution obtained under the procedure described above, one shall choose this profile $X(\zeta)$ that provides the minimum of the free energy \mathcal{F} , see Eq. (21) and Eq. (22). In Ref. [34] the following proposition has been proven

Proposition. *If $l_h \neq 0$ when it exist there is a single profile $X(\zeta)$ which is monotonic on the interval $(-1/2, 0)$, and for which $X(-1/2) = 0$, $X'(0) = 0$, and $l_h X(\zeta) \geq 0$.*

Performing numerically the procedure outlined above, one arrives at the behavior of the Casimir force shown in Figs. 2 and 3. We observe that under Dirichlet boundary conditions, and within the mean-field Ginzburg-Landau Ising type model, the force is *attractive* and non-monotonic.

Let us also mention that there is an alternative approach to the problem based on the explicit solution of the differential equation (12). Following [35], using the fact that the first integral is given by Eq. (17), one obtains that the order parameter is equal to

$$(28) \quad X(\zeta|l_t, l_h, X_m) = X_m + \frac{6X_m (\text{sign}(l_t) l_t^2 + 2X_m^2) - \sqrt{2/3} l_h^3}{12\wp(\zeta; g_2, g_3) - (\text{sign}(l_t) l_t^2 + 6X_m^2)},$$

$\wp(\zeta; g_2, g_3)$ is the Weierstrass elliptic function whose invariants g_2 and g_3 read

$$(29) \quad g_2 = \frac{1}{12} l_t^4 + p(l_t, l_h), \quad \text{and} \quad g_3 = -\frac{1}{216} [l_h^6 + l_t^6 - 36 p(l_t, l_h) l_t^2].$$

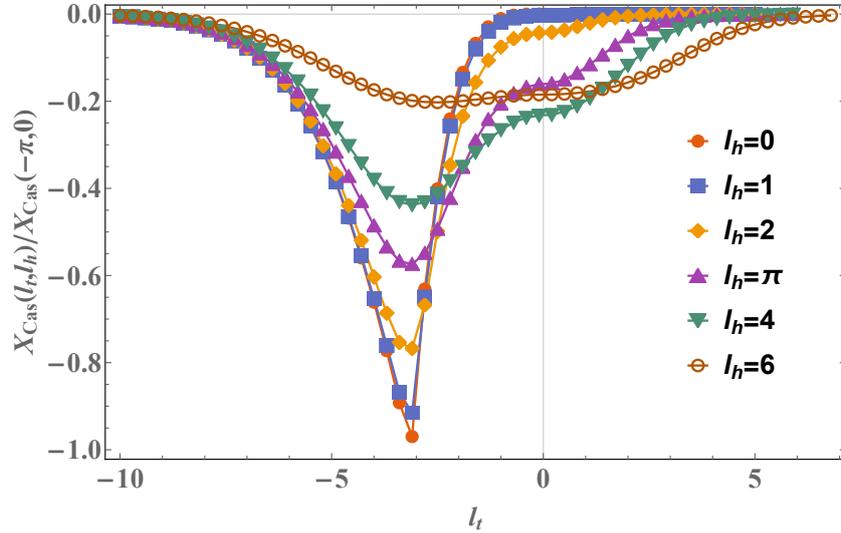


Fig. 2: The behavior of the scaling function of the Casimir force as a function of l_t for several fixed values of l_h . The function is normalized by its value at the critical point of the finite system. We observe that the force is *attractive* and non-monotonic.

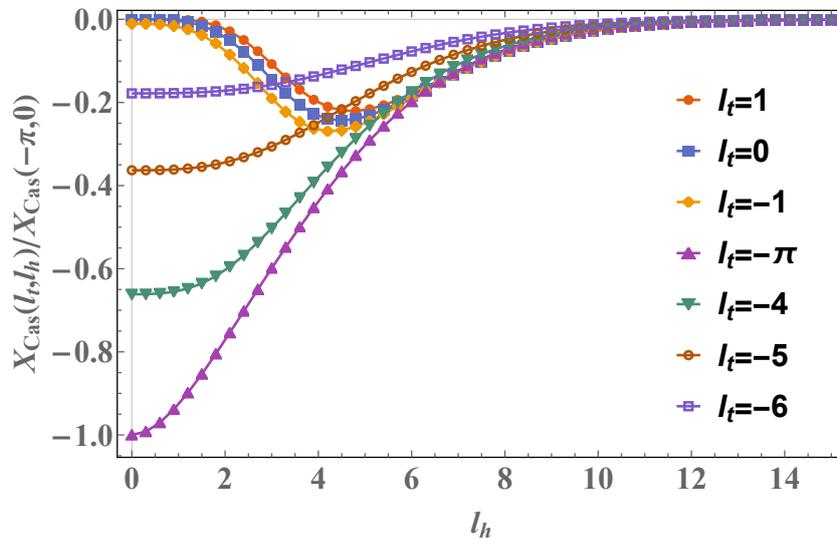


Fig. 3: The behavior of the scaling function of the Casimir force as a function of l_h for several fixed values of l_t . The function is normalized by its value at the critical point of the finite system. We observe that the force is *attractive* and non-monotonic.

Here X_m is to be determined from

$$(30) \quad 12\wp\left(\frac{1}{2}; g_2, g_3\right) - \text{sign}(l_t)l_t^2 - 6x_m^2 = 0,$$

so that one obtains a continuous order parameter profile in the interval $(-1/2, 1/2)$, satisfying the condition

$$(31) \quad 6\sqrt{3}x_m(\text{sign}(l_t)l_t^2 + 2x_m^2) - \sqrt{2}l_h^3 < 0.$$

4 DISCUSSION AND CONCLUDING REMARKS

This model we discussed here is normally considered to describe simple fluids and binary liquid mixtures. Using the grand canonical ensemble, we have obtained for that model the behavior of the Casimir force as a function of l_t and l_h . We have shown that the force is attractive, but is not monotonic. As outlined in the Introduction, one problem which we have attacked with Prof. Dr. Brankov long ago, see Ref. [10], that recently become of interest, is the issue of the behavior of the fluctuation induced forces in canonical ensemble, see, e.g., [11]. It is worthwhile also noting that due to the non-monotonicity, the Casimir force in the critical region is characterized by a highly nontrivial 3D relief map of the force. To these two problems we hope to return in the near future.

ACKNOWLEDGEMENTS

The author gratefully acknowledge the financial support via contract DN 02/8 with Bulgarian National Science Fund.

REFERENCES

- [1] J.G. BRANKOV, D.M. DANTCHEV, N.S. TONCHEV (2000) "The Theory of Critical Phenomena in Finite-Size Systems – Scaling and Quantum Effects". World Scientific, Singapore.
- [2] M.E. FISHER, M.N. BARBER (1972) Scaling Theory for Finite-Size Effects in the Critical Region. *Phys. Rev. Lett.* **28** 1516-1519.
- [3] M.N. BARBER (1983) Finite-size scaling. In: C. Domb, J.L. Lebowitz (Eds.), "Phase Transitions and Critical Phenomena", Vol. 8, Academic, London, Ch. 2, pp. 146-266.
- [4] J.L. CARDY (Ed.) (1988) "Finite-Size Scaling". North-Holland, Amsterdam.
- [5] V. PRIVMAN (Ed.) (1990) "Finite Size Scaling and Numerical Simulation of Statistical Systems". World Scientific, Singapore.
- [6] D. DANTCHEV, J. RUDNICK (2001) Subleading Long-Range Interactions and Violations of Finite Size Scaling. *European Physical Journal B* **21** 251-268.

- [7] J.G. BRANKOV, D.M. DANCHEV (1987) Ground State of an Infinite Two-Dimensional System of Dipoles on a Lattice With Arbitrary Rhombicity Angle. *Physica A* **144** 128-139.
- [8] Y. ZHANG, H. KERSELL, R. STEFAK, J. ECHEVERRIA, V. IANCU, U.G.E. PERERA, Y. LI, A. DESHPANDE, K.-F. BRAUN, C. JOACHIM, G. RAPENNE, S.-W. HLA (2016) Simultaneous and Coordinated Rotational Switching of All Molecular Rotors in a Network. *Nature Nanotechnology* **11** 706-712.
- [9] J.G. BRANKOV, D.M. DANCHEV (1987) On the Limit Gibbs States of the Spherical Model. *Journal of Physics A: Mathematical and General* **20** 4901-4913.
- [10] J.G. BRANKOV, D.M. DANCHEV (1989) A Probabilistic View on Finite-Size Scaling in Infinitely Coordinated Spherical Models. *Physica A* **158** 842-863.
- [11] C.M. ROHWER, A. SQUARCINI, O. VASILYEV, S. DIETRICH, M. GROSS (2019) Ensemble Dependence of Critical Casimir Forces in Films With Dirichlet Boundary Conditions. *Physical Review E* **99** 062103.
- [12] H.B. CASIMIR (1948) On the Attraction Between Two Perfectly Conducting Plates. *Proceedings of the Koninklijke Nederlandse Akademie van Wetenschappen* **51** p. 793.
- [13] P.W. MILONNI (1994) "The Quantum Vacuum". Academic, San Diego.
- [14] V.M. MOSTEPANENKO, N.N. TRUNOV (1997) "The Casimir Effect and Its Applications". Energoatomizdat, Moscow, in Russian; English version: Clarendon, New York.
- [15] M. KARDAR, R. GOLESTANIAN (1999) The "Friction" of Vacuum, and Other Fluctuation-Induced Forces. *Reviews of Modern Physics* **71** 1233-1245.
- [16] K.A. MILTON (2004) The Casimir Effect: Recent Controversies and Progress. *Journal of Physics A: Mathematical and General* **37** R209R277.
- [17] D. DALVIT, P. MILONNI, D. ROBERTS, F. DA ROSA (Eds.) (2011) "Casimir Physics". Springer, Berlin, vol. **834**, series *Lecture Notes in Physics*.
- [18] M.E. FISHER, P.G. DE GENNES (1978) Phénomènes aux parois dans un mélange binaire critique. *Comptes rendus de l'Académie des Sciences, Série B* **287** 207-209.
- [19] M. KRECH (1994) "Casimir Effect in Critical Systems". World Scientific, Singapore.
- [20] L.P. KADANOFF (1971) Critical Behavior Universality and Scaling. In: Proc. Intern. School of Physics "Enrico Fermi", Corso LI, Editor M.S. Green, Academic Press, New York, pp. 101-117.
- [21] R. EVANS (1990) Liquids at Interfaces. In: "Microscopic Theories of Simple Fluids and Their Interfaces". Editors J. Charvolin, J. Joanny, and J. Zinn-Justin, Les Houches Session, vol. XLVIII. Elsevier, Amsterdam.
- [22] J.L. CARDY Ed. (1988) "Finite-Size Scaling". North-Holland, Amsterdam.
- [23] V. PRIVMAN (1990) Finite-Size Scaling Theory. In: "Finite Size Scaling and Numerical Simulations of Statistical Systems". Editor V. Privman, World Scientific, Singapore, pp. 1-98.
- [24] M. KRECH, S. DIETRICH (1992) Free Energy and Specific Heat of Critical Films and Surfaces. *Physical Review A* **46** 1886-1921.

- [25] D.M. DANTCHEV, V.M. VASSILEV, P.A. DJONDJOROV (2016) Exact Results for the Behavior of the Thermodynamic Casimir Force in a Model with a Strong Adsorption. *Journal of Statistical Mechanics: Theory and Experiment* **2016**(9) 093209.
- [26] D.M. DANTCHEV, V.M. VASSILEV, P.A. DJONDJOROV (2018) Analytical Results for the Casimir Force in a GinzburgLandau Type Model of a Film with Strongly Adsorbing Competing Walls. *Physica A* **510** 302-315.
- [27] P.A. DJONDJOROV, D.M. DANTCHEV, V.M. VASSILEV (2017) Exact Results for the Casimir Force in a Model with Neumann-Infinity Boundary Conditions. *AIP Conference Proceedings* **1895** 090001.
- [28] D.M. DANTCHEV, V.M. VASSILEV, P.A. DJONDJOROV (2020) Boundary Conditions Influence on the Behavior of the Casimir Force: A Case Study via Exact Results on the Ginzburg-Landau Type Fluid System with a Film Geometry. *AIP Conference Proceedings* **2302** 100003.
- [29] F. SCHLESENER, A. HANKE, S. DIETRICH (2003) Critical Casimir forces in Colloidal Suspensions. *Journal of Statistical Physics* **110** 981-1013.
- [30] J. ZINN-JUSTIN (2002) "Quantum Field Theory and Critical Phenomena". Clarendon, Oxford.
- [31] A. PELISSETTO, E. VICARI (2002) Critical Phenomena and Renormalization-Group Theory. *Physics Reports* **368** 549-727.
- [32] A. GAMBASSI, S. DIETRICH (2006) Critical Dynamics in Thin Films. *Journal of Statistical Physics* **123** 929-1005.
- [33] R. ZANDI, A. SHACKELL, J. RUDNICK, M. KARDAR, L.P. CHAYES (2007) Thinning of Superfluid Films below the Critical Point. *Physical Review E* **76** 030601.
- [34] V.M. VASSILEV, P.A. DJONDJOROV, D.M. DANCHEV (2019) Analytic Representation of the Order Parameter Profiles and Compressibility of a Ginzburg-Landau Type Model with Dirichlet-Dirichlet Boundary Conditions on the Walls Confining the Fluid. *AIP Conference Proceedings* **2164** 100008.
- [35] E.T. WHITTAKER, G.N. WATSON (1963) "A Course of Modern Analysis". Cambridge University Press, London.