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Analytical results for the Casimir force in a Ginzburg–Landau type model of a film with strongly adsorbing competing walls

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HIGHLIGHTS

- The behaviour of the Casimir force in a Ginzburg–Landau type model is studied.
- Exact results for the force as a function of temperature and field are presented.
- We prove that the force experiences a single global maximum.
- The asymptotic behaviour of the force is determined.
- These results are in a perfect agreement with the finite-size scaling theory.

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ABSTRACT

We present both analytical and numerical results for the behaviour of the Casimir force in a Ginzburg–Landau type model of a film of a simple fluid or binary liquid mixture in which the confining surfaces are strongly adsorbing but preferring different phases of the simple fluid, or different components of the mixture. Under such boundary conditions an interface is formed between the competing phases inside the system which are forced to coexist. We investigate the force as a function of the temperature and in the presence of an external ordering field and determine the (temperature-field) relief map of the force. We prove the existence of a single global maximum of the force and find its position and value. We find the asymptotic behaviour of the force when any of the scaling fields becomes large while the other one is negligible. Contrary to the case of symmetric boundary conditions we find, as expected, that the finite system does not possess a phase transition of its own for any finite values of the scaling variables corresponding to the temperature and the ordering field. We perform the study near the bulk critical temperature of the corresponding bulk system and find a perfect agreement with the finite-size scaling theory.

1. Introduction

In the current article we study the behaviour of a system with $\infty^2 \times L$ film geometry. Let us recall that when at least one of the spacial extensions of the system is finite, one terms the corresponding system a finite one. In a system with a film geometry the pressure acting on its bounding surfaces differs, generally speaking, from the pressure that will be acting in the same system, characterized by the same thermodynamic parameters, but being infinite in extend. In different branches of science and in different range of parameters one uses the terms disjoining pressure, solvation force, or the thermodynamic Casimir force [1–3]. The Casimir like forces exist in any system where massless excitations are spatially limited by the

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presence of material bodies. The term thermodynamic Casimir force encompasses two cases with such massless excitations existing in thermodynamic (statistical mechanical) systems: near T_c, where they are the critical fluctuations of the order parameter and one speaks about the *critical Casimir force*, and below T_c, in systems with Goldstone modes, say ^{4}He, liquid crystals, where one sometimes speaks about off-critical Casimir force.

Let us consider a system with a film geometry at a temperature T exposed to an external ordering field h that couples to its order parameter—density, concentration difference, magnetization, etc., and let $(T = T_c, h = 0)$ is its bulk critical point in the (T, h) plane. The thermodynamic Casimir force $F_{\rm Cas}(T, h, L)$ 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.,

$$F_{\rm Cas}(T, h, L) = P_L(T, h) - P_b(T, h). \tag{1}$$

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 [1–3]

$$F_{\rm Cas}(T, h, L) \equiv -\frac{\partial \omega_{\rm ex}(T, h, L)}{\partial L} = -\frac{\partial \omega_L(T, h, L)}{\partial L} - P_b, \tag{2}$$

where $\omega_{\rm ex} = \omega_L - L\,\omega_b$ 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 Eqs. (1) and (2) comes from the observation that $\omega_b = -P_b$ and for the finite system with surface area A and thickness L one has $\omega_L = \lim_{A\to\infty} \Omega_L/A$, with $-\partial\omega_L(T, h, L)/\partial L = P_L$.

When a finite system is thermodynamically positioned close to its critical temperature its two-points correlation length ξ becomes comparable to L, and then the thermodynamic functions describing its behaviour depend on the dimensionless ratio L/ξ taking a scaling form given by the finite-size scaling theory [3–7].

When a *finite* system undergoes a phase transition its phase behaviour can be significantly different from that in the bulk counterpart [1,3–5,8–12]. One observes effects like shifts of the bulk critical points, that can be both with respect to T and h, or the appearance of phase transitions of its own at some new critical point $(T_{c,L}, h_L)$, like the capillary condensation phase transition, if the dimensionality of the finite system is large enough. Near the bulk critical point, the behaviour of the bulk system is characterized with critical exponents and scaling functions which depend only on gross features of the system like the dimensionality of the system d, the symmetry of the ordered state, normally denoted by n, and the long-ranginess of the interaction involved, i.e., on the so-called bulk universality class. The behaviour of the finite system, in addition, depends on the so-called surface universality class, which is determined by the boundary conditions on the surfaces of the finite system, as well as on its geometry. In a system with a film geometry if the finite system exhibits a phase transition of its own it belongs to the universality class of the $(d-1)$-dimensional infinite system. One of the quantities of especial interest in a finite critical system that is a subject of a plethora of studies, is the thermodynamic Casimir force and, more especially, that one which is observed near the critical point of the bulk system, often termed, as already explained above, *critical Casimir force*.

The critical Casimir effect has been already directly observed, utilizing light scattering measurements, in the interaction of a colloid spherical particle with a plate [13] both of which are immersed in a critical binary liquid mixture. Very recently the nonadditivity of critical Casimir forces has been experimentally demonstrated in [14]. Indirectly, as a balancing force that determines the thickness of a wetting film in the vicinity of its bulk critical point the Casimir force has been also studied in ^{4}He [15,16], as well as in ^{3}He–^{4}He mixtures [17]. In [18] and [19] measurements of the Casimir force in thin wetting films of binary liquid mixture are also performed. The studies in the field have also enjoined a considerable theoretical attention. Reviews on the corresponding results can be found in [20–25].

Before turning exclusively to the behaviour of the Casimir force, let us briefly remind some basic facts of the theory of critical phenomena. 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: $\xi_t^+ \equiv \xi(T \to T_c^+, h = 0) \simeq \xi_0^+ t^{-\nu}$, $t = (T - T_c)/T_c$, and $\xi_h \equiv \xi(T = T_c, h \to 0) \simeq \xi_{0,h}|h/(k_B T_c)|^{-\nu/\Delta}$, where ν and Δ are the usual critical exponents and ξ_0^+ and $\xi_{0,h}$ are the corresponding nonuniversal amplitudes of the correlation length along the t and h axes. For temperatures such that the correlation length ξ becomes comparable to L, the thermodynamic functions describing its behaviour depend on the ratio L/ξ and take scaling forms given by the finite-size scaling theory. For such a system the finite-size scaling theory [2–6,12] predicts for the Casimir force

$$F_{\rm Cas}(t, h, L) = L^{-d} X_{\rm Cas}(x_t, x_h); \tag{3}$$

where $x_t = a_t t L^{1/\nu}$, $x_h = a_h h L^{\Delta/\nu}$. Here 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., $a_t = 1/\left[\xi_0^+\right]^{1/\nu}$, and $a_h = 1/\left[\xi_{0,h}\right]^{\Delta/\nu}$.

In the next section we are going to consider the Casimir force within the Ginzburg–Landau mean-field model. Let us recall that the model we are going to consider is a standard model within which one studies phenomena like critical adsorption [22,26–39], wetting or drying [11,36,37,40–42], surface phenomena [9,10], capillary condensation [27,31,32,34,39,41,43,44], localization–delocalization phase transition [7,43,45], finite-size behaviour of thin films [3–7,31,39,43,46–50], the thermodynamic Casimir effect [34,50–56], etc. The results of the model have been also used to calculate the Casimir forces in systems with chemically or topographically patterned substrates, as well as, coupled with the Derjaguin approximation, for studies on interactions of colloids—see, e.g., the review [23] and the literature cited therein. Until very recently, i.e. before