Critical Casimir effect in $^3$He-$^4$He films

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Abstract. – Universal aspects of the critical Casimir force $f_C$ in wetting films of $^3$He-$^4$He mixtures near their bulk tricritical point are studied within models of the corresponding universality class. $f_C$ for such films of thickness $L$ is calculated along isotherms at several fixed concentrations of $^3$He. Nonsymmetric boundary conditions impose nontrivial concentration profiles leading to repulsive force which exhibit a rich crossover behavior between the tricritical point and the line of critical points. The theoretical results agree semiquantitatively with published experimental data and emphasize the importance of logarithmic corrections. The universal Casimir amplitude is the amplitude of the leading behavior $\sim L^{-3}(\ln L)^{1/2}$ dominating the contribution $\sim L^{-3}$ whose amplitude is nonuniversal and which is comparable with the background dispersion force contributions.

Finite-size contributions to the free energy of a fluid confined between two surfaces at a distance $L$ give rise to an effective force between them. Theory predicts that at the bulk critical point $T_c$ of such a system this force becomes long-ranged as a result of critical fluctuations of the corresponding ordering degrees of freedom. This is analogous to the well-known Casimir effect in electromagnetism. This so-called critical Casimir force $f_C$ per unit area and in units of $k_B T_c$ can be expressed in terms of universal scaling functions [1].

Only recently, sophisticated wetting experiments have provided detailed quantitative data for critical Casimir forces in various systems [2–6]. In the case of $^4$He wetting films near the superfluid transition, these experimental studies support quantitatively theoretical predictions for $f_C$ ($T \geq T_c$) corresponding to the universality class of the XY model [7]. For the case of $^3$He-$^4$He films near the bulk tricritical point some theoretical predictions are available [7], but those do not apply for the boundary conditions relevant for recent wetting experiments performed in these systems [4, 5]. However, the shape of the scaling function of the Casimir force depends sensitively on the type of boundary conditions (BC) and thus on the surface universality classes to which the confining surfaces belong [8]. The experiments of ref. [4]
report a repulsive \( f_C \) around the tricritical point which suggests nonsymmetric BC for the superfluid order parameter \((\text{OP})\). This is opposite to the case of pure \(^4\)He wetting films near the \( \lambda \)-point, where \( f_C \) was found to be attractive \([2,7]\). For the latter system the BC seem to be very well approximated by symmetric Dirichlet-Dirichlet BC \((O,O)\) forming the so-called ordinary \((O)\) surface universality class because the quantum-mechanical wave function describing the superfluid state vanishes at both interfaces \([1,2]\). In \(^3\)He-\(^4\)He wetting films a \(^4\)He-rich layer forms near the substrate-fluid interface, which may become superfluid already above the bulk \( \lambda \)-line \([9]\) whereas \(^3\)He has a preference for the fluid-vapor interface. Thus the two interfaces impose a nontrivial concentration profile which in turn couples to the superfluid OP. This suggests that the concentration profile induces indirectly nonsymmetric BC for the superfluid OP. It is not clear from the outset whether and to which extent this leads effectively to Dirichlet BC at the fluid-vapor interface and to symmetry-breaking (+) BC at the substrate-fluid interface \([10]\). We address this issue by explicit model calculations.

Here we consider two complementary approaches. Field-theoretical methods and renormalization group (RG) analyses are used to derive universal properties of the Casimir force at the tricritical point and the form of logarithmic corrections. However, these methods do not lend themselves to systematic studies of \( f_C \) along all thermodynamic paths followed in the aforementioned experiments. In order to be able to interpret the rich variation of \( f_C \) extracted from the capacity measurements in ref. \([4]\), to understand the emergence of the actual BC and, moreover, to predict the behavior of \( f_C \) in the crossover region between the tricritical and the critical points, we employ the vectoralized Blume-Emery-Griffiths model (VBEG) \([12]\) as a representative of the same universality class as the actual physical system. This lattice model is extended to the film geometry and treated within mean-field theory (MFT).

First we derive the leading asymptotic behavior of \( f_C \) at tricriticality for \((O,+):\) BC. To this end we consider the standard Ginzburg-Landau (GL) Hamiltonian for an \( O(n) \)-symmetric tricritical system (at \( T = T_c \), the tricritical temperature) in a film geometry:

\[
\mathcal{H}[\Phi] = \int d^{d-1}x \int_0^L dz \left\{ \frac{1}{2}(\nabla \Phi)^2 + \frac{u}{6!}(\Phi^2)^3 \right\},
\]

where \( L \) is the film thickness, \( \Phi \) is the \( n \)-component OP and \( z \) is the distance between the confining surfaces; \( u \) is a bare coupling constant. In a film geometry \( f_C = -(\partial f^{ex}/\partial L) = \langle T_{zz} \rangle \) is given by the stress tensor component \( T_{zz} \) \([1]\), where \( f^{ex}(L) \equiv (f - f_b)L \), \( f \) is the total free energy per unit area and per \( k_B T \) and \( f_b \) is the bulk contribution. The stress tensor is given by \([1]\) \( T_{ij} = \partial_i \Phi \cdot \partial_j \Phi - \delta_{ij} L - (d-2)/(4(d-1)) (\partial_i \delta_{ij} - \delta_{ij} \nabla^2) \Phi^2 \), where \( L \) is the integrand of \((1)\). We take \( \Phi = (m(z),0,\ldots,0) \). Determination of the tricritical Casimir force starts from the Euler-Lagrangian equation for the OP profile: \( m''(z) = (u/120)m^5(z) \) with \((O,+):\) BC, i.e., \( m(0) = 0 \) and \( m(L) = +\infty \). In this case the spatially constant \( \langle T_{zz} \rangle \) can be expressed as \((1/2)(m'(0))^2\). With the scaling ansatz

\[
m(z) = (u/360)^{-1/4} L^{-1/2} \varphi(z/L) \quad \text{and} \quad \langle T_{zz} \rangle = (90/u)^{1/2} L^{-3} \Theta,
\]

and after integrating directly the first integral of the Euler-Lagrange equation one obtains

\[
\Theta^{1/3} = \int_0^\infty dp/\sqrt{1 + p^2} \simeq 1.40218
\]
by implementing the above BC. Eventually, in units of $k_B T_t$ the MFT result for the tricritical Casimir force $f_C^l$ in the case of $(O, +)$ BC is
\[ f_C^l = 2.7568(4) \left( \frac{90}{u} \right)^{1/2} L^{-3}. \] (4)

Note that within MFT the parameter $u > 0$ remains undetermined. Its value follows from using standard RG arguments. In $d = 3 - \epsilon$ the above MFT result yields the leading contribution in an $\epsilon$-expansion. After removing the UV singularity via renormalization the asymptotic scaling behaviour of $f_C^l$ follows by substituting for $u$ the appropriate fixed-point value $u^* \propto \epsilon$.

At $d = d^*$, and under spatial rescaling by a factor $\ell$, $u$ flows to its RG fixed point value $u^* = 0$ according to $\bar{u}(\ell) = (240 \pi^2)/((3n + 22) \ln \ell) \ | \ell| [13]$. This limiting expression is correct to order $O(\ln |\ln \ell|/\ln^2 \ell)$ for $\ell \to 0$. With the rescaling factor $\ell = l_0/L$, where $l_0$ is some microscopic length scale of the order of a few Å, this yields a logarithmic correction to the power law $L$-dependence of the tricritical Casimir force:
\[ f_C^l \approx 0.54(3n + 22)^{1/2}(\ln L/l_0)^{1/2} L^{-3} \left[ 1 - c \frac{\ln \ln L/l_0}{\ln L/l_0} + \ldots \right]. \] (5)

Determining the constant $c$ requires work to extend ref. [13] which is left for future research. Gaussian fluctuations give contributions of at least $O(u^0)$ which are therefore subdominant (of order $L^{-3}$). We compare eq. (5) for $n = 2$ with the data obtained by Garcia and Chan [4] for their experimental value $L/l_0 \approx 520$ Å/1.3 Å. This gives $\vartheta_l \equiv f_C^l L^3 \approx 6.96$ whereas $\vartheta^{\text{exp}}_l = 8.4 \pm 1.7$, which suggests agreement with the experimental data. In order to extract the actual value of the universal Casimir amplitude (i.e., the numerical prefactor in eq. (5)) the experimental data require a reanalysis based on the functional form given by eq. (5) and to take into account the correction terms.

Now we turn to the VBEG model and consider a $d = 3$ simple cubic lattice consisting of $L$ parallel lattice layers at spacing $a$. Each layer has $A$ sites, labeled $i, j, \ldots$ and associated with an occupation variable $t_i = 0, 1$ and a phase $\theta_i (0 \leq \theta_i < 2\pi)$ which mimics the phase of the $^4$He wave function. A $^3$He ($^4$He) atom at site $i$ corresponds to $t_i = 0(1)$. The Hamiltonian is given by
\[ H = -J \sum_{\langle ij \rangle} t_i t_j \cos(\theta_i - \theta_j) - K \sum_{\langle ij \rangle} t_i t_j + \sum_i \Delta_i t_i, \] (6)

where the first two sums run over nearest-neighbor pairs and the last one is over all lattice sites. The field $\Delta_i$ is related to the chemical potentials of the two components of the mixture. $\Delta_1 = \Delta_1$ and $\Delta_1 = \Delta_2 = \Delta$, on the left and right surface layer, respectively, and $\Delta_1 = \Delta_2 = \Delta$ otherwise. The differences $\Delta_i - \Delta$, $i = 1, 2$, are a measure of the relative preferences of $^4$He atoms for the two surfaces such that $\Delta_1 < \Delta$ corresponds to the preference of $^4$He atoms for the solid substrate. At the opposite surface with the vapor we choose $\Delta_2 = \Delta$, the tricritical bulk value. Near the tricritical point this choice is consistent with the assumption made in ref. [4] for the concentration profile across the wetting film, whereby at the interface with the vapor the $^3$He mole fraction takes the bulk value.

Bulk properties of this model were studied within MFT and by Monte Carlo simulations in $d = 3$ in [12]. The resulting bulk phase diagram resembles that observed experimentally for $^3$He-$^4$He mixtures (see fig. 1). For the film geometry we have solved this model within MFT. This yields a set of self-consistent equations for the OP in the $l$-th layer, i.e., the concentration $Q_l = \langle t_i \rangle = 1 - X(l)$ of $^4$He, and the superfluid OP $M_l = (m_i^{(1)}, m_i^{(2)})$ with $m_i^{(1)} = \langle t_i \cos \theta_i \rangle$ and $m_i^{(2)} = \langle t_i \sin \theta_i \rangle$, where $t_i$ and $\theta_i$ denote the occupation number and the phase in the $l$-th
Fig. 1 – Phase diagram for the VBEG model obtained within MFT for $K/J = 0.5$ and $\Delta_1/J = -3$ exhibiting the bulk $\lambda$-line $T_s(X)$ of continuous superfluid transitions (long-dashed line), the phase separation curves (solid lines), the tricritical point $A = (T/T_s(0) = 2/3, X = 1/3)$, and the surface transition line (short-dashed line) which merges with the bulk $\lambda$-line at the special transition point $S = (T/T_s(0) \simeq 0.759, X \simeq 0.241)$. Vertical lines represent thermodynamic paths along which the Casimir force has been calculated (see fig. 3). ♦, •, (A), ▲: state points considered in fig. 2.

In the absence of helicity one has $M_l = (m_l(1), 0) \equiv (m_l, 0)$,

\begin{align}
Q_l &= I_0(\tilde{J}b_l)/\left(e^{-\tilde{K}a_l+\Delta_l/T} + I_0(\tilde{J}b_l)\right), \\
m_l &= I_1(\tilde{J}b_l)/\left(e^{-\tilde{K}a_l+\Delta_l/T} + I_0(\tilde{J}b_l)\right),
\end{align}

(7) (8)

$I_0(z)$ and $I_1(z)$ are modified Bessel functions and $\Delta_l = \Delta$ for $l \neq 1, L$; $\tilde{K} = qK/T$ and $\Delta_2/J = \Delta_t/J \simeq 0.61$ corresponding to the state points ♦, •, and ▲ indicated in fig. 1. Here $t = (T - T_t)/T_t$.

Fig. 2 – (a) Concentration $X(l) = 1 - Q_l$ of $^3$He in the $l$-th layer ($l$ is in units of the lattice constant $a \equiv 1$) and (b) superfluid OP $m_l$ profile for a VBEG film of width $L = 60$ for $K = 0.5J$, $\Delta_1/J = -3$, and $\Delta_2/J = \Delta_t/J \simeq 0.61$ corresponding to the state points ♦, •, and ▲ indicated in fig. 1. Here $t = (T - T_t)/T_t$. 
\[ J = qJ/T, \] where \( q = q_\perp + 2q' \) is the coordination number of the lattice. \( q_\perp \) is the in-layer coordination number while each site (but not in the first and last layers) is connected to \( q' \) atoms in each adjacent layer. We have introduced

\[ \begin{align*}
  b_l &\equiv m_{l-1} + q_\perp m_l + m_{l+1} & \text{for } & l \neq 1, L, \\
  a_l &\equiv Q_{l-1} + q_\perp Q_l + Q_{l+1} & \text{for } & l \neq 1, L,
\end{align*} \tag{9} \tag{10} \]

where \( b_1 \equiv q_\perp m_1 + m_2, b_L \equiv m_{L-1} + q_\perp m_L \) and \( a_1 = q_\perp Q_1 + Q_2, a_L = Q_{L-1} + q_\perp Q_L \). The coupled equations for \( Q_l \) and \( m_l \) are solved numerically; the acceptable solution minimizes the free energy.

First, we have analyzed the semi-infinite system. Close to the \( \lambda \)-line we observe a higher \( ^4\)He concentration near the left surface, which induces a local superfluid ordering (see fig. 2). By varying \( T \) and \( \Delta \) one obtains a whole line of continuous surface transitions corresponding to the onset of the formation of a superfluid film near the wall; it meets the \( \lambda \)-line at the special transition point whose position depends on the value of \( \Delta \) (see fig. 1). These findings are in agreement with the results of a Migdal-Kadanoff analysis [14]. In the film geometry the Casimir force is obtained by taking a finite difference after calculating \( f_{CS} \) for \( L_0 \) and \( L_0 + 1 \).

Figure 3 summarizes our result for a film of width \( L = 20, K/J = 0.5, \Delta_1/J = -3, \) and \( \Delta_2 = \Delta_t/J \approx 0.61 \). \( f_C \) is calculated along the thermodynamic paths indicated in fig. 1. Below \( T_t \), \( f_C \) is calculated along the coexistence line, infinitesimally on the superfluid branch of bulk coexistence. Our results are presented in terms of the scaling function \( \vartheta \equiv L^d f_C \) as a function of the scaling variable \( y \equiv tL^{1/\nu} = (L\xi_0/\xi)^{1/\nu} \), where \( t = (T - T_t)/T_t \). \( \xi_0 \) is the amplitude of the correlation length \( \xi \) and \( \nu = 1 \). The surface transition does not leave a visible trace in the behavior of \( f_C \). For \( ^3\)He concentration \( X < X_t \), upon crossing the \( \lambda \)-line there is a steep variation associated with a break in slope, giving rise to the formation of shoulders which are similar to those observed experimentally [4]. For \( X > X_t \), when \( T \) reaches the phase separation temperature \( f_C \) coincides with the curve common to all values of \( X \). This occurs with a discontinuous first derivative. The aforementioned common curve exhibits a pronounced maximum below \( T_t \) at \( y \approx -0.74 \) and gradually decreases to zero for \( y \to -\infty \).

Below \( T_t \), both the concentration and the superfluid OP profiles corresponding to this common curve display an interface-like structure separating two domains of the coexisting bulk phases (see \( t = -0.0625 \) in fig. 2). Features of \( f_C \) in this “soft mode” phase can be attributed to purely interfacial effects, as in Ising-like films with asymmetric BC [15]. Beyond MFT a positive sign of the force can be regarded as a consequence of entropic repulsion [16]. The maximum of \( f_C \) is expected to occur at the temperature \( T \) for which the interfacial width \( \sim \xi_b \sim L \), i.e., \( y \sim -1 \) [15] which checks with fig. 3 [17].

For \( X \leq X_t - 0.05 \) we observe a crossover to the critical superfluid behavior of pure \( ^4\)He and a gradual formation of a second, less pronounced local maximum located slightly below the \( \lambda \)-line. This local maximum decreases upon departure from \( X_t \) and finally disappears above the special transition \( S \). This is expected, because above \( S \) the BC turn into the type \((O,O)\) for which \( f_C \) vanishes within MFT. For lower \( T \), \( f_C \) increases steeply upon approaching bulk coexistence revealing that interfacial effects associated with the “soft mode” lead to a much stronger Casimir effect than near the critical \( \lambda \)-line.

The qualitative features of \( \vartheta \) extracted from the experimental data for \( X \approx X_t \) (see fig. 5 in ref. [4]) are very well captured by the present lattice model. Discrepancies can be attributed to fluctuation effects neglected in the present MFT VBEG approach: i) The discontinuities of slopes as obtained within MFT upon crossing the \( \lambda \)-line are expected to be smeared out by fluctuations. ii) The experimental scaling function \( \vartheta \) does not vanish at low temperatures, which may be due to Goldstone modes in the superfluid phase. However, the possibility that
this behavior is an artifact of an extreme change in the dielectric constant of the film cannot be excluded [18].

In the crossover regime to the critical behavior only few experimental data for the thickness of the wetting film are published. However, again the variation of film thicknesses agrees with our findings. In particular, one observes a rapid thickening of the films upon approaching the coexistence line; for some values of $X$ a small maximum located near the $\lambda$-line is also visible (compare fig. 3). A quantitative comparison is not possible because, for our realistic choices

\[ \vartheta(y) \text{ is rescaled to match the experimental data at the tricritical point } y = 0. \]
of surface terms in the Hamiltonian, the fixed-point BC \((O, +)\) cannot be reached within the VBEG model. In order to be able to extract universal properties—which requires attaining fixed-point boundary conditions—it would be necessary to introduce a surface field which couples to the superfluid OP so that the BC \((+)\) can be realized. Also MFT is not sufficient, even in \(d = d^*\). A naive correction of \(\vartheta\) by the logarithmic factor derived within the GL model will not give the proper universal behavior. Instead, renormalization group schemes or Monte Carlo simulations have to be employed. Nonetheless, our MFT results for \(X = X_t\), if matched at the tricritical point \(y = 0\) and after fixing a nonuniversal adjustable parameter, the amplitude \(\xi_0\), so that the positions of the maximum of the scaling function are the same (i.e., \(\xi_0^*/a \approx 0.065\)) reproduce very well the experimental curve (see fig. 4), especially near the maximum where we expect interfacial effects to be dominant. This is consistent because the “soft mode” phase does not depend on the details of the surface fields. Notice that the experimental data nominally for \(X = X_t\) more closely match the theory for \(X = X_t - 0.01\). This raises the question as to whether the \(^3\)He concentration in the film is shifted relative to the bulk one.

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