# INTERFACIAL ENTROPY PROFILE IN THE ONE-LOOP APPROXIMATION

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The near-critical interfacial entropy profile is calculated in the one-loop approximation of renormalized field theory. The shape of the profile is broadened by fluctuations and goes beyond the mean-field coupling between the entropy and the order parameter. The excess interfacial entropy and heat capacity are calculated by using the entropy profile. The interface creates corrections to the heat capacity and entropy of order $\xi/L$, where $\xi$ is the correlation length, and $L$ is a characteristic length of the system. These results are discussed in relation to finite-size scaling, surface critical phenomena, and the results of experiments and simulations.

## 1. Introduction

The near-critical interfacial entropy profile has received a significantly less attention than the near-critical interfacial order parameter profile (see [1] for a review of the later). This deficit is in part due to the fact that the order parameter profile is easily related to the most experimentally accessible interfacial property: the surface tension. However, there is at least one practical reason why the entropy profile is also worthy of investigation: it determines the interfacial heat capacity. In systems where the interfacial energy is significant relative to the bulk energy, the heat capacity can be expected to deviate from its bulk value. The study of these deviations requires a fluctuation-modified entropy profile.

After the first reviewing of the mean-field entropy profile in Section 2 and the near-critical thermodynamics in Section 3, we calculate the near-critical interfacial entropy profile using renormalization group techniques and the $\epsilon$ expansion in Section 4. The entropy profile is used to calculate the interfacial entropy and heat capacity contributions. Some implications of these results are discussed in Section 5 followed by a brief summary in Section 6.

## 2. Mean-field Entropy Profile

The Landau expansion of the Helmholtz energy density (in $\rho_c k_B T_c$ units, where $\rho_c$ is the critical density, $k_B$ is Boltzmann's constant, and $T_c$ is the critical temperature) is given by

$$f \approx \frac{1}{2}|\nabla m|^2 + \frac{1}{2}tm^2 + \frac{g}{4!}m^4, \quad (1)$$

where $m$ is the dimensionless order parameter, $g$ is a constant, and the reduced temperature is defined by $t = (T - T_c)/T_c$. The function $f$ is the critical part of the total Helmholtz energy density. Consequently, the entropy density and heat capacity calculated from the Landau expansion are zero above the critical point. Constants in front of the quadratic terms have been absorbed into the temperature and length scales. The order parameter is thermodynamically conjugate to the ordering field $h$ such that $h = (\delta f/\delta m)_t$. For a one-component fluid, the order parameter is identified, in the first approximation, with the density, namely $m = (\rho - \rho_c)/\rho_c$. When $t > 0$, the order parameter is zero for $h = 0$, and the system does not exhibit any spontaneous ordering. However, for $t < 0$ and $h = 0$, the system can separate into two phases, with $m \neq 0$, which are divided by an interfacial region. In this case, assuming a planar interface perpendicular to the $z$-direction, the order parameter is given by [1]

$$m(\hat{z}) = m_\infty(t) \tanh(\hat{z}), \quad (2)$$

where $m_\infty(t) = (6|t|/g)^{1/2}$ is the bulk order parameter, $\hat{z} = z/2\xi$, and the mean-field correlation length, which determines the interfacial thickness, is $\xi = |2t|^{-1/2}$. The corresponding entropy density is found to be

$$s(\hat{z}) = -\left(\frac{\partial f}{\partial t}\right)_m = -\frac{1}{2}m(\hat{z})^2. \tag{3}$$

The two bulk phases are located at $z = \pm\infty$ and are characterized by $s_\infty = -3|t|/g$. The entropy density takes on its maximum value at $z = 0$, where the bulk phases "mix" in equal proportion. Since the entropy of the bulk phases is asymptotically the same for both branches of the coexistence curve ($z = \pm\infty$), the interfacial entropy $S_\Sigma$ per unit area is calculated without reference to a particular dividing surface as

$$S_\Sigma/\Sigma = \int_{-\infty}^{\infty} [s(z) - s_\infty]\, dz = -4\xi s_\infty, \tag{4}$$

where $\Sigma$ is the area of the interface.

The zero-field interfacial heat capacity is related to the interfacial entropy by $C_\Sigma = (\partial S_\Sigma/\partial t)_{h=0}$. In the mean-field approximation, the interfacial heat capacity is found to be

$$C_\Sigma/\Sigma = -2\xi c_\infty, \tag{5}$$

where the bulk heat capacity at zero field is defined by $c_\infty = (\partial s_\infty/\partial t)_{h=0}$. For the Landau expansion, $c_\infty = 3/g$. The interfacial entropy makes two contributions to the interfacial heat capacity: the first is due to a variation of the interfacial width, and the second is due to a variation of the bulk entropy. The net result is a reduction of the heat capacity relative to the bulk value. Note that while $S_\Sigma$ is positive, $s_\infty$ and $C_\Sigma$ are negative.

From Eq. (5), we see that the interfacial heat capacity behaves as $C_\Sigma \sim -|t|^{-1/2}$. It is worth noting that this type of singularity is also seen when order parameter fluctuations are included, in the regime where the Landau expansion is valid, in the mean-field theory. Above $T_c$, the mean-field bulk heat capacity, which is zero in the absence of fluctuations, becomes $c = (1/6g)|t|^{-1/2}$ when fluctuations are included [2]. The ratio of the fluctuation-induced heat capacity with the mean-field heat-capacity discontinuity, $3/g$, resulting from Eq. (3), yields the Ginzburg number. The magnitude of the Ginzburg number determines the significance of critical fluctuations [3]. In contrast to the interface which lowers the heat capacity, the fluctuations increase it. Even though the physical origins of these two effects are different, they share the same temperature dependence since they both arise from the square-gradient term in the Helmholtz energy expansion.

## 3. Bulk Near-critical Thermodynamics

The preceding results are not expected to agree quantitatively with actual critical behavior, since the Landau theory does not properly account for fluctuations of the thermodynamic variables near the critical point. The fluctuations become long-ranged near the critical point, and significantly alter the mean-field results. In zero field, $h = 0$, the asymptotic bulk behavior of the order parameter and entropy are properly described by scaling theory [4]. Asymptotically,

$$m_\infty \approx \pm B|t|^\beta, \quad (t < 0), \tag{6}$$

$$s_\infty \approx \frac{A^\pm}{1-\alpha} t|t|^{-\alpha} - A_{\text{cr}} t, \tag{7}$$

where $\alpha \simeq 0.11$ and $\beta \simeq 0.326$ are universal critical exponents, and $B$, $A^+$, $A^-$, and $A_{\text{cr}}$ are system-dependent amplitudes [4]. In Eq. (6), $\pm$ correspond to the two branches of the coexistence curve. However, in Eq. (7), the superscript $\pm$ denote the different amplitudes above and below $T_c$. The term with coefficient $A_{\text{cr}}$ is the analytic fluctuation-induced contribution to the entropy. The bulk heat capacity in zero field is therefore

$$c_\infty \approx A^\pm |t|^{-\alpha} - A_{\text{cr}}. \tag{8}$$

## 4. Fluctuation-effected Entropy Profile

Our calculation of the fluctuation-modified entropy profile closely parallels Ohta and Kawasaki's work on the order parameter profile [5]. The renormalized Helmholtz energy density, in the one-loop approximation, is given by [6]

$$f \approx \frac{1}{2}|\nabla m|^2 + \frac{1}{2}Z_2 t m^2 + \frac{g}{4!}Z_4 m^4 + \frac{1}{2}\text{Tr}\ln H. \tag{9}$$

The renormalization constants are

$$Z_2 = 1 + \frac{1}{2}gJ, \quad Z_4 = 1 + \frac{3}{2}gJ, \tag{10}$$

with

$$J = \frac{1}{\epsilon}\left(1 + \frac{\epsilon}{2} + O(\epsilon^2)\right), \tag{11}$$

where $\epsilon = 4 - d$, $d$ being the dimensionality of the system. The fluctuation operator $H$ is

$$H(\mathbf{x}_1, \mathbf{x}_2) = \left\{-\nabla_1^2 + t + \frac{g}{2}m(z_1)^2\right\}\delta(\mathbf{x}_1 - \mathbf{x}_2), \tag{12}$$

where $m(z_1)$ is given by Eq. (2). Using the fixed point value of the coupling constant, $g^* = (2/3)\epsilon$ [6], one can show that Eq. (9) reduces to Eq. (1) in the limit $\epsilon \to 0$. This corresponds to the fact that, for $d > 4$, fluctuations do not affect the bulk thermodynamics in this approximation, and the mean-field results presented in Section 2 are valid near $T_c$.

Applying Eq. (3) to Eq. (9), we find

$$gs = -\frac{g}{2}m^2 - \frac{g}{2}\left(t + \frac{g}{2}m^2\right)J - \frac{g}{2}\mathrm{Tr}\{H^{-1}\}, \tag{13}$$

where we have multiplied the entropy density by the coupling constant $g$ for convenience, since the combinations $gs$ and $gm^2$ are both $O(1)$. In what follows, we will only retain terms up to $O(\epsilon)$. Ohta and Kawasaki [5] have previously evaluated the trace in the final term and found

$$\frac{g}{2}\mathrm{Tr}\{H^{-1}\} = (2|t|)^{-\epsilon/2}\left[\frac{1}{2}\left(1+\frac{\epsilon}{2}\right)\mathrm{sech}^2(\hat{z}) - \frac{1}{3}\right] -$$

$$-\frac{\epsilon\pi}{2\sqrt{3}}\,\mathrm{sech}^2(\hat{z})\tanh^2(\hat{z}). \tag{14}$$

The correlation length, contained in the reduced variable $\hat{z} = z/2\xi$, is now given by $\xi = \xi_0|t|^{-\nu}$, where $\nu = 1/2 + \epsilon/12$ is a universal critical exponent and $\xi_0 = (2)^{-1/2}(1 - \epsilon/6[\sqrt{3}\pi - 4 + \ln 2])$. Combining Eqs. (13) and (14), we arrive at

$$gs = -\frac{1}{2}gm^2 - \frac{\epsilon}{6}\left(t + \frac{g}{2}m^2\right)[1 + \ln(2|t|)] -$$

$$-\frac{\epsilon}{6}|t|\left\{3 - (3+\sqrt{3}\pi)\frac{g}{6|t|}m^2 + \sqrt{3}\pi\left(\frac{g}{6|t|}m^2\right)^2\right\}, \tag{15}$$

where we have used the mean-field order parameter profile in terms that are of order $O(\epsilon)$. The terms inside of the braces arise solely from the interface and sum to zero for $m = (6|t|/g)^{1/2}$. Equation (15) expresses $s$ as a function of $m$ and $t$. In zero field, the order parameter and, hence, the entropy density are solely functions of temperature.

Ohta and Kawasaki [5] have calculated the fluctuation-effected interfacial order parameter profile using Eq. (9) and found

$$m(\hat{z}) = B|t|^{\beta}\tanh(\hat{z})\left[1 - \frac{\pi\epsilon}{6\sqrt{3}}\mathrm{sech}^2(\hat{z})\right]. \tag{16}$$

The order-parameter amplitude is $B = (6/g)^{1/2}(1 + \epsilon/6[1 - \ln 2])$, and $\beta = 1/2 - \epsilon/6$. The fluctuations tend to smooth and broaden the order parameter profile. Using Eq. (16), we can rewrite the zero-field entropy ($t < 0$) as

$$s(\hat{z}) = \frac{A^-}{1-\alpha}t|t|^{-\alpha} - A_{\mathrm{cr}}t +$$

$$+\left(A^- - A^+/2^{\alpha}\right)t|t|^{-\alpha}\left[\Phi(\hat{z}) - 1\right], \tag{17}$$

where, in agreement with the first $\epsilon$-expansion, $\alpha = \epsilon/6$, and where

$$\frac{A^-}{1-\alpha} = \frac{4}{2^{\alpha}g}\left(1 + \frac{\epsilon}{6}\right), \tag{18}$$

$$\frac{A^+}{1-\alpha} = \frac{1}{g}\left(1 + \frac{7}{6}\epsilon\right), \tag{19}$$

$$A_{\mathrm{cr}} = \frac{1}{g}\left(1 + \frac{4}{3}\epsilon\right), \tag{20}$$

and

$$\Phi(\hat{z}) = m(\hat{z})^2\left[1 - \frac{\epsilon\pi}{6\sqrt{3}}\,\mathrm{sech}^2(\hat{z})\right], \tag{21}$$

where $m(\hat{z})$ is given by Eq. (16). The bulk entropy found $z = \pm\infty$ agrees with the expected result:

$$s_{\infty} = \frac{A^-}{1-\alpha}t|t|^{-\alpha} - A_{\mathrm{cr}}t. \tag{22}$$

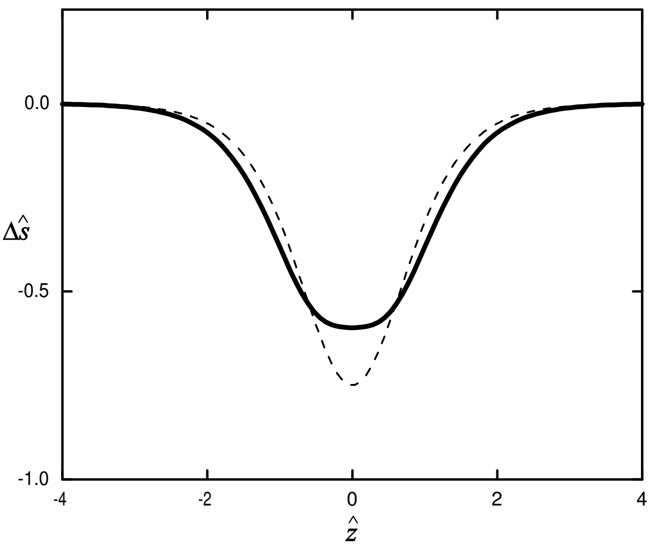
The reduced entropy profile, defined by $\Delta\hat{s} = [s(\hat{z}) - s_{\infty}]/s_{\infty}$, is plotted in the Figure alongside the mean-field profile for comparison.

Unlike the mean-field result, the fluctuation-modified entropy profile contains two terms which are independent of $z$, in addition to the profile-dependent term. The first term produces the asymptotic contribution to the bulk entropy below $T_c$ (*cf* Eq. (7)), while the second term $A_{\mathrm{cr}}t$ produces the well-known fluctuation-induced analytic contribution to the heat capacity [3]. The profile function given by Eq. (21) does not follow from the mean-field relationship between the entropy profile and the order-parameter profile found in Eq. (3). The amplitudes in Eqs. (18)–(20) agree with the bulk amplitudes found in the one-loop approximation and fully reproduce the amplitude ratio [7]

$$\frac{A^+}{A^-} = \frac{2^{\alpha}}{4}(1 + \epsilon). \tag{23}$$

Using Eq. (17), we find that the interfacial entropy becomes

$$S_{\Sigma}/\Sigma = -k\xi\frac{A^-}{1-\alpha}t|t|^{-\alpha}, \tag{24}$$




Reduced entropy profile (solid curve) found by using Eq. (17) and the corresponding mean-field result (dashed curve). Fluctuations broaden the profile and reduce the relative size of the peak at $z = 0$

with

$$k = 3\left(1 + \frac{\epsilon}{6}\left[\frac{\pi}{\sqrt{3}} - 3\right]\right), \tag{25}$$

and the interfacial heat capacity becomes

$$C_\Sigma/\Sigma = -k\left(1 - \frac{\nu}{1-\alpha}\right)\xi A^-|t|^{-\alpha}. \tag{26}$$

The interfacial heat capacity diverges with a universal power law as $C_\Sigma \sim -|t|^{-(\alpha+\nu)}$. The value of the corresponding critical exponent is $\alpha + \nu \simeq 0.74$, which leads to a stronger divergence than the mean-field prediction $C_\Sigma \sim |t|^{-1/2}$. If we extrapolate to $d = 3$ by taking $\epsilon \to 1$, we find $k \simeq 2.4$. The difference between this value of $k$ and the mean-field coefficient 4 (*c.f.* Eq. (4)) arises because the analytic background $A_{\mathrm{cr}}t$ is cancelled in Eq. (24).

## 5. Discussion

### *5.1. Dependence on dimensionality*

We have derived the interfacial entropy profile in an expansion around $d = 4$ and, by taking $\epsilon \to 1$, we have extrapolated the entropy profile to $d = 3$. This is the same approach taken by Ohta and Kawasaki in deriving the order-parameter profile. Our entropy profile therefore shares the same deficiencies as Ohta and Kawasaki's order-parameter profile. In particular, this approach skirts the issue of capillary waves [8], which are known to be relevant for $d = 3$. Calculating the order parameter profile around $d = 3$, Jasnow and Rudnick found that capillary-wave-like fluctuations destroy the profile in the absence of an external field (such as gravity for a fluid) [9]. In this treatment, the gravitational field makes a small non-universal contribution to the profile. This feature is also expected for an entropy profile calculation performed around $d = 3$. However, since Ohta and Kawasaki's profile yields results that are in close agreement with experimental surface tension measurements, we expect that our entropy profile is not too far off the mark.

### *5.2. Relation to surface phenomena*

The thermodynamics of interfaces is very closely related to the thermodynamics of surfaces, which has also been extensively investigated [10]. Much of the work on surface phenomena considers a semiinfinite domain extending from $z = 0$ to $z = \infty$, where the system is characterized by the bulk properties at $z = \infty$ and by special surface properties at $z = 0$. In a mean-field treatment, the surface effects are included by adding an additional term to the Helmholtz energy density

$$\hat{f} = f + \lambda^{-1}m(\partial m/\partial z), \tag{27}$$

where $\lambda$ is the so-called extrapolation length, which characterizes the deviation of the order-parameter at the surface from its bulk value. This term is normally excluded on the basis of translational invariance in bulk systems, a restriction that does not apply to semiinfinite systems. If the surface interactions are selected such that $m(z = 0) = 0$, the governing equations are identical to those describing an interface located at $z = 0$. Thus, the temperature dependence of the interfacial properties and the surface properties must be the same. Indeed, the surface heat capacity is predicted to scale as $C_s \sim |t|^{-(\alpha+\nu)}$ [10].

The similarity between surface phenomena and interfacial phenomena suggests that the interfacial entropy profile could be modified to describe the surface entropy. For non-zero values of the surface order parameter, the mean-field profile takes the form

$$m_s(\hat{z}) = m_\infty(t)\tanh(\hat{z} + \delta\hat{z}), \tag{28}$$

where the shift $\delta\hat{z}$ is related to the value of order parameter at the surface $z = 0$. This suggests that the surface entropy profile might be related to the interfacial entropy profile by a simple translation. More detailed calculations are needed to confirm this conjecture.

### *5.3. Relation to finite-size effects*

Our derivation of the entropy profile was made for a system of infinite spatial extent. To compare our predictions with experiments or simulations, the theory needs to be adapted to a finite system. For a finite system characterized by length $L$, we expect that interface-induced deviations from the bulk results will be determined by the ratio of the interfacial thickness and the system size $\sim \xi/L$. Explicitly,

$$C_\Sigma \simeq C_L \left[1 - k\left(1 - \frac{\nu}{1-\alpha}\right)\frac{\xi}{L}\right], \qquad (29)$$

where $L$ is the length of the system perpendicular to the interface, and $C_L$ is the finite-size heat capacity in the absence of the interface.

In Section 3, we described the way in which fluctuations modify bulk thermodynamic properties. In a finite-size system, the extent of fluctuations is constrained by the size of the system. This means that $C_\infty$ will also be modified by terms of order $\sim \xi/L$, such that

$$C_L \approx C_\infty \left(1 - a\frac{\xi}{L}\right), \qquad (30)$$

for $\xi/L \ll 1$, where $a$ is a positive constant. More details on finite-size scaling can be found in the review by Barber [11].

The interfacial reduction of the heat capacity only occurs below $T_c$, whereas the finite-size modifications of the heat capacity will be present above and below the critical point. This difference might allow the interfacial heat capacity reduction to be observed in simulations or experiments where other finite-size effects are present. However, the interfacial reduction will only be noticeable very close to $T_c$. Typically, for $t \simeq 10^{-4}$, $\xi \simeq 0.5$ $\mu$m. To make the effect detectable, one should have $L \lesssim 10$ $\mu$m.

## 6. Conclusion

In this work, we have calculated the fluctuation-affected interfacial entropy profile in the one-loop approximation. Just as in the case of the order-parameter profile, fluctuations were found to broaden the interfacial entropy profile. Additionally, we calculated the near-critical interfacial heat-capacity and found that it makes a negative contribution to the total heat capacity. The results were discussed in the context of the previous work, surface critical phenomena, and finite-size effects. The possibility of verifying these results via computer simulations seems promising.

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ПРОФІЛЬ ЕНТРОПІЇ ПОВЕРХНІ ПОДІЛУ
В ОДНОПЕТЛЬОВОМУ НАБЛИЖЕННІ

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Р е з ю м е

Розраховано профіль ентропій поверхні поділу поблизу критичної точки в однопетльовому наближенні ренормалізованої теорії поля. Профіль розширено флуктуаціями порівняно з наближенням середнього поля зі зв'язком між ентропією і параметром порядку. На цій основі розраховано надлишкові ентропія поверхні поділу і теплоємність. Наявність поверхні поділу приводить до поправок для теплоємності і ентропії порядку $\xi/L$, де $\xi$ – радіус кореляції, $L$ – характерна довжина системи. Ці результати обговорено у зв'язку з кінцеворозмірним скейлінгом, поверхневими критичними явищами, експериментом та результатами моделювання.