Coexistence at critical filling

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At the bulk liquid-gas coexistence the liquid film adsorbed on the corrugated substrate can exhibit a first-order thin-thick transition, provided the corrugation amplitude exceeds the critical value, specific for this kind of corrugation. We study the coexistence of thin and thick layer adsorbed on the sinusoidally corrugated substrate. We evaluate the line tension between these films in the vicinity of the filling critical temperature T_{CF}. The line $\mathcal{L}$ tension is positive and vanishes at the filling critical point according to the power law $\mathcal{L} \sim (T_{CF} - T)^{3/2}$.

I. INTRODUCTION

The adsorption of a fluid on a solid substrate can be influenced by the corrugation of a solid in two different ways. The wetting temperature can be decreased by the roughness; at the mean-field level it happens only when the wetting is a first-order transition. The second effect is more interesting; independently of the order of the wetting transition an additional thin-thick first-order transition can arise provided the amplitude of the corrugation exceeds a specific, critical value. This transition, called bending [1] or filling [2] transition, can depend not only on the roughness amplitude, but also on other geometrical properties of the substrate such as, for example, its local curvature.

In this paper we discuss the coexistence between thin and thick layer adsorbed on the sinusoidally corrugated substrate for the short-range interactions exhibiting the continuous wetting transition. We employ the mean-field approximation of the effective Hamiltonian theory. In this case the free energy of the system contains not only the bulk and surface contribution, but additionally the line contribution. We discuss the system close to the filling critical point, and we assume that the contact line is straight and perpendicular to the periodic structure of the substrate. Within the mean-field approximation critical quantities of the system are independent of its dimension. One expects that the singularity of the line tension obeys the same power law in the vicinity of the filling critical temperature T_{CF} like the surface tension in the vicinity of the wetting temperature T_W, i.e., vanishes with the critical exponent $\frac{1}{2}$. Indeed, we have found that the line tension is proportional to $(T_{CF} - T)^{3/2}$ when temperature grows to the filling critical temperature T_{CF}. Thus, the mean-field value of the critical exponent α_l connected to the singularity of the line tension is equal $\frac{1}{2}$. In Sec. II we recall the analysis described in [1,2]. In Sec. III we evaluate the mean-field value of the line tension at the temperature close to the critical filling temperature T_{CF}. Section IV contains the discussion of results.

II. THE ADSORPTION ON THE SINUSOIDALLY CORRUGATED SUBSTRATE

We discuss two-dimensional, corrugated substrate, described by the function

$$b(x,y) = A(1 - \cos qx). \tag{2.1}$$

The half space $z > b(x,y)$ is occupied by the fluid at the bulk liquid-gas coexistence, and infinitely far from the substrate the gas phase is stable. Due to the interactions of the fluid with the substrate, the adsorbed layer of the liquid appears on the wall. In this section we asume that the liquid-gas interface is (as the substrate) invariant in y direction. This assumption makes the problem one-dimensional; for this reason we denote the shape of the substrate simply by $b(x)$. We denote the film thickness by $l(x)$ and the position of the interface by $f(x)$, where $f(x) = b(x) + l(x)$. The interface has the same symmetry as the substrate. For this reason we can restrict our analysis to the one segment of the substrate. Thus the system is described by the Hamiltonian

$$\mathcal{H}[f] = \int_{-a}^{a} dx \left[\frac{\sigma}{2} f_x^2 + \omega(l) \right], \quad a = \frac{\pi}{q}, \tag{2.2}$$

supplemented by the boundary conditions

$$f_x(0) = f_x(a) = 0, \tag{2.3}$$

determined by the symmetry of the interface. Hamiltonian (2.2) is the appropriate one only when $qA \ll 1$. In Eq. (2.2) σ denotes the surface tension of the free liquid-gas interface and $\omega(l)$ is the effective interaction potential of the substrate. We discuss the potential of the form

$$\omega(l) = tW \exp(-p_\beta l) + U \exp(-2p_\beta l). \tag{2.4}$$

$t = (T - T_W)/T_W \lesssim 0$, where T_W is the wetting temperature of the planar substrate. The amplitudes W and U are positive; p_β is the inverse correlation length in the free liquid phase. The mean-field approach consists of the minimization of the Hamiltonian (2.2). In this way we obtain the Euler-Lagrange equation for the equilibrium position of the interface $\bar{f}(x)$

$$\sigma \bar{f}_{xx}(x) = \omega'(\bar{l}(x)). \tag{2.5}$$

The Hamiltonian (2.2) evaluated for this equilibrium position of the interface gives the mean-field free energy of the system.

Instead of solving Eq. (2.5) we can adopt an alternative procedure [1,2]. We approximate the film thickness up to its first harmonic

$$l(x) = l_0 + B \cos qx. \tag{2.6}$$

Next, we substitute Eq. (2.6) into Hamiltonian (2.2). This substitution reduces the Hamiltonian to the function of two variables,

$$\mathcal{H}(p_\beta l_0, p_\beta B) = \frac{\pi \sigma q}{2 p_\beta^2}(p_\beta B - p_\beta A)^2 + \frac{2\pi}{q}[tW e^{-p_\beta l_0}\Phi(p_\beta B)$$
$$+ U e^{-2 p_\beta l_0}\Phi(2 p_\beta B)], \tag{2.7}$$

where the function Φ is defined by the integral

$$\Phi(p_\beta B) = \frac{1}{\pi}\int_0^\pi dt \, e^{-p_\beta B \cos t}. \tag{2.8}$$

Minimization of the Hamiltonian with respect to l_0 gives

$$l_0 = l_\pi + p_\beta^{-1} \ln\left[\frac{\Phi(2 p_\beta B)}{\Phi(p_\beta B)}\right]. \tag{2.9}$$

$l_\pi = -\ln(-tW/2U)$ is the equilibrium film thickness on the planar substrate. Next we substitute $l_0(p_\beta B)$ into Eq. (2.7) and we obtain the Hamiltonian of the form

$$\Upsilon(p_\beta B) = \mathcal{H}(l_0(p_\beta B), p_\beta B)$$
$$= \frac{\pi \sigma q}{p_\beta^2}\left[\frac{1}{2}(p_\beta B - p_\beta A)^2 - \frac{1}{(q\xi_{\|\pi})^2}\frac{\Phi^2(p_\beta B)}{\Phi(2 p_\beta B)}\right]. \tag{2.10}$$

$\xi_{\|\pi}$ denotes the mean-field parallel correlation length on the planar substrate; this length is divergent at the wetting point. Minimization of the Hamiltonian (2.10) gives the equilibrium value $\bar{B}$ of the undulation amplitude of the film thickness. It satisfies equation

$$p_\beta A = p_\beta \bar{B} + \frac{2}{(q\xi_{\|\pi})^2}\frac{\Phi(p_\beta \bar{B})}{\Phi(2 p_\beta \bar{B})}\left[\frac{\Phi(p_\beta \bar{B})}{\Phi(2 p_\beta \bar{B})}\Phi'(2 p_\beta \bar{B})\right.$$
$$\left. - \Phi'(p_\beta \bar{B})\right], \tag{2.11}$$

where Φ' denotes the derivative of Φ with respect to its argument. Depending on the temperature and corrugation amplitude of the substrate Eq. (2.11) can have more than one solution. When there are three solutions of Eq. (2.11), the thin-thick coexistence can occur. Two of them are connected to the minima of Hamiltonian (2.10); we will denote them by $\bar{B}_1$ and $\bar{B}_3$. The third solution $\bar{B}_2$ $(\bar{B}_1 < \bar{B}_2 < \bar{B}_3)$ corresponds to the maximum of Hamiltonian. The mean-field free energy is then given by the expression

$$F(T, q, A) = \frac{\pi \sigma q}{(q\xi_{\|\pi})^2 p_\beta^2}\frac{\Phi^2(p_\beta \bar{B})}{\Phi(2 p_\beta \bar{B})}\left[\frac{2}{(q\xi_{\|\pi})^2}\Lambda(p_\beta \bar{B}) - 1\right], \tag{2.12}$$

where

$$\Lambda(p_\beta \bar{B}) = \frac{1}{\Phi(2 p_\beta \bar{B})}\left[\frac{\Phi(p_\beta \bar{B})}{\Phi(2 p_\beta \bar{B})}\Phi'(2 p_\beta \bar{B}) - \Phi'(p_\beta \bar{B})\right]^2. \tag{2.13}$$

At specific temperature $T_F(A)$ the free energy (2.12) evaluated for $\bar{B} = \bar{B}_1$ has the same value as the free energy evaluated for $\bar{B} = \bar{B}_3$. It is the filling transition temperature for the corrugation amplitude A. The line of such points is called the filling transition (or thin-thick) line. It terminates at the filling critical point defined by $p_\beta A_{CF} = 2.469$, and $(q\xi_{\|\pi})_{CF} = 0.492$.

When the temperature is less than the wetting temperature of the planar substrate T_W, the free energy of the system is negative due to the factor $(q\xi_{\|\pi})^{-2}$ into the square brackets, and continuously grows to 0 (it is the value of the free energy of the completely wet system) when temperature grows to T_W due to the factor $(q\xi_{\|\pi})^{-2}$ in front of the right-hand side (RHS) in Eq. (2.12). Thus the corrugated system displays the critical wetting at T_W.

III. THE COEXISTENCE OF TWO ADSORBED LAYERS

Now we take into consideration the thermodynamical conditions fixed at the thin-thick coexistence line $T_F(A)$ close to the critical filling point. We discuss the adsorbed liquid layer thin at $y = -\infty$ and thick at $y = \infty$ with the contact line situated at $y = 0$. The film thickness is represented by the function

$$l(x, y) = l_0(y) + B(y)\cos qx, \tag{3.1}$$

with the boundary conditions

$$l_0(-\infty) = \bar{l}_{01} = l_0(\bar{B}_1), \quad B(-\infty) = \bar{B}_1,$$

$$l_0(\infty) = \bar{l}_{03} = l_0(\bar{B}_3), \quad B(\infty) = \bar{B}_3, \tag{3.2}$$

where $\bar{l}_{01}$, $\bar{B}_1$, $\bar{l}_{03}$, and $\bar{B}_3$ denote the mean distance and the corrugation amplitude of the equilibrium thin or thick layer, respectively $(\bar{B}_1 < \bar{B}_3)$. The mean-field free energy of the thin and thick layer at the coexistence satisfy equations

$$F_1 = \mathcal{H}(p_\beta \bar{l}_{01}, p_\beta \bar{B}_1), \quad F_3 = \mathcal{H}(p_\beta \bar{l}_{03}, p_\beta \bar{B}_3), \quad F_1 = F_3. \tag{3.3}$$

Substituting $l(x, y)$ defined by Eq. (3.1) into the two-dimensional Hamiltonian analoguous to Hamiltonian (2.2)

$$\mathcal{H}[f] = \int_{-a}^{a} dx \int_{-\infty}^{\infty} dy \left[\frac{\sigma}{2}(\nabla f)^2 + \omega(l)\right], \tag{3.4}$$

and subtracting the surface contribuion, after a simple calculation we get the excess of the free energy connected to the thin-thick coexistence line. It is called the line tension

$$\mathcal{L} = \int_{-\infty}^{\infty} dy \left[\frac{\pi\sigma}{2q} \left(\frac{dB(y)}{dy} \right)^2 + \frac{\pi\sigma}{q} \left(\frac{dl_0(y)}{dy} \right)^2 \right.$$

$$\left. + \mathcal{H}(p_\beta l_0(y), p_\beta B(y)) - F_1 \right]. \tag{3.5}$$

Minimizing the line tension we obtain Euler-Lagrange equations

$$\frac{\pi\sigma}{q} \frac{d^2 B}{dy^2} = \frac{\partial \mathcal{H}}{\partial B}, \quad \frac{2\pi\sigma}{q} \frac{d^2 l_0}{dy^2} = \frac{\partial \mathcal{H}}{\partial l_0}. \tag{3.6}$$

Integrating these equations we obtain

$$\frac{\pi\sigma}{q} \left[\left(\frac{dl_0(y)}{dy} \right)^2 + \frac{1}{2} \left(\frac{dB(y)}{dy} \right)^2 \right] = \mathcal{H}(p_\beta l_0(y), p_\beta B(y)) - F_1. \tag{3.7}$$

The line tension can be rewritten as

$$\mathcal{L} = 2 \int_{-\infty}^{\infty} dy [\mathcal{H}(l_0(y), B(y)) - F_1]$$

$$= \frac{2\pi\sigma}{q} \int_{-\infty}^{\infty} dy \left[\left(\frac{dl_0(y)}{dy} \right)^2 + \frac{1}{2} \left(\frac{dB(y)}{dy} \right)^2 \right]. \tag{3.8}$$

It follows from Eq. (3.8) that the line tension is positive below the filling critical temperature. Close to the critical filling point $p_\beta(\bar{B}_3 - \bar{B}_1)$ and $p_\beta(\bar{l}_{03} - \bar{l}_{01})$ are small and in consequence we can linearize Eqs. (3.6) around $\bar{l}_{01}, \bar{B}_1$ for $y < 0$ and $\bar{l}_{03}, \bar{B}_3$ for $y > 0$:

$$l_0(y) = \bar{l}_{0k} + \delta l_{0k}(y), \quad B(y) = \bar{B}_k + \delta B_k(y), \quad k = 1, 3. \tag{3.9}$$

In this approximation Euler-Lagrange equations take the form

$$\frac{\pi\sigma}{q} \frac{d^2}{dy^2} \begin{pmatrix} \delta B_k \\ \delta l_{0k} \end{pmatrix} = \begin{pmatrix} \mathcal{H}_{BB}(k) & \mathcal{H}_{Bl_0}(k) \\ \frac{1}{2}\mathcal{H}_{Bl_0}(k) & \frac{1}{2}\mathcal{H}_{l_0 l_0}(k) \end{pmatrix} \begin{pmatrix} \delta B_k \\ \delta l_{0k} \end{pmatrix}$$

$$= \mathcal{A}(k) \begin{pmatrix} \delta B_k \\ \delta l_{0k} \end{pmatrix}, \tag{3.10}$$

where the matrix $\mathcal{A}(k)$ is evaluated at thin or thick equilibrium layer, respectively. The solution of these equations has the following form:

$$B(y) = \begin{cases} \bar{B}_1 + a_1 \exp(\gamma_1 y) + b_1 \exp(\eta_1 y) & \text{for } y \leq 0, \\ \bar{B}_3 + a_3 \exp(-\gamma_3 y) + b_3 \exp(-\eta_3 y) & \text{for } y \geq 0 \end{cases} \tag{3.11}$$

and

$$l_0(y) = \begin{cases} \bar{l}_{01} + c_1 \exp(\gamma_1 y) + d_1 \exp(\eta_1 y) & \text{for } y \leq 0, \\ \bar{l}_{03} + c_3 \exp(-\gamma_3 y) + d_3 \exp(-\eta_3 y) & \text{for } y \geq 0, \end{cases} \tag{3.12}$$

where γ_k and η_k $(k=1,3)$ are defined through eigenvalues s_{1k} and s_{2k} of the matrix $\mathcal{A}(k)$

$$\gamma_k = \sqrt{\frac{q s_{1k}}{\pi\sigma}}, \quad \eta_k = \sqrt{\frac{q s_{2k}}{\pi\sigma}}, \tag{3.13}$$

$$s_{1k} = \frac{1}{2} \frac{\mathcal{H}_{BB}(k) \mathcal{H}_{l_0 l_0}(k) - \mathcal{H}_{Bl_0}^2(k)}{\mathcal{H}_{BB}(k) + \frac{1}{2}\mathcal{H}_{l_0 l_0}(k)} = \frac{\det[\mathcal{A}(k)]}{\mathrm{Tr}[\mathcal{A}(k)]}, \tag{3.14}$$

$$s_{2k} = \mathcal{H}_{BB}(k) + \frac{1}{2}\mathcal{H}_{l_0 l_0}(k) - s_{1k} = \mathrm{Tr}[\mathcal{A}(k)] - s_{1k}. \tag{3.15}$$

The determinant of $\mathcal{A}(k)$ is related to the Hamiltonian (2.10) through the equation

$$\det[\mathcal{A}(k)] = p_\beta^2 (q\xi_{\|\pi})^{-2} \Psi(p_\beta \bar{B}_k) \left(1 - \frac{\Psi''(p_\beta \bar{B}_k)}{(q\xi_{\|\pi})^2} \right)$$

$$= p_\beta^2 (q\xi_{\|\pi})^{-2} \Psi(p_\beta \bar{B}_k) Y''(p_\beta \bar{B}_k), \tag{3.16}$$

where

$$\Psi(p_\beta B) = \frac{\Phi^2(p_\beta B)}{\Phi(2p_\beta B)}. \tag{3.17}$$

Since $\bar{B}_k$ is the minimum of Hamiltonian (2.10), $\det[\mathcal{A}(k)]$ is positive below the filling critical point, and vanishes at this point. For the same reason $\mathrm{Tr}[\mathcal{A}(k)]$ is positive independently of the temperature. Thus s_{1k} is positive below the filling critical point and vanishes at this point, while s_{2k} remains positive even at the filling critical point. The eigenvalues s_{1k}, s_{2k} are functions of $\bar{B}_k$, but close to the filling critical point one can replace its argument $\bar{B}_k$ by the undulation amplitude B_i at the filling critical point. Thus they have phase independent values s_1 and s_2, respectively. For this reason $a_3 = -a_1$, $b_3 = -b_1$ $c_3 = -c_1$, and $d_3 = -d_1$. The coefficients $a = a_1$, $b = b_1$, $c = c_1$, and $d = d_1$ in Eqs. (3.11) and (3.12) can be evaluated from the condition of continuity of $l_0(y)$, $B(y)$, and Eq. (3.10). The line tension is equal to

$$\mathcal{L} = \frac{2\pi\sigma}{q(\gamma + \eta)} \left[\frac{1}{2}\gamma\eta(a+b)^2 + \frac{1}{2}(\gamma a + \eta b)^2 + \gamma\eta(c+d)^2 \right.$$

$$\left. + (\gamma c + \eta d)^2 \right]. \tag{3.18}$$

The coefficients a, b, c, and d are evaluated in the Appendix. At the vicinity of the filling critical point the first and third contributions in square brackets dominate the second and fourth contributions. Thus the dominant contribution to the line tension in the vicinity of the filling critical point is equal

$$\mathcal{L} = \frac{\pi\sigma\gamma}{4q} \left(1 + 2l_0'(p_\beta B_i)^2 \right) (\bar{B}_3 - \bar{B}_1)^2. \tag{3.19}$$

Close to the filling critical point $(\bar{B}_3 - \bar{B}_1)^2$ and the line tension $\mathcal{L}$ is proportional to $(q\xi_{\|\pi})_{CF}^2 - (q\xi_{\|\pi})^2 \sim T_{CF} - T$ [2]. This result is obtained while expanding Hamiltonian (2.10) up to the fourth-order term in $(B - B_i)$ in the vicinity of the filling critical point, in the same way as standard Landau theory of

the bulk critical point, where the Landau Hamiltonian is expanded up to the fourth-order term of the order parameter. As $\gamma \sim \sqrt{T_{CF} - T}$ (Appendix), the asymptotic behavior of the line tension close to the critical filling temperature described by the power law

$$\mathcal{L} \sim A(T_{CF} - T)^{2-\alpha_l}, \tag{3.20}$$

for $T \lesssim T_{CF}$, gives the mean-field value of the critical exponent $\alpha_l = \frac{1}{2}$.

IV. SUMMARY AND CONCLUSIONS

We have obtained the mean-field value of the critical exponent describing the nonanalyticity of the line tension in the vicinity of the filling critical point. In accordance with the standard van der Waals result concerning the surface tension, $\alpha_l = \frac{1}{2}$.

Close to the filling critical temperature, the fluctuations of the film thickness become more and more pronounced as the system approaches T_{CF}. These fluctuations give an additional contribution to the true value of α_l. Here we do not discuss the influence of the fluctuation over the line tension; we only show that close to the filling critical point they are so strong that one cannot neglect them.

We describe the fluctuations in a very simplified way, taking into consideration a straight contact line, and assuming global fluctuations of l_0, and B, neglecting local fluctuations of the film thickness. Close to the filling critical point $\langle (\delta B)^2 \rangle = \langle (B - \bar{B}_k)^2 \rangle$ ($\bar{B}_k$ means $\bar{B}_1$ or $\bar{B}_3$, respectively) becomes greater than $(\bar{B}_3 - \bar{B}_1)^2$ and it is impossible to distinguish thin and thick film. We describe here the fluctuations of the undulation amplitude with the help of the Gaussian approximation

$$\langle (\delta B)^2 \rangle = \frac{1}{K} \int_0^\infty dl_0 \int_{-l_0}^{l_0} dB (\delta B)^2$$
$$\times \exp\left[-\frac{\beta}{2} (\delta B, \delta l) \begin{pmatrix} \mathcal{H}_{BB} & \mathcal{H}_{Bl_0} \\ \mathcal{H}_{Bl_0} & \mathcal{H}_{l_0 l_0} \end{pmatrix} \begin{pmatrix} \delta B \\ \delta l_0 \end{pmatrix} \right], \tag{4.1}$$

where the second derivative matrix is evaluated at $\bar{B}_3$ and $\bar{B}_1$ for thick and thin film, respectively. K is defined as

$$K = \int_0^\infty dl_0 \int_{-l_0}^{l_0} dB \exp\left[-\frac{\beta}{2} (\delta B, \delta l) \begin{pmatrix} \mathcal{H}_{BB} & \mathcal{H}_{Bl_0} \\ \mathcal{H}_{Bl_0} & \mathcal{H}_{l_0 l_0} \end{pmatrix} \begin{pmatrix} \delta B \\ \delta l_0 \end{pmatrix} \right]. \tag{4.2}$$

Because of the specific range of integration it is not easy to evaluate these integrals. Nevertheless, close to the filling critical point the leading, divergent term of the undulation amplitude fluctuations can be estimated as

$$\langle (\delta B)^2 \rangle \sim k_B T \frac{\partial}{\partial \mathcal{H}_{BB}} \ln(\det[\mathcal{H}'']) = \frac{k_B T}{\det[\mathcal{H}'']} \mathcal{H}_{l_0 l_0}. \tag{4.3}$$

Thus, very close to T_{CF} the fluctuation $\langle (\delta B)^2 \rangle$ is greater than $(B_3 - B_1)^2$ ($\det[\mathcal{H}'']$ vanishes at T_{CF}) and the mean-field approximation breaks down.

In the same way we can estimate

$$\langle (\delta l_0)^2 \rangle \sim \frac{k_B T}{\det[\mathcal{H}'']} \mathcal{H}_{BB} \tag{4.4}$$

and

$$\langle \delta B \delta l_0 \rangle \sim -\frac{k_B T}{\det[\mathcal{H}'']} \mathcal{H}_{Bl_0}. \tag{4.5}$$

All these quantities are divergent at the filling critical point but

$$\langle (\delta B)^2 \rangle \langle (\delta l_0)^2 \rangle - \langle \delta B \delta l_0 \rangle^2 \sim k_B T \tag{4.6}$$

remains finite.

A serious problem arises from the analysis described in Sec. I. The film thickness $l(x)$ has to be positive everywhere. However, in certain cases, depending on the amplitudes W, U of the effective potential $\omega(l)$, surface tension σ, and the temperature, this condition can be violated. In this case our analysis is not valid. In papers [1,2] the positivity of $l(x)$ was not discussed. The subsequent paper will be devoted to this problem.

ACKNOWLEDGMENTS

APPENDIX

In this appendix we evaluate coefficients a, b, c, and d present in Eq. (3.18). They are determined by the system of the linear equations

$$(\mathcal{H}_{BB} - s_1)a + \mathcal{H}_{Bl_0}c = 0,$$

$$(\mathcal{H}_{BB} - s_1)b + \mathcal{H}_{Bl_0}d = 0,$$

$$a + b = \frac{1}{2}(\bar{B}_3 - \bar{B}_1),$$

$$c + d = \frac{1}{2}(\bar{l}_{03} - \bar{l}_{01}) = \frac{1}{2}l'(p_\beta B_i)(\bar{B}_3 - \bar{B}_1). \tag{A1}$$

All derivatives of the Hamiltonian $\mathcal{H}$ are evaluated at $[B_i, l_0(p_\beta B_i)]$. As s_1 vanishes at the filling critical point, while $\mathcal{H}_{BB}$ does not vanish, we can neglect s_1 in the above equations. Solving Eqs. (A1) we obtain

$$a \simeq \frac{\bar{B}_3 - \bar{B}_1}{2 \operatorname{Tr}[\mathcal{A}]} \left(\frac{1}{2} \mathcal{H}_{l_0 l_0} - l'(p_\beta B_i) \mathcal{H}_{Bl_0} \right),$$

$$b \simeq \frac{\bar{B}_3 - \bar{B}_1}{2 \operatorname{Tr}[\mathcal{A}]} (\mathcal{H}_{BB} + l'(p_\beta B_i) \mathcal{H}_{Bl_0}). \tag{A2}$$

Explicit calculations show

$$\mathcal{H}_{Bl_0}(B_i, l_0(p_\beta B_i)) = -l'(p_\beta B_i)\mathcal{H}_{l_0 l_0}(B_i, l_0(p_\beta B_i)). \quad (A3)$$

With the help of this relation we finally obtain

$$a \simeq \frac{\bar{B}_3 - \bar{B}_1}{2\mathcal{H}_{l_0 l_0}\mathrm{Tr}[\mathcal{A}]}\left(\frac{1}{2}\mathcal{H}_{l_0 l_0}^2 + \mathcal{H}_{Bl_0}^2\right),$$

$$b \simeq \frac{\bar{B}_3 - \bar{B}_1}{\mathcal{H}_{l_0 l_0}\mathrm{Tr}[\mathcal{A}]}\det[\mathcal{A}]. \quad (A4)$$

Asymptotically, close to the filling critical point

$$a \sim t^{1/2}, \quad \gamma \sim t^{1/2}, \quad b \sim t, \quad a + b \sim t^{1/2}, \quad (A5)$$

and finally

$$\gamma\eta(a+b)^2 \sim t^{3/2}, \quad (\gamma a + \eta b)^2 \sim t^2. \quad (A6)$$

Analoguously we can obtain the asymptotic behavior of c and d.

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