Influence of inhomogeneous substrate curvature on line tension

P. Jakubczyk* and M. Napiórkowski

Instytut Fizyki Teoretycznej, Uniwersytet Warszawski, 00-681 Warszawa, Hoża 69, Poland
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Line tension accompanying equilibrium liquidlike films adsorbed at cylinder-shaped substrates equipped with chemical heterogeneities is studied within an effective interfacial Hamiltonian approach. The heterogeneity has the form of a stripe of width $2L$. The leading corrections to the line tension coefficient due to nonzero substrate curvature R^{-1} are derived. Their character is shown to be sensitively dependent on the system's temperature regime. For temperatures low enough that both the homogeneous components of the heterogeneous substrate remain nonwetted, the leading curvature correction is found to be proportional to R^{-1}. For temperatures such that one of the solid surface components is wetted by the fluid, one obtains corrections to the line tension of the order of either $(L/R)\ln R$ or $R^{-1/2}$ depending on the relative values of R and the heterogeneity width $2L$. For temperatures exceeding wetting temperatures of both the substrate components, the line tension is shown to decay to 0 in the limit $R \to \infty$ according to the power law $\eta \sim R^{-1/2}$.

I. INTRODUCTION

Adsorption of fluids at solid substrates equipped with chemical and geometrical structures has been a topic of increasing interest in recent years [1–17]. Theoretical studies have been stimulated by developments of experimental techniques allowing one to imprint solid surfaces with geometrical or chemical patterns of size down to the nanometer scale (see, e.g., [14–16].) Understanding the behavior of fluids in contact with such substrates is relevant in the context of microfluidics, e.g., when one wishes to transport a substance to desired locations where it is to undergo certain processes.

As extensive research reveals, the nature of adsorption crucially depends on the adsorbent geometry. Remarkable effort has been made to investigate the properties of physical quantities, like surface tensions and contact values of order parameters, in the particular cases of spherical and cylindrical geometries, in which the wetting transitions occurring in the planar case are prevented by the substrate's nonzero curvature [17–30].

It was shown by Hołyst and Poniewierski [17] (see also [28]) for systems of particles interacting via short-ranged forces, that the surface tension of the wall-gas interface σ_{WG} in the case of complete wetting of a substrate with positive curvature R^{-1} lacks an analytic expansion around $R^{-1}=0$. Explicitly, terms of the type l_{eq}/R, where $l_{eq} \sim \ln R$ is the equilibrium height of the adsorbed layer, enter the expansion of σ_{WG}.

In this paper we address the question of the structure of curvature contributions to the line free energy which arise when chemical inhomogeneity of a curved substrate is allowed. Interestingly, the character of the expansion of the line tension coefficient η around the zero-curvature limit is found to depend on temperature. The curvature corrections to η take the form of integer powers of R^{-1} provided the tem-

perature remains low enough, i.e., lower than the wetting temperatures of all homogeneous components of the heterogeneous adsorbent.

The system under study consists of a fluid in a thermodynamic state close to its bulk liquid-vapor coexistence in the presence of an infinite cylinder-shaped substrate. The substrate is equipped with a single, stripelike inhomogeneity placed on an otherwise chemically homogeneous surface (see Figs. 1 and 2). The heterogeneity border lines are assumed perpendicular to the cylinder axis, so that the interfacial morphology is invariant with respect to rotations around this axis. The substrate's chemical structure imposes nonuniformity of the adsorbed liquidlike layer, which gives rise to excess over the bulk and surface contributions to the system free energy. This contribution, evaluated per unit length of the inhomogeneity line (i.e., divided by $2\pi R$) is referred to as the line tension. The planar substrate case corresponding to $R^{-1}=0$ has been studied extensively from the point of view of both interfacial morphology characteristics and the properties of the line tension coefficient as a function of temperature and the inhomogeneity width $(2L)$ (see Refs. [7,31–33]). To our knowledge, the issue of the substrate curvature dependence of η has not been explored so far. In what follows, we apply the effective interfacial Hamiltonian approach for the case of short-ranged intermolecular forces in order to perform a perturbative expansion of the line tension
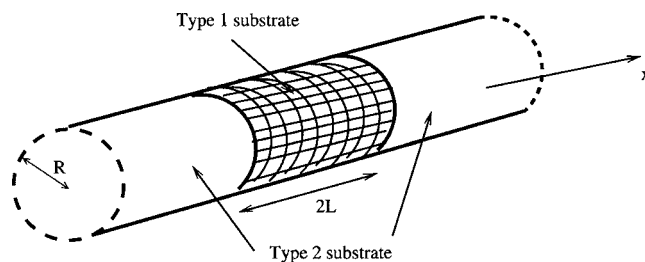

FIG. 1. A schematic illustration of the substrate under study. The infinite cylinder-shaped substrate of radius R contains a stripelike inhomogeneity of width $2L$.

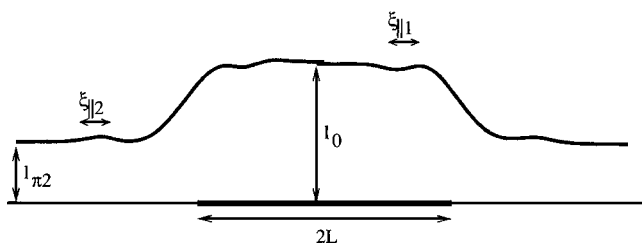*Corresponding author: Email address:
Pawel.Jakubczyk@fuw.edu.pl

FIG. 2. A cross section through a typical interfacial configuration above an inhomogeneous substrate. The wetting temperature of the stripe (T_{W1}) is assumed lower than the substrate wetting temperature (T_{W2}), so that the liquid phase is preferentially adsorbed in the vicinity of the stripe. The adsorbed liquid layer height corresponding to a homogeneous substrate of type 2 is denoted by $l_{\pi 2}$ and its height at the center of the heterogeneity by l_0. The interfacial correlation lengths $\xi_{\|1}$ and $\xi_{\|2}$ describe typical sizes of interfacial fluctuations for the case of adsorption at a homogeneous, planar substrate of types 1 and 2, respectively.

coefficient around the planar substrate limit, and show that the character of the leading curvature correction to η depends sensitively on the temperature regime and, in one of the regimes, also on the value of the parameter $L^2/(R\xi_B)$, ξ_B denoting the bulk correlation length in the adsorbed phase.

The work is arranged as follows. In Sec. II the model is introduced and the range of its applicability discussed. We outline the lines along which the line tension coefficient is evaluated. Section III contains our results together with the most relevant details of the calculations. In Sec. IV the results are summarized and discussed.

II. THE EFFECTIVE HAMILTONIAN MODEL

The analysis of the system is based on the effective interfacial Hamiltonian model, which in the considered case of two fluid phases coexisting in the presence of a cylinder-shaped substrate takes the form [20,34]

$$\mathcal{H}[l] = \int_0^{2\pi} d\phi \int_{-\infty}^{\infty} dx \left[\frac{\sigma}{2(l+R)} \left(\frac{\partial l}{\partial \phi} \right)^2 + \frac{\sigma}{2}(l+R) \left(\frac{\partial l}{\partial x} \right)^2 \right.$$
$$\left. + \sigma(l+R) + R\omega(x,l,R) \right]. \quad (1)$$

The function $l=l(x,\phi)$ denotes the position of the liquid-vapor dividing surface over the substrate. The x axis coincides with the cylinder axis and ϕ is the azimuthal angle. The first two terms, with σ being the surface tension between the fluid phases, describe the energetic cost of deviation of the interfacial shape from a cylindrical configuration of radius $R+l$. The term $\sigma(l+R)$ is the cost to create a unit length line in the x direction of the liquid-vapor interface at separation l above the substrate, and $\omega(x,l,R)$ denotes the effective potential of interaction between the substrate and the interface. The above effective Hamiltonian model describes the system on coarse-grained, mesoscopic length scales, i.e., length scales much larger than the bulk correlation length ξ_B.

The form of the effective Hamiltonian given in Eq. (1) was derived within Landau-Ginzburg-Wilson theory in Ref.

[34]. The derivation followed the ideas proposed by Jin and Fisher in Ref. [35] for the case of a planar substrate and amounted to introducing a constraint specifying the position of the liquid-vapor interface $l(x,y)$ and therefore limiting the accessible configurations of the bulk order parameter $m(\vec{r})$. The effective Hamiltonian has been identified as the logarithm of the partition function evaluated under this constraint. This derivation referred to a system with a chemically homogeneous substrate and was carried out within the mean-field approximation. A significant simplification of the model (1) is provided by the assumption that the crossover in $\omega(x,l,R)$ from $\omega_1(l,R)$ to $\omega_2(l,R)$, corresponding to homogeneous substrates of types 1 and 2, respectively, occurs over a distance of the magnitude of ξ_B. This assumption allows us to model $\omega(x,l,R)$ as [36]

$$\omega(x,l,R) = \Theta(L-|x|)\omega_1(l,R) + \Theta(|x|-L)\omega_2(l,R), \quad (2)$$

where $\Theta(x)$ is the Heaviside function.

The detailed structure of the effective potential $\omega_i(l,R)$ $(i=1,2)$ in the case of cylindrical geometry was discussed in Ref. [34]. To exploit the leading curvature corrections to the line tension it suffices to apply the asymptotic form, corresponding to a planar substrate [35],

$$\omega_i(l,R) = \tau_i e^{-l/\xi_B} + be^{-2l/\xi_B} + \cdots, \quad (3)$$

where the omitted terms are of the order e^{-3l/ξ_B} and $(\xi_B/R)e^{-l/\xi_B}$. The parameters $\tau_i=a(T-T_{Wi})$ (a being a positive constant) measure deviation of the temperature from the wetting temperature T_{Wi} of the ith substrate. We assume $T_{W1}<T_{W2}$, so that the fluid is preferentially adsorbed at the stripelike inhomogeneity. The parameter b controls repulsion of the interface from the substrate at short distances. Note that in order to simplify the formulas the same value of b is taken for both substrates within the present model.

The subsequent analysis is based on the mean-field approximation, which neglects interfacial fluctuations. For the case $\tau_1>0>\tau_2$ it was argued in Ref. [36] that asymptotically, i.e., for $L/\xi_B \gg 1$ and $x \simeq 0$, the net result of incorporating fluctuations amounts to replacing ξ_B with an effective (renormalized) correlation length. Possible additional effects caused by thermal fluctuations in the vicinity of the substrate inhomogeneity, and in the case of $\tau_i>0$ for $i=1,2$ in the homogeneous regions as well, are neglected in the present work.

Throughout the analysis the liquid-gas stiffness parameter $\Sigma(r)$, $r=R+l$, is assumed constant and equal to σ. As regards its dependence on r in the case of cylindrical interfaces, it has been argued [38] that a term of the order $\ln r/r$ is present in the expansion of Σ around the planar interface limit: $\Sigma =\Sigma(r)=\sigma(1+b_H \ln r/r+\cdots) \simeq \sigma(1+b_H \ln R/R)$, because $l \ll R$. The magnitude of the parameter b_H was, however, shown to be much smaller than ξ_B and conjectured equal to 0 for a specific system with short-ranged intermolecular interactions (see [28]). It can be checked that all the results of this work remain valid when σ is replaced by a quantity which depends on the substrate curvature $\Sigma(R)$. We come back to this point in the Discussion.

We also remark that the drumheadlike term in the interfacial Hamiltonian (see, e.g., [37]) has been replaced by the square gradient terms in Eq. (1). This approximation is justified provided spatial variation of the interfacial profile is not too strong, i.e., the condition $(\tau_1 - \tau_2)/\sigma \ll 1$ holds.

As was already mentioned, the equilibrium interfacial profile shows the cylindrical symmetry $\bar{l}(x,\phi) = \bar{l}(x)$, and in addition $\bar{l}(x) = \bar{l}(-x)$. This allows us to limit the considered range of x values to $x \in [0, \infty)$. Assuming $l \ll R$ (see, e.g., Ref. [17]) we rewrite Eq. (1) in the following form:

$$\mathcal{H}[l] = 4\pi R \int_0^\infty dx \left[\frac{\sigma}{2}\left(\frac{dl}{dx}\right)^2 + V(x,l,R) \right], \qquad (4)$$

with

$$V(x,l,R) = \omega(x,l) + \sigma\frac{l}{R}. \qquad (5)$$

Minimizing the functional (4) yields the Euler-Lagrange equation for the equilibrium profile

$$\sigma\frac{d^2\bar{l}}{dx^2} = \left.\frac{\partial V}{\partial l}\right|_{l=\bar{l}} \qquad (6)$$

together with the derivative continuity condition

$$\left.\frac{d\bar{l}}{dx}\right|_{x=L^-} = \left.\frac{d\bar{l}}{dx}\right|_{x=L^+}. \qquad (7)$$

In addition we require $\bar{l}(x=L^-) = \bar{l}(x=L^+)$, which for the considered discontinuous model of ω [Eq. (2)] does not follow from the free energy minimum condition. The boundary conditions, subject to which Eq. (6) is to be solved are $(d\bar{l}/dx)|_{x=0} = 0$ and $\lim_{x\to\infty} \bar{l}(x) = l_{\pi 2}(R)$, where $l_{\pi 2}(R)$ corresponds to the minimum of $V_2(l,R) = \omega_2(l) + \sigma l/R$. In what follows we shall omit the overbars and denote the equilibrium interfacial profile by l.

The first integral of Eq. (6) yields

$$\frac{dl}{dx} = \begin{cases} -\sqrt{\dfrac{2}{\sigma}[V_1(l) - V_1(l_0)]} & \text{for } 0 \leq x \leq L, \\[3mm] -\sqrt{\dfrac{2}{\sigma}[V_2(l) - V_2(l_{\pi 2})]} & \text{for } x > L, \end{cases} \qquad (8)$$

where $l_0 = l(x=0)$ remains to be determined from the continuity conditions at $x=L$.

The line tension coefficient is calculated as the line contribution to the free energy evaluated per unit length of a single interfacial inhomogeneity region around $x \simeq L$ according to the following convention [33]:

$$\eta(R,L) = \int_0^\infty dx \left[\frac{\sigma}{2}\left(\frac{dl}{dx}\right)^2 + V(x,l) - \Theta(L-x)V_1(l_{\pi 1}) \right. $$

$$\left. - \Theta(x-L)V_2(l_{\pi 2}) \right]. \qquad (9)$$

For another choice of convention see [7].

Let us note, that two linear inhomogeneities corresponding to $x \simeq L$ and $-L$ are present in the system. In consequence an expression for the full system's free energy contains two contributions involving η.

By substitution of Eq. (8) into this formula one obtains

$$\eta(R,L) = \eta_1(R,L) + \eta_2(R,L), \qquad (10)$$

where

$$\eta_1(R,L) = \sqrt{\frac{\sigma}{2}} \int_{l_L}^{l_0} \frac{dl[2V_1(l) - V_1(l_0) - V_1(l_{\pi 1})]}{\sqrt{V_1(l) - V_1(l_0)}},$$

$$\eta_2(R,L) = \sqrt{2\sigma} \int_{l_{\pi 2}}^{l_L} dl\sqrt{V_2(l) - V_2(l_{\pi 2})}. \qquad (11)$$

The parameters l_0 and $l_L = l(x=L)$ are functions of R and L. Their values are determined by the continuity conditions of $l(x)$ and dl/dx. For the assumed form of the interfacial potential Eq. (3) the derivative continuity condition (7) yields

$$e^{-l_L/\xi_B} = \frac{1}{\tau_1 - \tau_2}\left[\sigma\frac{l_0 - l_{\pi 2}}{R} + \omega_1(l_0) - \omega_2(l_{\pi 2}) \right]. \qquad (12)$$

The aim of the subsequent analysis is to solve the equations for l_0 and l_L up to the dominant order in R^{-1} and, keeping the leading R-dependent corrections, perform an expansion of $\eta_1(R,L)$, $\eta_2(R,L)$ around their values $\hat{\eta}_1(L)$, $\hat{\eta}_2(L)$ corresponding to $R^{-1}=0$:

$$\hat{\eta}_1(L) = \sqrt{\frac{\sigma}{2}} \int_{\hat{l}_L}^{\hat{l}_0} \frac{dl[2\omega_1(l) - \omega_1(\hat{l}_0) - \omega_1(\hat{l}_{\pi 1})]}{\sqrt{\omega_1(l) - \omega_1(\hat{l}_0)}}$$

$$\hat{\eta}_2(L) = \sqrt{2\sigma} \int_{\hat{l}_{\pi 2}}^{\hat{l}_L} dl\sqrt{\omega_2(l) - \omega_2(\hat{l}_{\pi 2})}, \qquad (13)$$

where all quantities marked with the caret refer to the planar case, i.e., $R^{-1}=0$.

III. RESULTS

Our analysis is restricted to the regime of small substrate curvatures, i.e., $\xi_B/R \ll 1$. In this regime the interfacial morphology depends on the system temperature and also—as we show below—on the value of the dimensionless parameter $L^2/(\xi_B R)$. In particular, the height of the adsorbed droplet at the center of the stripe $l(x=0) = l_0$ is a function of the cylinder's radius R, and its behavior in the limiting case $R^{-1}=0$ depends on the temperature regime. For temperatures T such that $T < T_{W1} < T_{W2}$ the height l_0 equals $\hat{l}_0 = \hat{l}_{\pi 1} + O(e^{-L/\xi_{\|1}})$ with $\xi_{\|1} = \sqrt{\sigma/\omega_1''(\hat{l}_{\pi 1})} = \xi_B\sqrt{2\sigma b/\tau_1^2}$ being the interfacial correlation length corresponding to the critical wetting of type 1 substrate and $\hat{l}_{\pi 1} = \xi_B \ln(-2b/\tau_1)$. On the other hand, for temperatures T such that $T_{W1} < T < T_{W2}$ the height $\hat{l}_0(L)$ is an increasing and unbounded function of the adsorbate width $2L$. For temperatures $T > T_{W2} > T_{W1}$ the height l_0 diverges in the limit $R^{-1} \to 0$ for any value of L. The asymptotic behavior

of the line tension coefficient is investigated separately in each of the above cases.

A. Case I: $T < T_{W1} < T_{W2}$

In this case, the parameter $l_0(R, L)$ converges to a finite value $\hat{l}_0(L)$ in the limit $R^{-1} \to 0$. As was shown in Ref. [33] the equilibrium droplet height $\hat{l}_0(L)$ adsorbed at a planar substrate with a stripelike inhomogeneity has the following expansion in the regime $\xi_{\|1}/L \ll 1$:

$$\hat{l}_0(L) = \hat{l}_{\pi 1} + \delta\hat{l}_0(L) = \hat{l}_{\pi 1} + \delta_1 e^{-L/\xi_{\|1}} + O(e^{-2L/\xi_{\|1}}), \quad (14)$$

where $\delta_1 = 2\xi_B(\tau_1 - \tau_2)/(\tau_1 + \tau_2) < 0$. To obtain the expression for the equilibrium height $l_0(R, L) = \hat{l}_0(L) + \delta l_0(R, L)$, we first expand Eq. (8) for $x < L$ and $\xi_B/R \ll 1$,

$$\int_0^L \sqrt{\frac{2}{\sigma}} dx = -\int_{l_0}^{l_L} \frac{dl}{\sqrt{\omega_1(l) - \omega_1(l_0)}}$$
$$+ \frac{\sigma}{2R} \int_{l_0}^{l_L} \frac{(l - l_0)dl}{[\omega_1(l) - \omega_1(l_0)]^{3/2}} + \cdots, \quad (15)$$

The integrals on the right-hand side (RHS) of (15) are performed in the asymptotic regime $\xi_{\|1}/R \ll 1$. The most relevant technical details of the calculations can be found in the Appendix. As a result, from Eq. (15) we obtain a simple equation for δl_0, which yields

$$\delta l_0 = -\frac{\xi_{\|1}^2}{R}\left[1 + O\left(\frac{\xi_{\|1}}{R}\right)\right]. \quad (16)$$

It follows that the equilibrium adsorbed droplet height may—in the present temperature regime—be expressed as

$$l_0 = \hat{l}_{\pi 1} + \delta\hat{l}_0(L) + \delta l_0(R), \quad (17)$$

where $\delta\hat{l}_0(L) \sim e^{-L/\xi_{\|1}}$ is the correction due to finite chemical inhomogeneity width, and $\delta l_0(R) \sim R^{-1}$ as given by Eq. (16) due to substrate curvature.

The expression for the line tension coefficient may be written as $\eta(L, R) = \hat{\eta}(L) + \delta\eta(L, R)$, where the line tension corresponding to the planar substrate has the form (see [33])

$$\hat{\eta}(L) = \xi_B \sqrt{\frac{\sigma}{2b}}\left[\tau_1 \ln\left(\frac{\tau_1 + \tau_2}{2\tau_1}\right) + \tau_2 \ln\left(\frac{\tau_1 + \tau_2}{2\tau_2}\right)\right]$$
$$+ \xi_B \tau_1 \sqrt{\frac{\sigma}{2b}}\left[-2\frac{\tau_1}{\tau_1 + \tau_2}e^{-L/\xi_{\|1}} + O\left(\frac{L}{\xi_B}e^{-2L/\xi_{\|1}}\right)\right]. \quad (18)$$

The integrands in η_1, η_2 in Eq. (11) are expanded around their values corresponding to $R^{-1} = 0$ given by Eq. (13) and only leading R-dependent terms are kept. Applying the formulea for l_0 given by Eqs. (16) and (17), the following expression for the line tension is obtained:
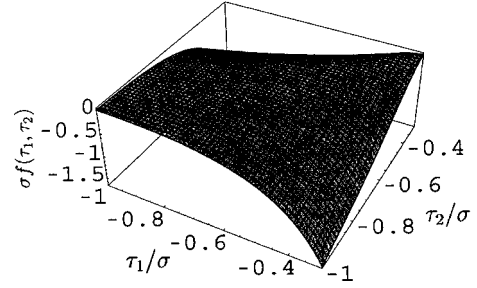

FIG. 3. Plot of the function $f(\tau_1, \tau_2)$ in Eq. (20). The leading curvature correction to the line tension coefficient is a nonpositive function of τ_1, τ_2. It takes the value 0 at $\tau_1 = \tau_2$ and decreases with increasing $|\tau_1 - \tau_2|$.

$$\eta = \hat{\eta}(L) + \sigma\xi_B\frac{\sqrt{2\sigma b}}{R}f(\tau_1, \tau_2) + 3\xi_B\sigma\frac{\sqrt{2\sigma b}}{\tau_1 R}\frac{\tau_1 - \tau_2}{\tau_1 + \tau_2}e^{-L/\xi_{\|1}}$$
$$+ \text{ higher order terms.} \quad (19)$$

In Eq. (19) only the dominant R- and L-dependent corrections to the planar line tension coefficient $\hat{\eta}$ are kept track of. The function $f(\tau_1, \tau_2)$ is given by

$$f(\tau_1, \tau_2) = -\left[\frac{1}{2\tau_1}\ln^2\left(\frac{\tau_1 + \tau_2}{2\tau_1}\right) + \frac{1}{\tau_1}L_2\left(\frac{\tau_1 - \tau_2}{2\tau_1}\right)\right.$$
$$\left. + \frac{1}{2\tau_2}\ln^2\left(\frac{\tau_1 + \tau_2}{2\tau_2}\right) + \frac{1}{\tau_2}L_2\left(\frac{\tau_2 - \tau_1}{2\tau_2}\right)\right], \quad (20)$$

with $L_2(x)$ being the dilogarithmic function [39]. The first curvature correction is of the order $\xi_{\|1}/R$ and negative in sign, while the next to leading term of the order $(\xi_{\|1}/R)e^{-L/\xi_{\|1}}$ is positive. The neglected terms are of the order $(\xi_\|/R)^2$ and $(L/R)e^{-2L/\xi_{\|1}}$. The function $f(\tau_1, \tau_2)$ is symmetric with respect to the interchange $\tau_1 \leftrightarrow \tau_2$ and its plot is provided by Fig. 3.

For reasons of clarity only the final result has been quoted in the main text. Details of the calculations can be found in the Appendix.

It is worthwhile to note that no assumption concerning the relative values of the parameters R and L was made in course of the calculations. This is a unique property of the presently analyzed temperature regime. In the remaining cases studied below one has to make assumptions concerning the relative values of parameters R and L. It is required, however, that the parameters $\xi_{\|1}/R$ and $\xi_{\|1}/L$ are small compared to unity. No obvious mechanism to generate higher order terms in the expansion of $\eta(R, L)$ that would contain logarithm or noninteger powers of R^{-1} arises in course of the calculations in this case.

B. Case II: $T_{W1} < T < T_{W2}$

The construction of the curvature expansion of the line tension coefficient in the present case follows the lines outlined in Sec. III A. However, a new aspect of the analysis appears and is related to the fact that $l_0(R, L) \to \infty$ in the limit $R^{-1}, L^{-1} \to 0$. As a consequence the asymptotic behavior of the adsorbed layer's morphology depends sensitively on the
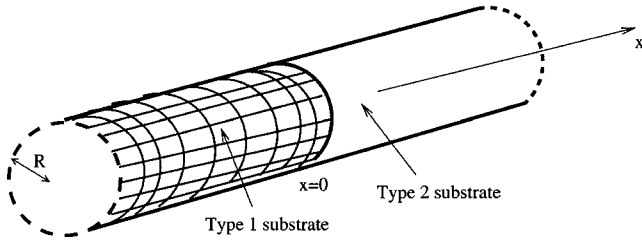
FIG. 4. Substrate consisting of two semi-infinite homogeneous cylinders of radius R meeting at $x=0$.

way the limits $R^{-1} \to 0$ and $L^{-1} \to 0$ are performed. In this section we consider two cases. First, keeping $\xi_B/L \ll 1$ and $\xi'/L = \xi_B \sqrt{2\sigma b}/\tau_1 L \ll 1$ fixed, we investigate the behavior of l_0 and η in the limit $\xi_B/R \to 0$. It appears that the curvature correction to the equilibrium droplet height is of the order $L^2/R\xi_B$ which is assumed small compared to 1. To explore the opposite case $R\xi_B/L^2=0$, we consider an inhomogeneous substrate consisting of two homogeneous semi-infinite cylinders meeting at $x=0$. This corresponds to putting $L^{-1}=0$ from the beginning. In the subsequent subsections we discuss
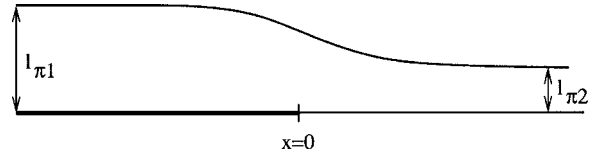

FIG. 5. A cross section of a typical interfacial configuration corresponding to the case $L^{-1}=0$.

the results obtained for these two regimes of R and L.

1. Regime $L^2/R\xi_B \ll 1$

Equation (15), which forms the starting point for determining l_0 (up to the leading R-dependent terms) remains valid also in the present case. However, due to divergence of l_0 in the limit R^{-1}, $L^{-1} \to 0$, the contribution from the integral $(\sigma/2R)\int_{l_0}^{l_L}(l-l_0)dl/[\omega_1(l)-\omega_1(l_0)]^{3/2}$ is of different type than in the temperature regime $T < T_{W1} < T_{W2}$ discussed in Sec. III A. In order to evaluate the asymptotic behavior of δl_0 we rewrite it the following way:

$$\frac{\sigma}{2R}\int_{l_0}^{l_L}\frac{(l-l_0)dl}{[\omega_1(l)-\omega_1(l_0)]^{3/2}} = \frac{\sigma}{2R\tau_1^{3/2}}\int_{l_0}^{l_L}\frac{dl(l-l_0)}{[e^{-l/\xi_B}-e^{-l_0/\xi_B}]^{3/2}[1+(b/\tau_1)(e^{-l/\xi_B}+e^{-l_0/\xi_B})]^{3/2}} \tag{21}$$

and perform the expansion of the integrand in $(b/\tau_1)(e^{-l/\xi_B}+e^{-l_0/\xi_B})$. It can then be shown (see the Appendix) that

$$\frac{1}{2R}\int_{l_0}^{l_L}\frac{(l-l_0)dl}{[\omega_1(l)-\omega_1(l_0)]^{3/2}} = \frac{\xi_B^2 e^{(3l_0)/(2\xi_B)}}{2R\tau_1^{3/2}}$$

$$\times \left[\int_0^\infty \frac{dx\,x}{(e^x-1)^{3/2}} + O\left(\frac{l_0-l_L}{R}e^{-3(l_0-l_L)/2\xi_B}, \frac{\xi_B e^{-l_0/\xi_B}}{R}\right)\right], \tag{22}$$

where $\kappa_\alpha = \int_0^\infty dx\,x/(e^x-1)^\alpha$, $\alpha > 0$, and $\kappa_{3/2} \simeq 1.93$. The equation for δl_0 yields

$$\delta l_0 = -\frac{2\kappa_{3/2}}{\pi^3}\frac{L^2}{R} + \text{higher order terms.} \tag{23}$$

Implicit in this calculation is the assumption that R is large enough that $L \gg (\xi_B^2/R)e^{3l_0/2\xi_B}$ which is equivalent to $L^2/(R\xi_B) \ll 1$. The line tension coefficient is evaluated along the lines sketched in Sec. III A and we refrain from describing the details. We obtain

$$\eta(R,L) = \widehat{\eta(L)} - \sigma\frac{l_{\pi1}}{R}L + \sigma\frac{\hat{l}_0}{R}L - \frac{\kappa_{1/2}}{\pi}\sigma\xi_B\frac{L}{R} + O\left(\frac{\ln L^2}{R}\right), \tag{24}$$

where the line tension corresponding to planar adsorbate is in this case given by [33]

$$\hat{\eta}(L) = \xi_B\sqrt{\frac{\sigma}{2b}}\left[\tau_1 \ln\left(\frac{\tau_1-\tau_2}{\tau_1}\right) - \tau_2\ln\left(\frac{2(\tau_2-\tau_2)}{\tau_2}\right)\right]$$

$$- \sigma\xi_B\left[\frac{\pi^2}{2}\frac{\xi_B}{L} + O\left(\left(\frac{\xi_B}{L}\right)^2\right)\right]. \tag{25}$$

We note that the dominant curvature-dependent term in Eq. (24) has the form $-\sigma l_{\pi1}L/R$, where $l_{\pi1} \simeq \xi_B \ln(\tau_1 R/\sigma\xi_B)$. This term originates from subtracting the surface contribution to the free energy when evaluating the line tension [see Eq. (9)]. The second to leading correction $\sigma\hat{l}_0 L/R$ is governed by the planar equilibrium droplet $\hat{l}_0 = \xi_B \ln(2\tau_1 L^2/\sigma\pi^2\xi_B^2) + O(\xi_B/R)$. The last computed term $-(\kappa_{1/2}/\pi)\sigma\xi_B L/R$ with $\kappa_{1/2} \simeq 4.36$ does not depend on the substrate parameters. It is worth noting that the parameters τ_2 and b do not enter the expression (24) up to the computed order.

2. Regime $L^{-1}=0$

To obtain the expansion for $\eta(R)$ in the case $L^{-1}=0$ we consider a substrate consisting of two homogeneous semi-infinite cylinders meeting at $x=0$ (see Figs. 4 and 5).

The Euler-Lagrange equation (6) is subject to the boundary conditions at $x \to \pm\infty$ and the continuity condition of $l(x)$ and dl/dx at $x=0$. The expression for the line tension is the same as in Eqs. (9) and (11) but l_L is substituted with $l(0)$ and l_0 with $l_{\pi1}$. Evaluation of line tension proceeds as de-

scribed in Sec. III A and the result appears to have the following structure:

$$\eta(R, L^{-1} = 0) = \hat{\eta}(L^{-1} = 0) - 5\sqrt{2}\sigma\xi_B^{3/2}\sqrt{\frac{1}{R}} + O\left(\frac{\ln R}{R}\right).$$

(26)

The leading curvature correction proportional to $R^{-1/2}$ is negative and is controlled by the adsorbent's geometry alone—i.e., independent of the substrate chemical properties described by the parameters τ_1, τ_2, b. It can be checked that terms containing the logarithm of R are also present in the expansion of $\eta(R)$ in this case and contribute to higher order corrections.

C. Case III: $T_{W1} < T_{W2} < T$

The analytic scheme along which line tension was discussed in Secs. III A and III B cannot be applied in the present case when the system temperature exceeds the wetting temperatures T_{W1} and T_{W2} of the corresponding homogeneous, planar substrates. This is due to the fact that neither of the terms under the square root of the integrand in Eq. (11) becomes dominant in the limit $R^{-1} \to 0$; both expressions $\omega_1(l) - \omega_1(l_{\pi1})$ and $(l - l_{\pi1})/R$ are asymptotically of the same order. The following analysis is restricted to the case $L^{-1} = 0$. Moreover, we assume the temperatures T_{W1} and T_{W2} to be close enough to each other such that the ratio $(\tau_1 - \tau_2)/\tau_2$ is small, i.e., $(\tau_1 - \tau_2)/\tau_2 \ll 1$. The continuity conditions of $l(x)$ and dl/dx at $x=0$ imply

$$e^{-l(0)/\xi_B} = \frac{\sigma}{\tau_1 - \tau_2}\left(\frac{\xi_B \ln(\tau_1/\tau_2)}{R} + O((\xi_B/R)^2)\right), \quad (27)$$

and the line tension coefficient Eq. (9) is given as $\eta = \eta_1 + \eta_2$ with

$$\eta_1 = \sigma\sqrt{\frac{2}{\sigma}}\int_{\xi_B \ln[(\tau_1-\tau_2)R/\sigma\xi_B \ln(\tau_1/\tau_2)]}^{\xi_B \ln(\tau_1 R/\sigma\xi_B)} \times dl \sqrt{\omega_1(l) - \frac{\sigma\xi_B}{R} + \sigma\frac{l - \xi_B \ln(\tau_1 R/\sigma\xi_B)}{R}},$$

$$\eta_2 = \sigma\sqrt{\frac{2}{\sigma}}\int_{\xi_B \ln(\tau_2 R/\sigma\xi_B)}^{\xi_B \ln[(\tau_1-\tau_2)R/\sigma\xi_B \ln(\tau_1/\tau_2)]} \times dl \sqrt{\omega_2(l) - \frac{\sigma\xi_B}{R} + \sigma\frac{l - \xi_B \ln(\tau_2 R/\sigma\xi_B)}{R}}. \quad (28)$$

The integrals in η_1 and η_2 are performed keeping track of the leading order dependence on R^{-1} and $\tau_1 - \tau_2$. As a result we obtain that the line tension coefficient converges to 0 in the limit $\xi_B/R \to 0$ according to the following power law:

$$\eta = \frac{\sigma\xi_B}{4}\left(\frac{\tau_1 - \tau_2}{\tau_2}\right)^2\left[1 + O\left(\frac{\tau_1 - \tau_2}{\tau_2}\right)\right]\frac{1}{\sqrt{R}}[1 + O(\xi_B/R)].$$

(29)

The decay of the line tension coefficient to 0 in the limit $R^{-1} \to 0$ may easily be deduced also for $L^{-1} \neq 0$ by analyzing

Eq. (11) [in which l_0 must be substituted with $l_{\pi1}$ and l_L with $l(0)$]. We note that all the terms in the integrands in Eq. (11) converge to 0 for $R^{-1} \to 0$. The range of integration variable $l \in [l_{\pi2}, l_{\pi1}]$ remains bounded, because for $\xi_B/R \to 0$ we have $l_{\pi1} - l_{\pi2} \to \xi_B \ln(\tau_1 R/\sigma\xi_B) - \xi_B \ln(\tau_2 R/\sigma\xi_B) = \xi_B \ln(\tau_1/\tau_2)$. This proves that $\eta(R, L)$ decays to 0 in the limit $\xi_B/R \to 0$ for any $L^{-1} \geq 0$ and $\tau_1 > \tau_2 > 0$.

We wish to point out that this observation is not trivial at all, as $\lim_{R\to\infty}(l_{\pi1} - l_{\pi2}) \neq 0$ and so the heterogeneity of the interfacial structure does not vanish in the limit $\xi_B/R \to 0$.

IV. SUMMARY AND DISCUSSION

In this paper the structure of the line tension coefficient η corresponding to heterogeneous liquid films adsorbed at chemically inhomogeneous and curved substrates has been determined in the case of short-ranged intermolecular forces. Our analysis was based on the effective Hamiltonian approach and the mean-field approximation; it allowed determination of the dominant curvature corrections to the line tension, valid in the limit of large substrate radii. Three cases were considered depending on the temperature regime: case I, $T_{W2} > T_{W1} > T$; case II, $T_{W2} > T > T_{W1}$; and case III, $T > T_{W2} > T_{W1}$. The computed curvature terms are different in each of the cases and—except for case III—are negative. In case II the character of the curvature corrections is predicted to depend additionally on the value of the parameter $L^2/(R\xi_B)$. Our conclusions, corresponding to different regimes of system's parameters, are as follows.

(1) When the system's temperature remains below the wetting temperatures T_{W1}, T_{W2} (case I), the leading curvature correction to the line tension coefficient is of the order $\xi_\parallel/R$. It is found to depend on all the system's parameters (i.e., τ_1, τ_2, σ, b) and exhibits a symmetry with respect to the interchange of the parameters $\tau_1 \leftrightarrow \tau_2$. The next-to-leading correction couples the curvature with the chemical inhomogeneity width and is proportional to $R^{-1}e^{-L/\xi_\parallel}$. The neglected higher order terms are of the type $(\xi_\parallel/R)^2$ and $e^{-2L/\xi_\parallel}/R$. Unlike the other cases, no obvious mechanism of generating terms that would include a logarithm of R or L arises in the course of calculations.

(2) Within the temperature range $T \in (T_{W1}, T_{W2})$ (case II), and for substrate radii R large enough such that the condition $L^2/(R\xi_B) \ll 1$ is satisfied, the leading curvature correction to the line tension is of the order $-l_{\pi1}L/R\xi_B = -[\ln(\tau_1 R/\sigma\xi_B)L]/R\xi_B$. However, when the system's full free energy including surface contributions is considered, this line contribution adds to 0 with the corresponding surface term. In consequence, the next-to-leading terms [see Eq. (24)] become of importance. These are shown to be of the order $[L \ln(L/\xi_B)]/R$, L/R and do not depend on values of the parameters τ_2, b.

(3) In the case $T \in (T_{W1}, T_{W2})$, $L^{-1} = 0$ (case II), the leading curvature correction to the line tension coefficient is of the order $(\xi_B/R)^{1/2}$. Its magnitude is found not to depend on any properties of the wetted substrate and is governed by the interfacial tension σ. The next-to-leading term is predicted to be of the order $(\ln R)/R$.

(4) The case $T > T_{W2} > T_{W1}$, $L^{-1} = 0$ was studied under the additional assumption that $(\tau_1 - \tau_2 / \tau_2) \ll 1$. The line tension is shown to decay as $R^{-1/2}$, with a positive coefficient of the order $[(\tau_1 - \tau_2)/\tau_2]^2$.

Throughout the analysis the liquid-gas stiffness coefficient in the interfacial Hamiltonian [see Eq. (1)] was assumed a constant parameter, i.e., we put $\Sigma(r) = \sigma$. There is currently discussion in the literature as regards the form of $\Sigma(r)$. In Ref. [38] it was proposed that $\Sigma(r) = \sigma(1 + \delta / r + \cdots)$, where $\delta \sim \ln r$ and $r = R + l$. However, simulation data do not recover the logarithmic term in the expansion of Σ around $r^{-1} = 0$ [28].

It is a demanding task to evaluate the line tension coefficient taking into account the dependence of Σ on the interfacial morphology $l(x)$. In this case the appropriate Euler-Lagrange equation determining $l(x)$ acquires an additional term including the derivative $\partial \Sigma / \partial l$. However, due to the fact that $l(x) \ll R$ at any x, one may conjecture, as we do, that the asymptotically relevant contribution to the quantities computed in this article following from the dependence of Σ on r is governed by the magnitude of R and not $l(x)$. In consequence, we assumed that in the considered regime $\xi_B / R \ll 1$, $\Sigma(r) \simeq \Sigma(R) = \sigma(1 + \delta / R + \cdots)$. One may check, that the results of our analysis remain correct when the dependence of the stiffness coefficient on R is allowed. One needs only to replace σ with $\Sigma(R)$ in all the obtained expressions, including $\hat{\eta}$. The corrections to η following from accounting for the R-dependent corrections to σ are most relevant in case I, where they generate a leading order R-dependent contribution, which equals $\hat{\eta} \delta / 2R$. In case II and for $L^2 / R \xi_B \ll 1$ the correction is relevant only if we assume $\delta \sim \ln R$. In this case it enters the expression for η as the second-to-leading curvature correction. In the regime $L^{-1} = 0$ of case II and in case III the corrections to $\eta(R)$ generated by the R-dependent stiffness coefficient turn out to be irrelevant.

APPENDIX

The most important technical details of the calculations leading to the curvature corrections to the adsorbed droplet's height δl_0 and the expressions for the line tension η are given in this appendix.

Case I

The first of the integrals on the RHS of Eq. (15) may be performed straightforwardly, while the second is evaluated up to terms of the leading order in $\xi_{\parallel 1} / R$ and $\xi_{\parallel 1} / L$. By expanding $\omega_1(l_0)$ around $\hat{l}_{\pi 1}$ one obtains

$$\frac{\sigma}{2R} \int_{l_0}^{l_L} \frac{(l - l_0)dl}{[\omega_1(l) - \omega_1(l_0)]^{3/2}} = \frac{\sigma e^{3\hat{l}_{\pi 1}/\xi_B}}{2Rb^{3/2}} \left(\int_{\hat{l}_{\pi 1} - l_0}^{\hat{l}_{\pi 1} - l_L} \frac{dx\, x}{(e^x - 1)^3} - (\hat{l}_{\pi 1} - l_0) \int_{\hat{l}_{\pi 1} - l_0}^{\hat{l}_{\pi 1} - l_L} \frac{dx}{(e^x - 1)^3} \right). \quad (A1)$$

The quantity $\epsilon = (\hat{l}_{\pi 1} - l_0)/\xi_B = (-\delta l_0 - \delta \hat{l}_0)/\xi_B$ converges to 0 for ξ_B / R, $\xi_B / L \to 0$ and the integrals of interest have the following asymptotic expansions:

$$\int_{\hat{l}_{\pi 1} - l_0}^{\hat{l}_{\pi 1} - l_L} \frac{dx\, x}{(e^x - 1)^3} = \frac{1}{\epsilon} + \frac{3}{2} \ln \epsilon + O(\text{const}), \quad (A2)$$

$$(\hat{l}_{\pi 1} - l_0) \int_{\hat{l}_{\pi 1} - l_0}^{\hat{l}_{\pi 1} - l_L} \frac{dx}{(e^x - 1)^3} = \frac{1}{2\epsilon} + O(\text{const}). \quad (A3)$$

By substituting Eqs. (A2) and (A3) into Eq. (A1), expressing l_L in terms of l_0 via Eq. (1) and expanding $l_0 = \hat{l}_0 + \delta l_0$ up to terms linear in δl_0 in Eq. (A1), the formula (15) yields the expression for δl_0 as given by Eq. (16).

To evaluate the line tension coefficient η we expand the integrands in Eq. (11) around their values corresponding to $R^{-1} = 0$. In this way one obtains the following expression for η_1:

$$\eta_1 = \sqrt{\frac{\sigma}{2}} \int_{l_L}^{l_0} \frac{dl[2V_1(l) - V_1(l_0) - V_1(l_{\pi 1})]\{1 - (1/2R)[\sigma(l - l_0)/\omega_1(l) - \omega_1(l_0)]\}}{\sqrt{\omega_1(l) - \omega_1(l_0)}} + \text{higher order terms}, \quad (A4)$$

in which the integrals on the RHS can be performed for $\xi_{1\parallel}/R \ll 1$ by expanding $l_0 = \hat{l}_0 + \delta l_0$ up to terms linear in $\delta l_0 \ll \hat{l}_0$.

For η_2 we note, that the difference $\omega_2(l) - \omega_2(l_{\pi 2})$ is negative for $l \in [l_{\pi 2}, l_{\pi 2}^*]$, where $l_{\pi 2}^* = \hat{l}_{\pi 2} + 2\sigma b \xi_B^2 / \tau_2^2 R + O((\xi_B / R)^2)$, and positive for $l > l_{\pi 2}^*$. However, one can check that $\int_{l_{\pi 2}}^{l_{\pi 2}^*} dl \sqrt{\omega_2(l) - \omega_2(\hat{l}_{\pi 2})}$ is of the order $(\xi_B / R)^2$, and may be neglected as compared to the remaining terms. Following this, one obtains

$$\eta_2 = \sqrt{2\sigma} \int_{l_{\pi 2}^*}^{l_L} dl \sqrt{\omega_2(l) - \omega_2(l_{\pi 2})}$$

$$+ \frac{\sigma^{3/2}}{\sqrt{2R}} \int_{l_{\pi 2}^*}^{l_L} dl \frac{l - l_{\pi 2}}{\sqrt{\omega_2(l) - \omega_2(l_{\pi 2})}} + \text{higher order terms}. \quad (A5)$$

The integrals in Eq. (A5) are now performed with l_0 given by Eq. (17) and l_L by Eq. (12). Analytic expressions are ob-

tained by expanding $\omega_2(l_{\pi 2})$ around its value corresponding to $R^{-1}=0$.

Case II

In order to obtain the expression for $l_0(R,L) = \hat{l}_0(L) + \delta l_0(R,L)$, we rewrite Eq. (21) in the following way:

$$\frac{\sigma}{2R\tau_1^{3/2}}\int_{l_0}^{l_L}\frac{dl(l-l_0)}{[e^{-l/\xi_B}-e^{-l_0/\xi_B}]^{3/2}[1+(b/\tau_1)(e^{-l/\xi_B}+e^{-l_0/\xi_B})]^{3/2}}$$

$$=\frac{\sigma e^{(3l_0)/(2\xi_B)}}{2R\tau_1^{3/2}}\int_{l_0}^{l_L}\frac{dl(l-l_0)}{(e^{(l_0-l)/\xi_B}-1)^{3/2}}$$

$$\times\left(1-\frac{3}{2}\frac{b}{\tau_1}(e^{-l/\xi_B}+e^{-l_0/\xi_B})+\cdots\right). \quad (A6)$$

Integrating shows that the last term is of the order

$b\tau_1^{-5/3}e^{l_0/(2\xi_B)}/R$ and may be neglected as compared to $[e^{(3l_0)/(2\xi_B)}/2R\tau_1^{3/2}]\int_0^{l_0-l_L}dxx/(e^x-1)^{3/2}$ provided the condition $L^2/(R\xi_B)\ll1$ holds. Moreover, substituting the upper integration limit l_0-l_L with ∞ is equivalent to neglecting terms of the order $[(l_0-l_L)/R]e^{-3(l_0-l_L)/(2\xi_B)}$. This way we obtain

$$\frac{1}{2R}\int_{l_0}^{l_L}\frac{(l-l_0)dl}{[\omega_1(l)-\omega_1(l_0)]^{3/2}}=\frac{e^{(3l_0)/(2\xi_B)}}{2R\tau_1^{3/2}}$$

$$\times\left[\int_0^\infty\frac{dxx}{(e^x-1)^{3/2}}+O\left(\frac{l_0-l_L}{R}e^{-3(l_0-l_L)/(2\xi_B)},\frac{e^{-l_0/\xi_B}}{R}\right)\right]$$

$$(A7)$$

as given in Sec. III B 1.

Evaluation of the line tension coefficient proceeds along the lines sketched in Sec. III A. The encountered technicalities are analogous to those dealt with while computing η and δl_0 in case I.

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