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# Finite-Size Effects in Surface Tension: Thermodynamics and the Gaussian Interface Model[1]

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It has been suggested by Kayser that finite-size effects associated with capillary waves might play a significant role in some surface tension measurements; for capillary rise between plates a distance $D$ apart, an effect varying as $1/D$ and apparently observable in measurements, was proposed. In reconsidering this problem, one must analyze the *thermodynamics* of finite-size corrections to surface tension. In particular, one sees that capillary rise between plates does not measure the interfacial free energy density but, rather, a derivative of the interfacial free energy with respect to a system dimension. The quantity needed to draw definite conclusions, the "finite-size residual" free energy, can be calculated within the harmonic or Gaussian capillary wave model in $d$ spatial dimensions with the aid of Poisson summation techniques and should yield the correct leading asymptotic behavior. For $d=3$ and experimentally relevant parameter values, the results are independent of the short-wavelength cutoff needed in the model and can be checked against the theory of conformal covariance at two-dimensional critical points. It is found that the finite-size effects in capillary-rise measurements of surface tension vary as $1/D^2$ (with a *universal* coefficient) but are too small to be seen in current experiments.

**KEY WORDS:** capillary rise; capillary waves; finite-size effects; Gaussian model; surface tension.

## 1. INTRODUCTION

The theory of finite-size effects in the vicinity of critical points has been a subject of great interest [1] since its original formulation nearly two decades ago [2]. It has proven valuable in the analysis of Monte Carlo

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and other theoretical studies of relatively small model systems, from which one wishes to estimate asymptotic critical behavior for infinite systems. However, the theory has had little application to *experimental* systems (a notable exception is the lambda transition in helium confined to small pores [3, 4]). Thus our interest was stimulated by a paper by Kayser [5], which suggested that finite-size effects in the surface tension of a fluid may have been evident in an experiment of Moldover and Gammon [6], who measured capillary rise between narrowly spaced plates. The observations are described in more detail shortly.

We have studied the issue theoretically: regrettably, our analysis shows that the proposed finite-size effects in surface tension are too weak to be measurable in the Moldover–Gammon experiment. An essential element of the discussion is an analysis, in Section 2, of the *thermodynamics* of finite-size effects in observations of surface tension. However, thermodynamic considerations alone are insufficient to draw definite conclusions about the character of the finite-size effects; rather, it turns out, one must calculate a quantity we have dubbed the "finite-size residual" of the interfacial free energy. To this end we have examined in detail a basic statistical mechanical model for interface fluctuations, namely, the Gaussian model of capillary waves; see Section 3. Our calculations of the finite-size residual for the Gaussian model in a $d'$-dimensional "box" are sketched in Section 4 for a variety of boundary conditions, as well as in various asymptotic regimes. Applications of the results of these calculations to the question of finite-size effects in capillary-rise experiments are previewed at the end of Section 2; a summary and further applications are given in Section 5.

Let us now consider the Moldover–Gammon experiment [6] and see how the issue of finite-size effects in surface tension arises there. The experiment measured the capillary rise of liquid $SF_6$ in coexistence with its vapor between narrowly spaced plates at temperatures close to the bulk critical point, $T_c$. The plates formed a wedge with an extremely small opening angle (about $10^{-4}$ rad). Thus a single experiment was, in effect, able to study capillary rise for spacings varying from 1 to 3 $\mu$m.

There are three relevant experimental facts. First, the classical formula for the capillary rise, $h$, was not obeyed. If $D$ denotes the spacing between the plates, which, like $h$, varies very slowly along the total length of the plates, $L$, the classical expression is

$$h = a_c^2/D \tag{1}$$

where the capillary length is defined by

$$a_c = (2\sigma/\Delta\tilde{\rho}g)^{1/2} \tag{2}$$

with $\sigma$ the surface tension, $\Delta\bar{\rho}$ the mass density difference between the coexisting fluid phases, and $g$ the gravitational acceleration.

Second, if we let $\xi$ denote the bulk correlation length, the condition

$$\xi \ll D \ll a_c \ll L \tag{3}$$

was always well satisfied. This is, in fact, the usual criterion for the applicability of the classical capillary rise formula.

Finally, most of the data could be well fit by a simple model in which $D$ in Eq. (1) was replaced by a shifted spacing $D - \Delta$. Moldover and Gammon proposed that the shift $\Delta$ represented the effect of the wetting layers of liquid $SF_6$ on the glass plates which act to reduce the effective spacing. In fact $\Delta$, defined this way, must depend on $D$ (or, rather, self-consistently, on $h$) as well as $T$. For the range of $D$ studied, $\Delta$ was nearly constant. Thus the wetting layers were responsible for corrections to the capillary rise formula of relative order $1/D$, roughly speaking.

Although Moldover and Gammon's model appeared to fit the data well, one key fitted parameter—the strength of the van der Waals interaction between glass and $SF_6$—came out to be approximately 50 times larger than had been expected. Furthermore, the expected value was later confirmed experimentally [7]. This discrepancy was only partly reduced by the theoretical work of Legait and de Gennes [8], who took into account interactions between the wetting layers which had been neglected previously. It is possible that the remaining discrepancy is due to systematic errors in the experimental determination of $D$. However, it is also worth considering [5] whether the problem might lie in a size dependence of $a_c$ or, more specifically, that $\sigma$ itself might have corrections of order $1/D$.

Such a finite-size effect seems quite plausible, at first glance. For an interface of dimensions $L_1 \times L_2$, one ought to expect rather generally to find edge/surface corrections to the interfacial free energy density of order $1/L_1$ and $1/L_2$. Furthermore, as we note in Section 3, the liquid–vapor interface constitutes a *critical system* even when the bulk is effectively noncritical ($\xi \ll D$). Thus it is reasonable to anticipate an even stronger influence on the surface tension due to the boundaries. This is one of the issues we address below: however, our conclusion is that with regard to the experimental determination of surface tension, only $1/D^2$, i.e., much smaller, corrections should be present.

## 2. THERMODYNAMICS OF FINITE-SIZE EFFECTS

As a first step, we discuss some aspects of the thermodynamics of finite-size effects in surface tension or, more generally, in free energy den-

sities such as overall pressure, line tension, and step free energy. The basic fact to be emphasized is that different ways of measuring surface tension, which will all agree in the thermodynamic limit, may entail quite different finite-size corrections. Then the question naturally arises: What exactly is measured by a capillary-rise observation? We attempt to answer this via an idealized treatment which ignores the wetting layers even though we know these do have a marked effect. Such a treatment should, nonetheless, describe the leading behavior of the corrections due to finite size *per se*. We are led to define a "finite-size residual," which is found to be the essential quantity to be understood.

Consider a system confined to a rectangular region of dimensions $L_1 \times \cdots L_{d'}$. Of present interest is an interface in $d$ spatial dimensions, with $d' = d-1$ and area $A = L_1 \cdots L_{d'}$. However, our considerations apply equally to bulk systems (with $d' = d$), steps on interfaces ($d' = d-2$), etc. As the $L_j \to \infty$, we expect that the total interfacial free energy, $F_\Sigma$, should, in leading order, vary simply as $A\sigma$, where $\sigma$ is the true, limiting bulk interfacial tension. The difference $(F_\Sigma - A\sigma)$ should then be dominated by the boundary or line tensions, say $\frac{1}{2}f_1, \frac{1}{2}f_2, \ldots$, associated with the various edges or $(d'-1)$-dimensional "faces." Next, provided $d' > 2$, will come further terms with coefficients $f_{1,2}, f_{1,3}$, etc. In sum we are led to define $F_\Sigma^{(\mathrm{ext})}$, the *extensive part* of the total free energy, via

$$F_\Sigma^{(\mathrm{ext})} = A\sigma + \left(\frac{A}{L_1} f_1 + \frac{A}{L_2} f_2 + \cdots\right) + \left(\frac{A}{L_1 L_2} f_{1,2} + \cdots\right) + \cdots + (L_{d'} f_{1,\ldots,d'-1} + \cdots) \tag{4}$$

where for $S$, a proper subset of $\{1,\ldots,d'\}$, the $f_S$ are equal (up to combinatorial or averaging coefficients) to the corresponding extensive boundary free-energy densities. Finally, the difference between $F_\Sigma$ and the sum of its extensive components is the *finite-size residual*

$$\mathscr{R} \equiv F_\Sigma - F_\Sigma^{(\mathrm{ext})} \tag{5}$$

Note that $\mathscr{R}$ will, in general, depend not only on the temperature, relative chemical potential, etc., and on the detailed boundary conditions, just like all the $f_S$, but also on the full set of $L_j$, although, asymptotically, it must be much smaller that any of the $L_j$.

For concreteness, consider the realistic case $d' = 2$, and ask "What is the surface tension in a finite system?" One natural answer is that it is the overall the surface free energy density, namely, for $d' = 2$,

$$\sigma_{(0)} \equiv \frac{F_\Sigma}{A} = \sigma + \frac{f_1}{L_1} + \frac{f_2}{L_2} + \frac{\mathscr{R}}{L_1 L_2} \tag{6}$$

However, a response motivated more by mechanics is that the tension is the appropriately normalized force exerted by the system on a pair of opposing boundary walls. Thus we may define

$$\sigma_{(1)} \equiv \frac{1}{L_2}\frac{\partial F_\Sigma}{\partial L_1} = \sigma + \frac{f_2}{L_2} + \frac{1}{L_2}\frac{\partial \mathscr{R}}{\partial L_1} \tag{7}$$

and, likewise, $\sigma_{(2)}$.

As $L_1$ and $L_2$ become infinite, both $\sigma_{(0)}$ and $\sigma_{(1)}$ approach the true surface tension, $\sigma$; but they are clearly distinct for finite systems. Thus take $L_2/L_1 \gg 1$, and consider the dependence on $L_1$. Then $\sigma_{(0)}(L_1) \approx \sigma + f_1/L_1$; however, to learn anything about $\sigma_{(1)}(L_1)$ we must know something about $\mathscr{R}$. If one has $\mathscr{R} \approx -r_1 L_2/L_1$, as turns out for the case describing the Moldover–Gammon experiment, then $\sigma_{(1)}(L_1) \approx \sigma + r_1/L_1^2$, where $r_1$ is a constant. Thus $\sigma_{(1)}$ has much weaker finite-size corrections than $\sigma_{(0)}$.

Which surface tension belongs in the capillary-rise formula (1), $\sigma$, $\sigma_{(0)}$, $\sigma_{(1)}$, or something else? Following the standard derivation (see, e.g., Refs. 9 and 10), capillary-rise results from a balance between the pressure difference $\Delta p$ across a cylindrical interface of radius $R = D/2$ and the gravitational pressure $\Delta\bar{\rho} g h$. (One assumes $h \gg R$, so that the variation of the gravitational pressure at different points on the interface may be neglected.) To determine $\Delta p$, one extremalizes the total grand potential for the system composed of a cylinder of fluid $\alpha$ surrounded by fluid $\beta$, namely,

$$\Omega = p_\alpha V_\alpha + p_\beta V_\beta + \sigma A \tag{8}$$

by setting $\partial\Omega/\partial R = 0$. Straightforward algebra and geometry then yield

$$\Delta p \equiv p_\alpha - p_\beta = \sigma(\partial A/\partial V_\alpha) = \sigma/R \tag{9}$$

To elucidate possible finite-size corrections, we must improve this derivation. In the first place Eq. (8) should be replaced by[3]

$$\Omega = p_\alpha V_\alpha + p_\beta V_\beta + F_\Sigma \tag{10}$$

It is also helpful to consider fluid $\alpha$ and fluid $\beta$ when separated by a thin planar barrier which is only broached along a slit of width $D = 2R$, through which fluid $\alpha$ protrudes as a result of a pressure differential, $\Delta p$, so that the $\alpha\beta$ interface forms a cylinder of semicircular cross section. After manipulations analogous to those leading to Eq. (9), one finds

$$\Delta p = \sigma_{(1)}/R \tag{11}$$

[3] Finite-size effects associated with the bulk terms are neglected here; see below.

Note that $L_1$ appearing in the definition of $\sigma_{(1)}$ now represents the length, $2D/\pi$, of the curved, semicircular cylindrical interface created in an ideal capillary-rise experiment (with no wetting layers). [We should note that our neglect of so-called *curvature corrections* to the surface tension is deliberate. A thorough discussion of this issue would lead too far afield, but the reader should be warned that much of the literature on this topic is misleading.]

In retrospect, it is not surprising that $\sigma_{(1)}$ is the surface tension probed by capillary rise, since the phenomenon is essentially one of mechanical balance. In consequence, as noted following Eq. (7), the effects of finite size in capillary observations are controlled by the nature of the finite-size residual.

What can be said about $\mathscr{R}$? Quite generally, if all the system dimensions $L_j$ are much greater than the correlation length $\xi$, and long-range forces play no role, one expects $\mathscr{R} \sim e^{-L/\xi}$, with $L$ a length related to the smallest of the $L_j$. This assertion is grounded in exact calculations for a variety of models, such as the two-dimensional Ising model [11], the spherical model [12, 13], and ideal quantal gasses [13], as well as the Gaussian model (see Section 4).

When $\mathscr{R}$ decays exponentially with system size, it may, for most purposes, be ignored entirely. Indeed, since $L_1, L_2 \gg \xi$ in the Moldover–Gammon experiment, this justifies our neglect of finite-size corrections to the bulk terms in the grand potential in Eq. (10). If $\xi$ were the only significant correlation length in a system composed of two phases with an interface between them, we would conclude that finite-size corrections to $\sigma_{(1)}$ should be exponentially small in $D$ [aside from the $O(1/L_2)$ term, which should normally also be negligible]. However, as stressed below, there is, in fact, another correlation length, associated specifically with the interface, which is *not* small relative to $L_1$. Thus further calculations are required to obtain the corrections to $\sigma_{(1)}$.

The results merit discussion at this point. As mentioned, we find $\Delta\sigma_{(1)} \equiv \sigma_{(1)} - \sigma \sim 1/L_1^2$; indeed, for $T \lesssim T_c$ and sufficiently large $D$, the finite-size effects may be cast in the form

$$\frac{\Delta\sigma_{(1)}}{\sigma} \simeq \omega \left(\frac{\xi}{D}\right)^2 \tag{12}$$

where $\omega = \lim_{T \to T_c^-} k_B T/6\pi\sigma\xi^2 \simeq 0.55$ is expected to be *universal* [14]. In the Moldover–Gammon experiment, this correction is too small to be detected: at the smallest $D$ and largest $\xi$ studied, it should produce at most a 0.4% effect on the capillary rise. In practice, Eq. (12) probably systematically overestimates $\Delta\sigma_{(1)}$; see the discussions of *nonideal boun-*

*daries* in Sections 3 and 4. Finite-size effects associated with the surface tension are thus negligible compared to the effects of wetting layers and do not resolve the present discrepancy between theory and experiments on capillary rise between narrowly spaced plates.

## 3. THE GAUSSIAN MODEL OF CAPILLARY WAVES

It has been recognized [15] for over two decades that capillary waves of long wavelength are the dominant low-energy fluctuations specifically associated with the presence of an interface. To describe those asymptotic features of the statistical mechanics of an interface which reflect the capillary waves, it is appropriate to use an *effective* Hamiltonian which is a functional of $z(\mathbf{y})$, the local transverse deviation of the interface from its mean position $z=0$ at a point $\mathbf{y}$ in the "plane" of the mean interface [16]. The corresponding Hamiltonian incorporates (a) the increase in local interfacial energy proportional to $\{(1+|\nabla z|^2)^{1/2}-1\}$ and (b) changes in local gravitational potential energy, varying as $\frac{1}{2}\Delta\bar{\rho}gz^2$. To describe the interesting long-wavelength behavior it suffices to expand in powers of $\nabla z$ and retain only the leading term [16]. One is thus led to the Gaussian model effective Hamiltonian

$$\mathscr{H}_G = \frac{1}{2}\sigma \int d\mathbf{y}[|\nabla z|^2 + (z/\xi_{||})^2] \tag{13}$$

in which $\xi_{||} = a_c/\sqrt{2}$ embodies the capillary length.

Various remarks regarding Eq. (13) are in order. (i) It is supposed that the bulk phases are noncritical so that $\xi$ is finite. Only fluctuations on length scales much greater than $\xi$ are correctly described by Eq. (13). (ii) Since $\mathscr{H}_G$ is Gaussian, one readily finds for an infinite system that the correlation function $\langle z(\mathbf{0})\, z(\mathbf{y})\rangle$ decays as $\exp(-|\mathbf{y}|/\xi_{||})$. Thus $\xi_{||}$ is, in fact, the relevant correlation length for the interface. Now the capillary length is typically a few millimeters, so one sees that the interface between two fluids should be regarded as a *critical system*: if the bulk correlation length of a fluid were as large, one would have $|T-T_c|/T_c \simeq 10^{-12}$, thus being *at* criticality as far as thermometry can currently specify!

(iii) As written, $\mathscr{H}_G$ is inadequate thermodynamically. Some high-wavenumber cutoff must be imposed so that the capillary wave or Gaussian free energy

$$F_G = -k_B T \ln \mathrm{Tr}\{\exp[-\mathscr{H}_G/k_B T]\} \tag{14}$$

exists. The presence of a cutoff reflects the renormalization or coarse graining up to some length scale larger than $\xi$ which is implicit in the

derivation of $\mathscr{H}_G$ [16]. (iv) Since the statistical variable $z(\mathbf{y})$ has dimensions of length, one needs a reference length, say $a_\perp$, to render the trace operation in Eq. (14) dimensionless. (v) The surface tension, $\sigma$, in Eq. (13) should be the true limiting bulk surface tension, *not* some "bare" surface tension (as proposed, for example, in Refs. 5 and 15). It transpires, however, that the results of principal interest here will be quite independent of $\sigma$ (provided it is neither zero nor unbounded). Accordingly, we comment no further on this issue. (vi) It is assumed, as is true for fluid–fluid interfaces, that the surface tension is independent of the orientation of the interface so that the "interfacial stiffness" is equal to $\sigma$ [17].

Consider now the choice of cutoff. A recognition of the finiteness of atomic or molecular sizes suggests the use of a spatial lattice. Thus the values of $\mathbf{y}$ may be restricted to a $d'$-dimensional hypercubic lattice with spacing $a$, that is, $y_i = l_i a$, with $l_i = 0,..., N_i - 1$ and $L_i = N_i a$. This is also mathematically clean. If $\mathbf{M} = [M_{ij}]$ is the corresponding lattice Laplacian matrix,[4] one has

$$\mathscr{H}_G = \frac{1}{2}\sigma a^{d'} \mathbf{z}^T (a^{-2}\mathbf{M} + \xi_{||}^{-2}\mathbf{I})\,\mathbf{z} \tag{15}$$

where $\mathbf{z}$ is the vector of values $z(\mathbf{y})$ at the discrete points $\mathbf{y}$. Performing the Gaussian trace integrals implicit in Eq. (14) yields

$$F_G = \frac{1}{2} k_B T \sum_q \ln(\bar{a}^2 \lambda_q) \tag{16}$$

where $\bar{a}^2 = a_\perp^2 a^{d'}\sigma/2\pi k_B T$, while the $\lambda_q$ are the eigenvalues of $-a^{-2}\mathbf{M} + \xi_{||}^{-2}\mathbf{I}$.

The eigenvalues depend on the boundary conditions. For what we may term "ideal" boundary conditions, they have the form

$$\lambda_q = \xi_{||}^{-2} + \frac{1}{a^2}\sum_{i=1}^{d'} (1 - \cos q_i a) \tag{17}$$

with the allowed $\mathbf{q}$ values forming a regular hyperrectangular lattice in $d'$ dimensions. Thus, for *periodic* boundary conditions (with $N_j$ odd) one has

$$q_j = 2\pi m_j / L_j, \qquad m_j = 0, \pm 1,..., \pm(N_j - 1)/2 \tag{18}$$

*Fixed* or *clamped* boundaries, $z = 0$ at $y_j = 0, (N+1)\,a$, yield

$$q_j = m_j \pi / L_j, \qquad m_j = 1, 2,..., N_j \tag{19}$$

[4] With $M_{ii} = -2d'$, $M_{ij} = 1$ if $|\mathbf{y}_i - \mathbf{y}_j| = a$, but $M_{ij} = 0$ otherwise, provided neither $\mathbf{y}_i$ nor $\mathbf{y}_j$ is on the boundary. On the boundaries $M_{ij}$ depends on the precise conditions.

while *free* boundary conditions at $y_j = a, (N_j + 1)\, a$ have the similar spectrum

$$q_j = m_j \pi / L_j, \qquad m_j = 0, 1, \ldots, N_j - 1 \tag{20}$$

*Antiperiodic* boundary conditions and *mixed* boundaries, for which $z$ is clamped on one side and free on the other, also yield regular lattices of modes in **q**-space. The form of Eq. (17) continues to hold if the various conditions apply to different pairs of opposing boundaries.

One can also handle theoretically *nonideal* boundaries, for which the $q_j$ are *not* uniformly spaced. For example, one might fix $z(y_j = 0) = z(y_j = L_j + a) = 0$ and also alter the coupling between the layers $y_j = 0$ and $y_j = a$ and between $y_j = L_j$ and $y_j = L_j + a$. In such cases, the $q_j$ are roots of a sequence of transcendental equations. Asymptotically, however (when $N_j \to \infty$ at fixed $m_j$), the effect on the $q_j$ amounts simply to a shift in $L_j$ by some fixed $\delta_j$.

For a fluid interface it can be argued that a lattice cutoff is somewhat unnatural since it destroys both translational and rotational invariance (although both are restored at long wavelengths). All one may wish to assume, beyond the cutoff's existence, is a definite associated length scale $a$ (which, for *fixed* bulk correlation length $\xi$, may be identified as a multiple of $\xi$, as proposed by Kayser [5], among others). For these reasons we focus only on cutoff-independent aspects of the model, which, fortunately, include the leading behavior of the residual $\mathscr{R}$.

For concreteness and simplicity we replace the true lattice cutoff [embodied in Eqs. (16) and (17), with the appropriate set of wavevectors] by using the approximation

$$F_G = \frac{1}{2} k_B T \sum_{\mathbf{q}} \ln[\bar{a}^2 (q^2 + \xi_{||}^{-2})]\; U(q) \tag{21}$$

The set of wavevectors in the sum is taken to be those determined above by the various ideal boundary conditions, except that the $m_j$ are allowed to run up to infinity. The cutoff is now contained entirely in the spherically symmetric function $U(q)$. In order that the basic properties of the summand at small $q$ are properly preserved, we assume a convergent expansion

$$U(q) = 1 + u_2 q^2 + u_4 q^4 + \cdots \tag{22}$$

It is also important that the cutoff function be well behaved physically in real space. Thus $U(q)$ must be smooth for all $q$: a sharp cutoff (such as proposed in Ref. 5) is not satisfactory since it implies long-ranged oscillations in real space which can yield quite misleading results. It suffices

to assume that $U(q)$ is monotonically decreasing in $|q|$, that it decays at least exponentially fast as $q \to \infty$, and that its analytic continuation into the complex plane is regular in a strip of width of order $1/a$ about the real axis.

What remains now is a mathematical task: in the following section we sketch the calculation of $\mathscr{R}$ within the Gaussian model in a variety of cases. A reader interested only in the physical results may skip the details but should note that, except for exponentially small corrections, the desired finite-size residual for $F_\Sigma$ should be the same as that for $F_G$.

## 4. CALCULATING THE FINITE-SIZE RESIDUAL

Systematic calculations of the finite-size residual are noticeably absent from the literature on finite-size effects in the Gaussian model [18, 19]—the focus of most calculations has been on the extensive boundary terms. Thus, for the sake of completeness, we go beyond our mandate to calculate $\mathscr{R}$ for experimentally relevant situations.

Consider, first, periodic boundary conditions which are the most straightforward because all terms beyond the first in Eq. (4) are absent. The formal expression is simply

$$\mathscr{R} = \frac{1}{2} k_B T \left[ \sum_{\mathbf{q}} - A \int \frac{d\mathbf{q}}{(2\pi)^{d'}} \right] \ln(q^2 + \xi_{\|}^{-2})\, U(q) \tag{23}$$

with the wavevectors in the sum given by Eq. (18) but with $m_j = 0, \pm 1, \ldots$. Note that here and below we omit the factors of $\bar{a}$ needed to render dimensionless the arguments of the various logarithms. It is appropriate to discuss the asymptotic behavior of $\mathscr{R}$ in three regimes distinguished by the relative magnitudes of the $L_j$ and the interfacial correlation length $\xi_{\|}$:

(A) *Large blocks* are systems with $\xi_{\|} \ll L_j$ for all $j$. The asymptotic behavior of $\mathscr{R}$ then follows from the Poisson summation formula (see, e.g., Ref. 20): generalized to $d'$ dimensions it states

$$\sum_{\mathbf{m}} f[(2\pi m_j/L_j)] = A \sum_{\mathbf{m}} \hat{f}[(L_j m_j)] \tag{24}$$

with $\mathbf{m}$ running over all $d'$-tuples of integers and the Fourier transform being

$$\hat{f}(\mathbf{k}) = \int \frac{d\mathbf{q}}{(2\pi)^{d'}} f(\mathbf{q})\, e^{-i\mathbf{q}\cdot\mathbf{k}} \tag{25}$$

If one moves the $\mathbf{m} = 0$ term from the right to the left in Eq. (24), it becomes evident that the leading asymptotic behavior of $\mathscr{R}$ as the $L_j \to \infty$

is determined by the decay of the Fourier transform $\hat{f}(\mathbf{k})$ of $\ln(q^2+\xi_{||}^{-2})\,U(q)$ at large values of $|\mathbf{k}|$. By shifting the contours of integration, this in turn follows from the location and nature of the singularity of $f(\mathbf{q})$ closest to the real axis. Since we suppose that any singularity of $U$ is further from the real axis than the singularities of $\ln(q^2+\xi_{||}^{-2})$ at $q=\pm i\xi_{||}^{-1}$, the controlling factor in $\hat{f}(\mathbf{k})$ at large $k$ is $e^{-k/\xi_{\|}}$. Consequently, the controlling factor in $\mathscr{R}$ is $e^{-L_{\min}/\xi_{\|}}$, where $L_{\min}\equiv \min_j L_j$: a result entirely in accord with expectations.

(B) *General strips* are characterized by $\xi_{\|}\ll L_j$ only for $j=d^{\dagger}+1,\ldots,d'$ but $\xi_{\|}\gg L_j$ for $j=1,\ldots,d^{\dagger}$. With $d'=2$ and $d^{\dagger}=1$, this is appropriate for capillary rise between plates. The first step is to replace the sum over the components $j=d^{\dagger}+1,\ldots,d'$ of $\mathbf{q}$ in Eq. (23) with an integral, since this incurs only exponentially small errors. One then has a sum-minus-integral over $\mathbf{q}^{<}$, the first $d^{\dagger}$ components of $\mathbf{q}$, of a $(d'-d^{\dagger})$-dimensional integral which has $\mathbf{q}^{<}$ as a parameter. The integral is singular although finite at $\mathbf{q}^{<}=0$ (but analytic for all other real vectors $\mathbf{q}^{<}$). Thus Eq. (24) may again be applied. After some analysis, one finds that the leading behavior is

$$\mathscr{R}\approx -k_{\mathrm{B}}Tf(d')\frac{A}{(L_1\cdots L_{d^{\dagger}})^{d'/d^{\dagger}}}E(l_j) \tag{26}$$

with a universal amplitude given by

$$f(\lambda)=2^{-\lambda}\pi^{(1-\lambda)/2}\Gamma(\lambda)/\Gamma((\lambda+1)/2) \tag{27}$$

while $E(l_j)$, with *shape parameters* $l_j=L_j/(L_1\cdots L_{d^{\dagger}})^{1/d^{\dagger}}$, is a $d^{\dagger}$-dimensional Epstein zeta function [21] defined by

$$E(l_j)=\sum_{\mathbf{m}}{}'\left(\sum_{j=1}^{d^{\dagger}} m_j^2 l_j^2\right)^{-d'/2} \tag{28}$$

where the prime indicates that the origin should be excluded from the sum.

For $d'=2$, $d^{\dagger}=1$, this result reduces to

$$\mathscr{R}\approx -k_{\mathrm{B}}T(\pi/6)(L_2/L_1) \tag{29}$$

in agreement with expressions based on conformal covariance [22, 23]. In this case we have checked not only that the terms omitted from Eq. (29) are of relative order $L_1/\xi_{\|}$ compared to the one displayed, but also that $\partial\mathscr{R}/\partial L_1$ [as needed in computing $\sigma_{(1)}$] is given by $k_{\mathrm{B}}T(\pi/6)(L_2/L_1^2)$ plus negligible corrections.

We note that the results obtained here by Poisson summation *cannot* be found simply by using the finite size of the system as a low-wavenumber

cutoff on an integral, as done in Ref. 5. Such a procedure fails to account for crucial differences between various boundary conditions: at best, for the case of clamped boundaries, it gives the correct form for the extensive part of the free energy, Eq. (4), but even then it cannot yield the correct residual.

(C) *Small blocks* have $\xi_\parallel \gg L_j$ for all $j \leqslant d'$. The first step is to separate the $q=0$ term from the sum in Eq. (23). For all other terms one has $q^2 \gg \xi_{||}^{-2}$, which motivates the overall decomposition

$$\ln(q^2 + \xi_{||}^{-2}) = \ln q^2 + \ln[1 + (q\xi_\parallel)^{-2}] \tag{30}$$

The contribution from $\ln q^2$ may be analyzed by a method detailed in Ref. 24 (slightly modified, in order to treat logarithmic rather than power-law singularities). The result is

$$\mathscr{R} = \frac{1}{d'} k_B T[\ln(A/\xi_{||}^{d'}) + C(l_j) + o(1)] \tag{31}$$

where now $l_j = L_j/(L_1 \cdots L_{d'})^{1/d'}$ so that $C(l_j)$ is a shape-dependent constant, or corner term. Note that the logarithmic prefactor is universal.[5] The piece of $\mathscr{R}$ arising from $\ln[1 + (q\xi_\parallel)^{-2}]$ may be bounded straightforwardly for $L_j/\xi_\parallel$ small. It proves to be of order $L_{\max}/\xi_\parallel$ for all $d'$, and so leaves Eq. (31) unchanged as $\xi_\parallel \to \infty$.

The leading behavior, Eq. (31), of $\mathscr{R}$ for small blocks (unlike strips) might not determine the leading behavior of derivatives such as $\partial\mathscr{R}/\partial L_1$ [since one can imagine corner terms $C(l_j)$ which, upon differentiation, dominate the order $1/L_1$ term arising from the logarithm]. We have not studied this problem carefully but the logarithmic term suffices for the leading behavior of *shape-maintaining* derivatives.

For *nonperiodic* but *ideal* boundaries, the strategy is to rewrite $F_G$ as a sum of free energies of periodic systems. We sketch one illustrative example here.

For $d'=2$ and fixed boundaries, the wavevectors in the sum, Eq. (21), for $F_G^{\text{fix}}(L_1, L_2)$ lie in the first quadrant, excluding the axes, and are spaced $\pi/L_j$ apart in the $j$th direction. Since $\mathbf{q} = (\pm q_1, \pm q_2)$ yield identical contributions, one can equally write $F_G^{\text{fix}}$ in terms of a sum over $\mathbf{q}$ in all four quadrants. Except for the missing values of $\mathbf{q}$ on the axes, we now have $F_G$

[5] Such universal logarithms may be expected to arise generally in critical systems [25]. In two dimensions the prefactor of $\ln A$ is proportional to the central charge [26]. Both Ref. 25 and Ref. 26 conclude, however, that the logarithm should be absent for periodic boundaries. The Gaussian model appears as an exception, since unless the $q=0$ mode is removed "by hand," the free energy at criticality diverges.

for a periodic system of size $2L_1 \times 2L_2$. The wavevectors on the axis generate a capillary-wave free energy for a *one*-dimensional system. Thus, in an obvious notation, we obtain

$$F_G^{fix}(L_1, L_2) = \tfrac{1}{4}[F_G^{per}(2L_1, 2L_2) - F_G^{per}(2L_1) - F_G^{per}(2L_2) + C_0] \quad (32)$$

where $C_0$ accounts for the zero mode, which would otherwise be double-counted in the two one-dimensional terms: the finite-size residual follows immediately. For a *strip* ($L_2 \gg \xi_\parallel \gg L_1$), one has

$$\mathscr{R} \approx -k_B T \frac{\pi}{24} \frac{L_2}{L_1} - \frac{1}{4} k_B T \ln L_1 \quad (33)$$

where the second term is negligible relative to the first; for a *small block* one obtains

$$\mathscr{R} \approx \tfrac{1}{4} k_B T (\tfrac{1}{2} \ln L_1 L_2 - \ln L_1 - \ln L_2) = -\tfrac{1}{8} k_B T \ln A \quad (34)$$

Of the remaining situations we quote a few specific results. For the $d' = 2$ *strip* with *free* boundaries the leading term in $\mathscr{R}$ is the same as for fixed boundaries, in agreement with the results from conformal covariance [22, 23], although the logarithmic term changes. Naturally, the leading behavior is also unaffected by the choice of boundary conditions on the short edges. [For *mixed* boundaries on the long edges, one must replace $-\pi/24$ in Eq. (33) by $+\pi/48$.] In contrast, for small blocks all boundaries are of comparable importance. For example, for fully fixed or fully free boundary conditions on a small block, the leading term is

$$\mathscr{R} \approx 2^{-d'} k_B T \sum_{n=0}^{d'-1} (-1)^{\varepsilon n} \sum_{|S|=n} \frac{1}{d'-n} \ln \left[ \prod_{j \notin S} L_j \right] \quad (35)$$

where $\varepsilon = 1$ for fixed boundaries but $\varepsilon = 0$ for free boundaries, while $|S|$ denotes the number of elements in a subset $S$ of $\{1, \ldots, d'\}$. The one-dimensional result $\mathscr{R} \approx \frac{1}{2} k_B T \ln L$ for fixed boundaries can be obtained in many other ways [27, 28].

Finally, there is the problem of evaluating $\mathscr{R}$ when the boundaries are not ideal. There are many possibilities, but it is clear that what matters for $\mathscr{R}$ is the spectrum of long-wavelength modes which enter the sums for $F_G$ in Eq. (21) or (16). In real capillary-rise experiments, with wetting layers present, the capillary waves are suppressed as the layers decrease in thickness up the sides of the capillary. In effect, there is a position-dependent $\xi_\parallel$ which takes its standard value on the main portion of the interface but decreases rapidly on moving up the wetting layers (as the square of the layer thickness, for nonretarded van der Waals interactions [29]). It seems

reasonable that a positive shift $\delta_1$ in $L_1$ (as described in Section 3) would account for this sort of nonideal boundary. However, we have not tried to estimate $\delta_1$, although such a calculation seems feasible.

## 5. CONCLUSIONS

The thermodynamic analysis of capillary rise indicates that a "tension," $\sigma_{(1)}$ as in Eq. (7), rather than the interfacial free energy density, $\sigma_{(0)}$, is the finite-size surface tension relevant to capillary rise. Consequently, the finite-size residual free energy, rather than some edge energy, is responsible for any finite-size corrections to the surface tension which might be relevant in interpreting experimental results. However the results, based on the Gaussian model of capillary waves, displayed in Eq. (12), are too weak to be seen in the experiment of Moldover and Gammon.

Finite-size effects associated with capillary waves *should* be relevant, however, in Monte Carlo simulations of surface tensions [30] and step free energies [31] in the Ising model [32]. [Note that these simulations measure $\sigma_{(0)}$ rather than some mechanical tension.] The relevant result for these cases is Eq. (31); the logarithm here also has implications for the finite-size scaling behavior of surface tensions and step free energies near the critical and roughening temperatures, respectively [32].

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