

Effect of capillary waves on surface tension

R. F. Kayser

Thermophysics Division, National Bureau of Standards, Gaithersburg, Maryland 20899

(Received 28 October 1985)

On fluid interfaces in finite-size systems, capillary waves longer than the system size are cut off, and the interfacial tension is higher than its infinite-system value σ . We quantify this increase using capillary-wave theory to calculate $\sigma_{2\pi/l}$, the surface tension of an interface with no capillary waves longer than l . The effect is small for a liquid-vapor interface near a triple point unless l is on the order of 10 molecular diameters. In contrast, $\sigma_{2\pi/l}/\sigma$ near a critical point can be significantly larger than unity for reasonably large values of l . We find that $\sigma_{2\pi/l}/\sigma = 1.6$ for $l = 20\xi$, with ξ the bulk correlation length in either coexisting phase. Because systems on the order of 20ξ are physically realizable, this result has important implications for surface tension in confined geometries. Our normalization of the capillary-wave partition function implies that $\sigma_{2\pi/l}$ also obeys finite-size scaling: $\sigma_{2\pi/l}/\sigma = F(l/\xi)$, where $F(x)$ depends on the shape of the confined geometry but is otherwise universal. The implications of these and other predictions are discussed in light of recent developments involving surface tension and confined geometries.

I. INTRODUCTION

The capillary-wave divergence of the thickness of a liquid-vapor interface was first predicted by Buff, Lovett, and Stillinger¹ in 1965. According to their theory, the mean-square displacement ($\langle \xi^2 \rangle$) of an interface from its nominal location diverges for an infinite system in the limit that the gravitational field (g) tends to zero. In three dimensions, $\langle \xi^2 \rangle$ is predicted to diverge as $\ln g^{-1}$. The physical explanation of this result is that capillary-gravity waves are thermally excited on the interface against surface tension and gravity. The long-wavelength modes, which resemble local vertical translations over large horizontal distances, require very little energy to create and exist with sufficient density to lead to the divergence.

The prediction of a divergent $\langle \xi^2 \rangle$ has been controversial because it raises questions about the commonly invoked concept of a density profile that interpolates smoothly between coexisting densities as one traverses a *thin* transition region separating two coexisting phases.² Prior to capillary-wave theory it was thought that such density profiles were intrinsic to the phase equilibrium itself and did not depend for their existence on the presence of an external field. An important step in reconciling the two views was made by Weeks,³ who argued that the two models apply on different length scales. The intrinsic-density-profile theories⁴ apply to cylindrical subsystems with interfacial cross-sectional areas on the order of the square of a bulk correlation length, whereas capillary-wave theory describes fluctuations between regions of the interface that are separated by many correlation lengths. In a very rough sense, density-profile theory provides the underlying interface whose deviations from planarity are described by capillary-wave theory. While these arguments are physically appealing, the scale where one description merges into the other is very difficult to define unambiguously.⁵

In this paper we calculate the increase in interfacial tension caused by cutting off capillary waves that are longer than a given wavelength. We focus for simplicity on three-dimensional systems and use capillary-wave theory to calculate σ_k , the surface tension of an interface where only those modes with at least one wave-vector component (k'_x, k'_y) greater than k are allowed. We also calculate the surface tension in the case that $|k'_x|$ and $|k'_y|$ must both be greater than k (all other modes cut off), and when only $|k'_x|$ must be greater than k . The second case (tension $\sigma_{k,\text{square}}$) corresponds to an interface of square cross-sectional area $(2\pi/k)^2$, and the third (tension $\sigma_{k,\text{slit}}$) to an interface confined in one direction but infinite in the other. The definitions of these quantities will become clear in Sec. III. A prominent feature of our analysis is a new "normalization" of the functional integral that yields the surface tensions.

The basic idea of capillary-wave theory is to "unfreeze" longer and longer wavelength distortions on a "bare" interface with bare surface tension σ_b . These quantities are defined here in an *a posteriori* fashion by estimating the shortest wavelength distortion that can be described using capillary-wave theory. We denote this shortest wavelength alternately by λ^* and $2l^*$ (and the corresponding wavevector by $k^* = 2\pi/\lambda^*$), and we identify the bare-surface tension with that of an interface with all modes longer than λ^* cut off. Modes shorter than λ^* and non-capillary-wave-like fluctuations cannot be described by the theory, but they do contribute to, and indeed determine, σ_b .

We are interested in the quantitative behavior of σ_k (used generically in the rest of this section) and its relation to the surface tension of a finite-size system. Our most surprising result is that σ_k can be significantly larger than the unconstrained surface tension $\sigma = \sigma_0$, even when $k \ll k^*$. This prediction of an enhanced surface tension, if correct, will have important implications for interfaces in confined geometries, where the small physical dimen-

sions of the system cut off capillary waves with wavelengths larger than the system size. We show that this can cause a 50% increase in the surface tension near a critical point in physically realizable confined geometries. The theory also predicts that σ and σ_k near a critical point are related by finite-size scaling.⁶ One then expects $(k^*)^{-1}$ to be on the order of a bulk correlation length,⁷ and we find that $\sigma_k = \sigma F(k/k^*)$, with $F(x)$ universal. These issues could be relevant for questions recently raised regarding two-scale-factor universality.⁸

Of past attempts to assess the effects of capillary waves on surface tension,^{1,3,9-13} our approach is closest to those of Atkins,¹¹ Stillinger,¹² and Weeks.³ (See also Huse, van Saarloos, and Weeks.¹³) Atkins, who built upon the work of Frenkel,¹⁴ showed that a substantial fraction of the surface tension of liquid He II at absolute zero could be attributed to the zero-point vibrations of the interface. He introduced the concept of an intrinsic, or bare, surface tension, in his case the surface tension of a hypothetical interface with the zero-point vibrations suppressed. Stillinger attempted to calculate the surface tension of near-critical droplets as a function of droplet size. He introduced the idea of renormalizing the surface tension, but his results depend explicitly on Planck's constant. Weeks attempted to calculate the difference between the macroscopic surface tension and the surface tension obtained from molecular-dynamics experiments. The periodic boundary conditions applied in the simulations cut off capillary waves larger than the cell size. Our analysis is similar to that of Weeks, although his treatment must be modified close to a critical point. Finally, Weeks has also discussed capillary-wave theory in the context of bulk critical phenomena. (See also Huse, van Saarloos, and Weeks.¹³) Starting with a bulk d -dimensional model, he argues that one obtains capillary-wave theory by integrating out degrees of freedom on scales shorter than a correlation length. The resulting model depends on renormalized parameters and describes fluctuations of a $(d-1)$ -dimensional interface on large length scales. The existence of an underlying coarse-graining procedure plays an essential role in our calculation of the surface tension in Sec. III.

The remainder of the paper is organized as follows. In Sec. II we review capillary-wave theory and the assumptions on which it is based. In Sec. III we calculate the effect of capillary waves on the surface tension and show how the theory can be formulated to obtain σ_k . In Sec. IV we discuss the limits of validity of the theory and the choice of l^* , and in Sec. V we present numerical examples. We conclude in Sec. VI with a discussion of implications, problems, and recent experimental and theoretical results.

II. REVIEW OF CAPILLARY-WAVE THEORY

We begin with a remark on the bare interface and associated bare surface tension σ_b . As noted earlier, these quantities are defined *a posteriori* in such a way that the shortest capillary wave that can be considered in either the x or y direction has wavelength λ^* , or in the notation used below, $2l^*$. It is shown in Sec. IV that l^* is some-

what larger than the range of correlations in the bulk liquid, and in particular that l^* is on the order of 10 bulk correlation lengths near a critical point. One would therefore expect σ_b near a critical point to scale in the usual way: $\sigma_b \propto (1 - T_c/T)^\mu$, with T_c the critical temperature and $\mu = 1.26$ the surface-tension exponent.¹⁵ It is shown in Sec. III that this is indeed the case.

We now consider N particles in a volume V . We assume that V has a square horizontal cross-sectional area $A = L^2$ and that N is such that the Gibbs dividing surface⁴ for the bare system lies in the xy plane of a coordinate system centered in V . With $(x, y, z) = (\mathbf{r}, z)$, capillary-wave theory treats single-valued distortions of the bare interface in which the local position of the Gibbs surface is given by $\zeta(\mathbf{r})$. The vertical displacements $\zeta(\mathbf{r})$ play a central role in the theory. By construction, $\zeta(\mathbf{r})$ can have no Fourier components with wavelengths smaller than $2l^*$: these smaller-scale fluctuations are already included in the bare-density profile and in σ_b . The basic assertion of the theory is that the probability of a spontaneous fluctuation $\zeta(\mathbf{r})$ is, from thermodynamic fluctuation theory,¹⁶

$$P[\zeta(\mathbf{r})] = C \exp(-\beta W), \quad (1)$$

where C is a normalization constant, β^{-1} is Boltzmann's constant times T , and W is the reversible work required to create the fluctuation.

An implicit assumption made in attempting to describe the fluctuations of the interface in terms of $\zeta(\mathbf{r})$ is that specification of $\zeta(\mathbf{r})$ alone is enough to determine W . To calculate W in general, however, one must specify not $\zeta(\mathbf{r})$, but rather the perturbation $\delta\rho(\mathbf{r}, z)$ of the density profile from its pre-fluctuation value $\rho_b(z)$. In fact, $\zeta(\mathbf{r})$ does not in general uniquely determine $\delta\rho(\mathbf{r}, z)$. The implicit assumption that we make is that $\delta\rho(\mathbf{r}, z) = \rho_b(z - \zeta(\mathbf{r})) - \rho_b(z)$. The validity of this for a mode of amplitude ζ_0 and wavelength λ requires

$$|\partial\delta\rho(\mathbf{r}, z)/\partial\mathbf{r}| \ll |\partial\delta\rho(\mathbf{r}, z)/\partial z|,$$

i.e., that $\zeta_0 \ll \lambda$. The theory formulated in terms of $\zeta(\mathbf{r})$ thus applies only to small amplitude oscillations.

We can now write W in the form

$$W = \int d\mathbf{r} \left[\sigma_b [(1 + |\nabla\zeta|^2)^{1/2} - 1] + \int dz [\rho_b(z - \zeta(\mathbf{r})) - \rho_b(z)] gz \right], \quad (2)$$

where the first term is the work done against surface tension in increasing the area of the interface, and the second term is the work done against gravity. A key assumption is that the surface tension in (2) is σ_b , the surface tension of the bare interface. This assumption is discussed in Sec. VI. For small amplitude oscillations, we have

$$(1 + |\nabla\zeta|^2)^{1/2} - 1 = \frac{1}{2} |\nabla\zeta|^2 + \dots, \quad (3)$$

and in the second term in (2) we expand about $\zeta=0$,

$$\rho_b(z - \zeta(\mathbf{r})) - \rho_b(z) = -\rho'_b(z)\zeta(\mathbf{r}) + \frac{1}{2}\rho''_b(z)\zeta(\mathbf{r})^2 + \dots. \quad (4)$$

The first term vanishes in (2) by definition of the Gibbs dividing surface

$$\int_{-\infty}^0 dz[\rho_b(-\infty) - \rho_b(z)] = \int_0^{\infty} dz[\rho_b(z) - \rho_b(\infty)],$$

while the second term is proportional to

$$\int_{-\infty}^{\infty} dz \rho_b''(z)z = \rho_l - \rho_v = \Delta\rho,$$

where ρ_l and ρ_v are the mass densities of the coexisting liquid and vapor phases. The contribution to (2) from the higher-order terms in (4) is identically zero. Using these results in (2), we have

$$W = \frac{1}{2} \int d\mathbf{r} (\sigma_b |\nabla\zeta|^2 + \Delta\rho g \zeta^2), \quad (5)$$

which one might call the canonical form of capillary-wave theory.¹ Since W is quadratic in the distortions, all averages, correlation functions, etc., can be calculated exactly, as in any quadratic field theory.

To further develop the notation, we calculate $\langle \zeta^2 \rangle$, the mean-square displacement of the interface from its nominal location at $z=0$. We assume that periodic boundary conditions apply at the vertical sides of the volume V , and we expand $\zeta(\mathbf{r})$ in a Fourier series

$$\zeta(\mathbf{r}) = \sum_{\mathbf{k}} a_{\mathbf{k}} \exp(i\mathbf{k}\cdot\mathbf{r}). \quad (6)$$

The allowed wave vectors \mathbf{k} are then

$$k_x, k_y = \pm 2\pi/L, \pm 2 \times 2\pi/L, \dots, \pm [L/(2l^*)] \times 2\pi/L, \quad (7)$$

$$\langle \zeta^2 \rangle = A^{-1} \int d\mathbf{r} \langle \zeta(\mathbf{r})^2 \rangle = \sum_{\mathbf{k}} \langle a_{\mathbf{k}} a_{-\mathbf{k}} \rangle$$

$$= k_B T (2\pi)^{-2} \int_{-\pi/l^*}^{\pi/l^*} dk_x \int_{-\pi/l^*}^{\pi/l^*} dk_y (\Delta\rho g + \sigma_b k^2)^{-1}, \quad (12)$$

where in the last line we have taken the thermodynamic limit ($A \rightarrow \infty$), and so replaced $A^{-1} \sum$ by $(2\pi)^{-2} \int d\mathbf{k}$. To exhibit the small- g behavior of $\langle \zeta^2 \rangle$ derived by Buff, Lovett, and Stillinger,¹ we replace the integration in (12) by integration over a circle of radius π/l^* , whence

$$\langle \zeta^2 \rangle = [k_B T / (4\pi\sigma_b)] \ln[1 + \frac{1}{2} a_b^2 (\pi/l^*)^2], \quad (13)$$

where $a_b = [2\sigma_b / (\Delta\rho g)]^{1/2}$ is the bare capillary length. $\langle \zeta^2 \rangle$ thus diverges as $\ln g^{-1}$, as asserted earlier. The divergence is believable because it is caused by small- k modes. A disturbing aspect of the result, on the other hand, is that the divergence of $\langle \zeta^2 \rangle$ involves σ_b and not σ , the full surface tension. This erroneous dependence would disappear in a self-consistent treatment (see Sec. VI).

III. CALCULATION OF SURFACE TENSIONS

A. Capillary-wave contribution to σ

The calculation of the surface tension in capillary-wave theory involves the evaluation of the partition function Z , associated with the surface distortions,

where we have excluded the $\mathbf{k}=0$ mode and all modes with wavelengths $\lambda = 2\pi/k < 2l^*$. The requirement that $\zeta(\mathbf{r})$ be real implies that $a_{\mathbf{k}} = a_{-\mathbf{k}}^*$, and one generally introduces a new set of variables $\{\alpha_{\mathbf{k}}, \beta_{\mathbf{k}}; k_x > 0, k_y \text{ unrestricted}\}$ by

$$a_{\mathbf{k}} = \alpha_{\mathbf{k}} + i\beta_{\mathbf{k}}. \quad (8)$$

With (6), (8), and the orthogonality implied by (7), (5) then becomes

$$W = A \sum_{k_x > 0, k_y} (\alpha_{\mathbf{k}}^2 + \beta_{\mathbf{k}}^2) (\Delta\rho g + \sigma_b k^2). \quad (9)$$

The probability of a distortion with $\alpha_{\mathbf{k}}$ in a small interval $d\alpha_{\mathbf{k}}$, etc., is now given by

$$P \propto \left[\prod_{k_x > 0, k_y} d\alpha_{\mathbf{k}} d\beta_{\mathbf{k}} \right] \exp(-\beta W), \quad (10)$$

and a straightforward calculation shows that we have independent modes with

$$\begin{aligned} \langle a_{\mathbf{k}} a_{-\mathbf{k}} \rangle &= \langle \alpha_{\mathbf{k}}^2 \rangle + \langle \beta_{\mathbf{k}}^2 \rangle \\ &= (k_B T / A) (\Delta\rho g + \sigma_b k^2)^{-1}. \end{aligned} \quad (11)$$

The mean-square displacement is given by

$$Z = \exp(-\beta F_{CW}) = \left[\prod_{\mathbf{k}} C \int da_{\mathbf{k}} \right] \exp(-\beta W). \quad (14)$$

The surface tension σ is then given by the sum of the bare surface tension and the contribution from capillary waves,

$$\sigma = \sigma_b + \sigma_{CW}, \quad (15)$$

where

$$\sigma_{CW} = \partial F_{CW} / \partial A. \quad (16)$$

While this calculation seems straightforward, the literature regarding σ and σ_{CW} is very confusing. The results that we derive below are closest in spirit to those of Weeks.³

When one attempts to calculate σ_{CW} , one immediately encounters an obstacle: the fluctuation variables $a_{\mathbf{k}}$ have the dimensions of length, yet Z must be dimensionless. The unknown reciprocal length C can be evaluated by changing from the variables $\{a_{\mathbf{k}}\}$ to a set which is dimensionless. We first write

$$\begin{aligned}
Z &= \sum_{\zeta(\mathbf{r})} \exp(-\beta W) \\
&= \sum_{\{\zeta(\mathbf{r}_i)\}} \exp(-\beta W) \\
&= \left[\prod_i C' \int d\zeta(\mathbf{r}_i) \right] \exp(-\beta W), \quad (17)
\end{aligned}$$

where we have represented the functions $\zeta(\mathbf{r})$ by sets of discrete values, $\{\zeta(\mathbf{r}_i)\}$, the \mathbf{r}_i defining the horizontal locations of tall cylinders of cross-sectional area $(l^*)^2$. The dimension l^* has been chosen to ensure that the number of variables $\zeta(\mathbf{r}_i)$ is equal to the number of allowed values of \mathbf{k} , i.e., $A/(l^*)^2$. To determine the new constant C' , we recall that one must integrate out bulk density fluctuations on scales smaller than the bulk correlation length to obtain capillary-wave theory. Thus, we consider the displacements $\zeta(\mathbf{r}_i)$ as arising from fluctuations in the number of coherent density fluctuations of size l_0 in each column, where l_0 is the correlation length in the liquid phase. Denoting the number of such "blobs" in the i th cell by N_i , we therefore have

$$\zeta(\mathbf{r}_i) = (N_i - \bar{N}) l_0^3 / (l^*)^2, \quad (18)$$

where \bar{N} is the average number of blobs in the i th cell. The main point is that we can now express W and Z in terms of the dimensionless fluctuation variables $N_i - \bar{N}$ and write

$$Z = \left[\prod_i \int d(N_i - \bar{N}) \right] \exp(-\beta W), \quad (19)$$

with a proportionality constant of exactly unity. It follows that C' is given by

$$C' = (l^*)^2 / l_0^3. \quad (20)$$

The constant C in (14) follows upon evaluation of the Jacobian of the transformation from $\{\zeta(\mathbf{r}_i)\}$ to $\{a_{\mathbf{k}}\}$, viz.,

$$\zeta(\mathbf{r}_i) = \sum_{\mathbf{k}} a_{\mathbf{k}} \exp(i\mathbf{k} \cdot \mathbf{r}_i),$$

thus,

$$C = C' [A / (l^*)^2]^{1/2}. \quad (21)$$

The combination $A / (l^*)^2$ is again the number of allowed values of k . Using these results and (8) and (9) in (14), we obtain the partition function in the following form:

$$\begin{aligned}
Z &= \prod_{k_x > 0, k_y} \left[[2(l^*)^2 A / l_0^6] \right. \\
&\quad \times \int d\alpha_{\mathbf{k}} \int d\beta_{\mathbf{k}} \exp[-\beta A (\alpha_{\mathbf{k}}^2 + \beta_{\mathbf{k}}^2) \\
&\quad \left. \times (\Delta\rho g + \sigma_b k^2) \right]. \quad (22)
\end{aligned}$$

The extra factor of 2 arises from the transformation from $(a_{\mathbf{k}}, a_{-\mathbf{k}})$ to $(\alpha_{\mathbf{k}}, \beta_{\mathbf{k}})$.

We can now perform a straightforward calculation of σ_{CW} . From (15), (16), and (22) we obtain, in the thermodynamic limit,

$$\beta\sigma = \beta\sigma_b + \frac{1}{2}(l^*)^{-2} \ln\left(\frac{1}{2}\beta\Gamma_b\right) + \frac{1}{2}(l^*)^{-2} F(G_b^2), \quad (23)$$

where

$$\Gamma_b = \sigma_b l_0^6 / [\pi(l^*)^4], \quad (24)$$

$$G_b^2 = 2(l^*)^2 \Delta\rho g / \sigma_b, \quad (25)$$

$$F(G_b^2) = (2\pi)^{-2} \int_{-\pi}^{\pi} dq_x \int_{-\pi}^{\pi} dq_y \ln\left(\frac{1}{2}G_b^2 + q^2\right). \quad (26)$$

Equation (23) is similar in form to the result obtained by Weeks [Ref. 3, Eq. (47)], and we have used his notation in defining Γ and G^2 . This is not so surprising when one considers the similarities between his calculation and that presented here. One difference is that in his formulation the two terms to the right of σ_b in (23) involve the surface tension σ instead of σ_b . He therefore assumes that capillary waves are unfrozen on an interface with tension σ . We argue in Sec. VI that neither σ nor σ_b is in fact correct. A more significant difference is that Weeks views the displacements $\zeta(\mathbf{r}_i)$ as arising from fluctuations in the number of particles in each cell, rather than in the number of blobs. The definition of the Gibbs dividing surface then leads to the erroneous result $C' = (l^*)^2 \Delta\rho / m$, where m is the mass of a molecule. It is essential that near a critical point one not ignore the coarse graining implicit in the formulation of capillary-wave theory. Far away from a critical point the difference is inconsequential: $(\Delta\rho/m)^{-1/3}$ and l_0 are then comparable microscopic lengths. The other differences between Week's result and (23) are minor and arise from his consideration of a particular discrete model [see Ref. 3, Eq. (34)]. Discretization of the model here leads to (23) through (26), but with q^2 in (26) replaced by

$$1 - \frac{1}{2} [\cos(2q_x) + \cos(2q_y)].$$

As a final point, the net correction to σ_b is *negative*, so that $\sigma < \sigma_b$. This is expected since σ_b pertains to a constrained interface: when capillary waves are unfrozen they lower the free energy associated with the interface.

We may simplify (23) by observing that G^2 is negligible except extremely close to a critical point—so close that the capillary length is on the order of a bulk correlation length. As gravity effects then play a major role,¹⁷ we avoid that region and ignore G^2 . (Equivalently, we simply take the limit $g \rightarrow 0$.) With the result

$$\begin{aligned}
(2\pi)^{-2} \int_{-\pi}^{\pi} dq_x \int_{-\pi}^{\pi} dq_y \ln q^2 &= 2 \ln \pi - 3 + \ln 2 + \pi/2 \\
&\equiv \ln E, \quad (27)
\end{aligned}$$

we then obtain

$$\beta\sigma = \beta\sigma_b + \frac{1}{2}(l^*)^{-2} \ln\{\beta\sigma_b l_0^6 E / [2\pi(l^*)^4]\}, \quad (28)$$

where $E = 4.7275 \dots$ and the leading-order correction is of order $g \ln g^{-1,3,10}$. The surface tension σ is thus well defined in the absence of an external field. An important consequence of (28) near a critical point follows upon noting that l^* is proportional to l_0 (see Sec. IV). Because σl_0^2 approaches a constant at a critical point,⁷ this means that σ_b and σ both scale as $(1 - T_c/T)^\mu$ for T near T_c , as noted in Sec. II. This lends credence to our evaluation of the constant C in (14).

B. Effects of capillary-wave cutoffs

In contrast to the calculation of σ (where all modes in the square $\{-k^* \leq k_x, k_y \leq k^*\}$ are unfrozen), one obtains surface tensions larger than σ when only subsets of modes are unfrozen. We consider the three capillary-wave cutoffs shown in Fig. 1, where the shaded regions denote unfrozen wavevectors and the unshaded regions wave vectors that are cut off. Case 1 (surface tension σ_k) does not correspond to any particular confined geometry, case 2 (surface tension $\sigma_{k,\text{square}}$) corresponds to a square confined geometry, and case 3 (surface tension $\sigma_{k,\text{slit}}$) corresponds to a slit, i.e., an interface confined in only one direction. It is clear that

$$\sigma_{k,\text{square}} > \sigma_{k,\text{slit}} > \sigma_k,$$

because the more modes that are cut off, the larger the surface tension. The quantity σ_k is useful as a lower bound.

To calculate σ_k we first rewrite (22) in the form $\exp[-2\beta F_{\text{CW}}(k)]$

$$= \prod_{\mathbf{k}'} \left[2(l^*)^2 A / l_0^6 \right. \\ \times \int d\alpha_{\mathbf{k}'} \int d\beta_{\mathbf{k}'} \exp[-\beta A(\alpha_{\mathbf{k}'}^2 + \beta_{\mathbf{k}'}^2) \\ \left. \times (\Delta\rho g + \sigma_b k'^2) \right]. \quad (29)$$

The product is over the shaded region for σ_k in Fig. 1, and the factor of 2 in the exponent on the left-hand side arises on elimination of the restricted product in (22). Since $F_{\text{CW}}(k)$ gives the lowering of the free energy due to the unfreezing of modes in the shaded region, we have

$$\sigma_k = \sigma_b + \partial F_{\text{CW}}(k) / \partial A. \quad (30)$$

To exhibit an explicit equation for σ_k , we need only carry out the integrations and pass to the thermodynamic limit. Doing this, we obtain

$$\beta\sigma_k = \beta\sigma_b + \frac{1}{2}[(k^*/\pi)^2 - (k/\pi)^2] \ln(\frac{1}{2}\beta\Gamma_b) \\ + \frac{1}{2}(k^*/\pi)^2 (2\pi)^{-2} \\ \times \int_{\pi k/k^* \leq |q_x|, |q_y| \leq \pi} dq_x \int dq_y \ln(\frac{1}{2}G_b^2 + q^2). \quad (31)$$

Note that σ_k reduces correctly to σ_b in the limit $k = k^*$, while in the limit of zero k it gives (23).

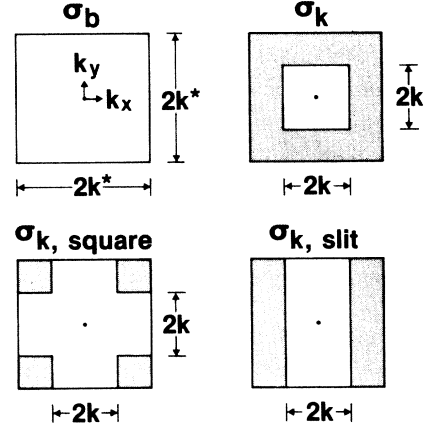


FIG. 1. Capillary-wave cutoffs in k space and their associated surface tensions. The shaded areas denote allowed wave vectors, and the unshaded regions wave vectors that are cut off. All modes would be allowed on an unconstrained interface and the squares would be entirely shaded in. We associate $\sigma_{k,\text{square}}$ with the surface tension of a square interface of edge $l = 2\pi/k$ in real space, where modes with $|k_x| \leq 2\pi/l$ or $|k_y| \leq 2\pi/l$ are cut off. Similarly, we associate $\sigma_{k,\text{slit}}$ with an interface which has width l in the x direction but is infinite in the y direction.

Equation (31) is convenient for studying σ_k in the neighborhood of k^* . It is more convenient to have an expression for σ_k that is accurate for small k . We set $G^2 = 0$ (as noted above, we assume that this term is negligible), subtract (23) from (31), and use (27). Writing $k = 2\pi/l$ and $k^* = 2\pi/(2l^*)$, we obtain

$$\beta\sigma_{2\pi/l} = \beta\sigma - 2l^{-2} \ln\{\beta\sigma_b l_0^6 E [2\pi(l^*)^4]^{-1} (2l^*/l)^2\}. \quad (32)$$

The bare surface tension can be eliminated completely by solving (28) for σ_b (see Sec. IV).

Equation (32) implies that $\beta\sigma_{2\pi/l}$ approaches the unconstrained surface tension slowly with increasing l , i.e., $\beta\sigma_{2\pi/l} - \beta\sigma \propto l^{-2} \ln l$ for large l . Because l_0 is a bulk correlation length near a critical point and l^* is a multiple of l_0 , $\sigma_{2\pi/l}$ also obeys finite-size scaling: $\sigma_{2\pi/l} = \sigma F(l/\xi)$. The function $F(x)$ depends on the shape of the allowed region in k space but is otherwise universal.

To calculate $\sigma_{k,\text{square}}$ and $\sigma_{k,\text{slit}}$, one needs to evaluate the product in (29) over the appropriate shaded regions in Fig. 1. Proceeding as for σ_k , we obtain

$$\beta\sigma_{2\pi/l,\text{square}} = \beta\sigma - 2[(l^*l)^{-1} - l^{-2}] \ln\{\beta\sigma_b l_0^6 / [2\pi(l^*)^4]\} + \frac{1}{2}(l^*)^{-2} [I(2l^*/l, 2l^*/l) - I(0,0)], \quad (33)$$

$$\beta\sigma_{2\pi/l,\text{slit}} = \beta\sigma - (l^*l)^{-1} \ln\{\beta\sigma_b l_0^6 / [2\pi(l^*)^4]\} + \frac{1}{2}(l^*)^{-2} [I(2l^*/l, 0) - I(0,0)], \quad (34)$$

where

$$I(a,b) = 4(2\pi)^{-2} \int_{\pi a}^{\pi} dx \int_{\pi b}^{\pi} dy \ln(x^2 + y^2) \\ = (1-a)(1-b)(2 \ln \pi - 3) + \ln 2 + \pi/2 + (a^2 - 1) \tan^{-1} a + (b^2 - 1) \tan^{-1} b - a \ln(1+a^2) - b \ln(1+b^2) \\ + ab \ln(a^2 + b^2) - a^2 \tan^{-1}(a/b) - b^2 \tan^{-1}(b/a). \quad (35)$$

Like $\sigma_{2\pi/l}$, $\sigma_{2\pi/l,\text{square}}$ and $\sigma_{2\pi/l,\text{slit}}$ obey finite-size scaling near a critical point, but with different functional forms for $F(x)$. That all three surface tensions obey finite-size scaling is a consequence of our normalization of the capillary-wave partition function. For large l we have the results

$$\beta\sigma_{2\pi/l,\text{slit}} - \beta\sigma = (\beta\sigma_{2\pi/l,\text{square}} - \beta\sigma)/2 \\ = -(l^*l)^{-1} [2(\ln\pi - 1) + \ln(\frac{1}{2}\beta\Gamma_b)], \quad (36)$$

which imply that $\beta\sigma_{2\pi/l,\text{slit}}$ and $\beta\sigma_{2\pi/l,\text{square}}$ approach $\beta\sigma$ very slowly (as l^{-1}) with increasing l . The numerical implications of (32) through (34) are investigated in Sec. V.

IV. CHOICE OF l^* , CALCULATION OF σ_b

To determine the range of validity of capillary-wave theory, we need to estimate the largest k for which we can believe calculations of σ_k , $\sigma_{k,\text{square}}$, and $\sigma_{k,\text{slit}}$. Since $k_{\text{max}} = k^* = 2\pi/(2l^*)$, we must choose l^* in such a way that the assumptions that we have introduced are valid.

$$\langle |\nabla\zeta|^2 \rangle = A^{-1} \int d\mathbf{r} \langle |\nabla\zeta(\mathbf{r})|^2 \rangle = \sum_{\mathbf{k}} k^2 \langle a_{\mathbf{k}} a_{-\mathbf{k}} \rangle \\ = k_B T (2\pi)^{-2} \int_{-\pi/l^*}^{\pi/l^*} dk_x \int_{-\pi/l^*}^{\pi/l^*} dk_y k^2 (\Delta\rho g + \sigma_b k^2)^{-1}. \quad (39)$$

It is simplest to replace this exact expression by an upper bound obtained by setting $g=0$ and substituting σ for σ_b . With (38) we obtain a result that can be written in the form

$$l_{\text{min}}^* = (0.1\beta\sigma l_0^2)^{-1/2} l_0. \quad (40)$$

Here, l_{min}^* is the smallest value of l^* for which capillary-wave theory can be considered valid, $2l_{\text{min}}^*$ is the shortest wavelength, and l_0 is an arbitrary scale factor (i.e., l_{min}^* is independent of l_0). For a pure fluid near its triple point we take l_0 to be a molecular diameter. For a near-critical interface we take $l_0 = \xi$, with $\xi = \xi_0 |1 - T/T_c|^{-\nu}$ the bulk correlation length of either coexisting phase. Here $\nu = 0.630$ is the correlation length exponent¹⁵ and ξ_0 is a nonuniversal amplitude on the order of $1 - 2 \times 10^{-8}$ cm.

Let us first consider the simple fluid SF₆ near its triple-point temperature T_t . Assuming the values¹⁹ $T_t = 223$ K, $\sigma = 11.4$ dyn/cm, and $l_0 = 3.1 \times 10^{-8}$ cm, we find

$$l_{\text{min}}^* = 5.3 l_0. \quad (41)$$

As stated in Sec. II, the theory in its present form is restricted to the treatment of small amplitude oscillations of the interface. Recall that for an individual mode of amplitude ζ_0 and wavelength λ this meant that $\zeta_0 \ll \lambda$. For many modes present simultaneously, on the other hand, we assumed that $|\nabla\zeta|^2 \ll 1$. The validity of the theory thus rests on the inequality¹²

$$\langle |\nabla\zeta|^2 \rangle \ll 1. \quad (37)$$

When this condition is not satisfied, modes with different wave vectors are strongly coupled, and it is not permissible to expand $(1 + |\nabla\zeta|^2)^{1/2}$ as in (3).¹⁸ As a practical matter we will define (37) to be satisfied when

$$\langle |\nabla\zeta|^2 \rangle \leq 0.1. \quad (38)$$

The leading-order term in the expansion of $(1 + |\nabla\zeta|^2)^{1/2} - 1$ is then 20 times larger than the first correction.

It is as straightforward to calculate $\langle |\nabla\zeta|^2 \rangle$ as it was to calculate $\langle \zeta^2 \rangle$ in Sec. II. We find

According to this, the theory correctly describes distortions with wavelengths as short as about 10 molecular diameters. We also record results for Ar near its triple point. With the values $\sigma = 14$ dyn/cm, $T_t = 85$ K, and $l_0 = 3.4 \times 10^{-8}$ cm, we find $l_{\text{min}}^* = 2.7 l_0$.

For a pure fluid near its critical point, we can use two-scale-factor universality²⁰ to express l_{min}^* in a universal form. According to this principle, the combination $\beta\sigma\xi^2$ approaches a constant, independent of any particular fluid, as T approaches T_c . Moldover's recent analysis⁸ of a wide variety of fluid data gives $\beta\sigma\xi^2 = 0.10$, where we have used the amplitude ratio²¹ $\xi_0(T > T_c)/\xi_0(T < T_c) = 2$ to write $\beta\sigma\xi^2$ in terms of $\xi_0(T < T_c)$. Equation (40) with $l_0 = \xi$ then becomes

$$l_{\text{min}}^* = 10\xi. \quad (42)$$

This result is consistent with assertions by Weeks³ and Huse *et al.*¹³ that $l_{\text{min}}^* = M\xi$, with M a fixed number much greater than unity. It would seem that at wavelengths of $2l^* = 20\xi$ most of the fluctuations responsible for the critical phenomena would have already been included in the parameter σ_b characterizing the bare interface.

TABLE I. Relevant data for SF₆ and Ar near their triple points.

Fluid	T_{triple} (K)	σ (dyn/cm)	l_0 (Å)	l_{min}^*/l_0	$\beta\sigma l_0^2$	σ_b/σ
SF ₆	223	11.4	3.12	5.3	0.36	1.38
Ar	85	14.0	3.40	2.7	1.38	1.19

TABLE II. The ratios $\sigma_{k,\text{square}}/\sigma$ and $\sigma_{k,\text{slit}}/\sigma$ for SF₆ and Ar near their triple points, with $k = 2\pi/l$. l_{min} is 33.1 Å for SF₆ and 18.4 Å for Ar.

l/l_{min}	SF ₆		Ar	
	$\sigma_{k,\text{square}}/\sigma$	$\sigma_{k,\text{slit}}/\sigma$	$\sigma_{k,\text{square}}/\sigma$	$\sigma_{k,\text{slit}}/\sigma$
1	1.379	1.379	1.187	1.187
1.5	1.342	1.264	1.172	1.137
2	1.294	1.203	1.151	1.107
3	1.224	1.139	1.118	1.075
4	1.179	1.106	1.095	1.058
5	1.149	1.085	1.080	1.047
6	1.127	1.071	1.069	1.040
7	1.111	1.061	1.061	1.034
8	1.099	1.054	1.054	1.030
9	1.089	1.048	1.049	1.027
10	1.081	1.043	1.044	1.024
25	1.034	1.018	1.019	1.010

With (41) and (42) for l^* , we can calculate σ_b/σ from (28). The results for SF₆ and Ar near their triple points are collected in Table I, while near a critical point σ_b/σ always has the value 1.57. That σ_b/σ is significantly larger than unity is important because $\sigma_{2\pi/l}$, $\sigma_{2\pi/l,\text{square}}$, and $\sigma_{2\pi/l,\text{slit}}$ each reduce to σ_b as l decreases to its minimum value $2l^*$. The smaller the value of l_{min}^* the larger the ratio σ_b/σ , and vice versa.

V. NUMERICAL EXAMPLES

Equations (32)–(34) are useful for computation. Information for SF₆ and Ar near their triple points is given in Table I, and calculated values of $\sigma_{2\pi/l,\text{square}}/\sigma$ and $\sigma_{2\pi/l,\text{slit}}/\sigma$ as functions of l/l_{min} are given in Table II. The surface tension ratios near a critical point are presented graphically in Fig. 2—these are universal when plotted as functions of l/ξ . Unscaled parameters are tabulated for SF₆ in Table III.

For SF₆ near its triple point, (41) implies that $l_{\text{min}} = 2l^*_{\text{min}} = 10.6l_0$. For $l_0 = 3.12$ Å, we have $l_{\text{min}} = 33.1$ Å. We see from Table II that $\sigma_{2\pi/l,\text{square}}/\sigma = 1.38$ for $l/l_{\text{min}} = 1$, corresponding to a 38% enhancement of the surface tension over its infinite-system value. This is presumably what one would find in the computer simulation of a system of SF₆ 10.6-molecular diameters across. For Ar we find $l_{\text{min}} = 5.4l_0 = 18.4$ Å, and we obtain

TABLE III. Data for SF₆ for the critical curves shown in Fig. 2. Here $t = (T - T_c)/T_c$, $T_c = 319\text{K}$, $\sigma = 48 \times |t|^{1.26}$ dyn/cm, and $\xi = 0.94 \times |t|^{-0.63}$ Å (see Ref. 19). l_{min} is equal to 20ξ and $\sigma_b/\sigma = 1.57$.

$ t $	σ (dyn/cm)	ξ (Å)	l_{min} (μm)
10^{-2}	1.45×10^{-1}	17	0.03
10^{-3}	7.97×10^{-3}	73	0.15
10^{-4}	4.38×10^{-4}	311	0.62
10^{-5}	2.41×10^{-5}	1328	2.66
10^{-6}	1.32×10^{-6}	5664	11.33

$\sigma_{2\pi/l,\text{square}}/\sigma = 1.19$ for $l/l_{\text{min}} = 1$. This increase pertains to the computer simulation of a system of Ar 5.4-molecular diameters across. For a more realistic system 10.8 diameters across, we would predict a 15% enhancement, which is not unreasonable in terms of simulations that have been done and in view of the difficulties in simulating interfaces (see Ref. 4, Chap. 6). The predicted finite-size effects depend weakly on l in the range of system sizes accessible to simulation.

Near a critical point (42) implies that $l_{\text{min}} = 20l_0 = 20\xi$, with ξ a bulk correlation length. We find $\sigma_{2\pi/l}/\sigma = 1.57$ for $l/l_{\text{min}} = 1$, and an identical result holds for the square and slit geometries (see Fig. 2). Taking the reduced temperature $|t| = 10^{-4}$ as an example, we find $l_{\text{min}} = 6220$ Å for SF₆. This might mean that measurements of capillary rise in a capillary 0.6 μm in diameter would lead to anomalously large apparent surface tensions. Alternatively, if one thought that one knew the surface tension, the fluid would rise 1.57 times higher than one would think.

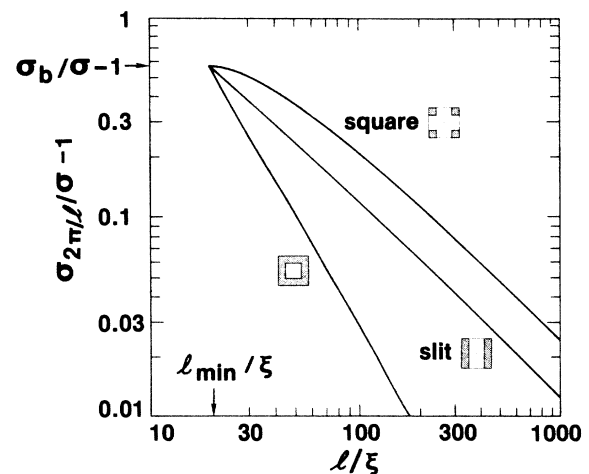


FIG. 2. Log-log plots of $\sigma_{2\pi/l}/\sigma - 1$ vs l/ξ near a critical point, with ξ the bulk correlation length of either coexisting phase. The curves depend on the geometry of the allowed region in k space (see Fig. 1) but are otherwise universal. All curves converge to $\sigma_b/\sigma - 1$ at $l_{\text{min}} = 20\xi$, our estimate of where capillary-wave theory breaks down. Values of σ , ξ , and l_{min} for SF₆ are given in Table 3.

Note that the effects of capillary-wave cutoffs decay very slowly with increasing l for the square and slit geometries: for $l = 100\xi$, we find $\sigma_{2\pi/l, \text{square}}/\sigma = 1.22$ and $\sigma_{2\pi/l, \text{slit}}/\sigma = 1.12$. For SF₆ at $|t| = 10^{-4}$, 100ξ equals $3.2 \mu\text{m}$, a system size which is easily realized experimentally. While the surface-tension enhancement factors are certainly significant for T near T_c and l near l_{\min} , the surface tension itself is very small. This is shown in Table III, where we collect results for SF₆ at several reduced temperatures.

VI. CONCLUDING REMARKS

We have used capillary-wave theory to calculate the effect that cutting off capillary waves has on surface tension. The fact that modes are cut off causes the surface tension to be larger than its unconstrained value σ . The surface tensions σ_k , $\sigma_{k, \text{square}}$, and $\sigma_{k, \text{slit}}$ pertain to infinite interfaces with certain sets of capillary waves cut off (see Fig. 1). We have shown in Sec. V that the ratios of these constrained tensions to σ can be significantly larger than unity, especially near a critical point and for the smallest k 's ($k = 2\pi/l$) that the theory can be said to legitimately describe. Results for SF₆ and Ar near their triple points are given in Table II, while results for any system near its critical point are presented in Fig. 2.

There are two predictions of the theory. The first of these is that the surface tension of a fluid in a confined geometry can be 1.5 (or possibly more) times larger than the surface tension in a large system. This effect might provide some insight into the results obtained by Moldover and Gammon,²² who measured the capillary rise of SF₆ between two very closely-spaced (1–4 μm) laser mirrors. They observed rises substantially larger than predicted by hydrostatic theory with the macroscopic surface tension—for example, a 30–40% increase for $|t| = 2.1 \times 10^{-4}$ and a spacing of 1 μm . Our results for $\sigma_{2\pi/l, \text{slit}}$ imply a 24% enhancement. Moldover and Gammon tried to explain their results in terms of wetting layers on the glass plates (which were envisioned to effectively reduce the plate spacing), but this led to the prediction of anomalously thick wetting layers. We now believe that the wetting layers in their system would have been too thin to explain the capillary rise measurements.²³ Moreover, we now know that there was a significant uncertainty in the determination of the plate spacing because of an unknown phase shift arising from the use of the multilayer dielectric mirrors. In light of this, it would be very interesting to do the Moldover-Gammon experiment over again. It is encouraging that the shapes of the capillary-rise curves as a function of plate spacing in their experiment do not vary as the reciprocal of the real or effective plate spacing, as they would if the conventional theory of capillary rise were applicable. Rather, the discrepancy between the measured and theoretical values of the capillary rise increases as the spacing between the plates decreases. This is consistent with an interpretation of their experiment in terms of finite-size effects. We remark that interface curvature and the effects of wetting layers need to be considered to decide what interface fluctuations are actually cut off.

The second prediction deals with how σ_k and the other constrained surface tensions scale near a critical point. According to (32), $\sigma_{2\pi/l}/\sigma$ is a universal function of l/ξ , where ξ is the correlation length of either bulk phase. The results are thus in agreement with the proposal of finite-size scaling for the surface tension.⁶

The finite-size effects shown in Fig. 2 may be relevant for questions recently raised concerning two-scale-factor universality for fluids, according to which $\beta\sigma\xi^2$ is a universal constant. Moldover⁸ has recently shown that $\beta\sigma\xi^2$ for a wide variety of fluids apparently is a constant, but its value is about 1.4 times larger than that predicted theoretically. Most of the measurements were extrapolated to T_c from far from T_c , however, and it is possible that those made near T_c were influenced by finite-size effects. Such effects would lead to apparent surface-tension amplitudes which would be too large. Note that the range of significant finite-size effects in Fig. 2 decays very slowly with system size near a critical point.

We conclude with a discussion of two open questions. The first concerns the smallest length scale $2l_{\min}^*$ on which capillary-wave theory can be applied. As noted in Sec. IV, our results for σ_b/σ depend sensitively on this length. Near a critical point we have estimated that $2l_{\min}^* = 20\xi$, but the value could be somewhat lower or somewhat higher. It is often stated that l_{\min}^* is on the order of ξ . To estimate l_{\min}^* more accurately would require the development of a theory that bridges the gulf between length scales somewhat smaller than ξ and length scales much greater than ξ . An experiment designed to probe finite-size effects would provide valuable information in this regard.

A second question concerns the way in which distortions are usually unfrozen in capillary-wave theory. Let us imagine that we unfreeze all modes with wavelengths greater than λ^* but less than some arbitrarily long wavelength λ . If we inquire as to what surface tension the mode of wavelength λ sees, capillary-wave theory responds σ_b , the bare surface tension. But the long-wavelength mode should see essentially σ , the unconstrained surface tension. We conclude that the long-wavelength mode sees a “renormalized” surface tension—a surface tension that differs from σ_b because of the unfrozen modes of shorter wavelength. Such effects have not been included in the version of capillary-wave theory considered here. At the very least, one would have to replace σ_b in (29) with a generalized wave vector-dependent quantity $\sigma(k'; k, k^*)$ representing the surface tension that a mode of wave vector k' sees given that modes with wave vector components between k and k^* have been unfrozen. Limiting cases are $\sigma(0; k, k^*) = \sigma_{k, \text{square}}$, which is one of the surface tensions calculated in Sec. III, and $\sigma(k; 0, k^*) \equiv \sigma(k)$, which is the response of an unconstrained interface to a mode of wave vector k . One would also expect $\sigma(k'; k, k^*)$ to be a monotonically increasing function of k (because larger k 's correspond to more constrained interfaces), and of k' (because the renormalizing effect of modes in the interval (k, k^*) should diminish as k' increases). While a theory for $\sigma(k'; k, k^*)$ does not yet exist, its effect on our calculations would be to increase the ratios of σ_k , $\sigma_{k, \text{square}}$, and

$\sigma_{k,\text{slit}}$ to σ . The response function $\sigma(k)$ would be interesting to calculate for two-scale-factor universality because $\sigma(k)$ is the surface tension measured in quasi-elastic light scattering from capillary waves. If $\sigma(k)$ were significantly larger than σ , this would help to reduce the present discrepancy between experiment and theory.

ACKNOWLEDGMENTS

The author acknowledges informative discussions with P. C. Albright, M. R. Moldover, and J. D. Weeks. This work was supported in part by NASA under Contract No. H-27954-B.

-
- ¹F. P. Buff, R. A. Lovett, and F. H. Stillinger, *Phys. Rev. Lett.* **15**, 621 (1965).
- ²For a recent review of capillary-wave and density-profile theories, see D. Jasnow, *Rep. Prog. Phys.* **47**, 1059 (1984). See also Refs. 4 and 10.
- ³J. D. Weeks, *J. Chem. Phys.* **67**, 3106 (1977).
- ⁴See J. S. Rowlinson and B. Widom, *Molecular Theory of Capillarity* (Oxford University Press, Oxford, 1982).
- ⁵It is likely that a definition of intrinsic profile that does not involve some element of arbitrariness is impossible. For a recent discussion, see D. B. Abraham, *Phys. Rev. B* **29**, 525 (1984); and D. A. Huse (unpublished).
- ⁶K. K. Mon and D. Jasnow, *Phys. Rev. A* **30**, 670 (1984); **31**, 4008 (1985).
- ⁷B. Widom, *J. Chem. Phys.* **43**, 3892 (1965); B. Widom, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic, New York, 1972), Vol. 2.
- ⁸M. R. Moldover, *Phys. Rev. A* **31**, 1022 (1985).
- ⁹H. T. Davis, *J. Chem. Phys.* **67**, 3636 (1977).
- ¹⁰R. Evans, *Adv. Phys.* **28**, 143 (1979).
- ¹¹K. R. Atkins, *Can J. Phys.* **31**, 1165 (1953).
- ¹²F. H. Stillinger, *J. Chem. Phys.* **47**, 2513 (1967).
- ¹³D. A. Huse, W. van Saarloos, and J. D. Weeks, *Phys. Rev. B* **32**, 233 (1985).
- ¹⁴J. Frenkel, *Kinetic Theory of Liquids* (Oxford University Press, Oxford, 1946), Chap. 6.
- ¹⁵We use values of the critical exponents predicted by renormalization group theory. See D. Z. Albert, *Phys. Rev. B* **25**, 4810 (1982); and J. C. Le Guillou and J. Zinn-Justin, *Phys. Rev. B* **21**, 3976 (1980).
- ¹⁶L. D. Landau and E. M. Lifshitz, *Statistical Physics*, revised and enlarged by E. M. Lifshitz and L. P. Pitaevskii (Pergamon, New York, 1980), Chap. 12, Part 1.
- ¹⁷For a review of gravity effects in fluids, see M. R. Moldover, J. V. Sengers, R. W. Gammon, and R. J. Hocken, *Rev. Mod. Phys.* **51**, 79 (1979).
- ¹⁸The breakdown of the theory when (33) fails is serious. The significance of the single-valued functions $\zeta(r)$ as good variables is lost, as noted prior to (2).
- ¹⁹We use the SF₆ data of W. Rathgen and J. Straub, *Wärme-Stoffübertrag* **14**, 59 (1980); W. Rathgen and J. Straub, in *Proceedings of the Seventh Symposium on Thermophysical Properties*, edited by A. Cezairliyan (American Society of Mechanical Engineers, New York, 1977), p. 839; and D. S. Cannell, *Phys. Rev. A* **12**, 225 (1975).
- ²⁰D. Stauffer, M. Ferer, and M. Wortis, *Phys. Rev. Lett.* **29**, 345 (1972).
- ²¹H. B. Tarko and M. E. Fisher, *Phys. Rev. B* **11**, 1217 (1975); E. Brezin, J. C. Le Guillou, and J. Zinn-Justin, *Phys. Lett.* **47A**, 285 (1974).
- ²²M. R. Moldover and R. W. Gammon, *J. Chem. Phys.* **80**, 528 (1984).
- ²³R. F. Kayser, J. W. Schmidt, and M. R. Moldover, *Phys. Rev. Lett.* **54**, 707 (1985).

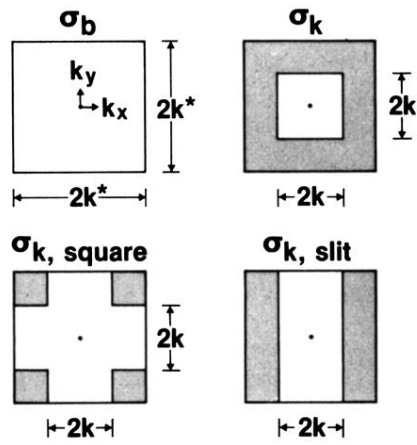


FIG. 1. Capillary-wave cutoffs in k space and their associated surface tensions. The shaded areas denote allowed wave vectors, and the unshaded regions wave vectors that are cut off. All modes would be allowed on an unconstrained interface and the squares would be entirely shaded in. We associate $\sigma_{k,\text{square}}$ with the surface tension of a square interface of edge $l = 2\pi/k$ in real space, where modes with $|k_x| \leq 2\pi/l$ or $|k_y| \leq 2\pi/l$ are cut off. Similarly, we associate $\sigma_{k,\text{slit}}$ with an interface which has width l in the x direction but is infinite in the y direction.

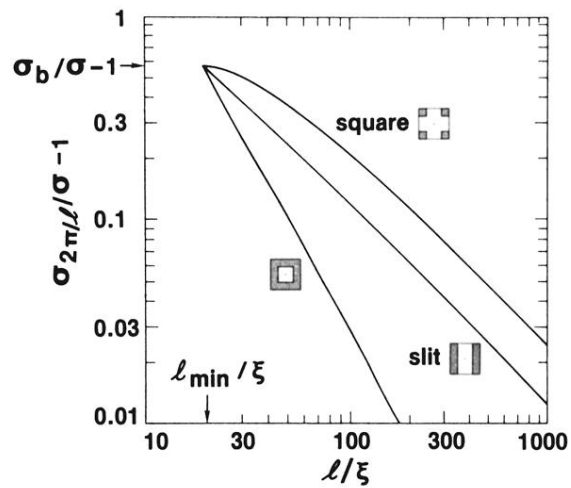


FIG. 2. Log-log plots of $\sigma_{2\pi/l}/\sigma - 1$ vs l/ξ near a critical point, with ξ the bulk correlation length of either coexisting phase. The curves depend on the geometry of the allowed region in k space (see Fig. 1) but are otherwise universal. All curves converge to $\sigma_b/\sigma - 1$ at $l_{\min} = 20\xi$, our estimate of where capillary-wave theory breaks down. Values of σ , ξ , and l_{\min} for SF_6 are given in Table 3.