

Capillary waves of a vapor-liquid interface near the critical temperature

J. V. Sengers

*Institute for Physical Science and Technology, University of Maryland, College Park, Maryland 20742
and Thermophysics Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899*

J. M. J. van Leeuwen

Instituut-Lorentz voor Theoretische Natuurkunde, Rijksuniversiteit Leiden, Nieuwsteeg 18, 2311 SB Leiden, The Netherlands

(Received 28 November 1988)

An attempt is made to develop the picture of an interface near the critical temperature as an intrinsic Fisk-Widom interface broadened by capillary waves. We propose a method for determining the free parameters appearing in the capillary-wave theory by requiring that the capillary waves smoothly renormalize the surface tension from the bare to the experimental value. We evaluate the effect of the capillary waves on the width of the interface and make a comparison with experimental reflectivity measurements obtained by Wu and Webb [Phys. Rev. A **8**, 2065 (1973)] for SF₆ and also with the renormalization results of Jasnow and Rudnick [Phys. Rev. Lett. **41**, 698 (1978)].

I. INTRODUCTION

The interface between coexisting vapor and liquid phases is commonly pictured as an intrinsic interface broadened by the presence of thermally excited capillary waves.¹⁻³ A phenomenological theory of the intrinsic interface is provided by the mean-field or van der Waals theory which, for fluids near the critical point, has been extended by Fisk and Widom.⁴ An outstanding problem is how to combine the theory of an intrinsic interface with the capillary-wave theory to obtain a quantitative description of interface properties such as surface tension, interfacial thickness, and interfacial structure.⁵⁻⁷

A major difficulty is the lack of a suitable first-principle theory in which the capillary waves are incorporated. The usual approach presupposes a theory which yields an intrinsic interface with a "bare" surface tension, and then considers the effect of the capillary waves on this interface.^{8,9} In order to make the theory well behaved a short-wavelength cutoff has to be imposed. Neither the bare surface tension nor the cutoff can be obtained from the capillary-wave theory itself, but must follow from the underlying theory yielding the intrinsic interface. The renormalization theory can in principle provide an answer, as shown by Jasnow and Rudnick.^{10,11} In practice, however, it appears difficult to implement the renormalization program to obtain accurate results for three-dimensional fluids.

Introducing a column model, Weeks has proposed a conceptual justification for adding the capillary waves to an intrinsic interface.⁶ However, as noted by Kayser,⁷ this column model contains an ambiguity concerning the relationship between the amplitude of the capillary waves and the bulk correlation length. This ambiguity becomes apparent in the calculation of the contribution of the capillary waves to the surface tension. As will be further elucidated in Sec. II, the column model assumes the existence of two different cutoffs: one as the minimum al-

lowable capillary wavelength, and another specifying the minimum height unit in the columns.

In this paper we shall treat the vapor-liquid interface near the critical point as a fluctuating Fisk-Widom interface. We propose a method for determining the two cutoffs mentioned above by requiring that the capillary waves smoothly renormalize the surface tension from the bare to the experimental value. The result is a wavelength-dependent surface tension varying from the bare surface tension, associated with the capillary waves at the short-wavelength cutoff, to the experimentally observed surface tension in the long-wavelength limit. We then evaluate the effect of the capillary waves on the interfacial density profile and make a comparison with experimental reflectivity measurements¹² and with the renormalization results of Jasnow and Rudnick.^{10,11}

The results presented in this paper pertain to temperatures near the critical temperature where the properties of the fluid can be represented by their asymptotic critical power laws.¹³ They cease to be valid, however, at temperatures so close to the critical temperature that gravitational effects associated with the large compressibility become important.^{14,15} An analysis of the capillary waves when these compressibility effects become significant will be presented in another publication.¹⁶

II. CAPILLARY-WAVE MODEL

We consider the gravitational field directed in the negative z direction and take the plane $z=0$ at the Gibbs dividing surface of the interface, where the density ρ is equal to the critical density ρ_c . Our picture is similar to that of Weeks,⁶ Huse *et al.*,¹⁷ and Kayser⁷ in which the capillary waves account for fluctuations larger than the bulk correlation length ξ , so that the capillary-wave Hamiltonian involves a coarse graining over length scales up to or slightly larger than ξ . For this purpose Weeks⁶ proposed a column model in which the space is divided

into rectangular columns with base width l . As pointed out by Kayser,⁷ to effect the coarse graining correctly, so as to obtain the appropriate scaling relations near the critical point, the columns must be subdivided into cells with height l' . We thus consider the space divided into cells with volume $l'l^{d-1}$, where d is the dimensionality of the system. Although we are interested in the $d=3$ case, we keep the dimensionality d unspecified initially in order to elucidate the role of d . The cell lengths l and l' are expected to be of the order of ξ , but we postpone a more detailed discussion of the size and shape of the cells to Sec. V.

The cell division is employed to evaluate the partition function in two steps: first, sum over all configurations subject to the constraint that cell i contains N_i particles, and then sum over all distributions $\{N_i\}$. Let us assume that the first step leads to the constrained partition function $Z[N_i]$, which we write as the product of an ideal-gas contribution, and a factor accounting for a constrained free energy $F_{\text{int}}(N_i)$ due to the interaction

$$Z[N_i] = (l'l^{d-1})^{\sum_i N_i} \exp(-F_{\text{int}}[N_i]/k_B T), \quad (2.1)$$

where k_B is Boltzmann's constant and T the temperature, and where the square brackets indicate functionals rather than functions. The second step then requires the evaluation of the grand-canonical sum

$$Z_{\text{gr}} = \sum_{\{N_i\}} \frac{(z_a l'l^{d-1})^{\sum_i N_i}}{\prod_i N_i!} \exp(-F_{\text{int}}[N_i]/k_B T), \quad (2.2)$$

where z_a is the activity of the system.

It is advantageous to transform (2.2) to a continuum description by introducing the density field $n(\mathbf{r})$ defined as

$$n(\mathbf{r}_i) = N_i / l'l^{d-1}, \quad (2.3)$$

where \mathbf{r}_i represents the location of the center of cell i . Then

$$\sum_i N_i = \sum_i (l'l^{d-1}) n(\mathbf{r}_i) \simeq \int d\mathbf{r} n(\mathbf{r}) \quad (2.4)$$

and

$$\begin{aligned} \prod_i N_i! &\simeq \prod_i \left(\frac{N_i}{e} \right)^{N_i} \\ &= \exp \left[\sum_i N_i \ln \left(\frac{N_i}{e} \right) \right] \\ &\simeq \exp \left[\int d\mathbf{r} n(\mathbf{r}) \ln \left(\frac{n(\mathbf{r}) l'l^{d-1}}{e} \right) \right]. \end{aligned} \quad (2.5)$$

As a consequence, (2.2) can be written in the form

$$Z_{\text{gr}} = \sum_{\{N_i\}} \exp \left[\int d\mathbf{r} \Omega[n(\mathbf{r})] / k_B T \right], \quad (2.6)$$

with

$$\Omega[n(\mathbf{r})] = n(\mathbf{r}) k_B T \ln \left(\frac{z_a n(\mathbf{r})}{e} \right) - f_{\text{int}}[n(\mathbf{r})], \quad (2.7)$$

where $f_{\text{int}} = F_{\text{int}}/V$ is the interaction free energy per unit volume. In (2.6) we have deliberately not yet replaced the sum over $\{N_i\}$ by a functional integration over $n(\mathbf{r})$; as pointed out by Kayser⁷ this additional step requires some care.

The sum in (2.6) can be performed by first determining the density distribution $\hat{n}(z)$, which optimizes $\Omega[n(\mathbf{r})]$, and then incorporating the influence of the fluctuations $\Delta N_i = N_i - \hat{N}_i$ around this optimum profile $\hat{N}_i = l'l^{d-1} \hat{n}(z_i)$. The basic assumption of the column model is that the capillary waves of the optimum profile are the most important fluctuations when the cell distribution is chosen appropriately. A capillary fluctuation can be represented by a displacement $Z(\mathbf{r}_\perp)$ of the original profile,⁶ where \mathbf{r}_\perp is a vector perpendicular to the z axis specifying a location in the dividing surface

$$\Delta N_i = l'l^{d-1} [\hat{n}(z_i + Z(\mathbf{r}_{i\perp})) - \hat{n}(z_i)]. \quad (2.8)$$

In order for this expression to signify a new cell occupation, we impose the condition that $Z(\mathbf{r}_{i\perp})$ be a multiple of l' :

$$Z(\mathbf{r}_{i\perp}) = l' h_i, \quad (2.9)$$

where $h_i = h(\mathbf{r}_{i\perp})$ is the height of the column at $\mathbf{r}_{i\perp}$ in terms of the number of cells in the column. Thus the sum in (2.6) can be replaced by the contribution of the optimum profile and the sum over all integer height distributions $\{h_i\}$. We then obtain

$$Z_{\text{gr}} = \hat{Z}_{\text{gr}} Z_{\text{CW}}, \quad (2.10)$$

where \hat{Z}_{gr} is the partition function associated with the intrinsic profile, such that

$$k_B T \ln \hat{Z}_{\text{gr}} = \int d\mathbf{r} \Omega[\hat{n}(z)], \quad (2.11)$$

while Z_{CW} is the partition function associated with the capillary waves

$$Z_{\text{CW}} = \sum_{\{h_i\}} \exp \left[-\frac{H[h_i]}{k_B T} \right]. \quad (2.12)$$

The capillary-wave Hamiltonian $H[h_i]$ is the energy of a fluctuation $Z(\mathbf{r}_\perp)$ and is generally taken to be of the form

$$H[Z] = \frac{\sigma_b}{2} \int d\mathbf{r}_\perp \{ |\nabla_\perp Z(\mathbf{r}_\perp)|^2 + \lambda_0 Z^2(\mathbf{r}_\perp) \}. \quad (2.13)$$

Here σ_b is the bare surface tension (surface tension of the intrinsic interface) associated with the optimum profile $\hat{n}(z)$. The term in (2.13) involving the squared gradient represents the contribution to the free energy from the enlargement of the interface area in a capillary wave, while the second term in (2.13) accounts for the gravitational energy of the wave. In Sec. IV we shall derive a capillary-wave Hamiltonian of the type (2.13) on the basis of the Fisk-Widom theory.

With the explicit form (2.13) for H , the capillary-wave partition function can be readily evaluated. One introduces normal modes

$$h(\mathbf{q}_\perp) = \sum_j h_j \exp(i\mathbf{q}_\perp \cdot \mathbf{r}_{j\perp}), \quad (2.14)$$

which diagonalize the Hamiltonian (2.13). The wave number \mathbf{q}_\perp must fit into the lattice cells. For a square system with length L , q_x can assume the values

$$q_x = \frac{2\pi}{L} m_x \quad \text{with } m_x = -\frac{L}{2l}, \dots, +\frac{L}{2l}. \quad (2.15)$$

The other components of \mathbf{q}_\perp must satisfy similar constraints. The total number of modes is $(L/l)^{d-1}$, which equals, of course, the number of columns. Thus \mathbf{q}_\perp is constrained to a Brillouin zone B of area $(2\pi/l)^{d-1}$. The summation over the normal modes has been carefully discussed by Kayser.⁷ The result is

$$\ln Z_{\text{CW}} = -\frac{L^{d-1}}{2(2\pi)^{d-1}} \int_B d\mathbf{q}_\perp \ln \left[\frac{\sigma_b(q_\perp^2 + \lambda_0)(l')^2 l^{d-1}}{2\pi k_B T} \right]. \quad (2.16)$$

Note that l' appears in the result because the displacement Z had to be translated into a dimensionless height variable h in order to perform the Gaussian integration over $h(\mathbf{q}_\perp)$.

Equation (2.16) shows that $\ln Z_{\text{CW}}$ is proportional to the area L^{d-1} . Thus the capillary waves yield a contribution $\Delta\sigma$ to the surface tension given by

$$\begin{aligned} \Delta\sigma &= -\frac{k_B T}{L^{d-1}} \ln Z_{\text{CW}} \\ &= \frac{k_B T}{2(2\pi)^{d-1}} \int_B d\mathbf{q}_\perp \ln \left[\frac{\sigma_b(q_\perp^2 + \lambda_0)(l')^2 l^{d-1}}{2\pi k_B T} \right]. \end{aligned} \quad (2.17)$$

We conclude that both dimensions l' and l of the cells appear in the contribution $\Delta\sigma$ of the capillary waves to the total surface tension $\sigma = \sigma_b + \Delta\sigma$. This is not the case for the mean-squared displacement $\langle Z^2 \rangle$ of the interface due to capillary waves which is given by

$$\langle Z^2 \rangle = \frac{1}{(2\pi)^{d-1}} \int_B d\mathbf{q}_\perp \frac{k_B T}{\sigma_b(q_\perp^2 + \lambda_0)}. \quad (2.18)$$

In (2.18) the base length l of the cells enters through the boundary of the integration over the Brillouin zone, but the integral does not depend on the height l' of the cells. The reason why the influence of the shape of the cells on the surface tension has been overlooked in the literature may be that one was primarily interested in $\langle Z^2 \rangle$.

III. THEORY OF FISK AND WIDOM FOR THE INTERFACE

The free-energy density Ψ is related to the function Ω in the expression (2.6) for the grand-canonical partition function by $\Omega(\rho) = \mu\rho - \Psi(\rho)$, where μ is the chemical potential and ρ the mass density. Here we consider Ω and Ψ as a function of the mass density $\rho(\mathbf{r})$ rather than the number density $n(\mathbf{r})$. In the squared-gradient theory, employed by Fisk and Widom,⁴ Ψ is assumed to have the form²

$$\begin{aligned} \Psi(\rho(\mathbf{r})) &= \rho_c \mu(\rho_c) - P(\rho_c) - W(\rho(\mathbf{r})) + \frac{1}{2} A |\nabla\rho(\mathbf{r})|^2 \\ &\quad + gz(\rho(\mathbf{r}) - \rho_c), \end{aligned} \quad (3.1)$$

where $\mu(\rho)$ and $P(\rho)$ are the chemical potential and the pressure P , respectively, of the homogeneous system with density ρ at the given temperature T , while g is the gravitational acceleration constant. The function $W(\rho)$ is an even function of $\Delta\rho = \rho - \rho_c$, where ρ_c is the critical density; it is defined by its derivative

$$-\left[\frac{\partial W(\rho)}{\partial \rho} \right] = \mu(\rho) - \mu(\rho_c) \quad (3.2)$$

and the condition that W vanishes at the densities ρ_{vap} and ρ_{liq} of the vapor and the liquid at coexistence. The squared gradient term in (3.1) represents the interaction between cells with different densities. The coefficient A is related to the correlation length ξ and the "symmetrized" compressibility $\chi = (\partial\rho/\partial\mu)_T$ of the homogeneous system with density ρ by

$$A = \xi^2 / \chi. \quad (3.3)$$

The last term in (3.1) represents the additional contribution from the gravitational field. In the theory of Fisk and Widom⁴ the effect of the gravitational field is neglected, and the interfacial density profile is restricted to densities between ρ_{vap} and ρ_{liq} . For these intermediate densities the coefficient A is identified with

$$A = \xi_{\text{coex}}^2 / \chi_{\text{coex}}. \quad (3.4)$$

In this paper we adopt the convention that the index coex means that the value is that of the homogeneous system at coexistence.

The quantitative predictions of the theory of Fisk and Widom depend on the form chosen for the function $W(\rho)$ in the coexistence region. It is argued^{6,17} that cells of a volume ξ^d lead to an effective free-energy density for which the Fisk-Widom function may be a reasonable approximation. Fluctuations on scales less than ξ^d renormalize the mean-field equation of state to the scaled equation of state, and the expression for W adopted by Fisk and Widom yields a smooth interpolation between the compressibility factors outside the coexistence region.

To discuss the theory of Fisk and Widom, it is convenient to introduce dimensionless quantities. For this purpose we define

$$\Delta\rho^* = (\rho - \rho_c), \quad \Delta T^* = (T - T_c) / T_c, \quad \chi^* = \chi P_c / \rho_c^2, \quad (3.5)$$

where ρ_c , T_c , and P_c are the density, temperature, and pressure of the critical point. As a next step we define

$$\tilde{z} = z / \xi_{\text{coex}}, \quad (3.6a)$$

$$\Delta\tilde{\rho} = \Delta\rho^* / |\Delta\rho_{\text{coex}}^*|, \quad (3.6b)$$

$$\tilde{W} = W \chi_{\text{coex}}^* / P_c |\Delta\rho_{\text{coex}}^*|^2, \quad (3.6c)$$

$$\tilde{g} = g \rho_c \chi_{\text{coex}}^* \xi_{\text{coex}} / P_c |\Delta\rho_{\text{coex}}^*|. \quad (3.6d)$$

In terms of these tilde variables, the free energy can be written in the dimensionless form

$$\frac{1}{k_B T_c} \int d\mathbf{r} \Psi(\rho(\mathbf{r})) = \frac{\rho_c \mu(\rho_c) - P(\rho_c)}{k_B T_c} + \bar{R}_\psi \int d\mathbf{r} [-\bar{W}(\Delta\bar{\rho}(\mathbf{r})) + \frac{1}{2} |\bar{\nabla}\Delta\bar{\rho}(\mathbf{r})|^2 + \bar{g} z \Delta\bar{\rho}(\mathbf{r})], \quad (3.7)$$

with

$$\bar{R}_\psi = \xi_{\text{coex}}^d (\Delta\rho_{\text{coex}}^*)^2 P_c / \chi_{\text{coex}}^* k_B T_c. \quad (3.8)$$

The theory of Fisk and Widom is applicable at temperatures sufficiently close to the critical temperature so that the properties of the homogeneous phases at coexistence satisfy the asymptotic power laws¹³

$$\xi_{\text{coex}} = \xi_- |\Delta T^*|^{-\nu}, \quad (3.9a)$$

$$|\Delta\rho_{\text{coex}}^*| = B |\Delta T^*|^\beta, \quad (3.9b)$$

$$\chi_{\text{coex}}^* = \Gamma_- |\Delta T^*|^{-\gamma}, \quad (3.9c)$$

where ν , β , and γ are universal critical exponents, such that $d\nu = 2\beta + \gamma$, while ξ_- , B , and Γ_- are system-dependent amplitudes. Substitution of (3.9) into (3.8) yields

$$\bar{R}_\psi = \xi_-^d B^2 P_c / \Gamma_- k_B T_c, \quad (3.10)$$

and we note that \bar{R}_ψ is a universal constant as follows from two-scale-factor universality.¹⁸

The nonclassical expression adopted by Fisk and Widom^{2,4} for \bar{W} has the simple form

$$-\bar{W}(\Delta\bar{\rho}) = \frac{1}{\delta^2 - 1} \left[|\Delta\bar{\rho}|^{\delta+1} - \frac{\delta+1}{2} |\Delta\bar{\rho}|^2 + \frac{\delta-1}{2} \right], \quad (3.11)$$

where $\delta = 1 + \gamma/\beta$. Note that \bar{W} and $\partial\bar{W}/\partial\Delta\bar{\rho}$ indeed vanish at the phase boundary $|\Delta\bar{\rho}| = 1$, while the prefactor on the right-hand side of (3.11) is determined by the condition that $\partial^2\bar{W}/\partial\Delta\bar{\rho}^2 (= -1)$ be continuous at the phase boundary.

$$\begin{aligned} 4K &= \int_{-\infty}^{+\infty} \frac{d^2\Delta\bar{\rho}_{\text{FW}}}{d\bar{z}^2} d\bar{z} = 2 \int_0^{\Delta\bar{\rho}_{\text{coex}}} [-2\bar{W}(\Delta\rho)]^{1/2} d\Delta\bar{\rho} \\ &= 2 \left[\frac{2}{\delta^2 - 1} \right]^{1/2} \int_0^1 dy \left[y^{\delta+1} - \frac{\delta+1}{2} y^2 + \frac{\delta-1}{2} \right]^{1/2} = 0.576. \end{aligned} \quad (3.18)$$

Just as \bar{R}_ψ , two-scale-factor universality implies that $\bar{\sigma}$, and hence $\bar{\sigma}_b$, are universal.¹⁹⁻²³

In our actual calculations we continue to use the exponent values adopted in related previous publications^{14,15,24}

$$\beta = 0.325, \quad \gamma = 1.240, \quad (3.19)$$

which imply $\delta = 1 + \gamma/\beta = 4.815$ and $\nu = (\gamma + 2\beta)/3 = 0.630$, in good agreement with the theoretical values predicted for three-dimensional Ising-like systems.^{13,25} To determine \bar{R}_ψ we make use of the theoretical values

In the squared-gradient theory the interfacial density profile is obtained by optimizing (3.7) with respect to $\Delta\bar{\rho}$. The density profile then satisfies the differential equation¹⁴

$$\frac{d^2|\Delta\bar{\rho}|}{d\bar{z}^2} = \Delta\bar{\mu} + \bar{g} z, \quad (3.12)$$

with

$$\Delta\bar{\mu} \equiv \frac{\partial\bar{W}}{\partial\Delta\bar{\rho}}. \quad (3.13)$$

Fisk and Widom did not consider the explicit effect of the gravitational field. Instead of (3.12), the density profile $\Delta\bar{\rho}_{\text{FW}}$ of the Fisk-Widom theory satisfies the differential equation

$$\frac{d^2|\Delta\bar{\rho}_{\text{FW}}|}{d\bar{z}^2} = \Delta\bar{\mu}(\Delta\bar{\rho}_{\text{FW}}), \quad (3.14)$$

which has an integral of motion

$$\frac{1}{2} \left[\frac{d\Delta\bar{\rho}_{\text{FW}}}{d\bar{z}} \right]^2 + \bar{W}(\Delta\bar{\rho}_{\text{FW}}) = 0. \quad (3.15)$$

Associated with the Fisk-Widom interface is a so-called bare surface tension σ_b . Defining a dimensionless surface tension as

$$\bar{\sigma} = \frac{\sigma \xi_{\text{coex}}^2}{k_B T_c}, \quad (3.16)$$

one obtains for the Fisk-Widom interface¹⁴

$$\bar{\sigma}_b = 4K \bar{R}_\psi, \quad (3.17)$$

where the coefficient $4K$ is determined by the integral²

calculated for the following amplitude ratios:^{26,27}

$$\xi_+ (A_+ P_c / k_B T_c)^{1/3} = 0.2699 \pm 0.0008, \quad (3.20a)$$

$$\Gamma_+ / \Gamma_- = 4.77 \pm 0.30, \quad (3.20b)$$

$$A_+ \Gamma_+ / B^2 = 0.0594 \pm 0.0011, \quad (3.20c)$$

so that

$$\bar{R}_\psi = (1.58 \pm 0.14) R_\xi^{-3}. \quad (3.21)$$

Here, ξ_+ , A_+ , and Γ_+ are the amplitudes of the critical

power laws for the correlation length, specific heat, and compressibility of the homogeneous system at $\rho = \rho_c$ above the critical temperature, while $R_\xi = \xi_+ / \xi_-$. Brézin *et al.*²⁸ have reported $R_\xi = 1.91$ from a renormalization calculation to second order in $\epsilon = 4 - d$. Tarko and Fisher²⁹ found $R_\xi = 1.96$ from an analysis of the series expansions for the three-dimensional Ising model, while the analysis made by Ritchie and Essam³⁰ implied $R_\xi = 1.93$. We have therefore adopted the compromise value

$$R_\xi = \xi_+ / \xi_- = 1.93 \pm 0.03, \quad (3.22)$$

so that

$$\tilde{R}_\psi = 0.22 \pm 0.03. \quad (3.23)$$

Experimental values for the universal surface-tension amplitude (3.16) have been reported by Moldover and co-workers^{21,31} and by Gielen *et al.*,³²

$$\bar{\sigma}_{\text{expt}} = (0.386 \pm 0.03) R_\xi^{-2}. \quad (3.24)$$

The actual values of \tilde{R}_ψ , $\bar{\sigma}_b$, and $\bar{\sigma}_{\text{expt}}$ depend on the accuracy of the available universal amplitude ratios. Subsequent to this work, Liu and Fisher have therefore reconsidered the numerical results for the three-dimensional Ising model to obtain²⁵

$$\Gamma_+ / \Gamma_- = 4.95 \pm 0.15, \quad (3.25a)$$

$$A + \Gamma_+ / B^2 = 0.0581 \pm 0.0010, \quad (3.25b)$$

$$R_\xi = 1.96 \pm 0.01. \quad (3.25c)$$

Adoption of the latter values would imply $\tilde{R}_\psi = 0.222 \pm 0.016$, $\bar{\sigma}_b = 0.128 \pm 0.009$, and $\bar{\sigma}_{\text{expt}} = 0.100 \pm 0.009$. The analysis presented in this paper is still based on the estimates given by (3.20) and (3.22), except that we have used the results of Liu and Fisher to reduce the error estimates of \tilde{R}_ψ and $\bar{\sigma}_b$ to

$$\tilde{R}_\psi = 0.22 \pm 0.02, \quad (3.26)$$

$$\bar{\sigma}_b = 0.126 \pm 0.013. \quad (3.27)$$

In comparing the bare surface tension given by (3.17) and (3.21) with the experimental surface tension given by (3.24), we note that

$$\bar{\sigma}_{\text{expt}} / \bar{\sigma}_b = 0.82 \pm 0.15. \quad (3.28)$$

The macroscopically observed surface tension $\bar{\sigma}_{\text{expt}}$ is smaller than the bare surface tensions σ_b associated with the Fisk-Widom interface. In this paper we adopt the point of view that this difference is due to the presence of capillary waves, which lead to a reduction of the surface tension, as further discussed in Sec. V.

It should be noted that the actual value $\bar{\sigma}_{\text{expt}} / \bar{\sigma}_b$ given by (3.28) depends on the choice of the phenomenological interpolation function for \tilde{W} proposed by Fisk and Widom, and hence we do not know how reliable this value is. However, there is limited freedom if one sticks with a similar interpolation which meets all the requirements. One way to investigate the dependence of $\bar{\sigma}_b$ on the shape of \tilde{W} is to vary the value of δ in (3.11); we find that

the value of $\bar{\sigma}_b$ is surprisingly insensitive to the value of δ .

IV. CAPILLARY WAVES OF THE FISK-WIDOM INTERFACE

To treat the capillary waves we consider fluctuations around the optimum profile $\Delta\tilde{\rho}_{\text{FW}}$ of the squared-gradient theory

$$\Delta\tilde{\rho} = \Delta\tilde{\rho}_{\text{FW}} + \Delta\tilde{\rho}_1, \quad (4.1)$$

and expand (3.7) to second order in $\Delta\tilde{\rho}_1$:

$$\frac{1}{k_B T_c} \int d\mathbf{r} \Psi(\rho(\mathbf{r})) = \frac{\rho_c \mu(\rho_c) - P(\rho_c)}{k_B T_c} + \frac{L^2}{\xi_{\text{coex}}^2} (\bar{\sigma}_b + \Delta\bar{\sigma}), \quad (4.2)$$

with

$$\Delta\bar{\sigma} = \frac{1}{2} \tilde{R}_\psi \int d\tilde{\mathbf{r}} [\tilde{V}(\tilde{z}) (\Delta\tilde{\rho}_1)^2 + |\tilde{\nabla} \Delta\tilde{\rho}_1|^2]. \quad (4.3)$$

The potential $\tilde{V}(\tilde{z})$ is given by

$$\tilde{V}(\tilde{z}) = \frac{\partial \Delta\tilde{\mu}(\Delta\tilde{\rho}_{\text{FW}})}{\partial \Delta\tilde{\rho}_{\text{FW}}} = \frac{1}{\delta - 1} (\delta |\Delta\tilde{\rho}_{\text{FW}}|^\delta - 1). \quad (4.4)$$

The last equality in (4.4) holds for $|\Delta\tilde{\rho}| \leq 1$ and has to be extended appropriately for $|\Delta\tilde{\rho}| \geq 1$ when effects from the gravity term in (3.12) become important.^{14,15} The minimum of $\tilde{V}(\tilde{z})$ occurs for $\tilde{z} = 0$ and has the value $-1/(\delta - 1)$.

Expression (4.3) can be diagonalized by considering the Schrödinger-type eigenvalue equation

$$\left[-\frac{d^2}{d\tilde{z}^2} + \tilde{V}(\tilde{z}) \right] \chi_n(\tilde{z}) = \tilde{\lambda}_n \chi_n(\tilde{z}). \quad (4.5)$$

Expanding $\Delta\tilde{\rho}_1$ in the eigenfunctions

$$\Delta\tilde{\rho}_1 = \sum_n \frac{1}{(2\pi)^{d-1}} \int d\mathbf{q}_1 v_{nq_1} \chi_n(\tilde{z}) \exp(i\tilde{\mathbf{q}}_1 \cdot \tilde{\mathbf{r}}_1), \quad (4.6)$$

we rewrite (4.3) as

$$\Delta\bar{\sigma} = \frac{1}{2} \tilde{R}_\psi \sum_n \frac{1}{(2\pi)^{d-1}} \int d\tilde{\mathbf{q}}_1 (\tilde{\lambda}_n + \tilde{q}_1^2) |v_{nq_1}|^2, \quad (4.7)$$

assuming that the $\chi_n(\tilde{z})$ are normalized.

The Fisk-Widom interface and hence the expression (4.4) for the potential $\tilde{V}(\tilde{z})$ correspond to the limit $\tilde{g} \rightarrow 0$. In this limit³³ the potential $\tilde{V}(\tilde{z})$ develops an eigenvalue $\tilde{\lambda}_0$ which vanishes as \tilde{g} :

$$\tilde{\lambda}_0 = \frac{\tilde{g}}{2K}, \quad (4.8)$$

with the corresponding normalized eigenfunction.

$$\chi_0(\tilde{z}) = \frac{1}{(4K)^{1/2}} \frac{d\Delta\tilde{\rho}_{\text{FW}}}{d\tilde{z}}. \quad (4.9)$$

In this limit the lowest mode becomes very easy to excite with the consequence that $\Delta\tilde{\rho}_1$ is dominated by this mode. Thus restricting the excitations to this mode, we may write

$$\Delta\bar{\rho}_1(\bar{\mathbf{r}}) \simeq \frac{d\Delta\bar{\rho}_{\text{FW}}}{d\bar{z}} \bar{Z}(\bar{\mathbf{r}}_1), \quad (4.10)$$

with

$$\bar{Z}(\bar{\mathbf{r}}_1) = (4K)^{-1/2} \frac{1}{(2\pi)^{d-1}} \int d\bar{\mathbf{q}}_1 v_{0q} \exp(i\bar{\mathbf{q}}_1 \cdot \bar{\mathbf{r}}_1). \quad (4.11)$$

Substituting (4.10) into (4.1) and treating (4.1) as the first two terms of an expansion,³⁴ we write

$$\Delta\bar{\rho}_{\text{FW}} + \Delta\bar{\rho}_1 \simeq \Delta\bar{\rho}_{\text{FW}}(\bar{z} + \bar{Z}(\bar{\mathbf{r}}_1)), \quad (4.12)$$

which is the counterpart of (2.8). Keeping only the sliding mode $\chi_0(\bar{z})$, we find the Hamiltonian of the capillary waves from (4.7), (4.11), and (3.17),

$$H_{\text{CW}}/k_B T_c = \frac{1}{2} \bar{\sigma}_b \int d\bar{\mathbf{r}}_1 [|\bar{\nabla}_1 \bar{Z}(\bar{\mathbf{r}}_1)|^2 + \tilde{\lambda}_0 \bar{Z}^2(\bar{\mathbf{r}}_1)], \quad (4.13)$$

which corresponds to (2.13). We note that in this picture of the capillary waves the thermodynamic surface tension (3.17) associated with the Fisk-Widom interface also appears as the coefficient of the squared-gradient term in the capillary-wave Hamiltonian.

V. SELF-CONSISTENT SURFACE TENSION AND CHOICE OF CUTOFFS

In the Fisk-Widom free-energy expression the inhomogeneity effect is represented by a squared-gradient term only. As a consequence, the resulting capillary-wave Hamiltonian (4.13) contains the same bare surface tension $\bar{\sigma}_b$ for all capillary-wave excitations. For short wave-

lengths near the cutoff this is to be expected, but in the long-wavelength limit the full surface tension would seem to be a more appropriate measure for the change of free energy associated with the surface enlargement by capillary waves. On this large length scale there is no reason to make a distinction between the microscopic configurations that contribute to the bare surface tension and the short-wavelength fluctuations that contribute to the full surface tension.

The viewpoint of Kayser⁷ that the shorter waves renormalize the surface tension for the longer waves is very suggestive. While there does not exist a theoretical foundation for this picture, the idea can be readily implemented mathematically. First, we rewrite relation (2.17) in terms of the reduced variables

$$\bar{\sigma} = \bar{\sigma}_b + \frac{1}{2(2\pi)^2} \int_{\bar{q}'_1 \leq \bar{q}_{\text{max}}} d\bar{\mathbf{q}}'_1 \ln \left[\frac{\bar{\sigma}_b [(\bar{q}'_1)^2 + \tilde{\lambda}_0] (\bar{I}')^2 \bar{I}^2}{2\pi} \right], \quad (5.1)$$

putting $d=3$ and introducing the scaled cutoff parameters

$$\bar{I} = l/\xi_{\text{coex}}, \quad \bar{I}' = l'/\xi_{\text{coex}}. \quad (5.2)$$

In addition, we have replaced the Brillouin zone by a circular integration area of equal area, so that

$$\bar{q}_{\text{max}} = 2\sqrt{\pi/\bar{I}}. \quad (5.3)$$

As earlier proposed by Kayser,^{7,35} a renormalization of the surface tension is achieved by considering $\bar{\sigma}$ as a function of \bar{q}^2 , replacing the integration interval by $\bar{q} < \bar{q}'_1 < \bar{q}_{\text{max}}$, and inserting $\bar{\sigma}(\bar{q}'^2)$ in the integrand:

$$\bar{\sigma}(\bar{q}^2) = \bar{\sigma}_b + \frac{1}{8\pi} \int_{\bar{q}^2}^{\bar{q}_{\text{max}}^2} d(\bar{q}')^2 \ln \left[\frac{[\bar{\sigma}(\bar{q}'^2)(\bar{q}')^2 + \tilde{\lambda}_0 \bar{\sigma}_b] (\bar{I} \bar{I}')^2}{2\pi} \right], \quad (5.4)$$

where \bar{q}' is the magnitude of the two-dimensional wave vector $\bar{\mathbf{q}}'$. Thus the waves with $\bar{q}' > \bar{q}$ contribute to the surface tension associated with the capillary wave with wave number \bar{q} . We note that $\bar{\sigma}_b$ is not replaced by $\bar{\sigma}((\bar{q}')^2)$ in the second term of the argument of the logarithm, since the product $\tilde{\lambda}_0 \bar{\sigma}_b$ in (5.1) simply stands for $2\bar{g} \bar{R}_\psi$ in accordance with (3.24) and (4.8). For the surface tension, the term with $\tilde{\lambda}_0$ is less important than for the mean-squared displacement (2.18) as (5.4) converges for $\tilde{\lambda}_0 \rightarrow 0$. In the Fisk-Widom limit $\bar{g} \rightarrow 0$, the term with $\tilde{\lambda}_0$ vanishes and we do not need to consider this term here.

We are now in a position to discuss our choice for the cutoffs \bar{I} and \bar{I}' . For this purpose we take $\bar{q}^2 = x$ and replace (5.4) by the equivalent differential equation

$$\frac{d\bar{\sigma}(x)}{dx} = -\frac{1}{8\pi} \ln \left[\frac{\bar{\sigma}(x)x (\bar{I} \bar{I}')^2}{2\pi} \right], \quad (5.5)$$

with the boundary condition

$$\bar{\sigma}(x_{\text{max}}) = \bar{\sigma}(4\pi/\bar{I}^2) = \bar{\sigma}_b. \quad (5.6)$$

Generally one expects that the surface tension will be lowered by the capillary waves,⁷ since they represent degrees of freedom not included in the optimization procedure yielding $\bar{\sigma}_b$. This implies that the argument of the logarithm in (5.5) is less than unity. In particular, it then follows that at the boundary $x = x_{\text{max}} = 4\pi/\bar{I}^2$,

$$2\bar{\sigma}_b (\bar{I}')^2 \leq 1. \quad (5.7)$$

Condition (5.7) implies that $\bar{\sigma}(x) < \bar{\sigma}_b$, and that $\bar{\sigma}(x)$ will be an increasing function of x for $x \leq x_{\text{max}}$. On the other hand $\bar{\sigma} = \bar{\sigma}_b$ independent of x for $x > x_{\text{max}}$. In order to have the least variation of $\bar{\sigma}$ with x , we implement (5.7) as an equality. Then $\bar{\sigma}(x)$ merges smoothly (i.e., with zero derivative) with the Fisk-Widom surface tension $\bar{\sigma}_b$ at $x = x_{\text{max}}$ and

$$\bar{I}' = (2\bar{\sigma}_b)^{-1/2} = 1.99 \pm 0.10. \quad (5.8)$$

Note that condition (5.8) does not involve \bar{I} but only \bar{I}' (which would not be the case for $d \neq 3$).

The second length \bar{l} , or equivalently the upper limit $x_{\max} = 4\pi/\bar{l}^2$, can be adjusted so as to recover, in the long-wavelength limit $x=0$, the macroscopically observed surface tension $\bar{\sigma}_{\text{expt}}$. For that purpose we integrate (5.5) from various upper boundaries x_{\max} to $x=0$. The resulting values for $\bar{\sigma}(0)/\bar{\sigma}_b$ are plotted in Fig. 1 as a function of the upper boundary x_{\max} . Intersecting this curve with $\bar{\sigma}_{\text{expt}}/\bar{\sigma}_b = 0.82 \pm 0.15$ as given by (3.28), we obtain $x_{\max} = 0.54 (\pm 0.4)$ or for $\bar{q}_{\max} = \sqrt{x_{\max}}$:

$$\bar{q}_{\max} = 0.74 (\pm 0.3). \quad (5.9)$$

The value $\bar{q}_{\max} \simeq 0.74$ corresponds to $\bar{l} = 4.8$.

The differential equation (5.1), with the cutoff \bar{q}_{\max} given by (5.9) yields, in effect, an interpolation function for $\bar{\sigma}$ as a function of \bar{q}^2 from its bare value at $\bar{q} = \bar{q}_{\max}$ to its macroscopic value for $\bar{q} = 0$. This function $\bar{\sigma}(\bar{q}^2)$ is shown in Fig. 2. We note from (5.5) that for small values \bar{q}^2 the surface tension $\bar{\sigma}(\bar{q}^2)$ will vary as $\bar{q}^2 \ln \bar{q}$. This is related to the earlier statement dating back to Buff *et al.*⁸ that the capillary waves contribute to the surface tension $\bar{\sigma}(0)$, a term which goes as $g \ln g$, as one finds from (5.1) for small g .

VI. REFLECTIVITY

The reflectivity of an interface is related to the gradient of the refractive-index profile. Close to the critical point the refractive index n varies as^{36,37}

$$n = n_c + n'_c \Delta \rho^*, \quad (6.1)$$

where n_c is the refractive index at the critical point and n'_c a system-dependent constant. For normal incidence the reflectivity R is then related to the density gradient by^{34,38}

$$R(k) = \left[\frac{n'_c}{2n_c} \int_{-\infty}^{+\infty} dz \frac{d\Delta \rho^*}{dz} \exp(-2ikz) \right]^2, \quad (6.2)$$

where $k = 2\pi n_c/\lambda$ is the wave number of the light. We

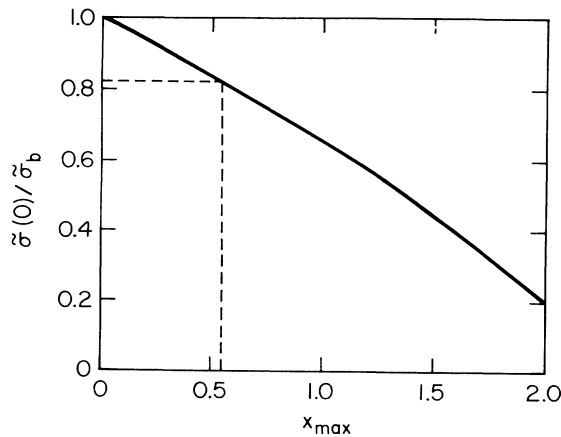


FIG. 1. Calculated long-wavelength surface tension $\bar{\sigma}(0)$, relative to the bare surface tension $\bar{\sigma}_b$, as a function of the cutoff $x_{\max} = \bar{q}_{\max}^2$. For $x_{\max} = 0.54$ we recover $\bar{\sigma}_{\text{expt}}/\bar{\sigma}_b = 0.82$.

can define a scaled reflectivity \bar{R} as a function of the scaled wave number $\bar{k} = k \xi_{\text{coex}}$ by taking out the Fresnel contribution (i.e., the contribution of a sharp interface)

$$R = d_0 |\Delta T^*|^{2\beta} \bar{R}, \quad (6.3)$$

where $d_0 = (n'_c B / 2n_c)^2$ is a nonuniversal scale,²⁴ which is not important as one measures in practice relative reflectivities.¹² The scaled reflectivity $\bar{R}(\bar{k})$ is then related to the scaled density profile by

$$\bar{R}(\bar{k}) = \left[\int_{-\infty}^{+\infty} dz \left[\frac{d\Delta \bar{\rho}}{dz} \right] e^{-2i\bar{k}z} \right]^2. \quad (6.4)$$

The capillary-wave theory gives the average profile $\Delta \bar{\rho}$ as a Gaussian average of the fluctuating profile³⁴ (4.12)

$$\Delta \bar{\rho}(\bar{z}) = \frac{1}{\bar{Z}_{\text{CW}}} \int \mathcal{D}Z e^{-\bar{H}_{\text{CW}}(\bar{Z})} \Delta \bar{\rho}_{\text{FW}}(\bar{z} + \bar{Z}), \quad (6.5)$$

where $\bar{H}_{\text{CW}}(\bar{Z})$ is the scaled capillary-wave Hamiltonian given by the right-hand side of (4.13) and \bar{Z}_{CW} the corresponding capillary-wave partition function. Taking the derivative with respect to \bar{z} and performing a Fourier transform as indicated in (6.4), one finds

$$\bar{R}(\bar{k}) = \bar{R}_{\text{FW}}(\bar{k}) \langle e^{+2i\bar{k}\bar{Z}} \rangle^2, \quad (6.6)$$

where $\bar{R}_{\text{FW}}(\bar{k})$ is the scaled reflectivity of the intrinsic Fisk-Widom interface,

$$\bar{R}_{\text{FW}}(\bar{k}) = \left[\int_{-\infty}^{+\infty} dz \frac{d\Delta \bar{\rho}_{\text{FW}}}{dz} e^{-2i\bar{k}z} \right]^2, \quad (6.7)$$

and where the average $\langle \dots \rangle$ in (6.6) is to be taken over a capillary-wave ensemble as indicated in (6.5). Since the waves are Gaussian distributed we have

$$\langle e^{2i\bar{k}\bar{Z}} \rangle = \exp(-2\bar{k}^2 \langle \bar{Z}^2 \rangle), \quad (6.8)$$

so that

$$\bar{R}(\bar{k}) = \bar{R}_{\text{FW}}(\bar{k}) \exp(-4\bar{k}^2 \langle \bar{Z}^2 \rangle). \quad (6.9)$$

The formula for the mean squared displacement $\langle \bar{Z}^2 \rangle$ is

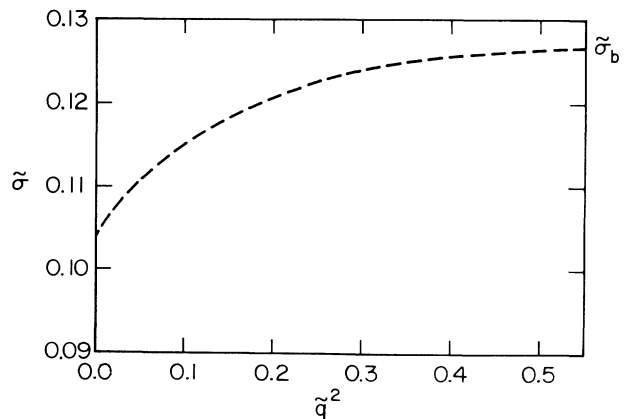


FIG. 2. Reduced surface tension $\bar{\sigma} = \sigma \xi_{\text{coex}}^2 / k_B T_c$ as a function of $\bar{q}^2 = q^2 \xi_{\text{coex}}^2$.

given by (2.18) which for $d=3$ becomes, in terms of the reduced variables,

$$\langle \tilde{Z}^2 \rangle = \frac{1}{4\pi} \int_{\tilde{q}_{\min}^2}^{\tilde{q}_{\max}^2} d\tilde{q}^2 \frac{1}{\bar{\sigma}(\tilde{q}^2)\tilde{q}^2 + 2\tilde{R}_{\psi}\tilde{g}}. \quad (6.10)$$

We have again replaced the Brillouin zone by a circular area bounded by \tilde{q}_{\max} , as given by (5.3). To be consistent we treat the surface tension $\bar{\sigma}$ in the integral as a function of the wave number \tilde{q} , while $\tilde{\lambda}_0\bar{\sigma}_b$ has been identified again with $2\tilde{R}_{\psi}\tilde{g}$. Meunier and Langevin have argued that reflectivity experiments effectively involve a lower capillary-wave cutoff

$$\tilde{q}_{\min} = \tilde{k} \sin \theta, \quad (6.11)$$

where 2θ is the collection angle.^{5,39} With \tilde{q}_{\max} given by (5.9) and the function $\bar{\sigma}(\tilde{q}^2)$ as determined in Sec. V, we can calculate the mean-squared displacement $\langle \tilde{Z}^2 \rangle$ from (6.10).

Reflectivity measurements of a vapor-liquid interface near the critical point at various wave numbers k have been reported by Wu and Webb for sulfurhexafluoride.¹² To make a comparison of (6.10) with these experimental data, we have adopted the critical-region parameters^{18,37,40} presented in Table I. From (6.3) and (6.9) it follows that one can deduce experimental values for the mean squared displacement of the interface due to the capillary waves from the experimental reflectivity data R_{expt} as

$$\langle \tilde{Z}^2 \rangle_{\text{expt}} = -\frac{1}{4\tilde{k}^2} \left[\ln \left(\frac{R_{\text{expt}}}{\tilde{R}_{\text{FW}} |\Delta T^*|^{2\beta}} \right) - C \right], \quad (6.12)$$

where C is an adjustable constant which converts the relative reflectivities into absolute reflectivities. For each experimental run, i.e., for each k , the values of $\ln(R_{\text{expt}}/\tilde{R}_{\text{FW}}|\Delta T^*|^{2\beta})$ deduced from the original experimental data⁴¹ could be fitted to a linear function of $\tilde{k}^2 = k^2 \xi_{\text{coex}}^2$ well within the experimental accuracy, thus yielding C . For $\langle \tilde{Z}^2 \rangle_{\text{expt}}$ we find

$$\langle \tilde{Z}^2 \rangle_{\text{expt}} = 11 \pm 2 \quad (6.13)$$

for $T_c - T \leq 1$ K and independent of k . The actual values deduced from the experimental reflectivities obtained at $\lambda = 4880$ Å, which corresponds to $k = 0.1405 \times 10^8$ m⁻¹, are shown in Fig. 3. In the analysis we have restricted ourselves to temperatures within 1° from T_c for two reasons. First, for $T_c - T > 1$ K, one must expect correc-

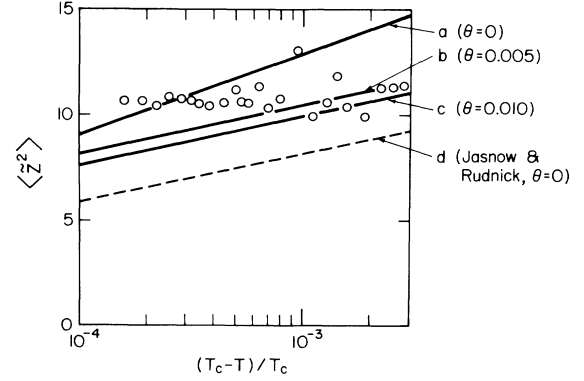


FIG. 3. Mean squared displacement $\langle \tilde{Z}^2 \rangle$ as a function of $(T_c - T)/T_c$. The circles represent values deduced from the experimental reflectivity data at $k = 0.1405 \times 10^8$ m⁻¹ obtained by Wu and Webb (Refs. 12 and 41) for SF₆. Curves (a), (b), and (c) represent the values calculated from (6.10) with $\tilde{q}_{\min} = \tilde{k} \sin \theta$ for $\theta = 0$, $\theta = 0.005$, and $\theta = 0.010$ rad, respectively. Curve (d) indicates values calculated from the theoretical formula of Jasnow and Rudnick (Ref. 10).

tion terms to the asymptotic power laws (3.9).⁴² Second, for $T_c - T > 1$ K, the values deduced for $\langle \tilde{Z}^2 \rangle$ from the experimental reflectivities become very inaccurate.

A comparison with (6.10) is complicated by the fact that the collection angle θ , and hence the lower cutoff \tilde{q}_{\min} , is not well known for these experiments.^{5,39} As was done by Meunier,⁵ we have evaluated (6.10) for $\theta = 0$, $\theta = 0.005$, and $\theta = 0.010$ rad, and the results are represented by the solid curves (a), (b), and (c) in Fig. 3. For $\theta = 0$, the cutoff is determined by gravity through

$$\begin{aligned} \tilde{g} &= \frac{g\Gamma - \xi - \rho_c}{BP_c} |\Delta T^*|^{-(\beta\delta + \nu)} \\ &= 1.10 \times 10^{-15} |\Delta T^*|^{-(\beta\delta + \nu)}. \end{aligned} \quad (6.14)$$

For $\theta = 0.005$ and $\theta = 0.010$, the value of the integral (6.10) is determined by the experimental cutoff. [The uncertainty in the cutoff wave number (5.9) affects the values calculated for $\langle \tilde{Z}^2 \rangle$ by less than 0.5.] Curves (a) and (c) are expected to provide upper and lower bounds for $\langle \tilde{Z}^2 \rangle$. From Fig. 3 we note that the theory provides values for $\langle \tilde{Z}^2 \rangle$ of the correct order of magnitude, but the expected temperature dependence of $\langle \tilde{Z}^2 \rangle$ is not seen in the experimental data. In fact, the absence of this temperature dependence justifies the procedure described above for determining the constant C .

Since the experimental cutoff $\tilde{q}_{\min} = \tilde{k} \sin \theta$ depends on $\tilde{k} = k\xi$, at a given k the mean squared displacement $\langle \tilde{Z}^2 \rangle$ should depend on temperature, and at a given temperature it should depend on k , although the range of experimental k values may not have been sufficiently large to resolve the latter effect. When $\theta = 0$, $\langle \tilde{Z}^2 \rangle$ should still depend on temperature through the temperature dependence of \tilde{g} as given by (6.14). It would be desirable to perform new reflectivity measurements (including turbidity corrections) in which the reflectivity is carefully in-

TABLE I. Critical region parameters for SF₆.

$T_c = 318.69$ K
$\rho_c = 730$ kg m ⁻³
$P_c = 3.761$ MPa
$n_c = 1.091$
$B = 1.62$
$\Gamma_+ = 0.046$
$\Gamma_- = 0.0096$
$\xi_+ = 0.189$ nm
$\xi_- = 0.098$ nm

vestigated as a function of the collection angle θ . When $\bar{q}_{\min} = \bar{k} \sin \theta$, $\langle \bar{Z}^2 \rangle$ should vary with temperature as $(2\nu/4\pi\bar{\sigma}_{\text{expt}}) \ln |\Delta T^*|$. When $\bar{q}_{\min} = 0$, the cutoff is provided by gravity and $\langle \bar{Z}^2 \rangle$ should vary with temperature as $[(\beta\delta + \nu)/4\pi\bar{\sigma}_{\text{expt}}] \ln |\Delta T^*|$.

Beysens and Robert³ have recently calculated the reflectivity with the traditional capillary-wave formula with a constant surface tension, so that (6.10) is approximated by

$$\langle \bar{Z}^2 \rangle = \frac{1}{4\pi\bar{\sigma}_b} \ln \frac{\bar{q}_{\max}^2}{\bar{q}_{\min}^2}. \quad (6.15)$$

They estimated the short-wavelength cutoff \bar{l} , and hence \bar{q}_{\max} , from the experimentally observed interface thickness (which includes capillary-wave effects), obtaining values for \bar{l} ranging from 8 to 10 in our notation. No attempt was made to identify $\bar{\sigma}_b$ in (6.15) with the Fisk-Widom surface tension. We note that also, with the approximate equation, $\langle \bar{Z}^2 \rangle$ should be expected to vary with temperature.

Jasnow and Rudnick have derived an expression for the reflectivity of the interface using renormalization techniques.^{10,11,34} Their result has the same form as (6.9) but with

$$\langle \bar{Z}^2 \rangle = c_1 \ln [c_2 (a/2\xi_{\text{coex}})^{(\beta\delta + \nu)/\nu} / h_0 a^{(d+2)/2}]. \quad (6.16)$$

Here $c_1 = 0.44$, $c_2 = 1.73$, and a is a microscopic length parameter, while h_0 represents the external field, such that

$$h_0 \simeq \frac{\rho_c g}{k_B T_c} a^{d/2}. \quad (6.17)$$

(The correlation length ξ employed by Jasnow and Rudnick must be identified with $2\xi_{\text{coex}}$.) In terms of the scaled gravity \bar{g} given by (6.14), the expression (6.16) of Jasnow and Rudnick becomes

$$\langle \bar{Z}^2 \rangle = -c_1 \ln(q_0 \bar{g}), \quad (6.18)$$

with

$$q_0 = \frac{2^{(\beta\delta + \nu)/\nu}}{c_2} \left(\frac{\xi_-}{a} \right)^{-\beta/\nu} \frac{\bar{R}_\psi}{B}. \quad (6.19)$$

This expression for q_0 is identical to the formula presented in a previous paper,²⁴ except that $2\xi_-$ had been replaced by ξ_+ , previously. General renormalization arguments show that the coefficient q_0 must be a universal constant,²⁴ although this is not apparent from the expression (6.19) found by Jasnow and Rudnick.¹⁰ Estimating a as $m/2\rho_c$, where m is the molecular mass, we find from (6.19) for SF₆ $q_0 = 2.1$. The results then obtained from (6.18) for $\langle \bar{Z}^2 \rangle$ are shown in Fig. 3 as curve (d). The theoretical result of Jasnow and Rudnick corresponds to $\bar{q}_{\min} = 0$, and therefore cannot be compared directly with the experimental reflectivities; it should be compared with curve (a) obtained from our equations. Equation (6.18) implies that $\langle \bar{Z}^2 \rangle$ should vary with temperature as

$c_1(\beta\delta + \nu) \ln |\Delta T^*|$, and the coefficient $c_1 = 0.44$ is to be compared with $1/4\pi\bar{\sigma}_{\text{expt}} = 0.77$ in our results. [In Ref. 24 the symbol Q in Sec. 5 should be replaced with \bar{R}_ψ , and Eq. (5.5) should read $c_1 = 1/4\pi\bar{\sigma}_b = 0.61$ with $\bar{\sigma}_b = 4K\bar{R}_\psi$.]

VII. DISCUSSION

The capillary-wave theory is a mesoscopic description of the system, and therefore needs a phenomenological input. It has been widely appreciated that the bare surface tension and a short wavelength cutoff are required to make the capillary-wave Hamiltonian complete. These two parameters are, of course, not unrelated: the smaller the short wavelength cutoff, the larger will be the difference between the bare and the experimentally measured surface tension. In addition to these parameters, a third constant is needed to relate the amplitude of the capillary waves to the bulk correlation length, as earlier pointed out by Kayser.⁷ This additional constant enters in the effect of the capillary waves on the surface tension, while it does not enter in the calculation of the correlation functions of the interface.

We have determined these parameters by taking the Fisk-Widom value⁴ for the bare surface tension, and requiring that the difference between the bare and the measured surface tension are due to capillary waves. We have made this renormalization of the surface tension by capillary waves more precise by using the principle that the capillary waves with shorter wavelengths contribute to the surface tension "felt" by capillary waves with longer wavelengths. This principle has no firm theoretical foundation but it is intuitively attractive. Within the traditional capillary-wave model the influence of the shorter waves on the longer waves is absent, because the capillary waves are noninteracting. A consequence of our renormalization procedure is a dispersion of the surface tension; in the long-wavelength limit $\sigma(q) - \sigma(0)$ behaves as $q^2 \ln q$. We emphasize that our choice of parameters leads to the minimum dispersion in the surface tension.

Having fixed the free parameters of the capillary-wave model by tying them to the behavior of the surface tension, the mean squared displacement of the fluctuating Fisk-Widom interface can be calculated without further fitting parameters, and the results have been compared with the reflectivity data of Wu and Webb¹² for sulfur hexafluoride. The calculated reflectivities appear to be of the same order of magnitude as those observed experimentally, but the capillary-wave theory predicts a variation of the reduced mean squared displacement $\langle \bar{Z}^2 \rangle$ with temperature that has not yet been observed experimentally.

Meunier⁵ has recently proposed a mechanism for coupling between capillary waves by considering higher-order terms in the capillary-wave Hamiltonian (4.13). His theory yields a dispersion of the surface tension (which differs from that obtained in this paper) and a natural cutoff for the capillary waves. In this picture the interface is described as a thin interface with capillary waves, even near the critical temperature. It is difficult to

see how a fluctuating sharp interface at all temperatures below T_c is smoothly connected with the continuous profiles above the critical temperature.¹⁷

Schmidt⁴³ has recently reported new ellipticity measurements of liquid-liquid interfaces of binary mixtures near the critical point of mixing, which he analyzed with the aid of the equations presented in this paper. In contrast to the results found by us for SF₆, Schmidt concludes that the theory overestimates the ellipticity coefficient of the interface. It is difficult to imagine that the structure of the interface of liquid mixtures near the critical point of mixing would be different from that of a vapor-liquid interface near the critical point. Measurements of both the reflectivity and ellipticity for the same

system, combined with a critical examination of the relationship between the observed ellipticity and the structure of the interface,⁴⁴ could possibly contribute to the resolution of this issue.

ACKNOWLEDGMENTS

The authors acknowledge stimulating discussions with D. Bedeaux, M. E. Fisher, M. P. Gelfand, R. F. Kayser, A. J. Liu, M. R. Moldover, J. W. Schmidt, W. van Saarloos, and R. K. P. Zia. The research at the University of Maryland was supported by National Science Foundation Grant No. DMR-8814439.

- ¹B. Widom, Faraday Symp. Chem. Soc. (London) **67**, 7 (1981).
²J. S. Rowlinson and B. Widom, *Molecular Theory of Capillarity* (Clarendon, Oxford, 1982).
³D. Beysens and M. Robert, J. Chem. Phys. **87**, 3056 (1987).
⁴S. Fisk and B. Widom, J. Chem. Phys. **50**, 3219 (1969).
⁵J. Meunier, J. Phys. (Paris) **48**, 1819 (1987).
⁶J. D. Weeks, J. Chem. Phys. **67**, 3106 (1977).
⁷R. F. Kayser, Phys. Rev. A **33**, 1948 (1986).
⁸F. P. Buff, R. A. Lovett, and F. H. Stillinger, Phys. Rev. Lett. **15**, 621 (1965).
⁹D. Bedeaux, in *Fundamental Problems in Statistical Mechanics*, edited by E. G. D. Cohen (Elsevier, Amsterdam, 1985), p. 125.
¹⁰D. Jasnow and J. Rudnick, Phys. Rev. Lett. **41**, 698 (1978).
¹¹D. Jasnow, in *Phase Transitions and Critical Phenomena*, edited by J. L. Lebowitz and C. Domb (Academic, New York, 1986), Vol. 10, p. 269.
¹²E. S. Wu and W. W. Webb, Phys. Rev. A **8**, 2065 (1973).
¹³For a recent review, see J. V. Sengers and J. M. H. Levelt Sengers, Annu. Rev. Phys. Chem. **37**, 189 (1986).
¹⁴J. M. J. van Leeuwen and J. V. Sengers, Physica A **132**, 207 (1985).
¹⁵J. H. Sikkenk, J. M. J. van Leeuwen, and J. V. Sengers, Physica A **139**, 1 (1986).
¹⁶J. M. J. van Leeuwen and J. V. Sengers, Physica A (to be published).
¹⁷D. A. Huse, W. van Saarloos, and J. D. Weeks, Phys. Rev. B **32**, 233 (1985).
¹⁸J. V. Sengers and M. R. Moldover, Phys. Lett. **66A**, 44 (1978).
¹⁹K. Binder, Phys. Rev. A **25**, 1699 (1982).
²⁰E. Brézin and S. Feng, Phys. Rev. B **29**, 472 (1984).
²¹M. R. Moldover, Phys. Rev. A **31**, 1022 (1985).
²²K. K. Mon and D. Jasnow, J. Stat. Phys. **41**, 273 (1985).
²³K. K. Mon, Phys. Rev. Lett. **60**, 2749 (1988).
²⁴J. M. J. van Leeuwen and J. V. Sengers, Physica A **138**, 1 (1986).
²⁵A. J. Liu and M. E. Fisher, Physica A **156**, 35 (1989).
²⁶C. Bervillier and C. Godrèche, Phys. Rev. B **21**, 5427 (1980).
²⁷C. Bagnuls, C. Bervillier, D. I. Meiron, and B. G. Nickel, Phys. Rev. B **35**, 3585 (1987).
²⁸E. Brézin, J. C. Le Guillou, and J. Zinn-Justin, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic, New York, 1976), Vol. 6, p. 125.
²⁹H. B. Tarko and M. E. Fisher, Phys. Rev. B **11**, 1217 (1975).
³⁰D. S. Ritchie and J. W. Essam, J. Phys. C **8**, 1 (1975).
³¹H. Chaar, M. R. Moldover, and J. W. Schmidt, J. Chem. Phys. **85**, 418 (1986).
³²H. L. Gielen, O. B. Verbeke, and J. Thoen, J. Chem. Phys. **81**, 6154 (1984).
³³R. Evans, Mol. Phys. **42**, 1169 (1981).
³⁴D. Jasnow, Rep. Prog. Phys. **47**, 1059 (1984).
³⁵R. F. Kayser (unpublished).
³⁶W. T. Estler, R. J. Hocken, T. Charlton, and L. R. Wilcox, Phys. Rev. A **12**, 2118 (1975).
³⁷M. R. Moldover, J. V. Sengers, R. W. Gammon, and R. J. Hocken, Rev. Mod. Phys. **51**, 79 (1979).
³⁸J. S. Huang and W. W. Webb, J. Chem. Phys. **50**, 3677 (1969).
³⁹J. Meunier and D. Langevin, J. Phys. (Paris) Lett. **43**, L-185 (1982).
⁴⁰J. V. Sengers and J. M. J. van Leeuwen, Physica A **116**, 345 (1982).
⁴¹E. S. Wu, Materials Science Center, Cornell University, Report No. 1992, 1973.
⁴²J. M. H. Levelt Sengers and J. V. Sengers, in *Perspectives in Statistical Physics*, edited by H. J. Raveché (North-Holland, Amsterdam, 1981), p. 239.
⁴³J. W. Schmidt, Phys. Rev. A **38**, 567 (1988).
⁴⁴D. Bedeaux, E. M. Blokhuis, and J. W. Schmidt, Intern. J. Thermophys. (to be published).