Thermal Fluctuations of Thin Wetting Films on Disordered Solids

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We consider thin liquid layers which completely wet nonideal (either rough or heterogeneous in composition) solid surfaces. Two different sources of fluctuations of the liquid surface are identified, and the competition between them is investigated. For thick enough films (but still in the submicrometer range), the liquid surface fluctuations are dominated by thermally induced capillary waves. For thin films, capillary waves are strongly damped and the liquid surface fluctuations are correlated with the disorder of the underlying solid surface. The fluctuation spectrum is explicitly calculated for a van der Waals liquid and for several different types of solid disorder. Our findings are in agreement with recent X-ray specular reflection and diffuse scattering experiments.

1. Introduction

Wetting of solid surfaces has been an extremely active area of research for some time.[1-4] Most previous research has been restricted to wetting of idealized smooth solid surfaces of homogeneous composition. Recent theoretical[5-11] and experimental[12-16] studies, however, have focused on the effects of disorder in the solid support on wetting processes. As almost all surfaces are either rough or heterogeneous in composition, this is the situation most relevant in practice. In addition, surface heterogeneity can be obtained in a controlled fashion using techniques such as molecular beam epitaxy, allowing systematic experimental and theoretical study of the wetting properties of nonideal surfaces.

Recent theoretical work has considered the effects of surface disorder on the static properties of wetting

layers[8,10,11] and contact angle hysteresis.[5-7,9] In the former studies, analytic results in the case of weak solid disorder and numerical calculations for solids with one-dimensional square grooves both indicate the same general trends: thin wetting films are much more susceptible to roughness induced by the solid support than thicker films, and the liquid response is strongly wavelength dependent. A characteristic length scale ξ (the so-called "*healing length*"), determined by the competition between the liquid-vapor surface tension and the long-range component of the molecular interactions, governs this response; the liquid interface follows the solid for undulations of wavelength greater than ξ, while undulations of shorter wavelength are strongly damped.

Several recent experiments have examined the effects of solid inhomogeneity on the properties of wetting layers. One class of experiments uses X-ray reflectometry (at grazing angles) to study the root mean square (rms) fluctuations of aqueous wetting layer precursor films on rough substrates.[12] This technique allows independent measurement of the height-height autocorrelation function of the rough solid surface and of the free surface of the liquid layer. The roughness of the liquid-vapor interface was measured to be approximately 3.6-4.2 Å for wetting layers of mean thickness between 70 and 100 Å. This value is slightly greater than the value of 3.2 Å reported for bulk water surface roughness.[15]

Recent X-ray specular reflection and surface diffuse scattering experiments[13] of cyclohexane films on a silicon surface clearly indicate that the roughness of the free liquid surface of such wetting films is the sum of contributions from the static roughness induced by (and correlated with) the inhomogeneity of the solid support and from thermal fluctuations of the liquid interface itself. For very thin liquid films, the capillary fluctuations are found to be strongly damped, and hence the liquid roughness is dominated by the static contribution. Furthermore, the specific functional form of the correlations between the solid and liquid surfaces is in quantitative agreement with theoretical predictions.[10,11] For substantially thicker films, on the other hand, the roughness induced by the molecular interactions between the liquid and the disordered solid

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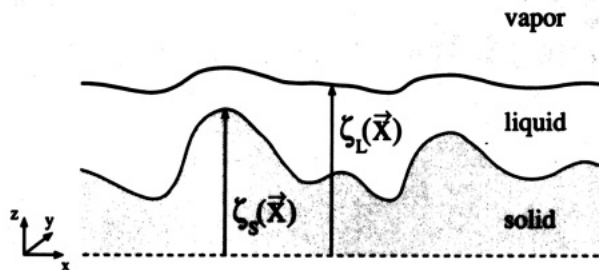(16) Pfeifer, P.; Wu, Y.; Cole, M. W.; Krim, J. *Phys. Rev. Lett.* **1989,** *62,* 640.

Figure 1. A continuous liquid film covering a rough solid surface. The liquid and solid surfaces are at height $\zeta_L(\tilde{x})$ and $\zeta_S(\tilde{x})$, respectively, above the $z = 0$ reference plane.

is negligible, and the liquid roughness is dominated by capillary fluctuations of the liquid interface.[17-22] In another series of experiments,[14] direct visualization of thin wetting films of poly(dimethylsiloxane) on various surfaces has been made using a special microscopic imaging ellipsometer. It was reported that the static thickness fluctuations of the wetting films are roughly inversely proportional to the local average film thickness. In all of the measurements outlined above, quantitative analysis of experimental data would be facilitated by explicitly including in the theory the contribution of thermal fluctuations to the total liquid surface roughness.

The outline of this paper is as follows: In section 2, we briefly review the formalism needed to derive the equilibrium liquid interface profile and show how it may be extended to provide the spectrum of thermal fluctuations about this equilibrium interface. Then, we present the special cases of rough solid supports of homogeneous composition (section 3) and smooth but chemically heterogeneous solids (section 4). Finally, in section 5 we summarize and discuss our results, and make comparisons with recent experiments.

2. General Formalism

We consider a thin fluid film wetting a rough solid surface in the presence of a third phase, which may be either vapor or another liquid. Roughness of the solid support results in undulations of the interface between the wetting layer and the third phase (called the liquid surface below), as shown in Figure 1. We limit our consideration to surfaces without overhangs or nonzero average curvature. Hence, the solid surface profile may be specified by a single valued function $\zeta_S(\tilde{x})$ [$\tilde{x} = (x,y)$] giving the local height of the solid with respect to a reference plane, which we take to be the $z = 0$ plane. Similarly, the liquid surface profile is specified by its local height above the reference plane, $\zeta_L(\tilde{x})$. For convenience, we choose the position of the reference plane so that the spatial average of the solid profile vanishes, $\langle \zeta_S \rangle = 0$, and $\langle \zeta_L \rangle = e$, the average wetting film thickness. Alternatively, we may consider the case of heterogeneous solids, in which

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the composition of the solid support is inhomogeneous. The general case may be treated as follows.

Taking as a reference state the coexistence of the solid surface and the third phase (denoted V in the following, but which can be either vapor or another liquid) in the absence of the liquid phase, the mean field free energy of the three-phase system has the general form

$$F = \int d^2\tilde{x} \left[(\gamma_{SL} - \gamma_{SV})(1 + |\vec{\nabla}\zeta_S|^2)^{1/2} + \gamma(1 + |\vec{\nabla}\zeta_L|^2)^{1/2} + P[\zeta_L(\tilde{x})] + \Delta\mu(\zeta_L - \zeta_S) \right] \quad (1)$$

where $\vec{\nabla}$ denotes the two-dimensional gradient operator, and where γ_{SL}, γ_{SV}, and γ are the interfacial tensions between solid and wetting liquid, between solid and the third phase, and between the third phase and wetting liquid, respectively. The first two terms are the change in interfacial energy of the solid and liquid interfaces relative to the reference state. The third term, $P[\zeta_L(\tilde{x})]$, is the effective interaction energy of the solid and liquid interfaces, which is due only to the long-range components of the interactions between molecules of the solid and liquid phases. Expressed in terms of two-body interactions, $P[\zeta_L(\tilde{x})]$ has the form

$$P[\zeta_L(\tilde{x})] = \int_{\zeta_L(\tilde{x})}^{\infty} dz \int d^2\vec{\rho} \int_{-\infty}^{\zeta_S(\vec{\rho})} dz' \, w(\vec{r},\vec{r}') \quad (2)$$

where $w(\vec{r},\vec{r}') = n_L^2 U_{LL}(\vec{r},\vec{r}') - n_L n_S(\vec{r}) \, U_{LS}(\vec{r},\vec{r}') - n_V n_L U_{LV}(\vec{r},\vec{r}') + n_V n_S(\vec{r}') \, U_{SV}(\vec{r},\vec{r}')$ is the local interaction energy difference per unit volume squared between the S-V reference state and the S-L-V three-phase wetting state, where n_i and U_{ij} for i, j = S, L, V are, respectively, the particle number densities of the i molecules and the pair interactions between molecules of types i and j, and where $\vec{r}' \equiv (\vec{\rho},z')$ and $\vec{r} \equiv (\tilde{x},z)$. The $\vec{r}$ dependence of the $n_S(\vec{r})$ expresses the heterogeneous features of the solid support. The short-range components of the pair interactions U_{ij} in $w(\vec{r},\vec{r}')$ contribute only to a finite size correction to the liquid-phase self-energy and corrections to the interfacial energies. For detailed discussion of this point, see ref 10. The last term in eq 1 is the chemical potential difference integrated over the volume of the wetting film. The form of this chemical potential difference depends on the nature of the L and V phases; several interesting cases are discussed in refs 10 and 11.

Minimization of the free energy functional with respect to the liquid surface profile, $\delta F/\delta \zeta_L = 0$, gives an equation for the equilibrium liquid surface profile $\zeta_L^{eq}(\tilde{x})$. In the limit of weak solid inhomogeneity, one may employ a linear response approximation to obtain an analytical estimate of the form of $\zeta_L^{eq}(\tilde{x})$ and its dependence on the properties of the liquid layer and on the solid support roughness.[10,11] In this case, minimization with respect to ζ_L yields a linear integrodifferential equation for ζ_L^{eq}, which is easily solved in Fourier space, yielding the q space equilibrium profile, $\zeta_L^{eq}(\tilde{q})$.

Superimposed on the equilibrium profile $\zeta_L^{eq}(\tilde{q})$ are the thermal fluctuations of the liquid surface,[17-22] $\delta\zeta_L(\tilde{q})$. The total liquid surface roughness is the sum of these two contributions: $\zeta_L(\tilde{q}) = \zeta_L^{eq}(\tilde{q}) + \delta\zeta_L(\tilde{q})$. One can obtain an estimate of $\delta\zeta_L(\tilde{q})$ using an equipartition of energy argument, as follows. Let $F_q[\zeta_L(\tilde{q})]$ be the Fourier components of the mean field free energy functional given in eq 1 expanded to second order in $\zeta_L - e$ and the relevant disorder parameter. Equipartition of energy assigns $k_B T$ of energy to each q mode of the capillary fluctuations of the liquid surface. Thus, we have

$$\langle \Delta F_q \rangle_T = k_B T \quad (3)$$

where $\Delta F_q = F_q[\zeta_L(\tilde{q})] - F_q[\zeta_L^{eq}(\tilde{q})]$ is the incremental

energy due to the capillary mode $\delta\zeta_L(\vec{q})$, and where the brackets denote thermal averaging. Equation 3 gives a relation for $\langle|\delta\zeta_L(\vec{q})|^2\rangle_T$ in terms of the properties of the liquid layer and the nature of the solid–liquid interaction. As we will see, in the linear response regime $\langle|\delta\zeta_L(\vec{q})|^2\rangle_T$ only depends on the average properties of the solid support; the inhomogeneity of the solid does not couple to the capillary fluctuations at this level of approximation.[23] In the following two sections, we present the special cases of rough solid supports of homogeneous composition and smooth solids of heterogeneous composition.

3. Wetting Films on Rough Solids

In the case of rough solids of homogeneous composition, the form of the effective interaction potential between liquid and solid interfaces is particularly simple; $w(\vec{r},\vec{r}')$ only depends on the relative distance between $\vec{r}$ and $\vec{r}'$; $w = w(|\vec{r}-\vec{r}'|)$. Hence, one can write $P[\zeta_L]$ from eq 2 in the simplified form[10,11]

$$P[\zeta_L(\vec{x})] = \int_{\zeta_L(\vec{x})}^{\infty} dz \int d^2\vec{\rho} \int_{-\infty}^{\zeta_S(\vec{x}+\vec{\rho})} dz' \, w(\vec{\rho},z'-z) \quad (4)$$

The corresponding linear response free energy functional is given by eq 1, with $P = P[\zeta_L(\vec{x})]$ from eq 4 expanded to second order in $\zeta_L - e$ and ζ_S and the assumption of slowly varying liquid interfacial profiles, $|\vec{\nabla}\zeta_L(\vec{x})| \ll 1$:

$$F^{(lr)} = \int d^2\vec{x} \, [(\gamma/2)|\nabla\zeta_L|^2 + P^{(lr)}[\zeta_L(\vec{x})] +$$
$$\Delta\mu(\zeta_L - \zeta_S) + F_0] \quad (5)$$

where F_0 contains only terms in eq 1 that are independent of ζ_L. Minimization of $F^{(lr)}$ with respect to ζ_L leads to expressions for the mean thickness of the wetting film and for the equilibrium liquid surface profile $\zeta_L^{eq}(\vec{x})$. The solution in Fourier space is given by

$$\zeta_L^{eq}(\vec{q}) = \frac{K(\vec{q})\,\zeta_S(\vec{q})}{1 + q^2\xi^2} \quad (6)$$

where $\xi(e)$ is the previously mentioned healing length defined by $\xi^2(e) = \gamma/\int d^2\vec{\rho}\, w(\vec{\rho},e)$, e is the mean thickness of the wetting film, where $K(\vec{q}) = (\xi^2/\gamma)w(\vec{q},e)$ and where the Fourier transformed quantities $f(\vec{q})$ are defined by $f(\vec{q}) = \int d^2x\, f(\vec{x})\exp(i\vec{q}\cdot\vec{x})$, with $\zeta_L^{eq}(\vec{q})$ being the Fourier transform of $\zeta_L^{eq}(\vec{x}) - e$. The static contribution to the intensity of the scattered signal is determined by $\zeta_L^{eq}(\vec{q})$; for instance, in an X-ray reflectivity experiment, $I_{eq}(\vec{q}) \approx \langle|\zeta_L^{eq}(\vec{q})|^2\rangle$. In general, there is also a contribution to $I(\vec{q})$ from thermal fluctuations of the liquid profile around the static profile $\zeta_L^{eq}(\vec{q})$. To estimate this contribution, we write $F^{(lr)}$ from eq 5 in terms of its Fourier components; one finds $F^{(lr)} = (2\pi)^2\int d^2\vec{q}\, F(\vec{q})$, with $F(\vec{q})$ given by

$$F(\vec{q}) = (1/2)[\gamma q^2 + \int d^2\vec{\rho}\, w(\vec{\rho},e)]|\zeta_L(\vec{q})|^2 -$$
$$w(\vec{q})\,\zeta_L(-\vec{q})\,\zeta_S(\vec{q}) + F_0(\vec{q}) \quad (7)$$

Using eq 7, we may determine $\Delta F(\vec{q}) = F[\zeta_L^{eq}(\vec{q}) + \delta\zeta_L(\vec{q})] - F[\zeta_L^{eq}(\vec{q})]$, the incremental free energy of a capillary fluctuation $\delta\zeta_L(\vec{q})$. Within the linear response approximation appropriate in the weak solid roughness limit, $\delta\zeta_L$ is not correlated with the solid roughness ζ_S[23] and the capillary fluctuations are those of an interface bound to

a smooth solid substrate.[22] Using equipartition of energy, $\langle\Delta F(\vec{q})\rangle_T = k_B T$, we obtain

$$\langle|\delta\zeta_L(\vec{q})|^2\rangle_T = \frac{k_B T\xi^2/\gamma}{1 + q^2\xi^2} \quad (8)$$

where the brackets denote a thermal average and where we have used $\langle\delta\zeta_L(\vec{q})\rangle_T = 0$ and $\langle\delta\zeta_L(\vec{q})\,\zeta_L^{eq}(\vec{q})\rangle_T = 0$, i.e., the linear response approximation. The total scattered intensity $I(\vec{q})$ from the liquid surface measured in an X-ray reflectivity experiment should be proportional to the sum of the static and capillary contributions computed from eqs 6 and 8:

$$I(\vec{q}) \propto \langle|\zeta_L^{eq}(\vec{q})|^2\rangle + \langle|\delta\zeta_L(\vec{q})|^2\rangle_T \quad (9)$$

In order to illustrate these effects, we will focus in the following on the specific case of van der Waals liquid–solid interactions and solid surfaces with *self-affine correlated* roughness.[24] For van der Waals interactions, $w(r) = (A/\pi^2)r^{-6}$ where A is the standard Hamaker constant proportional to the effective molecular polarizability of the S–L–V system. The corresponding healing length is $\xi = e^2/a$ where $a = (A/2\pi\gamma)^{1/2}$ is a microscopic length typically of the order of a few angstroms, while the interaction kernel $K(q)$ has the simple form $K(q) = (1/2)(qe)^2K_2(qe)$ where K_2 is the modified Bessel function of the second kind of order 2. In a recent study, liquid films of thickness $e = 22$, 44, and 128 Å on rough solids were investigated using X-ray diffraction at grazing angles.[13] For the thin films, $I(q)$ was fitted with eq 6 with $K(q) = 1$ (the local Deryagin approximation[11]), and correlations with the solid roughness were observed. For the thick film, however, $I(q)$ was fitted with an expression assuming capillary fluctuations like our eq 8 but considering van der Waals interactions exclusively.

Recent efforts aimed at understanding the properties of rough solid surfaces have focused on fractal or self-affine models of roughness.[8,16,24] In particular, self-affine surfaces provide an attractive description of surface roughness. However, such models suffer from divergent roughness at large length scales. Physically, the rms roughness of a given sample surface must saturate at some finite value. Clearly, a long length cutoff must be imposed in such models. Indeed, the finite size of experimental samples provides a natural cutoff. A *reduced self-affine* scaling law has been proposed[24] that has such a long length cutoff explicitly included:

$$\langle|\zeta_S(\vec{x}+\vec{\rho}) - \zeta_S(\vec{x})|^2\rangle = 2\alpha^2(1 - \exp[-(\rho/\sigma)^{2\beta}]) \quad (10)$$

where β is the self-affine roughness exponent, α is the saturated rms roughness at long length scales, and σ is the crossover length from self-affine to saturated roughness behavior. The Fourier components of the corresponding height–height correlation function $\langle|\zeta_S(\vec{q})|^2\rangle$ are obtained from eq 10. For simplicity and without loss of generality, we restrict our attention to a particular value of the roughness exponent β for which $\langle|\zeta_L^{eq}(\vec{q})|^2\rangle$ may be obtained analytically. For $\beta = 1/2$, the Fourier space correlation function is given by

$$\langle|\zeta_S(\vec{q})|^2\rangle = \frac{2\pi\alpha^2\sigma^2}{[1 + q^2\sigma^2]^{3/2}} \quad (11)$$

The corresponding equilibrium liquid surface profile is obtained by substitution of eq 11 into eq 6 using the form of the kernel $K(q)$ appropriate to van der Waals inter-

(23) However, in the nonlinear regime coupling between the capillary fluctuations of the liquid interface and the disorder of the underlying solid does appear.

(24) Sinha, S. K.; Sirota, E. B.; Garoff, S.; Stanley, H. B. *Phys. Rev. B* **1988**, *38*, 2297.

actions, as described above. We find

$$\langle |\zeta_L{}^{eq}(\vec{q})|^2\rangle = \frac{\pi\alpha^2\sigma^2}{2}\frac{(qe)^4K_2{}^2(qe)}{[1+q^2\sigma^2]^{3/2}[1+q^2\xi^2]^2} \qquad (12)$$

The nature of the total liquid surface roughness is determined by competition between the equilibrium surface roughness given by eq 12, and capillary fluctuations around the equilibrium profile, as given by eq 8. As expected, in the case of thin wetting layers or surface roughness with long-range correlations, the liquid roughness induced by the rough solid dominates over the capillary fluctuations. On the other hand, for thick wetting layers or surface roughness with short-range correlations, capillary fluctuations will dominate over the static contributions to the liquid surface roughness. However, there will be a range of parameters for which both effects will play an important role. Consider, for example, a wetting layer at room temperature of mean thickness $e = 100$ Å, surface tension $\gamma = 40$ dyn/cm, a healing length $\xi = 1000$ Å (set by an appropriate value of the Hamaker constant A), and a reduced self-affine solid support with saturated rms roughness $\alpha = 5$ Å. In Figure 2, we show plots of the static and capillary contributions to $\langle |\zeta_L(\vec{q})|^2\rangle$ vs wavenumber q for these parameters and for a self-affine cutoff length $\sigma = 400$ Å. In this case, we see a crossover from static dominated roughness at low q ($q\xi < 1$) to capillary dominated roughness at higher q ($q\xi > 1$).

Such behavior is not restricted to the case of self-affine solid roughness. For instance, the case of Gaussian correlated solid roughness, in which $\langle |\zeta_S(\tilde{x}+\vec{\rho})\,\zeta_S(\tilde{x})|^2\rangle \propto \exp[-(x/\sigma)^2]$, yields similar crossover behavior for appropriate values of the solid and liquid parameters. In fact, the nature of the static liquid surface roughness is dominated by the Lorentzian decay and is relatively insensitive to the precise form of $\langle |\zeta_S(\vec{q})|^2\rangle$ except at quite large wave numbers, $q > 1/e$. Hence, as long as the dominant solid disorder is on length scales larger than e, the nonlocal features of the interaction kernel $K(q)$ are of little consequence. For such solids, the Deryagin approximation, $K(q) \simeq 1$, should give good qualitative results.

4. Wetting Films on Heterogeneous Solids

A second type of solid disorder that we consider is heterogeneity in the solid composition that may be characterized by fluctuations of the solid–liquid and solid–vapor interaction coupling strength due to local variation in the solid composition. Thus, following ref 11, we assume the functional form of the interactions are unaffected by the solid disorder, and we write $w(\vec{r},\vec{r}') = \epsilon(\vec{r}')\,w_0(\vec{r}-\vec{r}')$, where $\epsilon(\vec{r}')$ describes the local solid composition and w_0-$(\vec{r}-\vec{r}')$ is the spatially averaged interaction potential. The normalization of $w_0(\vec{r}-\vec{r}')$ is chosen to make $\langle \epsilon(\vec{r}')\rangle = 1$. We focus on the case where $\epsilon(\vec{r}')$ is separable; e.g., the solid has a *columnar* or a *lamellar* structure and $\epsilon(\vec{r}') = 1 + \phi(\vec{\rho})\,f(z')$.

The effective interaction potential between liquid and such heterogeneous (but smooth) solid interfaces has the form

$$P[\zeta_L(\tilde{x})] =$$
$$\int_{\zeta_L(\tilde{x})}^\infty dz \int d^2\vec{\rho} \int_{-\infty}^0 dz'\,[1 + \phi(\tilde{x}+\vec{\rho})\,f(z')]w_0(\vec{\rho},z'-z) \qquad (13)$$

The corresponding linear response free energy functional is given by eq 1, with $P = P[\zeta_L(\tilde{x})]$ from eq 13 expanded to second order in $\zeta_L - e$ and $\epsilon(\vec{r}) - 1$ and the assumption of slowly varying liquid interfacial profiles, $|\vec{\nabla}\zeta_L(\tilde{x})| \ll 1$.
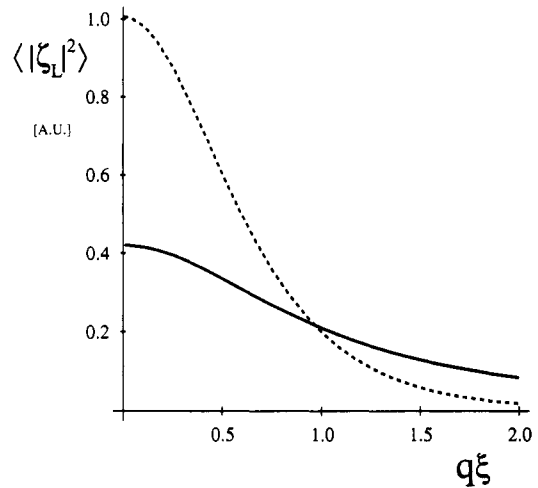

Figure 2. Static (dashed line) and thermally excited capillary (solid line) roughness of the liquid surface as a function of $q\xi$. The solid roughness is characterized by self-affine height–height correlation with a long wavelength cutoff. The parameters chosen are mean film thickness $e = 100$ Å, surface tension $\gamma = 40$ dyn/cm, healing length $\xi = 1000$ Å, rms solid roughness $\alpha = 5$ Å, and self-affine cutoff length $\sigma = 400$ Å.

Within the linear response approximation, the form of the capillary fluctuations $\langle |\delta\zeta_L(\vec{q})|^2\rangle$ is identical to that given in eq 8 with $w = w_0(\vec{r}-\vec{r}')$; as before, the capillary effects are determined by the average interaction between the solid and liquid phases and are insensitive to the precise details of the solid disorder.[23] On the other hand, the equilibrium liquid surface profile couples directly to the solid disorder; the Fourier components of the equilibrium liquid surface profile are given by

$$\zeta_L{}^{eq}(\vec{q}) = \frac{G(\vec{q})\,\phi(\vec{q})}{1+q^2\xi^2} \qquad (14)$$

where $\phi(\vec{q})$ is the Fourier transform of $\phi(\tilde{x})$, $\xi = \xi(e)$ is the effective healing length defined in the previous section, and $G(q)$ is given in terms of $f(z)$, the healing length $\xi(z)$, and the average interaction kernel $K(q,z)$ discussed in the previous section by

$$G(q) = \xi^2(e)\int_e^\infty dz\,\xi^{-2}(z)\,K(q,z)\,f(e-z) \qquad (15)$$

In order to illustrate our results, we focus on the case of van der Waals interactions and solid supports that are homogeneous in the z direction; i.e., $f(z) = 1$. In this situation, $\phi(\tilde{x})$ represents the lateral fluctuations of the Hamaker constant A. The resulting simplified $G(q)$ is given by eq 15 with $f = 1$, $\xi(z) = z^2/a$ with $a = (A/2\pi\gamma)^{1/2}$, and $K(q,z) = (1/2)(qz)^2K_2(qz)$. As in the previous section, we will characterize the lateral solid inhomogeneity by a reduced self-affine scaling law with exponent $\beta = 1/2$. The resulting Fourier transformed composition–composition correlation function has the form

$$\langle |\phi(\vec{q})|^2\rangle = \frac{2\pi\delta^2\sigma^2}{[1+q^2\sigma^2]^{3/2}} \qquad (16)$$

where δ is the saturated rms fluctuation of the Hamaker constant $\delta = \Delta A/A$, and σ is the crossover length from self-affine to saturated solid disorder. The corresponding equilibrium liquid surface profile is obtained by substitution of eq 16 and $G(q)$ from eq 15 into eq 14.

The total liquid roughness follows the same general trends as in the case of wetting films on rough supports discussed in the previous section. Quantitatively, solid roughness couples more effectively to the liquid fluctu-
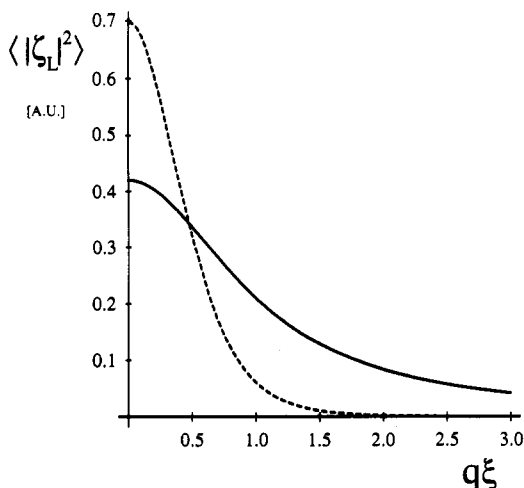
Figure 3. Static (dashed line) and thermally excited capillary (solid line) roughness of the liquid surface as a function of $q\xi$. The solid disorder is characterized by self-affine composition correlation with a long wavelength cutoff. The parameters chosen are mean film thickness e = 100 Å, surface tension γ = 40 dyn/cm, healing length ξ = 1000 Å, rms Hamaker constant variation δ = 0.05, and self-affine cutoff length σ = 1000 Å.

ations than does chemical heterogeneity. One may see this by setting $\alpha^2 = (\delta e)^2$ in eq 11, and comparing the resulting equilibrium profiles for reduced self-affine roughness and lateral composition fluctuations with identical crossover lengths σ. As before, there will be a range of film thickness and solid heterogeneity for which both static and capillary effects play an important role. Consider, for example, a wetting layer at room temperature of mean thickness e = 100 Å, surface tension γ = 40 dyn/cm, a healing length ξ = 1000 Å, and a reduced self-affine solid support with rms fluctuations of the Hamaker constant δ = 0.05 and cutoff length σ = 1000 Å. In Figure 3, we plot separately the static and capillary contributions to $\langle|\zeta_L(\vec{q})|^2\rangle$ vs wavenumber q, indicating a crossover from static dominated roughness at low q ($q\xi < 0.5$) to capillary dominated roughness at higher q ($q\xi > 0.5$). As discussed in the previous section, such behavior is not restricted to the case of self-affine solid roughness. For instance, the case of Gaussian correlated composition fluctuations yields similar crossover behavior for appropriate values of the solid and liquid parameters.

5. Discussion

We have considered the contribution of capillary fluctuations to the roughness of wetting films on weakly rough or chemically heterogeneous solid supports. Both types of solid disorder display similar trends. For thick wetting films or short-range solid disorder, long-range liquid–solid interactions (e.g., van der Waals) are weak and capillary fluctuations dominate. For thin wetting films or long-range solid disorder, capillary fluctuations are strongly damped and liquid surface roughness is induced by and correlated to the underlying solid disorder. These two limiting behaviors have been recently confirmed by X-ray specular reflection and diffuse scattering experiments[13] on thin cyclohexane films on rough silicon surfaces. Capillary waves (eq 8) have been shown to be the main contribution to the liquid surface fluctuations for films thicker than 60 Å. For thinner films, the scattering

function has been fitted with an expression equivalent to eq 6 in the limit $qe \ll 1$ but $q\xi > 1$. This local Deryagin limit,[11] $K(qe) \simeq 1$, is justified in the scattering experiments where the in-plane q vector is of the order of 10^{-2}–10^{-3} Å^{-1} and the film thickness is $e \lesssim 60$ Å. It is important to note that the X-ray scattering provided a *direct* proof of the correlation between the solid and liquid surfaces for thin enough films, as well as of the lack of such correlation for thick films, which are dominated by capillary fluctuations.

We have calculated the fluctuation spectrum explicitly for physically realizable van der Waals liquids and several types of solid disorder. Rough solid surfaces characterized by self-affine height–height correlations with an upper spatial cutoff in the correlation function were studied. Chemically heterogeneous (but smooth) solids with reduced self-affine lateral (columnar) composition fluctuations were also considered. In both cases, we find an intermediate region exists for which static liquid fluctuations induced by the solid disorder, and capillary fluctuations, are of equal importance (c.f. Figures 2 and 3). However, one should note that the extent of this intermediate regime is quite limited; for most reasonable choices of the solid disorder and liquid parameters (surface tension, Hamaker constant, and film thickness), either capillary waves or the solid disorder dominates the liquid fluctuations.

For simplicity, we have limited our discussion to weakly disordered solids for which a linear response treatment could be given. In this case, the capillary fluctuations of the liquid interface are not coupled to the underlying solid disorder. However, higher order couplings of the capillary fluctuations and the solid disorder may be analyzed within the theoretical framework presented in this paper. Such an extension of the theory may be important for understanding the thermal fluctuations of wetting films on very rough or heterogeneous solids.

In the future, it would be interesting to test these theoretical predictions in a systematic manner by, for instance, using several different well-characterized rough or heterogeneous solid surfaces. Solid disorder can be introduced in a controlled fashion by using molecular beam epitaxy, or other surface preparation techniques. Another possibility for future experimental investigation is to use inelastic light scattering to study the hydrodynamic surface fluctuations of wetting films on disordered solids. Such experiments have been performed on free soap films, in which a thin liquid layer has two fluctuating interfaces.[25] Finally, a possible theoretical extension of this work would be to generalize our results for films of simple liquids to the case of complex fluids such as polymer or surfactant solutions.

(25) Joosten, J. G. H. *J. Chem. Phys.* **1984**, *80*, 2363, 2383.