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Scattering of light by capillary waves in critical wetting interfaces

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Abstract : The intensity distribution in scattered light, due to scattering by capillary waves in critical wetting interfaces, is derived. It is seen that the intensity is confined within an angle $<\theta^2> \sim \sigma^{-1} \sim t^{1.33}$ around the specular direction, σ being the surface tension of the interface. The quantity $<\theta^2>$ is seen to be independent of the thickness of the layer. A temporal measurement, measuring the temporal rate of change of scattered intensity in any direction is seen to probe the dispersion relation of the capillary waves and is hence very sensitive to the layer thickness, for very thin layers.

Keywords : Wetting, critical point, interface, light scattering.

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1. Introduction

Wetting phenomenon, near the critical point of a binary liquid mixture is an interesting phenomenon where a heavier liquid resides on top of a lighter liquid. The observation of wetting has been reported in many systems (Cahn 1977, Moldover and Cahn 1980, Vani *et al* 1983). Observations on the effect of hydrodynamic instabilities in the wetting layers has been reported by us (Chatterjee *et al* 1985). Whenever the cell dimensions are small enough such that hydrodynamic instabilities are absent, an important role is played by the surface capillary waves in determining the thickness of the wetting layer. Chatterjee and Gopal (1988) have discussed the effect of the capillary waves on the thickness of the wetting layer and in particular, have shown that because of the influence of the capillary waves, the thickness of the wetting layer goes to zero as one approaches the critical point, provided the forces are of long range type. For

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Cahn-Hilliard type short range forces, the thickness has a complicated dependence on $t=|(T-T_0)/T_0|$.

As has been shown (Chatterjee *et al* 1985) stability of the wetting layer is very critically decided by the dispersion relation of the capillary waves. In the above paper, the authors considered the well known dispersion relation

$$\omega^2(k)=(1/\rho)[(g\Delta\rho+\sigma k^2)k\tanh(kl)]$$

l being the thickness of the wetting layer. This shows that

$$\omega^2(k)\sim(\sigma/\rho)k^4l$$

for very thin layers and leads to a free energy contribution $F_{\text{capillary}}\sim -l^{-x}$ where x changes from l in extreme low t limit to 1/2 for higher t values. This particular behaviour of $F_{\text{capillary}}$ with respect to l is an important determining factor as far as the dependence of l on t is concerned. Hence, we consider that the single most important justification in favour of our 'capillary wave' model can be obtained, if a direct evidence of the above dispersion relation can be found for the surface ripples.

With this motivation in mind, we discuss the possibility of experimental verification of the presence of capillary waves. We take light as the probe and consider the scattering of light by capillary waves, which render the surface irregular (Beckmann and Spizzichino 1963). We derive in the following, an expression for the intensity of the reflected light from a wetting interface and show that it follows a distinct scaling behaviour which may be verified experimentally.

We propose two experiments, in one of which a broad beam of light is incident on the wetting interface and the reflected beam is converged using a lens and then projected on a screen. The wetting surface being irregular, because of displacements caused by capillary waves, the reflected beam will proceed in random directions and hence the point of focus on the screen will broaden out into a patch if the exposure time be large. In this case, the width of the patch follows a fixed scaling behaviour. In the second experiment, we have a narrow beam of light incident on a given spot in the wetting interface. The movement of the reflected light on the screen is determined by the tilt of the surface. This gives the behaviour of grad ξ. The temporal changes of Grad ξ depend on $\omega(K)$ dispersion and hence explicitly on the thickness of the wetting layer and should follow the behaviour derived in the following section. The temporal changes in the intensity are related to the time evolution of the displacements of the surface ripples. We show that this in both cases one studies the change in coherence properties of the reflected light. In the first experiment, one studies the distortion of the wavefront on reflection. In the second one, we take the temporal change in coherence for a very narrow reflected beam of light.

2. Theory

2a. Light scattering by capillary waves : static experiment

Figure 1 shows the wetting situation in a binary liquid mixture. L_1 and L_2 are the two liquids and L_1L_2 is the interface showing the bulk phase separation. A thin wetting layer of L_1 forms on top of L and L_2L_1 is the wetting interface.

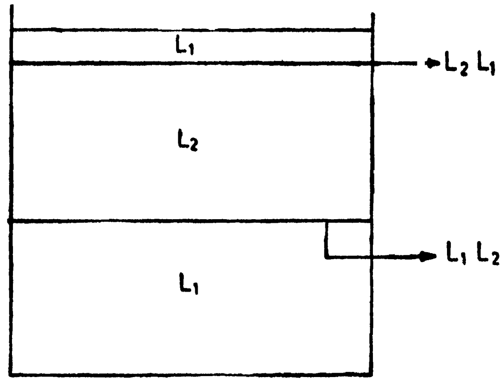

Figure 1. Schematic diagram of the wetting phenomena.

We consider the distortion of the interface, due to capillary waves and the scattering of a plane wave front of light by these distortions on the wetting interface.

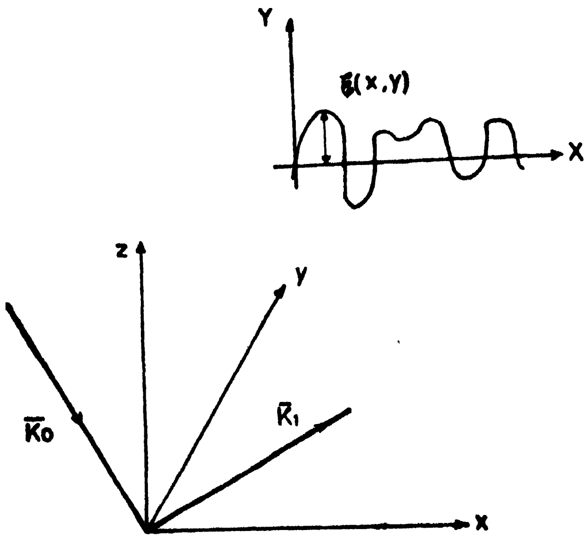

Figure 2. Sketch of the scattering geometry.

The capillary waves at the surface are considered to be a random rough surface in two dimensions. As shown in Figure 2, let a plane front be incident on the interface.

Let $\mathbf{s}k_0$ be the wave vector of the scattered light, with $s(s_x, s_y, s_z)$ being the direction of scattering. Let s_x^o, s_y^o, s_z^o be the direction cosines for the specular direction and $\xi(x, y)$ be the elevation of the surface at any point x, y.

Then the intensity in any direction (s_x, s_y, s_z) is

$$I(v)=(E\Gamma/\lambda^2)\iint e_x^{iv}(x_1-x_2)e_y^{iv}(y_1-y_2)e_z^{iv}[\xi(x_1, y_1)-\xi(x_2, y_2)]dxdy$$

where

$$x=x_1-x_2$$

$$y=y_1-y_2$$

(x_1, y_1), (x_2, y_2) being points in the x, y plane.

with

E=Total energy incident on the surface.

$\lambda=2\pi/k_0$=wavelength of light

and

$$\nu=k_0(s-s_0)$$

Γ=Reflection coefficient of the surface

We know $(\xi_1-\xi_2)$ to be a zero mean random variable, whose distribution is Gaussian. Then it can be shown,

$$\langle e_z^{iv}(\xi_1-\xi_2)\rangle=e_z^{-v^2}\langle\xi_1-\xi_2)^2\rangle/2 \tag{6}$$

where $\langle(\xi_1-\xi_2)^2\rangle$ is the average over all possible realisations of the interface.

The integral in (1) is therefore,

$$I(v_x, v_y)=(E\Gamma/\lambda^2)\iint e_x^{iv}(x_1-x_2).e_y^{iv}(y_1-y_2).e_z^{-v^2}\langle(\xi_1-\xi_2)^2\rangle/2\ dxdy \tag{7}$$

We now Fourier analyse,

$$\xi(x, y)=\sum\tilde{\xi}(p, q)e^{i(px+qy)} \tag{8}$$

Now, the displacement $\xi(x, y)$ being real, we must have

$$\xi^*(p, q)=\xi(-p, -q) \tag{9}$$

Also, we consider the Fourier components to be correlated as,

$$\langle\xi(p', q')\tilde{\xi}^*(p, q)\rangle=\langle|\xi(p, q)|^2\rangle\,\delta(p-p')\delta(q-q') \tag{10}$$

Using (8) to (10) one obtains,

$$\langle|\xi_1-\xi_2|^2\rangle=\sum_{p, q}\langle|\xi(p, q)|^2\rangle\sin^2\{p(x_1-x_2)+q(y_1-y_2)\} \tag{11}$$

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To evaluate $I(v_x, v_y)$ (Landau and Lifshitz 1959) we must now evaluate $\langle |\xi_1-\xi_2|^2 \rangle$.

From (11), we first calculate the thermal average for $\langle |\xi(p, q)|^2 \rangle$, for the capillary waves which we now proceed to do.

2b. Calculation of thermal averages $\langle |\tilde{\phi}(p, q)|^2 \rangle$:

To calculate the thermal averages $\langle |\xi(p, q)|^2 \rangle$ we first obtain the expression for the energy of the capillary waves.

Let us assume that a displacement $\xi(\boldsymbol{r}, t)=\xi(\boldsymbol{k}, t) \cos(\boldsymbol{k}.\boldsymbol{r})$ be created at any point $\boldsymbol{r}=(x, y)$ on the interface, located at $z=1$. We know that the velocity potential for the flow of the fluid, at any height z, is given by (Landau and Lifshitz 1959),

$$\phi=\phi(k, T) \cosh kz \tag{12}$$

$$\phi_z=v_z=k\phi(k, t) \sinh kz \tag{13}$$

Now the z-component of the velocity at the surface is given by

$$\phi_z(l)=\phi(k, T)k \sinh kl=\partial\xi(k, t)/\partial t \tag{14}$$

$$\phi(k, t)=\xi(k, t)/(k \sinh kl) \tag{15}$$

$$v_z=k(1/k \sinh kl)) \sinh (kz)\xi(k,t) \tag{16}$$

The kinetic energy is then given by,

$$\int_0^1 (\rho/2).v_z^2 \, dxdydz=(1/4)A\rho\dot{\xi}^2(k, t)/(k\tanh kl) \tag{17}$$

A being the area of the surface.

Potential energy has a contribution both from the buoyancy term and the surface tension term.

The contribution to the potential energy from the buoyancy term is the well known gravitational energy.

$$(P.E.)_B=(1/2)g\Delta\rho\iint |\xi(k, t)|^2dxdy \tag{18}$$

The contribution from the surface tension term is calculated from the product of the increase in surface area and surface tension.

The surface area at any instant is given by,

$$\iint_{xy} dxdy(1+\xi_x^2+\xi_y^2)^{1/2} \tag{19}$$

The change in area,

$$\iint dxdy(1/2)(\xi_x^2+\xi_y^2) \tag{20}$$

on substituting and simplifying yields,

$$(1/2)\iint(\xi_x^2+\xi_y^2)dx\,dy=A/2\sum_{k_x,k_y}(k_x^2+k_y^2)\tilde{\xi}(k_x,k_y)\hat{\xi}(-k_x,-k_y) \qquad (21)$$

Thus the surface energy is,

$$(A/2)\sigma\sum(k_x^2+k_y^2)\mid\tilde{\xi}(k_x,k_y)\mid^2 \qquad (22)$$

The total energy of the system is given by adding the terms in (17), (18) and (22), which gives us,

$$H=A\sum\{1/2(g\Delta\rho+\sigma k^2)\mid\xi(k)\mid^2+(\rho/(k\tanh kl))\mid\dot{\xi}(k)\mid^2 \qquad (23)$$

Comparing (23) with the expression for the energy of a simple harmonic oscillator and from the theorem of equipartition of energy, for a simple harmonic oscillator, we find the dispersion relation to be

$$\omega^2(k)=(1/\rho)(g\Delta\rho+\sigma k^2)kth(kl) \qquad (23a)$$

$$\langle K.E.\rangle=\langle P.E.\rangle=K_BT/2 \qquad (24)$$

we have,

$$A\langle\mid\xi(k)\mid^2\rangle=(K_BT/2)(g\Delta\rho+\sigma k^2) \qquad (25)$$

2c. $I(v_x, v_y)$ for capillary waves :

The quantities $\langle\mid\xi(k)\mid^2\rangle$ being known, we now substitute (25) in (11) to get

$$\langle\mid\xi_1-\xi_2\mid^2\rangle=(k_BT/8\Gamma(2))(1/\sigma)[K_{max}^2/2-(g\Delta\rho/2\sigma\ \ln(g\Delta\rho+\sigma K_{max}^2))]R^2 \qquad (26)$$

With $R^2=(X_1-X_2)^2+(Y_1-Y_2)^2$ and K_{max} being an upper cut off wave vector for the capillary waves. As can be seen from (26), the quantity $\langle(\xi_1-\xi_2)\rangle^2$ is not determined by the height of the interface.

Thus we have from (26),

$$\exp(-v_z^2\langle(\xi_1-\xi_2)^2\rangle/2)=\exp(-v_z^2a^2R^2/2)$$

where

$$a^2=(K_BT/8\Gamma(2))(1/\sigma)[K_{max}^2-(g\Delta\rho/2\sigma)\ln((g\Delta\rho+\sigma K_{max}^2)/)] \qquad (26.1)$$

Thus, the integral in (7) can be easily written as,

$$I(v_x,v_y)=(A2\pi/a^2)\exp(-(v_x^2+v_y^2)/2v_z^2a^2) \qquad (27)$$

The Gaussian nature of (27) shows that the intensity is maximum along the specular direction and the intensity is broadened to a patch of size

$$\langle v_x^2+v_y^2\rangle=2v_z^2a^2 \qquad (28)$$

or to an angle θ around the specular direction, such that

$$\langle \sin^2\theta \rangle = 2k^2a^2/k^2 = 2a^2 \tag{29}$$

It is seen that a^2 is independent of the wavelength of light. This conclusion is infact a result of the approximation $\langle (\xi_1-\xi_2)^2 \rangle \sim R^2$ which always arises in the low R limit. However, for $R \to \infty$, $\langle (\xi_1-\xi_2)^2 \rangle \to$ constant and this should give rise to a k dependence in a^2.

Thus if F is the distance from the source to the screen, the size of the patch δX is given by,

$$\langle |\delta X|^2 \rangle = f^2 \langle \sin^2\theta \rangle = 2a^2f^2 \tag{30}$$

from the expression for a^2,

$$a^2 \approx 1/\sigma \approx 1/t^{1\cdot 3} \tag{31}$$

the size of the patch should scale as $1/t^{1\cdot 3}$ which should be the result expected from this static experiment, where a broad beam of light is focussed on the wetting interface. As mentioned in the introduction, the average intensity profile obtained above contains average over all realisations of the interface and hence has no information about the dynamics.

2d. Light scattering by capillary waves : dynamic experiment :

To obtain information about the dispersion relation of the capillary waves, a dynamic experiment is required. If we note the temporal rate of change $\dot{I}(t)$ we shall be studying the behaviour of $\dot{\xi}(x, y)$. This explicitly involves the dispersion relation as we show below.

Differentiating eq. (2) with respect to time,

$$\dot{I}(\dot{x}, y) = (E/\lambda^2) \iint e_x^{iv}(x_1-x_2).e_y^{iv}(y_1-y_2)_z^{iv}(\dot{\xi}_1-\dot{\xi}_2)e_z^{iv}(\xi_1-\xi_2)dxdy \tag{32}$$

We consider the case along the specular direction i.e, $v_x = v_y = 0$. This gives,

$$\dot{I}(0, 0) = (E\Gamma/\lambda^2)\, i \iint v_z(\dot{\xi}_1-\dot{\xi}^2)e_z^{iv}(\xi_1-\xi_2)dxdy \tag{33}$$

The integrand in (33) is a zero mean random variable, so that $\langle \dot{I}(0,0) \rangle = 0$. However, the quantity $\langle \dot{I}(0, 0)^2 \rangle$ can be easily estimated as follows.

We have seen from (26 and 26.1) the quantity in the exponent correlated within $R \leqslant r_0$ such that

$$(1/2)v_z^2a^2r_0^2 = 1$$

or

$$r_0^2 = 2/(v_z^2a^2) \tag{34}$$

Thus, over a blob of radius r_0, we have

$$\iint [(\dot{\xi}_1-\dot{\xi}_2)]dxdy \sim [\dot{\xi}_x(x_1-x_2)+\dot{\xi}_y(y_1-y_2)]r_0^2 \tag{35}$$

where $\dot{\xi}_x$ and $\dot{\xi}_y$ are also random variables, correlated within the blob.

Thus for every blob,

$$\langle [\iint_{r0} [(\dot{\xi}_1-\dot{\xi}_2)]dxdy]^2 \rangle \sim [\langle \dot{\xi}_x^2 \rangle + \langle \dot{\xi}_y^2 \rangle]\, r_0^6 \equiv \alpha^2 \tag{36}$$

The interface has $N \sim A/r_0^2$ blobs. Hence from the law of large numbers,

$$\begin{aligned}\langle [\dot{I}(0,0)]^2 \rangle &= (E\Gamma/\lambda^2)^2 v_z^2 N\alpha^2 \\ &= (E\Gamma/\lambda^2)^2 v_z^2 (A/r_0^2)[\langle \dot{\xi}_x^2 \rangle + \langle \dot{\xi}_y^2 \rangle] r_0^6 \\ &= (E\Gamma/\lambda^2)^2 v_z^2 A \langle \dot{\xi}_r^2 \rangle\, r_0^4 \\ &= 4(E\Gamma/\lambda^2)^2 A \langle \dot{\xi}_r^2 \rangle / (v_z^2 a^4)\end{aligned} \tag{37}$$

Now

$$\langle \dot{\xi}_r^2 \rangle = \langle \dot{\xi}_x^2 \rangle + \langle \dot{\xi}_y^2 \rangle = \sum_k k^2\omega^2(k) \langle |\xi(k)|^2 \rangle$$

which from (25) reads

$$=(k_B T/\rho)\int_0^{k_{max}} k^4 th kl dk \tag{38}$$

For $k_{max} l \ll 1$ one finds

$$\langle \dot{\xi}_r^2 \rangle \sim (k_B T/\rho)(k_{max}^6\, l)/6 \tag{39}$$

i.e, it follows l, increasing as t increases,

while for $k_{max} l \gg 1$ we have $t < (d_0/k)^{1/2}$

$$\langle \dot{\xi}_r^2 \rangle = (k_B T/\rho)(1/5)[k_m^5 - (1/l^5 \int_0^\infty x^5 \operatorname{sech}^2 x dx)] \tag{40}$$

i.e. there is a slow rise as l increases or as t increases.

Equation (37) shows that $\langle \dot{I}^2 \rangle \propto A$. Also $\langle I \rangle \propto A$. Hence for effective detection of $\langle \dot{I}^2 \rangle$ in the background of $\langle I \rangle$ one must have the ratio $\langle \dot{I}^2 \rangle / \langle I \rangle^2$ large i.e. the size of the light beam must be small.

3. Effect due to finite thickness of the interface

The total dependence of $\langle \dot{I}^2 \rangle$ also contains the reflectivity of the interface. In this respect, the model of the interfacial thickness is necessary, to ascertain the reflectivity of the interface. We consider here the dielectric constant to vary according to the Epstein model (Epstein 1930)

$$\epsilon(z)=(\epsilon_1+\epsilon_2)/2+[(\epsilon_1-\epsilon_2)/2]\ th\ (z/d) \tag{41}$$

where $2d$ is the intefacial thickness. It is immediately seen that $\epsilon(z) \to \epsilon_1$ as $z \to \infty$ and $\epsilon(z) \to \epsilon_2$ as $z \to -\infty$. The reflectivity in such a case is given by (8),

$$\Gamma=[sh(\pi kd(n_1-n_2)/2)/sh(\pi kd(n_1+n_2)/2)]^2 \tag{42}$$

It is seen that for $\pi kd/2 \ll l$, Γ is approximated as,

$$\Gamma=(n_1-n_2/n_1+n_2)^2$$
$$\sim \Gamma_0^2 t^{2\beta} \tag{43}$$

being decided by the difference of the refractive indices and being insensitive to the interfacial thickness.

For $\pi kd/2 \gg 1$, on the other hand, the reflectivity follows,

$$\Gamma=\exp\ [-\pi kd(n_1+n_2)] \tag{44}$$

being insensitive to the refractive index differences, but following the interfacial thickness.

Now we know, $d \sim d_0 t^{-1/2}$ which means that with decreasing t, the reflectivity follows a decay,

$$\Gamma \sim \exp\ (-d_0 t^{-1/2}/\lambda). \tag{45}$$

The magnitude of $\langle \dot{l}^2 \rangle$ thus depends crucially upon the quantity $k_m l$. For all practical purposes one must have $k_m \ll l/d$ or $k_m l \ll 1/d \ll 1$, in order that an interface can be defined. Hence equation (40) is the valid equation for all ranges. Also if one performs experiments at $t > 10^{-6}$, in the visible range, one finds conditions proper for the application of eq. (43).

Thus, in these cases, retaining only the t-dependent terms, one has,

$$\langle [\dot{l}(0,0)]^2 \rangle/A \propto t^{2\beta} t^{2\mu} [k_m^5-(1/l^5)\int_0^\infty x^5\ \text{sech}^2 x dx] \tag{46}$$

where $\beta \sim 0.33$, $\mu \sim 1.33$, $k_m \sim t^{1/2}$ and $l \sim 0.66$.

Thus the first two factors in (44) give $t^{2(\beta+\mu)} \sim t^{3\cdot 32}$, on inserting the factor $[\cdots]$ in (44) one finds $\langle \dot{l}(0,0)]^2 \rangle$ to fall faster than $t^{3\cdot 32}$ as T_c is approached, owing to the faster variation of l^{-5} term $(\sim t^{-3\cdot 3})$ that k_m^5 $(\sim t^3)$ as $t \to 0$. Thus as the two terms become comparable $\langle \dot{l}(0,0)^2 \rangle$ would abruptly vanish.

4. Conclusion

The motivation of the present paper is to explore the possibility of direct observation of capillary waves in the interface of wetting layers. Their existence can be easily 'seen' in the scattering of light by the interface of the wetting layers. In absence of the distortion of the interface, one would obtain a perfectly specular reflection, maintaining the angle of incidence equal to the angle of reflection. The capillary wave distortions, would cause departures from this specular condition. In contrast, the scattered beam would be seen to arrive at angle θ, with respect to the specular direction where $\langle \theta \rangle = 0$ and $\langle \theta^2 \rangle = t^{-1}$. This scaling is seen to be determined by the scaling laws of the surface tension $\sigma \approx t^{1.88}$ and $\Delta\rho \approx t^{0.88}$, being independent of the layer thickness. The dynamic experiment involving the measurement of $\langle i^2 \rangle$ is seen to be strongly t dependent as given by equations (38) and (40). A combination of these two simple experiments would unmistakably establish the importance of capillary waves in determining the stability of wetting layers.

Recently, Dieterich and Schack (1987) have considered a case where the interface is of mesoscopic nature i.e., the interface cannot be considered by a well defined thickness and studied the case of specular reflection. The interplay of capillary and the mesoscopic interfaces in reflectivity of surfaces promises to be one of rich prospects.

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