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Wetting of a binary liquid mixture on glass

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When two fluids coexist above a substrate, a thin layer of the upper fluid often intrudes between the lower fluid and the substrate. For such intruding layers to be stable against gravity, it is necessary that the short- and long-range interactions between the substrate and the two fluid phases both favor the presence of the upper phase near the substrate. We consider the consequences of this for the carefully studied case of partially miscible mixtures of nitromethane and carbon disulfide in contact with borosilicate glass. A careful calculation based on the Dzyaloshinskii-Lifshitz-Pitaevskii theory of dispersion forces shows that dispersion forces do not favor the formation of the nitromethane-rich layer that has been observed to intrude between the carbon disulfide–rich phase and the glass. If the observed layers are an equilibrium phenomenon, their existence requires a protagonist force stronger than dispersion forces. It is plausible that electrostatic forces which arise from ionization of the glass surface are the required long-range force.

I. INTRODUCTION

Wu, Schlossman, and Franck[1] have studied wetting in binary liquid mixtures of nitromethane plus carbon disulfide in contact with borosilicate glass (BK-7).[2] When the two components are partially miscible, a carbon disulfide-rich phase (c) coexists with a nitromethane-rich phase (n) at a height L above the glass (g) (see Fig. 1). For L on the order of 1 cm, Wu *et al.* measured the thicknesses of gravity-thinned wetting layers of phase n that were observed to intrude between phase c and the glass. It was found that the wetting layer thickness d was sensibly constant for T a few degrees or more below the consolute temperature of the c and n phases ($T_c \simeq 335$ K). This constant value of d varied from 400 to 600 nm in ostensibly identical experiments. A novel aspect of the experiments was that the system was stirred continuously by a glass-encapsulated magnetic mixer that was suspended at the n-vapor interface and spanned phase n. The stirring was sufficiently gentle (stirring rates on the order of 1 Hz) that the c-n interface waved but did not break up.[1] A goal of the present paper is to understand the very thick wetting layers of phase n that were observed to form two or more degrees below the consolute point of the mixture.

The equilibrium thickness of a wetting layer, $d(L)$, is often, but not always,[3] determined by a competition between gravity and dispersion forces. If the observed wetting layers of phase n are stabilized by dispersion forces alone, $d(L)$ should be given by

$$F(d)+\Delta\rho g L = 0\ , \qquad (1)$$

where $F(d)$ is the dispersion-force term, $\Delta\rho=\rho_c-\rho_n$ is the mass density difference between the c and n phases, and g is the acceleration due to gravity. $F(d)$ is the force acting per unit area on each of the two semi-infinite phases, g and c, when they are separated by a gap of width d occupied by phase n. By convention, positive values of F correspond to attraction between the two half spaces and negative values to repulsion. $F(d)$ is often given in the generic form

$$F(d)=A/d^3\ , \qquad (2)$$

where $6\pi A$ is the materials-dependent Hamaker constant.[4] Repulsive forces ($A<0$) are required for stable wetting layers.

Equation (2) is often used with a microscopic prescription for A,[5,6] but it is not quantitative compared to the definitive theory developed by Dzyaloshinskii, Lifshitz, and Pitaevskii[7] (DLP). The DLP theory includes nonadditivity of intermolecular forces and retardation effects, and it gives an expression for $F(d)$ in terms of the absorption spectra of the bulk phases. The theory ignores the short-range structure near phase boundaries, but this

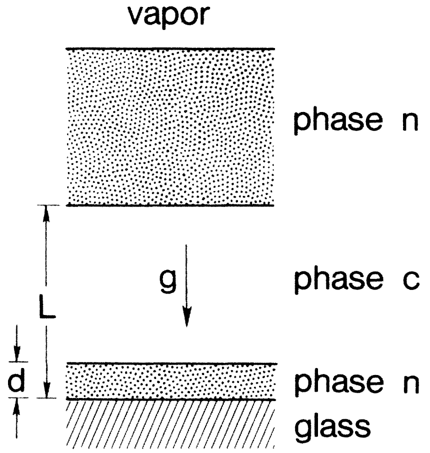

FIG. 1. A binary liquid mixture in contact with a solid substrate near the miscibility gap of the mixture. In the experiments of Wu *et al.* (Ref. 1), the mixture was nitromethane plus carbon disulfide and the substrate was borosilicate glass. Thick wetting layers of the nitromethane-rich phase (n) were observed to intrude between the denser carbon disulfide–rich phase (c) and the glass (g).

causes a negligible error when the correlation lengths in the bulk materials are much smaller than d. The ratio of the correlation length to d is very small in the g-n-c system for the thick wetting layers observed far from T_c. A "slab model" is therefore entirely appropriate. The form of $F(d)$ in the DLP theory is discussed below.

Described herein are attempts to calculate the equilibrium wetting layer thickness $d(L)$ in the context of the DLP theory. The calculations lead to a surprising result: $F(d)$ in Eq. (1) is *positive* for all values of d and T. This means that dispersion forces act in a direction to *destabilize* wetting layers of the nitromethane-rich phase. Without another stabilizing mechanism the layer thickness would decrease to a value on the order of a correlation length, in contrast to what is observed.

If the observed wetting layers are an equilibrium phenomenon, they must be stabilized by a long-range force other than dispersion forces. Electrostatic forces resulting from ionization of the glass surface are one possibility. Forces arising from impurities are perhaps another. It has already been shown[8] that electrostatic forces combined with the effects of continuous stirring[9] can lead to wetting layers as thick as those observed. The calculations presented here provide further motivation for the study of long-range forces other than dispersion forces.

The DLP theory applies in the case of arbitrary media, 1, 2, and 3, corresponding to g, c, and n above, respectively. $F(d)$ is in general given by[7]

$$F(d)=(k_BT/\pi c^3)\sum_{j=0}^{\infty}{}' \epsilon_3^{3/2}\xi_j^3 \int_1^{\infty} p^2dp\{[f_1(1)f_2(1)\exp(2p\xi_j\epsilon_3^{1/2}d/c)-1]^{-1} + [f_1(\epsilon_1/\epsilon_3)f_2(\epsilon_2/\epsilon_3)\exp(2p\xi_j\epsilon_3^{1/2}d/c)-1]^{-1}\}\ , \tag{3}$$

where

$$f_i(x)=(s_i+px)/(s_i-px)\ ,$$

and

$$s_i=(\epsilon_i/\epsilon_3-1+p^2)^{1/2},\quad i=1,2\ .$$

The quantity k_B is Boltzmann's constant, c is the speed of light, $\xi_j=2\pi jk_BT/\hbar$, $2\pi\hbar$ is Planck's constant, and ϵ_1, ϵ_2, and ϵ_3 are the frequency-dependent dielectric constants of the three media evaluated at the imaginary frequencies $\omega=i\xi_j$: $\epsilon\equiv\epsilon(i\xi_j)$. The prime attached to the summation sign denotes that the term with $j=0$ is to be given half weight. Note that $F(d)$ can be calculated exactly if the inputs $\epsilon(i\xi_j)$ are known. As these are related to the absorption spectra of the bulk phases, the DLP theory enables one in principle to evaluate $F(d)$ without adjustable parameters. Expressions for $F(d)$ in limiting cases have been given by DLP.[7]

To calculate $F(d)$ for the g-n-c system one needs to model the quantities $\epsilon(i\xi)$ for the g, c, and n phases using optical properties data. The data required to use the DLP theory almost never exist in practice and one must resort to models. A secondary goal of the present paper is to apply the DLP theory systematically in a concrete case. It is hoped that this will facilitate the application of the theory in future work. The relevant data and models are presented in Sec. II, results for $F(d)$ as a function of d and T are presented in Sec. III, and conclusions follow in Sec. IV.

II. MODELS FOR $\epsilon(i\xi)$

The function $\epsilon(i\xi)$ for a given material is often represented in the Ninham-Parsegian form,[10]

$$\epsilon(i\xi)=1+\sum_{i=1}^{N} C_i/[1+(\xi/\omega_i)^2]\ , \tag{4}$$

where the ω_i are absorption frequencies and $\pi\omega_iC_i/2$ are oscillator strengths. The C_i must satisfy

$$\epsilon(0)=1+\sum_{i=1}^{N} C_i\ , \tag{5}$$

which is a sum rule. A lucid discussion of $\epsilon(i\xi)$ and a derivation of Eq. (4) have been given by Hough and White.[11] When the relaxation frequencies ω_i are widely spaced, $\epsilon(i\xi)$ between absorptions (or bands of absorptions) is nearly constant and coincident with $\epsilon'(\xi)$, the real part of the complex dielectric constant. One often writes

$$\epsilon(i\xi)=1+\sum_{i=1}^{N}[\epsilon'(\omega_i^-)-\epsilon'(\omega_i^+)]/[1+(\xi/\omega_i)^2]\ , \tag{6}$$

where $\epsilon'(\omega_i^-)$ and $\epsilon'(\omega_i^+)$ are the constant values of $\epsilon(i\xi)$ for ξ far below and above ω_i, respectively. This enables one to partition the sum into contributions from the ultraviolet (uv), infrared (ir), and microwave (mw) regions of the electromagnetic spectrum. In regions of no absorption $\epsilon'(\xi)$ equals $n^2(\xi)$, where $n(\xi)$ is the frequency-dependent refractive index. In the context of Eq. (4), $\epsilon'(\xi)$ is in general given by[11]

$$\epsilon'(\xi)=1+\sum_{i=1}^{N} C_i/[1-(\xi/\omega_i)^2]\ . \tag{7}$$

This relation is needed below.

The functions $\epsilon(i\xi)$ in Eq. (3) are required at evenly spaced frequencies $\xi_j=j\Delta\xi$, where $\Delta\xi=2\pi k_BT/\hbar$. Near room temperature $\Delta\xi$ is about 3×10^{14} rad/s, which is a frequency in the infrared region of the spectrum. Thus, the first ten terms in the sum on j cover the frequency range from zero frequency up to visible frequencies. The major contributions to F for a given value of d occur for $\xi_j \lesssim c/d$. For thin films ($d \lesssim 5$ nm), $F(d)$ is usually dominated by contributions from the ultraviolet region of the spectrum; exceptions occur only when the uv responses of media 2 and 3 are sufficiently similar. In contrast, absorptions at ir and zero frequency matter when films are very thick. One would expect the low-frequency absorptions in the g-c-n system to make substantial contributions to $F(d)$ for the large values of d (500 nm) that are observed.

The simplest way to model the optical properties of the mixture phases c and n is to use the Clausius-Mossotti (CM) relation. For a homogeneous mixture of A and B molecules, the CM relation states that

$$f(\epsilon(i\xi))=4\pi[n_A\alpha_A(i\xi)+n_B\alpha_B(i\xi)]\ , \tag{8}$$

where

$$f(x)=(x-1)/(x+2)\ . \tag{9}$$

The function $f(x)$ is the CM function, n_A and n_B are the number densities of the A and B molecules in the mixture, and α_A and α_B are their frequency-dependent polarizabilities. It is more convenient to express the composition of the mixture in terms of the volume fraction of component A, $\phi\equiv V_A/(V_A+V_B)$, where V_A and V_B are the volumes of the A and B phases at the temperature of the measurement before mixing. The volume after mixing is denoted by V_{A+B}, and V_{A+B} is not in general equal to V_A+V_B. In terms of volume fractions Eq. (8) becomes

$$f(\epsilon(i\xi))=\Omega[\phi f(\epsilon_A(i\xi))+(1-\phi)f(\epsilon_B(i\xi))]\ , \tag{10}$$

where

$$\Omega=(V_A+V_B)/V_{A+B}\ . \tag{11}$$

The phases g, c, and n will be identified, as before, with media 1, 2, and 3, respectively. Similarly, pure liquid carbon disulfide and pure liquid nitromethane will be referred to as A and B. Thus, $\epsilon_2(i\xi)$ and $\epsilon_3(i\xi)$ are given by

$$\begin{aligned} f(\epsilon_i(i\xi))=\Omega_i[\phi_i f(\epsilon_A(i\xi)) \\ +(1-\phi_i)f(\epsilon_B(i\xi))],\quad i=2,3\ , \end{aligned} \tag{12}$$

where ϕ_i is the volume fraction of carbon disulfide in phase i.

The following data are needed to calculate $F(d)$: ϕ_i, Ω_i, $\epsilon_1(i\xi)$, $\epsilon_A(i\xi)$, and $\epsilon_B(i\xi)$. For the coexistence curve of the c and n phases near their consolute point one has

$$T_c=335.143\ \mathrm{K}\ , \tag{13}$$

$$\phi_c=0.601\ , \tag{14}$$

$$t=(T-T_c)/T_c\ , \tag{15}$$

$$(\phi_2+\phi_3)/2=\phi_c-0.0014(T_c-T)\ \mathrm{K}^{-1}\ , \tag{16}$$

$$\phi_2-\phi_3=(-t)^{\beta}[1.63+0.77(-t)^{1/2}-2.43(-t)]\ , \tag{17}$$

$$\beta=0.325\ . \tag{18}$$

Equations (13), (14), and (16) are from the work of Gopal *et al.*,[12] and Eq. (17) is from Greer's analysis[13] of the Gopal data. Greer's result for the exponent β (0.315 ± 0.008) has been replaced for simplicity by the currently accepted theoretical value.[14] The raw data of Gopal *et al.* is tabulated in Ref. 15.

The volume factors Ω_i are determined by requiring consistency between the Lorenz-Lorentz (LL) relation and optical data at visible wavelengths. The LL relation is obtained by replacing $\epsilon(i\xi)$ in Eq. (12) by $\epsilon'(\xi)\simeq n^2(\xi)$. The following data at $\lambda_0=632.8$ nm ($\omega_0=2.977\times10^{15}$ rad/s) are used:

$$n_{2,3}(\omega_0)=[(1.485\,39)^2\pm0.75\times1.64\times0.5(-t)^{\beta}]^{1/2}\ , \tag{19}$$

$$n_A(\omega_0)=1.592\,38+6.70\times10^{-4}(T_c-T)\ \mathrm{K}^{-1}\ , \tag{20}$$

$$n_B(\omega_0)=1.361\,68+4.50\times10^{-4}(T_c-T)\ \mathrm{K}^{-1}\ . \tag{21}$$

The upper and lower signs in Eq. (19) correspond to phases 2 and 3, respectively. Equation (19) is the result of Wu *et al.*[1] and Eqs. (20) and (21) are obtained by interpolation in Table I. With the exception of dn/dT for nitromethane,[16] the measurements in Table I were made by Malitson.[17] When these results are used in Eq. (12) one obtains

$$\Omega_{2,3}=0.983\pm0.036(-t)^{\beta}\ , \tag{22}$$

which is correct to order $(-t)^{\beta}$. The relative volume change on mixing is therefore positive and on the order of 2%. The temperature corrections in Eqs. (20) and (21) do not contribute to $\Omega_{2,3}$ to order $(-t)^{\beta}$. These corrections are small for T near T_c and are ignored from this point onward.

With little extra effort one can estimate the mass density at the consolute point (ρ_c), and the mass density difference ($\Delta\rho=\rho_2-\rho_3$) to order $(-t)^{\beta}$. The mass density of phase i is related to Ω_i by $\rho_i=\Omega_i[\phi_i\rho_A+(1-\phi_i)\rho_B]$, where ρ_A and ρ_B are the mass densities of the pure phases. With the values[18,16] $\rho_A=1.200$ g/cm^3, $\rho_B=1.078$ g/cm^3 for $T=T_c$, one finds

$$\rho_c=1.131\ \mathrm{g/cm^3}\ , \tag{23}$$

$$\Delta\rho=0.278(-t)^{\beta}\ \mathrm{g/cm^3}\ . \tag{24}$$

The density difference appears in Eq. (1) for the equilibrium thickness of a wetting layer.

With the CM relation, the functions $\epsilon(i\xi)$ need to be modelled only for glass and the two pure liquids. Consistent with Eq. (4), each function can be written in the form

$$\begin{aligned} \epsilon(i\xi)=1+(\epsilon_{\mathrm{vis}}-1)/[1+(\xi/\omega_{\mathrm{uv}})^2] \\ +(\epsilon_{0+}-\epsilon_{\mathrm{vis}})/[1+(\xi/\omega_{\mathrm{ir}})^2]\ , \end{aligned} \tag{25}$$

where ω_{uv} and ω_{ir} characterize the important absorptions in the uv and ir, and $\epsilon_{\mathrm{vis}}-1$ is an as yet undetermined weight. The interpretation of ϵ_{0+} depends on whether or

TABLE I. Index of refraction data for pure liquid carbon disulfide and pure liquid nitromethane as a function of wavelength at 25.1 °C. The index measurements were performed by Malitson. The index values are accurate within 3×10^{-5}.

λ (μm)	Source	$n(\mathrm{CS_2})$	$n(\mathrm{CH_3NO_2})$
0.4047	Hg	1.688 86	1.395 87
0.4358	Hg	1.669 37	1.391 38
0.4800	Cd	1.650 09	1.386 78
0.5461	Hg	1.631 57	1.382 10
0.5876	He	1.623 61	1.380 01
0.6438	Cd	1.615 48	1.377 85
0.7065	He	1.608 93	1.376 05
$-10^4(dn/dT)$ K		6.7	4.5

TABLE II. Parameters in Eq. (25) used to model $\epsilon(i\xi)$ for glass, pure liquid carbon disulfide, and pure liquid nitromethane.

Material	$\epsilon(0)$	ϵ_{0+}	ϵ_{vis}	$\omega_{\text{ir}}\times 10^{-14}$ (rad/s)	$\omega_{\text{uv}}\times 10^{-16}$ (rad/s)
borosilicate glass (BK-7)	4.8	4.8	2.28	1.9	2.0
CS_2 (liquid)	2.53	2.53	2.42	2.8	1.1
CH_3NO_2 (liquid)	33.7	5.6	1.87	3.0	1.6

not there are significant microwave absorptions. Glass and carbon disulfide exhibit negligible absorption and ϵ_{0+} can be identified with $\epsilon(0)$, the static dielectric constant [see Eq. (5)]. This is not the case for nitromethane, however, and ϵ_{0+} must be identified with the value of $\epsilon(i\xi)$ in the far-infrared region, i.e., at frequencies lower than the important infrared absorptions but higher than the microwave relaxations. The zero-frequency behavior of nitromethane has to be considered separately. Considerations of this type are always necessary when one is considering highly polar fluids.

The determination of ω_{uv} is considered first. Spectral data in the relevant frequency range [from $(1-3)\times 10^{16}$ rad/s] are not available and one must resort to models. The optimal procedure is to assume, as in Eq. (25), that there is a single frequency that characterizes the absorption of each material in the uv, and to determine this frequency by constructing a Cauchy plot.[11] This can be done when the index of refraction of a material is known as a function of frequency (wavelength) at visible frequencies. The linearity of the plot is a check on the assumptions of a single frequency and of no absorption in the visible. To construct a Cauchy plot, one first writes the analog of Eq. (25) for $\epsilon'(\xi)$ [see Eq. (7)]. Ignoring the infrared term, one has

$$\epsilon'(\xi)=1+(\epsilon_{\text{vis}}-1)/[1-(\xi/\omega_{\text{uv}})^2]\ , \tag{26}$$

which with $\epsilon'(\xi)\simeq n^2(\xi)$ can be written

$$n^2(\xi)-1=[n^2(\xi)-1](\xi^2/\omega_{\text{uv}}^2)+(\epsilon_{\text{vis}}-1)\ . \tag{27}$$

Thus, a plot of $n^2(\xi)-1$ versus $[n^2(\xi)-1]\xi^2$ at visible frequencies ($\omega_{\text{uv}}^2 \gg \xi^2 \gg \omega_{\text{ir}}^2$) should yield a straight line of slope ω_{uv}^{-2}. The infrared term does not make a significant contribution to ω_{uv}.

The values of ω_{uv} for glass and the two pure liquids as determined by Cauchy plots are given in Table II. Index of refraction data for borosilicate crown glass (BK-7) were obtained from Ref. 19, and for pure carbon disulfide and pure nitromethane from Table I. The Cauchy plots of the data at 25 °C were almost perfectly linear. The weak temperature dependence of the refractive indices is not significant in the present model and the uv frequencies are assumed to be independent of temperature.

The assumed values of ω_{ir} and ϵ_{0+} are given in Table II. The value of ω_{ir} for glass was obtained from Ref. 11 and the values for carbon disulfide and nitromethane from Ref. 20. The value of ϵ_{0+} for glass was obtained from Ref. 21 and for carbon disulfide from Ref. 22. The value of ϵ_{0+} for nitromethane was obtained by reanalyzing the dielectric dispersion data in Ref. 23 assuming a Debye form for the dispersion. All ϵ_{0+} values apply at $T=T_c$. Note that the dielectric relaxation time in nitromethane is 3×10^{-12} s, which corresponds to a frequency of about 3×10^{11} rad/s. This is 1000 times smaller than the smallest nonzero frequency needed in Eq. (3).

The values of ϵ_{vis} in Table II are calculated from ϵ_{0+}, ω_{uv}, ω_{ir}, and the requirement that Eq. (7) for $\epsilon'(\xi)\simeq n^2(\xi)$ be consistent with index of refraction data at $\omega_0=2.977\times 10^{15}$ rad/s. It is assumed that[1] $n_1(\omega_0)=1.515\,09$ and that $n_2(\omega_0)$, $n_3(\omega_0)$ are given by Eqs. (20) and (21) evaluated at $T=T_c$. The values of ϵ_{vis} are similar to the corresponding values of $n^2(\omega_0)$.

Equation (25) and the data in Table II determine $\epsilon(i\xi)$ for glass and carbon disulfide at all frequencies, and $\epsilon(i\xi)$ for nitromethane at all frequencies greater than the frequency characterizing the microwave absorption. This information in conjunction with the CM relation [Eq. (10)] is sufficient to evaluate every term in the sum in Eq. (3) except for the zero-frequency term ($j=0$). To calculate

TABLE III. The functions $\epsilon(i\xi)$ at $-t=10^{-2}$. The only frequencies needed to calculate $F(d)$ are the integral multiples of $\Delta\xi\simeq 3\times 10^{14}$ rad/s. The first column gives the approximate number of relevant frequencies in each decade of ξ.

Number of terms in sum	$\log_{10}\xi$	$\epsilon_1(i\xi)$ (glass)	$\epsilon_2(i\xi)$ (c)	$\epsilon_3(i\xi)$ (n)
1	$-\infty$	4.80	3.54	6.90
	13.0	4.79	2.93	3.81
	13.2	4.78	2.93	3.81
	13.4	4.76	2.93	3.80
	13.6	4.69	2.92	3.79
	13.8	4.55	2.91	3.75
	14.0	4.25	2.89	3.67
3	14.2	3.76	2.83	3.50
	14.4	3.19	2.72	3.20
	14.6	2.74	2.58	2.80
	14.8	2.49	2.44	2.45
	15.0	2.36	2.35	2.22
30	15.2	2.30	2.28	2.10
	15.4	2.27	2.23	2.03
	15.6	2.23	2.15	1.96
	15.8	2.16	1.99	1.85
	16.0	2.02	1.74	1.66
300	16.2	1.78	1.45	1.43
	16.4	1.50	1.23	1.23
	16.6	1.26	1.10	1.11
	16.8	1.12	1.04	1.05
	17.0	1.05	1.02	1.02

$\epsilon(i\xi)$ for phase n at zero frequency one must use the static dielectric constant of pure nitromethane instead of ϵ_{0+}, which applies at frequencies just above the microwave absorption. The value of $\epsilon(0)$ given in Table II was calculated at $T=T_c$ from Ref. 23.

Calculations of $\epsilon(i\xi)$ for glass and the coexisting c and n phases of the mixture are given in Table III for the reduced temperature $-t=10^{-2}$. Note that the relative ordering of $\epsilon_1(i\xi)$, $\epsilon_2(i\xi)$, and $\epsilon_3(i\xi)$ is different at different frequencies.

III. CALCULATIONS OF $F(d)$

The DLP form of $F(d)$ was evaluated with the inputs described in the previous section. The integrals in Eq. (3) were expressed in terms of the variable $u=1/p$ and were evaluated using Simpson's rule. The spacing was decreased until the relative absolute error in the evaluation of the integral was less than 10^{-6}. Spacings on the order of 5×10^{-4} were required. The sum was computed by adding terms until the last three terms divided by the accumulated sum were each less than 10^{-5} in magnitude. The number of terms required was on the order of 300 for $d=10$ nm but was less than 50 for $d>100$ nm.

Values of $F(d)d^3/\Delta\rho g$ at selected values of d are given in Table IV for the reduced temperatures $-t=10^{-1},10^{-2},10^{-3},10^{-4},10^{-5}$. The following features are evident: (a) $F(d)$ is *positive* for all values of d and t; (b) $F(d)d^3/\Delta\rho g$ approaches a limit for small d; (c) $F(d)d^3/\Delta\rho g$ approaches a limit for large d; (d) $F(d)d^3/\Delta\rho g$ is not in general a monotonic function of d; (e) $F(d)d^3/\Delta\rho g$ decreases monotonically with T at fixed d.

Feature (a) can be easily understood if the g, c, and n phases are first regarded as rigid macroscopic bodies. $F(d)$ is then the force per unit area on each of two half spaces, g and c, which are separated by a layer of width d consisting of phase n. The positive sign of $F(d)$ indicates (by sign convention) an attractive force between the half spaces for all separations. Such a force acting on a fluid layer of phase n in a gravitational field would cause the layer to thin to a thickness on the order of the correlation length in the fluid. Such a situation is one of adsorption rather than wetting.

Features (b), (c), and (d) have a common interpretation. When d is small, every term in the sum in Eq. (3) varies as $1/d^3$. $F(d)d^3$ therefore approaches a constant, as expected from Eq. (2). As d increases, the higher-frequency terms in the sum become retarded before the lower-frequency terms. The higher-frequency terms then vary as $1/d^4$, which causes $F(d)d^3$ to decrease. Because the relative ordering of the functions $\epsilon(i\xi)$ is different at high and low frequencies, $F(d)d^3$ can then either continue to decrease or even increase as d increases further. Finally, for large values of d all terms in the sum are retarded except for the zero-frequency term, which always varies as $1/d^3$. Thus, $F(d)d^3$ again approaches a constant.

The values of $F(d)d^3/\Delta\rho g$ for $d\geq200$ nm are dominated by the zero-frequency term. The $j=0$ term in Eq. (3) can be written in the form

$$(k_BT/16\pi d^3)\int_0^\infty x^2dx/(1+Q^{-1}e^x) = -(k_BT/8\pi d^3)Q(1+Q/8+\cdots)\,, \quad (28)$$

where

$$Q=-\frac{[\epsilon_1(0)-\epsilon_3(0)][\epsilon_3(0)-\epsilon_2(0)]}{[\epsilon_1(0)+\epsilon_3(0)][\epsilon_3(0)+\epsilon_2(0)]}\,. \quad (29)$$

This contribution is always *positive* for the assumed "*g*-*n*-*c*" ordering of the phases. The static dielectric constant of the nitromethane-rich phase simply never lies between those of glass and the carbon disulfide–rich phase.

Calculations of $F(d)$ require many judgments. It is therefore desirable to check the stability of the results to variations in the input. The input parameters are the uv and ir frequencies in Table II, and the values of $\epsilon(0)$ for glass, carbon disulfide, and nitromethane, and ϵ_{0+} for nitromethane. (Recall that the values of ϵ_{vis} are determined once these other quantities are specified.) The dielectric parameters are relatively certain compared to the frequencies and only the latter are varied here. The results of varying all frequencies independently by 10% are given in Table V for $-t=10^{-2}$. Note that in no case is the sign of $F(d)$ negative. Moreover, the variation of $F(d)d^3/\Delta\rho g$ for $d\geq200$ nm is small compared to the value computed with the data in Table II. This reflects an important fact: the zero-frequency term, which is certainly positive, dom-

TABLE IV. Calculated values of $F(d)d^3/\Delta\rho g$ at selected values of d and t. The results were obtained using the parameters in Table II.

	$[F(d)d^3/\Delta\rho g]\times10^{17}$ (cm^4)				
d (Å)	$-t=10^{-1}$	10^{-2}	10^{-3}	10^{-4}	10^{-5}
50	1.160	0.779	0.585	0.500	0.462
100	1.125	0.755	0.565	0.482	0.445
500	0.694	0.394	0.245	0.181	0.152
1000	0.510	0.255	0.130	0.0760	0.0520
2000	0.422	0.195	0.0843	0.0371	0.0159
3000	0.400	0.182	0.0757	0.0303	0.0099
4000	0.391	0.178	0.0736	0.0290	0.0090
5000	0.387	0.177	0.0732	0.0292	0.0094
10 000	0.377	0.175	0.0750	0.0324	0.0133
50 000	0.371	0.175	0.0766	0.0350	0.0163

TABLE V. Sensitivity of $F(d)d^3/\Delta\rho g$ to variations in the input frequencies in Table II. The lists of symbols are in correspondence with the frequencies (a) uv (glass), (b) uv (CS_2), (c) uv (CH_3NO_2), (d) ir (glass), (e) ir (CS_2), (f) ir (CH_3NO_2). The symbol $+$ $(-)$ represents a 10% increase (decrease) in the corresponding frequency and 0 represents no change. The extreme values are given and $-t=10^{-2}$.

	$[F(d)d^3/\Delta\rho g]\times 10^{17}$ (cm^4)															
d (Å)	Table II	min	a	b	c	d	e	f	max	a	b	c	d	e	f
500	0.394	0.324	$-$	$-$	$+$	$+$	$-$	$+$	0.471	$+$	$+$	$-$	$-$	$+$	$-$
1000	0.255	0.235	$-$	$-$	$+$	$+$	$-$	$+$	0.275	$+$	$+$	$-$	$-$	$+$	$-$
2000	0.195	0.187	$-$	$-$	$+$	$+$	$-$	0	0.207	$+$	$+$	$-$	$-$	$+$	$+$
3000	0.182	0.174	$-$	$-$	$+$	$+$	$-$	$-$	0.194	$-$	$+$	$-$	$-$	$+$	$+$
4000	0.178	0.170	$+$	$-$	$+$	$+$	$-$	$-$	0.189	$-$	$+$	$+$	$-$	$+$	$+$
5000	0.177	0.169	0	$-$	$+$	$+$	$-$	$-$	0.187	$-$	$+$	$+$	$-$	$+$	$+$

inates $F(d)d^3/\Delta\rho g$ for large values of d. Similar tests with 20% variations at $-t=10^{-2}$ and with 10% and 20% variations at $-t=10^{-4}$ likewise produced only positive values of $F(d)$. Note that 10% (20%) changes in the frequencies represent 20% (40%) variations in the relative ordering of the frequencies; this consideration overrides that of the small uncertainties in the low-frequency dielectric properties.

IV. CONCLUSIONS

Calculations of the dispersion force term in Eq. (1) have been carried out for partially miscible mixtures of nitromethane and carbon disulfide in contact with borosilicate glass. The DLP theory[7] has been used for $F(d)$ and it has been assumed that a gravity-thinned layer of the nitromethane-rich phase (n) intrudes between the denser carbon disulfide–rich phase (c) and the glass (g). This assumption is consistent with the experiments of Wu *et al.*,[1] which indicate that very thick wetting layers of phase n form when the mixture is continuously stirred. Wu *et al.* observe $d \simeq 500$ nm for $-t \gtrsim 10^{-2}$ and $L \simeq 1$ cm. If the observed layers are to be interpreted in terms of van der Waals forces, it is necessary that $F(d)$ be *negative*: otherwise Eq. (1) has no solutions with d and L both positive. The calculations presented here, however, indicate that $F(d)$ is *positive* for all values of d and t. In particular, $F(d)$ for $d \simeq 500$ nm is determined almost entirely by the zero-frequency term in Eq. (3), and it is inconceivable that the static dielectric constants of the g, c, and n phases could be sufficiently in error to reverse the sign of $F(d)$. An interpretation of the observed thicknesses in terms of van der Waals forces is therefore untenable.

If the observed wetting layers are stable, they must be stable because of the action of a long-range force. Electrostatic forces similar to those that occur in water are a natural candidate.[8] It is known from the work of Langmuir[24] that surface charges can cause very thick wetting layers of liquid water to form on glass in contact with slightly undersaturated water vapor. Moreover, such layers can be much thicker than those stabilized by dispersion forces.[25] Electrostatic forces play a role when a fluid can induce chemical groups on the surface of a substrate to dissociate, and this is determined largely by the polarity of the fluid. The large static dielectric constant of nitromethane in the g-n-c system enables phase n to induce surface dissociation to a much greater extent than phase c. With stirring, the degree of dissociation is sufficient to stabilize wetting layers of phase n that are as thick as those observed.[8] The effect of stirring is to replace the value of L in Eq. (1) by a much smaller value that depends on the stirring rate.[9]

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