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ELLIPSOMETRIC STUDY OF THE SURFACE OF SIMPLE LIQUIDS

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The coefficient of ellipticity $\bar{\rho}$ has been measured for liquid argon between 85 and 120 K and carbon tetrachloride between 20°C and 40°C. The experimental technique which is ideally suited to this measurement is described in detail. From $\bar{\rho}$ one is able to derive the thickness of the liquid–vapour interface. Theories of the liquid–vapour interface are reviewed and predictions compared with experiment. Theoretical uncertainties are emphasised.

$$\bar{\rho} = i\frac{\pi}{\lambda}\frac{\sqrt{\varepsilon_1+\varepsilon_2}}{\varepsilon_1-\varepsilon_2}\cdot\int\frac{(\varepsilon-\varepsilon_1)(\varepsilon-\varepsilon_2)}{\varepsilon}dz$$

Coefficient of Ellipticity

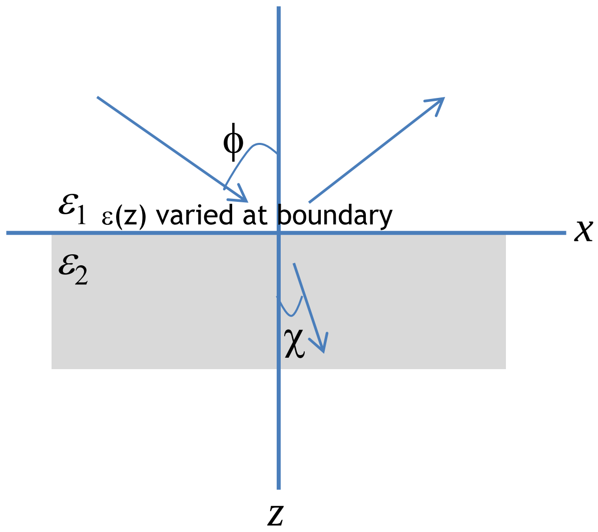
$$\left\langle \xi_w^2 \right\rangle = \frac{k_B T}{2\pi\sigma}\ln\frac{k_{\max}}{k_{\min}}$$

Surface Wave Excitation Theory
(the mean square displacement of the surface due to excitation)

Seok, Sangjun -15OCT2010-

Background – coefficient of ellipticity

$r_p / r_s = \tan \Psi e^{i\Delta}$



In plane wave

$$u = R_{s,p} \cos[(k \cdot r - \omega t) + \delta]$$

u is the part of the complex quantity

$$u = R_{s,p} e^{i[(k \cdot r - \omega t) + \delta]}$$

Writing now

$$u = R_{s,p} e^{i\delta} = \mathrm{R}_{\mathrm{S,P}}$$

Proportional to the thickness “l”

⋮ I will be replaced by the complex amplitudes

$$\frac{\mathrm{R_P}}{\mathrm{E_P}} = \frac{\cos\phi\sqrt{\varepsilon_2} - \cos\chi\sqrt{\varepsilon_1}}{\cos\phi\sqrt{\varepsilon_2} + \cos\chi\sqrt{\varepsilon_1}} \left\{ \mathrm{I} + i\frac{4\pi}{\lambda}\cos\phi\sqrt{\varepsilon_1}\frac{-p\cos^2\chi - l\varepsilon_2^2\sin^2\chi}{\varepsilon_2\cos^2\phi - \varepsilon_1\cos^2\chi} \right\} \ldots 1$$

$$\frac{\mathrm{R_S}}{\mathrm{E_S}} = \frac{\cos\phi\sqrt{\varepsilon_1} - \cos\chi\sqrt{\varepsilon_2}}{\cos\phi\sqrt{\varepsilon_1} + \cos\chi\sqrt{\varepsilon_2}} \left\{ \mathrm{I} + i\frac{4\pi}{\lambda}\cos\phi\sqrt{\varepsilon_1}\frac{l\varepsilon_2 - p}{\varepsilon_1\cos^2\phi - \varepsilon_2\cos^2\chi} \right\} \ldots 2$$

Incidence light is plane-polarized at 45° and the Brewster angle

Snell’s law

$$\sqrt{\varepsilon_1}\sin\phi = \sqrt{\varepsilon_2}\sin\chi$$

For from this it follows that

$$\varepsilon_1\cos^2\phi - \varepsilon_2\cos^2\chi = \varepsilon_1 - \varepsilon_2$$

$$\varepsilon_2\cos^2\phi - \varepsilon_1\cos^2\chi = \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_2}(\varepsilon_1\sin^2\phi - \varepsilon_2\cos^2\phi)$$

$$\frac{\mathrm{R_P}}{\mathrm{R_S}} = -\frac{\cos(\phi+\chi)}{\cos(\phi-\chi)} \left\{ \mathrm{I} + i\frac{4\pi}{\lambda}\frac{\varepsilon_2\sqrt{\varepsilon_1}}{\varepsilon_1 - \varepsilon_2} \cdot \frac{\cos\phi\sin^2\phi}{\varepsilon_1\sin^2\phi - \varepsilon_2\cos^2\phi}\eta \right\}$$

$$\eta = p - l(\varepsilon_1 + \varepsilon_2) + q\varepsilon_1\varepsilon_2$$

At the Brewster angle

$$\frac{\mathrm{R_P}}{\mathrm{R_S}} = i\frac{\pi}{\lambda}\frac{\sqrt{\varepsilon_1 + \varepsilon_2}}{\varepsilon_1 - \varepsilon_2}\eta$$

Background – coefficient of ellipticity

$$\frac{R_P}{R_S} = i\frac{\pi}{\lambda}\frac{\sqrt{\varepsilon_1+\varepsilon_2}}{\varepsilon_1-\varepsilon_2}\eta \qquad \eta = p - l(\varepsilon_1+\varepsilon_2) + q\varepsilon_1\varepsilon_2 \qquad \int_1^2 dz = l, \int_1^2 \varepsilon dz = p, \int_1^2 \frac{1}{\varepsilon} dz = q$$

$$R_P = R_p \cdot e^{i\delta_p}, R_P = R_s \cdot e^{i\delta_s} \qquad \frac{R_P}{R_S} = \frac{R_P}{R_S} e^{i(\delta_P-\delta_s)} = \rho \cdot e^{i\Delta}$$

ρ is the amplitudes and Δ the difference in phase of the two components.

$$\bar{\rho} = i\frac{\pi}{\lambda}\frac{\sqrt{\varepsilon_1+\varepsilon_2}}{\varepsilon_1-\varepsilon_2}\eta, \ \Delta = \pi/2$$

$$\bar{\rho} = i\frac{\pi}{\lambda}\frac{\sqrt{\varepsilon_1+\varepsilon_2}}{\varepsilon_1-\varepsilon_2}\cdot\int\frac{(\varepsilon-\varepsilon_1)(\varepsilon-\varepsilon_2)}{\varepsilon}dz$$

Coefficient of ellipticity $\Rightarrow$ $\bar{\rho}_{21} = -\bar{\rho}_{12}$

Ellipsometry techniques

If the angle of incidence is set to θ_B when $\Delta=\pi/2$(by adjusting θ until Re(r)=0) then includes residual static phase shift has only a small effect on Im(r)

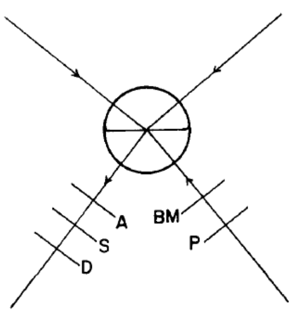


Fig. 1. The optical arrangement. Light beams reflected from the liquid–vapour and vapour–liquid surfaces are shown. P Polariser, BM birefringence modulator; A analyser; S horizontal slit; D detector.

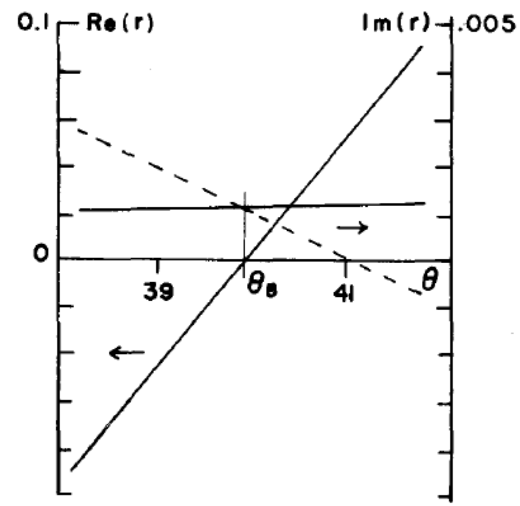


Fig. 2. Calculated θ variation of r_{12} for a uniform film (ϵ = 1.22, t = 15 Å) on a bulk medium (ϵ_2 = 1.5). The dashed line shows Im(r) when a stray Δ_1 of 0.02 rad is present. The Re(r) is not affected on this scale.

Results – Carbon tetrachloride

Table I
Summary of data for carbon tetrachloride

Constants d = 5.16 Å (45% packing fraction)

	σ (erg/cm^2)[a]	ϵ_1[b]	ϵ_2[b]	$\bar{\rho} \times 10^4/\eta$	$\eta/t(F)$ (Å^{-1})	η/t (erg Å^{-1})	η/k_{max} (Å[c])
18°C	27	1.0011	2.132	−7.77	−0.194	−0.188	−1.88
40°C	24	1.0017	2.102	−7.95	−0.186	−0.180	−2.15

Experiment

from the surface excitation theory $k_{max} = 2\pi / t$

	$\bar{\rho}_{12} \times 10^4$	$\bar{\rho}_{21} \times 10^4$	$\lvert\bar{\rho} \times 10^4\rvert_{av}$	t(F) (Å)	t(Erf) (Å)	k_{max} (Å)$^{-1}$	t_m (Å)	
18°C	11.8 ± 0.3	−12.9 ± 0.3	12.3 ± 0.3	8.2	8.5	0.85	7.4	$\bar{\rho}_{21}(40°C)/\bar{\rho}_{21}(18°C) = 1.10 \pm 0.04$

Other work

Reference	$\bar{\rho}_{12} \times 10^4$	T°C
3	8.4	Room temperature
4	12.6 ± $\frac{1}{2}$	12$\frac{1}{2}$
5	10.5 ± $\frac{1}{2}$	15–18 no T dependence to 140°C
6	17.8 ± 1$\frac{1}{2}$	20, $\bar{\rho}$ rising to 26 at 40°C

[a] International Critical Tables, vol. 4, p. 447.
[b] Interpolated from International Critical Tables, vol. 7, p. 12.
[c] Using σ experimental.

$\bar{\rho}_{21} / \bar{\rho}_{12} = 1.093 \pm 0.05$ at 18°C

This difference points to an inadequacy of the assumption of the Drude model

Space averaged density profile (error fn form)

$$\rho_{\mathrm{Erf}}(z) = \frac{\rho_l + \rho_v}{2} + \frac{\rho_l - \rho_v}{2} \mathrm{Erf}\left(\frac{z}{\sqrt{2}\xi_{\mathrm{rms}}}\right).$$

Fermi profile

$$\eta(F) = (\epsilon_2 - \epsilon_1) \ln \frac{\epsilon_1}{\epsilon_2} \delta$$

Results – Liquid argon

The reservoir was cooled to 77 K using liquid nitrogen

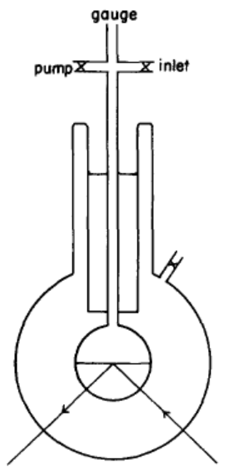


Fig. 3. The pyrex glass cell used for the liquid argon studies.

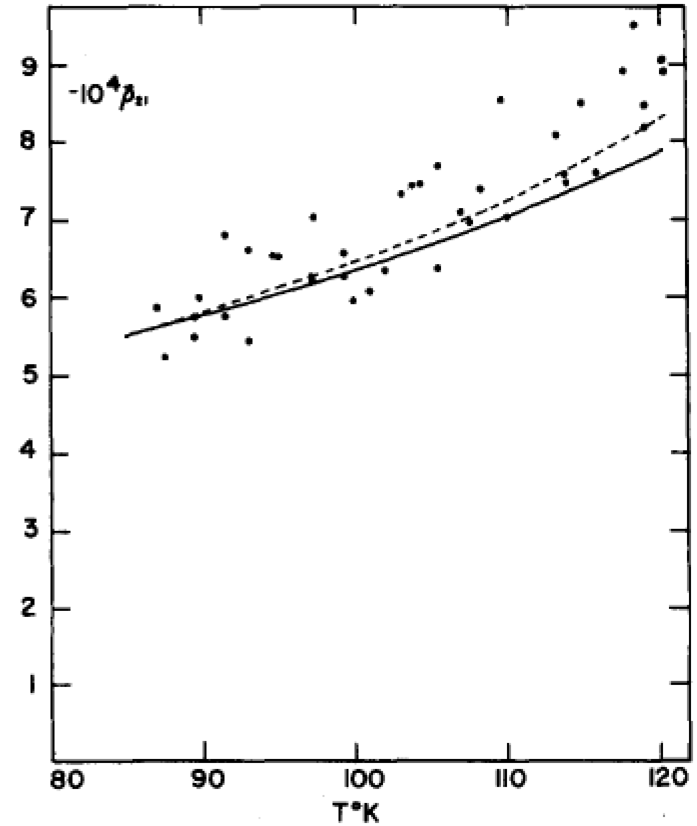


Fig. 4. p_{21} measured for liquid argon in 3 warming cycles between 85 K and 120 K. The full line shows the variation of p predicted by the surface wave excitation theory with $k_{min} = 2\pi/\lambda$, $k_{max} = 2\pi/t$, using the experimental value of surface tension, while the dashed line holds k_{max} constant.

The mean square displacement

$$\langle \xi_w^2 \rangle = \frac{k_B T}{2\pi\sigma} \ln \frac{k_{max}}{k_{min}} ,$$

Results – Liquid argon

$$\epsilon(z) = 1 + \frac{n\alpha/\epsilon_0}{1 - n\alpha/3\epsilon_0}$$

From the Clausius-Mossotti

Density variation

Surface tension

Table II
Summary of liquid argon data

Constants $d = 3.40$ Å, $T_c = 150.9$ K

T (K)	ϵ_1[a]	ϵ_2[a]	θ_B (°)	ρ_l[b] (g/cm³)	ρ_v[b] (g/cm³)	σ[c] (erg/cm²)	$\bar{\rho}/\eta$	η/t(F)	η/t(Erf)	η/k_{max}[d] (Å²)
85	1.0015	1.5147	39.11	1.402	0.0046	13.12	-1.535×10^{-3}	−0.0483	−0.0467	−0.281
90	1.0025	1.5026	39.24	1.374	0.0080	11.86	1.571	0.0461	0.0445	0.314
100	1.0056	1.4750	39.55	1.309	0.0180	9.42	1.668	0.0409	0.0395	0.390
110	1.0103	1.4450	39.90	1.238	0.0328	7.10	1.787	0.0354	0.0343	0.493
120	1.0183	1.4137	40.32	1.160	0.0580	4.95	1.961	0.0295	0.0285	0.645

Experiments

$$\eta(F) = (\epsilon_2 - \epsilon_1) \ln \frac{\epsilon_1}{\epsilon_2} \delta$$

$$\rho_{Erf}(z) = \frac{\rho_l + \rho_v}{2} + \frac{\rho_l - \rho_v}{2} \mathrm{Erf}\left(\frac{z}{\sqrt{2}\xi_{rms}}\right).$$

$$k_{max} = 2\pi / t$$

T (K)	$-\bar{\rho}_{21} \times 10^4$ e	$-\bar{\rho}_{21} \times 10^4$ f	$-\eta$ (Å)		t(F) (Å)		t(Erf) (Å)		k_{max} (Å⁻¹)		t_m (Å)
85	4.7 ± 0.4	(5.4 ± 0.4)	0.306	(0.352)	6.33	(7.30)	6.55	(7.54)	1.09	(1.25)	5.8 (5.0)
90		5.7 ± 0.4		0.363		7.9		8.2		1.16	5.4
100		6.5 ± 0.4		0.390		9.5		9.9		1.00	6.3
110		7.5 ± 0.4		0.420		11.9		12.2		0.85	7.4
120		8.8 ± 0.6		0.450		15.2		15.8		0.70	9.0

Predictions

$$\sigma_0 = \sigma + \frac{3}{16\pi} k_B T k_{max}^2.$$

T (K)	t_w[g] (Å)	t_w[h] (Å)	σ_0 (erg/cm²)[i]	t_{w0}[i] (Å)	t_l[j] (Å)
85	7.64	7.59	20.52	6.22	4.3
90	8.22	8.22	18.78	6.67	4.8
100	9.62	9.72	15.38	7.70	6.2
110	11.47	11.74	11.87	9.09	8.1
120	14.12	14.69	8.57	11.03	11.3

Temperature variation

T (K)	$t_m(T)/t_m(90)$[k]	$t(\mathrm{Erf}, T)/t(\mathrm{Erf}, 90)$[k]	$t_w(T)/t_w(90)$	$l(T)/l(90)$
85	0.93	0.92	0.93	0.95
90	1	1	1	1
100	1.17	1.21	1.17	1.12
110	1.37	1.49	1.39	1.29
120	1.67	1.93	1.72	1.54

[a] Extrapolated from the data of Sinnock and Smith, ref. 29 using the Clausius–Mossotti expression. [b] Ref. 30. [c] Ref. 31. [d] Using σ experimental. [e] Average of 3 samples. [f] Average of 3 warming cycles, value in parentheses extrapolated to 85 K. [g] $k_{min} = 2\pi/\lambda$, $k_{max} = 2\pi/t$, σ experimental. [h] $k_{min} = 2\pi/\lambda$, k_{max} constant $= 2\pi/t(90)$, σ experimental. [i] $k_{min} = 2\pi/\lambda$, $k_{max} = 2\pi/t$, σ_0 bare. [j] $t_l^2 = t^2(\mathrm{Erf}) - t_{w0}^2$. [k] Experimental values.