

## Adequacy of the Lifshitz Theory for Certain Thin Adsorbed Films

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(Received 22 March 1995)

We have employed a quartz crystal microbalance technique to study the thickness versus pressure dependence of a variety of thin (0–5 nm) liquid films (water, cyclohexane, nitrogen, krypton, and xenon) adsorbed on metal surfaces. We observe the Lifshitz theory of van der Waals forces to provide an excellent description of nitrogen adsorption, and an inadequate description of water adsorption, with the remaining gases spanning the two extremes.

PACS numbers: 68.15.+e, 67.70.+n

The interactions which control gas adsorption on solid surfaces are basic to a variety of physical phenomena such as surface melting of single phase materials [1], gas separation processes [2], and the wetting [3] and spreading [4] behavior of liquid films on solid surfaces. The pressure dependence of the thickness  $d$  of a film adsorbed on a flat solid surface reveals basic information on the nature of these interactions, and thus has been of continuing interest for at least half a century. One approach to this problem, which is believed to include retardation as well as very general many-body effects, is that of Dzyaloshinskii, Lifshitz, and Pitaevskii (DLP) [5]. The DLP approach leads to an expression which relates the film thickness at temperature  $T$  to the vapor pressure relative to saturation  $P/P_0$  [6],

$$k_B T \ln(P/P_0) = -\gamma(d)d^{-3}, \quad (1)$$

where  $\gamma(d)$  is a coefficient reflecting both substrate-adsorbate and adsorbate-adsorbate interactions. This coefficient varies slowly in the thin film regime ( $d < 5$  nm), where Eq. (1) is well approximated by the form  $k_B T \ln(P/P_0) = \gamma(0)d^{-3}$ . Retardation effects become increasingly important for film thicknesses beyond  $\approx 15$  nm [6], and eventually cause the right side of Eq. (1) to cross over to a  $d^{-4}$  dependence. Equation (1) is applicable only in cases where the adsorbed film completely wets the substrate [7].

Among a number of adsorption experiments which have been carried out in recent decades to specifically investigate the adequacy of Eq. (1) (see Table I), the 1973 analysis of Sabisky and Anderson for He adsorption on  $\text{SrF}_2$  yielded the most remarkable agreement between theory and experiment [8]. Other data reported for He/Au and He/quartz [9] exhibited, however, systematic deviations from theory [6]. Such apparent discrepancies have proven difficult to resolve: interpretation of most experimental work has been complicated by the extreme sensitivity of adsorption data to roughness [10,11], porosity [12], and/or chemical inhomogeneity [13] in the substrate, as well as the intrinsic width of the film-vapor interface [14]. In 1991, Beaglehole *et al.* [15] reported adsorption data for  $\text{H}_2\text{O}$  and  $\text{C}_6\text{H}_{12}$  recorded on a mica substrate free of the aforementioned complications. They observed

clear disagreement with the Lifshitz theory, and noted that unequivocal experimental reports presenting agreement of thin film adsorption data with the DLP theory were nonexistent [16,17]. Experimental support for the DLP theory is, in fact, quite sparse, and has been limited to studies of thick films at low temperature [8,11]. For example, the measurements of Sabisky and Anderson [8], which showed a very good agreement with DLP theory, were recorded for thicknesses greater than 1.2 nm ( $\approx 5$  layers of helium atoms). Indeed, it has become widely accepted in certain communities that for thin films [18–20] and/or metal [21,22] substrates the DLP theory provides an incorrect form for film-substrate interactions, since Eq. (1) provides an incorrect functional form for adsorption data and underestimates the thickness of the adsorbed film. Our purpose here is to report adsorption isotherms on both metal substrates and in the thin film regime which are entirely consistent with the DLP theory, and to demonstrate that the previously reported discrepancies can be attributed to properties of the adsorbate rather than substrate.

Our adsorption measurements were obtained by means of a quartz crystal microbalance (QCM) technique [23,24]. The QCM consists of a single crystal of quartz which oscillates in transverse shear motion with a quality factor  $Q$  near  $10^5$ . Au or Ag film electrodes, which serve as substrates for adsorption, were evaporated *in situ* onto the major surfaces of the QCM. The Ag film electrodes were prepared by collimated thermal evaporation at  $10^{-8}$  torr and 0.05–0.1 nm/s onto optically polished 5 or 8 MHz quartz crystals held 50 cm above a tungsten boat evaporation source. (The topology of samples produced in this manner is discussed extensively in Palasantzas and Krim [25].) Au films were thermally evaporated at  $10^{-9}$  torr onto identical crystals held 12 cm above a tungsten wire basket source. Adsorption isotherms were carried out by transferring the sample, in either a vacuum or flowing argon gas environment, to a small vacuum chamber whose temperature could be regulated between 77.4 K and room temperature. Adsorbate gas was then admitted to the chamber, and the frequency shift of the oscillator was measured under equilibrium conditions. Gas-phase corrections to the frequency shift were included (at  $T = 77.4$  K the gas pressure con-

tribution to the frequency shift for an 8 MHz quartz crystal is about  $-2$  Hz, near monolayer completion for a nitrogen film, and it becomes far less important at higher film coverages; see Ref. [26] for further details and references). The corrected frequency shift (proportional to the mass per unit area of the adsorbed film) was converted to film thickness by assuming the film had the same density as the bulk liquid. The data were not corrected for adsorbate film slippage effects [27,28] (which arise if the film is unable to track the oscillatory motion of the substrate, and would cause the thickness to be underestimated) or for substrate roughness effects [26] (which would cause the thickness to be overestimated). Such effects result in an uncertainty on the order of 10% for film thicknesses reported here beyond monolayer coverage (the uncertainty is much greater for submonolayer and monolayer films). Although they could have been incorporated into the present data analysis, they would have served only to complicate it: the conclusions of the work remain unchanged.

In order to avoid artifacts in the data analysis associated with sample height (i.e., gravitational potential shifts), adsorbate wetting behavior, and/or potential cold points in the sample cell, the saturated vapor pressure  $P_0$  was identified from the data set itself via the intercept ( $\ln P_0$ ) of a plot of  $\delta f^3$  versus  $\ln P$  [7]. This procedure, discussed in detail in Ref. [7], assured *identical* treatment of the data sets obtained from the various runs, so that comparisons with theory could be performed in an objective manner. In the discussion which follows, we refer to data points which fall within experimental error of theoretical prediction as "agreeing with theory," and take the thickness range over which this agreement occurs as a measure of the quality of the agreement.

Data for a representative selection of adsorbate-substrate combinations are presented in Figs. 1–3. All of the isotherms were recorded at temperatures well above the melting points of the respective films, so the layering transitions typically associated with adsorption on a uniform surface are not in evidence [30]. We note that layering transitions for data sets recorded at lower temperatures on identical substrates are, in fact, quite apparent [28], indicating that the substrates are highly uniform. We have not employed such data sets for comparisons with theory, however, since they frequently correspond to films which do not wet their respective substrates [7], thus greatly limiting the range of film thickness available for study [28].

The solid lines in Figs. 1–3 depict the predictions of the DLP theory [6,31,32]. We note that there are *no* adjustable parameters employed in comparing the data to the theory. Let us first focus on the data presented by circles in the upper sections of Figs. 1 and 2. These data sets were recorded on a 75 nm thick Au film deposited at room temperature. The water isotherm was recorded on the *same* Au substrate immediately after recording the nitrogen isotherm. While the nitrogen data are within

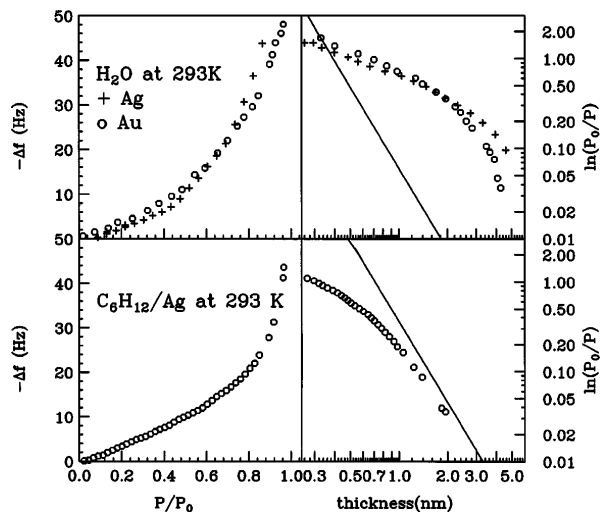


FIG. 1. Frequency shift ( $1 \text{ Hz} = 8.85 \text{ ng/cm}^2$ ) versus partial pressure (water ( $0.998 \text{ g/cm}^3$ ) and cyclohexane ( $0.7785 \text{ g/cm}^3$ ) films adsorbed at room temperature. The same data are depicted as  $\ln(P_0/P)$  vs film thickness on the right side of the figure. The solid lines represent theoretical prediction for water [ $\gamma(0) = 17700 \text{ K} \text{ \AA}^3$  [32]] and cyclohexane [ $\gamma(0) = 106000 \text{ K} \text{ \AA}^3$  [29]] on gold.

experimental error of the DLP theory for all thicknesses beyond  $\approx 0.6$  nm, the water adsorption data are clearly not described by the DLP theory. This is the essential result which we seek to report: we have recorded hundreds of isotherms for a variety of adsorbates (including pyridine, benzene, cyclohexane, water, nitrogen, oxygen, and the

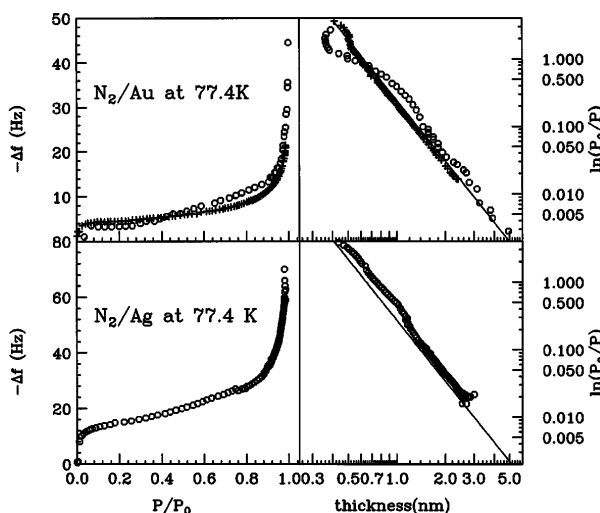


FIG. 2. Frequency shift versus partial pressure for nitrogen films ( $0.804 \text{ g/cm}^3$ ) adsorbed on Au ( $1 \text{ Hz} = 8.85 \text{ ng/cm}^3$ ) and Ag ( $1 \text{ Hz} = 3.45 \text{ ng/cm}^3$ ) substrates at 77.4 K. The same data are depicted as  $\ln(P_0/P)$  vs thickness on the right side of the figure. On the top part, the circles are for the same substrate as the Fig. 1 (top part) data represented by circles. The crosses are nitrogen data recorded on a 100 nm thick Au film evaporated at 400 K. The solid lines represent theoretical prediction for nitrogen/Au [ $\gamma(0) = 19000 \text{ K} \text{ \AA}^3$  [6]] and nitrogen/Ag [ $\gamma(0) = 20963 \text{ K} \text{ \AA}^3$  [31]].

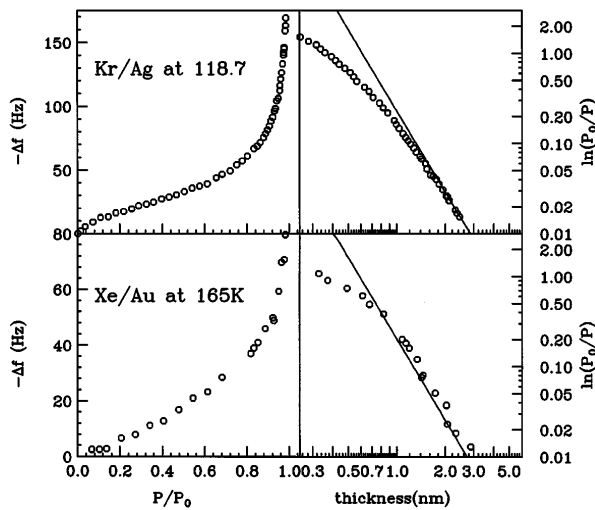


FIG. 3. Frequency shift versus partial pressure for Kr films on Ag ( $2.40 \text{ g/cm}^3$ ;  $1 \text{ Hz} = 3.45 \text{ ng/cm}^2$ ) at 118.5 K and Xe films on Au ( $3.08 \text{ g/cm}^3$ ;  $1 \text{ Hz} = 8.85 \text{ ng/cm}^2$ ) at 164 K. The same data are depicted as  $\ln(P_0/P)$  vs thickness on the right side of the figure. The solid lines represent the theoretical prediction for Kr/Ag [ $\gamma(0) = 27454 \text{ K \AA}^3$ [31]] and Xe/Au [ $\gamma(0) = 33300 \text{ K \AA}^3$ [6]].

rare gases) on gold and silver substrates, and we have never observed room temperature adsorption to be well described by the DLP theory. Low temperature adsorp-

tion onto identical substrates regularly results in data sets which are in excellent agreement with the DLP theory, even for thin films on metal surfaces.

The additional data sets presented in Figs. 1–3 are meant to provide a representative sampling of our observations. Data sets for nitrogen on 100 nm thick Au evaporated at 400 K (Fig. 2 crosses) and nitrogen on 150 nm thick Ag evaporated at 300 K (Fig. 2) are in excellent agreement with theory. Data for xenon on 150 nm thick Au evaporated at 300 K (Fig. 3), krypton on 150 nm thick Ag evaporated at 300 K (Fig. 3), and cyclohexane on 150 nm thick Ag postannealed to 400 K exhibit progressively shorter regions of agreement with theory. Data for water recorded on the 150 nm thick Ag film meanwhile exhibit no overlap whatsoever with theory (Fig. 1, crosses). While factors such as surface roughness, deviations of film density from the bulk value, and film slippage can potentially account for the discrepancies between the low temperature adsorption data and theory, they cannot account for the size of the discrepancies observed in the room temperature data sets.

It has been suggested [22] that the results of Beaglehole for the adsorption of cyclohexane and water onto mica might be an artifact due to the fact that mica is an easily charged material. Our results for the adsorption of cyclohexane and water on metal surfaces would indicate

TABLE I. Relevant works on the behavior of adsorbed films and their comparison with the DLP theory. An \* denotes the reported agreement with theory has been disputed in the literature [15] (ML = monolayer).

Authors/ref.	System	Thickness range	Agreement with DLP theory reported	$T(\text{K})$
Sabisky <i>et al.</i> , 1973/[8] <sup>a</sup>	He/SrF <sub>2</sub>	$\geq 12 \text{ \AA}$ ( $\geq 5 \text{ ML}$ )	Yes	1.38
Hemming, 1971/[6,9] <sup>c</sup>	He/Au	$\geq 175 \text{ \AA}$	No	2.13
	He/quartz	$\geq 175 \text{ \AA}$	No	2.10
Blake <i>et al.</i> , 1971/[16] <sup>b</sup>	alkanes/Al	1 – 5 ML	Yes, *	294
Gee <i>et al.</i> , 1988/[17] <sup>c</sup>	<i>n</i> -alkanes/quartz	$\geq 10 \text{ \AA}$	Yes, *	294
Beaglehole <i>et al.</i> , 1991/[15] <sup>c</sup>	C <sub>6</sub> H <sub>12</sub> /mica	0–2 nm	No	291
	H <sub>2</sub> O/mica	$\leq 5 \text{ ML}$	No	291
Vukusic <i>et al.</i> , 1992/[22] <sup>d</sup>	alcohols/Au	0.2–20 $\text{ \AA}$	No	
Bradberry <i>et al.</i> , 1992/[22] <sup>d</sup>	alkanes/Au	0.2–10 nm	No	297.8
This work <sup>e</sup>	C <sub>6</sub> H <sub>12</sub> /Au	$\leq 4 \text{ ML}$	Poor	293
	H <sub>2</sub> O/Ag(Au)	$\leq 16 \text{ ML}$	No	293
	N <sub>2</sub> /Ag(Au)	$\leq 8(13) \text{ ML}$	Yes	77.4
	Kr/Ag	$\leq 7 \text{ ML}$	Moderate	118.5
	Xe/Au	$\leq 7 \text{ ML}$	Good	165

<sup>a</sup> Acoustic interferometry. <sup>b</sup> Gravimetric adsorption. <sup>c</sup> Ellipsometry.

<sup>d</sup> Surface plasmon resonance. <sup>e</sup> Quartz crystal microbalance.

that the results of [15] are not due to this suggested artifact, but originate in the intrinsic properties of water and cyclohexane. We believe the simplest explanation of the fact that some adsorbates are described by the DLP theory while others are not is that the DLP theory represented by Eq. (1) can be followed only when van der Waals forces dominate other forces, and in addition are strong enough to reduce thermal fluctuations of the film-vapor interface. Given these constraints, it should be of no surprise that so few systems display excellent agreement with Eq. (1). Thermal fluctuations, which increase the film-vapor interfacial width, can greatly alter the functional form of an isotherm derived from DLP interactions [33], and room temperature adsorbates may be more susceptible to such effects. An adsorbate such as water is meanwhile susceptible to both thermal fluctuations and non-van der Waals forces (electrostatic, for example) so it should be of no surprise that the data bear little resemblance to Eq. (1). Although DLP-consistent isotherms may be unlikely for adsorption occurring at room temperature, we do *not* claim that *all* low temperature data are consistent with theory. Deviations between theory [6,34] and experiment clearly exist for low temperature data reported for He adsorption on Au [6,9], quartz [6,9], and H<sub>2</sub> [35].

In conclusion, we have reported adsorption data for thin liquid films adsorbed on silver and gold substrates which are consistent with isotherms associated with DLP interactions down to monolayer thicknesses. Our results demonstrate that previously reported discrepancies with theory originate in properties of the adsorbate, and are not due to the metallic nature of the substrate.

We acknowledge E. T. Watts, D. H. Solina, and J. Digel for assistance in sample preparation. M. W. Cole, T. H. Ellis, and K. R. Mecke are gratefully acknowledged for useful discussions. Support was provided by the NSF, Grant No. DMR9202044.

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