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Retardation and many-body effects in multilayer-film adsorption

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A discussion is presented of the relation between the film thickness d and the coexisting vapor pressure P for a physisorbed film. The theory of Dzyaloshinskii, Lifshitz, and Pitaevskii (DLP) is used to calculate the chemical potential $\Delta\mu \equiv -\gamma(d)d^{-3}$ relative to the value for bulk liquid. The relation is established between the DLP theory and a many-body expansion, of which the Frenkel-Halsey-Hill (FHH) theory is a first approximation to the nonretarded limit. Numerical calculations are performed for the cases of ^{4}He, Ne, H_2, N_2, Ar, O_2, CH_4, Kr, and Xe films on glass, gold, graphite, Si, quartz, and Al. Typically, the effect of retardation is to reduce the thickness by 20% for $d \sim 200$ Å. The function $\gamma(d)$ is shown to have a universal retardation behavior with a thickness scale ($d_{1/2}$) depending on both adsorbate and substrate characteristic frequencies.

I. INTRODUCTION

Much attention is currently directed to the nature of multilayer physisorbed films on planar substrates.[1–13] One question of interest is whether the adsorbate wets the surface under given experimental conditions of pressure P and temperature T. Quantitative questions pertain to the film thickness (d) and structure. Of particular interest because of its apparent simplicity is the case of a thick liquid film which wets the surface. Then one might deem the substrate to present only a minor perturbation on the thermodynamic properties of the film and so lead to a simple connection between T, p, and d. Such a relation is the subject of this paper.

There are two classic formulations of this problem; each assumes the fluid to be a structureless continuum which is essentially identical to the bulk fluid at temperature T and saturated vapor pressure P_0. One approach is that of Dzyaloshinskii, Lifshitz, and Pitaevskii (DLP), believed to include quite general many-body effects and retardation.[14] This leads to an expression for the difference in chemical potential between film and bulk liquid:

$$\Delta\mu = \mu - \mu_0 \,, \tag{1a}$$

$$-\Delta\mu \equiv \gamma(d) d^{-3} \,, \tag{1b}$$

where $\gamma(d)$ is a coefficient discussed below. If the coexisting vapor is ideal at saturation, then the corresponding difference in the vapor phase satisfies

$$-\Delta\mu_{\text{ideal}} = k_B T \ln(P_0/P) \,, \tag{2}$$

so that the right-hand sides of Eqs. (1b) and (2) agree. We show below that for He near 2 K, there is needed a small correction to this relation due to nonideality of the vapor. In any case, the coefficient in Eq. (1b) is given by an intimidating double integral:[15]

$$\gamma(d) = -\frac{\hbar d^3}{2\pi^2 c^3 n} \int_0^\infty d\omega \int_1^\infty dp\, p^2 \omega^3 \epsilon_a^{3/2} \left[\left[\frac{(S_1+p)(S_2+p)}{(S_1-p)(S_2-p)} \exp(d/\delta) - 1 \right]^{-1} + \left[\frac{(S_1+p\,\epsilon_s/\epsilon_a)(S_2+p/\epsilon_a)}{(S_1-p\,\epsilon_s/\epsilon_a)(S_2-p/\epsilon_a)} \exp(d/\delta) - 1 \right]^{-1} \right] , \tag{3}$$

$$S_1 \equiv (p^2 - 1 + \epsilon_s/\epsilon_a)^{1/2}, \quad S_2 \equiv (p^2 - 1 + 1/\epsilon_a)^{1/2} \,, \tag{4a}$$

$$\delta \equiv c/[2p\omega(\epsilon_a)^{1/2}] \,. \tag{4b}$$

Here, c is the speed of light and n is the adsorbate number density. The quantities ϵ_a and ϵ_s are the dielectric functions of the adsorbate and substrate, respectively, evaluated at imaginary frequency $i\omega$.[14] These are real, monotonically decreasing functions of ω, as will be seen below. The general behavior following from these equations is that $\gamma(d)$ decreases with d from a limiting value $\gamma(0)$ to an asymptotic d^{-1} behavior due to retardation.[15] The characteristic thickness at which retardation becomes a substantial effect is just where $d \sim \delta$ in the exponential of Eq. (3) for characteristic frequencies (ω_a or ω_s) in Eq. (4b); this means that the photon traversal time of the film is of order a vibrational period. Typically, this becomes $d \sim 100$–200 Å.

An alternative approach to this problem is the so-called Frenkel-Halsey-Hill (FHH) theory,[16,17] which purports to describe the nonretarded regime only. It then predicts Eq. (1), with the value of the coefficient $\gamma(0)$ given by

$$\gamma_{\mathrm{FHH}}(0)=\Delta C_3\equiv C_3^{a\text{-}s}-C_3^{a\text{-}a}\ , \tag{5}$$

where $C_3^{a\text{-}s}$ is the coefficient of the z^{-3} nonretarded van der Waals potential between the adatom and the surface:

$$V_{a\text{-}s}\sim -C_3^{a\text{-}s}z^{-3}\ ,$$

$$C_3^{a\text{-}s}=\frac{\hbar}{4\pi}\int_0^\infty d\omega\,\alpha(i\omega)g_s(i\omega)\ , \tag{6}$$

$$g_s(i\omega)=\frac{\epsilon_s(i\omega)-1}{\epsilon_s(i\omega)+1}\ . \tag{7}$$

Here, $\alpha(i\omega)$ is the adatom polarizability (spherically averaged for molecules) and $C_3^{a\text{-}a}$ is the analogous term with ϵ_a substituted for ϵ_s. In contrast to Eq. (3), Eq. (5) has a simple heuristic interpretation in terms of the relative energies of adding a particle to film or bulk material (see Sec. II).

This paper has two purposes. One is to describe the relationship between these two approaches; it will be shown that in the absence of retardation the FHH expression is the leading term in a many-body expansion involving the parameter

$$\eta_0=\frac{4\pi n\alpha_0}{3}\ , \tag{8}$$

where α_0 is the adsorbate atom's static polarizability. The next two terms in the series are derived; altogether, these account well for the case of gas adsorption in the range $\eta_0\lesssim 0.2$. The second purpose is to provide numerical results using the general DLP theory for all combinations of nine adsorbates and six substrates (borosilicate glass, gold, quartz, Si, Al, and graphite). Quite similar behavior is seen in all of these cases.

Since the basis of this paper is the DLP theory, it is appropriate to review it briefly. It is based on quantum field theory at finite T for the electromagnetic field in the presence of uniform media characterized by their bulk dielectric properties. In practice, the result in Eq. (2) does not depend on T because ordinarily the film thickness is small compared to the thermal wavelength of light (0.2 cm/T); also assumed is that there is a negligible T dependence of the dielectric function.[17] Possibly a more important approximation is the omission of the effects of interfacial diffuseness[18] and finite-size effects associated with boundary conditions on the excitations of the systems, which influence the thermodynamic properties.[19] It is obvious, for example, that λ-point fluctuations in *bulk* ^{4}He will not play the same role in the film; this difference is not considered in the theory.

The DLP theory was stimulated by experiments of Derjaguin's group,[20] which identified many-body effects and retardation in the force between two solid bodies. Subsequent experiments have tended to support the theory for that geometry, except in the cases of very small separation, surface roughness, or electrical forces due to charged layers.[4,21–23] On the other hand, the DLP theory has *not* been particularly successful in predicting film thickness. This may be due to experimental difficulties associated with the fact that P must be very close to P_0 for d to be large; see Eqs. (1) and (2). A notable exception to this assessment is the Sabisky and Anderson experiment,[24] which was remarkably consistent with the DLP theory. We hope that the present calculations provide a stimulus for further experimental tests of this problem.

This paper is organized as follows. In Sec. II, a series of analytic calculations is presented concerning limiting behavior of the DLP theory. In Sec. III we present calculations of $\gamma(d)$ for many adsorption systems. In Sec. IV we discuss these in relation to available data. In Sec. V we summarize our results.

II. ANALYTIC RESULTS IN LIMITING CASES

A. Small-*d* expansion

For small d, the general expression for $\gamma(d)$ simplifies to[14]

$$\gamma(d)=\frac{\hbar}{16\pi^2 n}\int_0^\infty d\omega\int_{y(\omega)}^\infty dx\,x^2(f^{-1}e^x+1)^{-1}\ , \tag{9}$$

$$y(\omega)\equiv\frac{2\omega d(\epsilon_a)^{1/2}}{c}\ , \tag{10}$$

$$f\equiv\frac{\epsilon_s-\epsilon_a}{\epsilon_s+\epsilon_a}\,\frac{\epsilon_a-1}{\epsilon_a+1}\ . \tag{11}$$

In these expressions, the argument $i\omega$ is implicit in the dielectric functions. In the case of small η, we may obtain an expansion in the small function f. This yields

$$\gamma(d)=\frac{\hbar}{16\pi^2 n}\int_0^\infty d\omega\int_y^\infty dx\,x^2 f e^{-x}(1-fe^{-x}+\cdots)\ , \tag{12}$$

$$\gamma(d)\simeq\frac{\hbar}{8\pi^2 n}\int_0^\infty d\omega\,f\,e^{-y}(1+y+y^2/2) \tag{13}$$

to lowest order in f. Substituting Eq. (10) and expanding in d, we obtain the small-thickness expansion,

$$\gamma(d)\simeq\gamma(0)[1-(\tilde{\omega}d/c)^3+\cdots]\ , \tag{14}$$

where

$$\gamma(0)=\frac{\hbar}{8\pi^2 n}\int_0^\infty d\omega\,f(i\omega)\ , \tag{15}$$

$$\tilde{\omega}^3\equiv\frac{4\int_0^\infty d\omega\,f(i\omega)\omega^3\epsilon_a^{3/2}}{3\int_0^\infty d\omega\,f(i\omega)}\ . \tag{16}$$

Equation (15) gives the nonretarded limit, discussed further in subsection B below. Note that it depends on the function f over the whole frequency domain. The expansion (14) indicates that retardation can be neglected if d is small compared to the distance light moves in a characteristic vibrational period $\sim\tilde{\omega}^{-1}$, which depends in a complicated way, Eq. (16), on both adsorbate and substrate. Using an estimate $\hbar\bar{\omega}\sim 20$ eV, discussed below, we find $c/\bar{\omega}=100$ Å. Thus retardation may be safely neglected *only* when $d \ll 100$ Å.

B. Relation between DLP and FHH theories

We consider the nonretarded limit next, Eq. (15), and explore its relation to the FHH expression, Eq. (5). To do so, we expand Eq. (9) with $y(\omega)=0$ in the small-η limit, using the Clausius-Mossotti expression:[25]

$$\frac{\epsilon_a-1}{\epsilon_a+2}=\frac{4\pi}{3}n\alpha=\eta\ . \tag{17}$$

To second order in η (or α) we arrive at the expressions

$$\gamma(0)\simeq C_3^{a\text{-}s}-\frac{n\pi}{6}C_6-\frac{n\pi}{18}C_{S1}+\frac{7n\pi}{48}C_{S2}\ , \tag{18}$$

$$\gamma(0)\cong\gamma_{\text{FHH}}(0)-\frac{n\pi}{6}(C_{S1}/3-\tfrac{7}{8}C_{S2})\ , \tag{19}$$

where we have used

$$C_3^{a\text{-}a}=\frac{n\pi}{6}C_6=\frac{n\hbar}{2}\int_0^\infty d\omega\,\alpha^2\ , \tag{20}$$

$$C_{S1}=\frac{3\hbar}{\pi}\int_0^\infty d\omega\, g_s\alpha^2\ , \tag{21}$$

$$C_{S2}=\frac{3\hbar}{\pi}\int_0^\infty d\omega\, g_s^2\alpha^2\ . \tag{22}$$

The last two coefficients appear in the McLachlan theory of the substrate-mediated interaction between atoms.[26] Note that each of the last three terms of Eq. (18) is essentially a factor η smaller than the first term. For the gases in Table I, $\eta_0 \lesssim 0.2$.

We may understand these results as follows. The FHH model obtains the first two terms of Eq. (18) as the difference between the *energy* $(-C_3^{a\text{-}s}d^{-3})$ of adding an atom to a film of thickness d and the corresponding value $(-C_3^{a\text{-}a}d^{-3})$ for a hypothetical substrate constructed of the same material as the adsorbate; entropy and many-body effects are neglected. Those correction terms to FHH arising from the omitted many-body energy contributions involve the influence of the substrate on the interaction between adatoms. This substrate-mediated interaction between atoms at $\mathbf{r}_1$ and $\mathbf{r}_2$ is[26]

$$\phi(\mathbf{r}_1,\mathbf{r}_2)=C_{S1}\lambda(\mathbf{r}_1,\mathbf{r}_2)-C_{S2}\beta(\mathbf{r}_1,\mathbf{r}_2)\ , \tag{23}$$

where λ and β are functions of the adatom positions relative to the substrate. We consider the effect of these terms on $\Delta\mu$. For simplicity, we use a discrete lattice model in the analysis; it simplifies the derivation but does not affect the result. In this model, the film is decomposed into $N=d/l$ layers, where l is the layer spacing. If an atom is added to the film at the film's surface ($z=d$), its substrate-mediated interaction with layer j has a lateral (x-y) average given by[27]

$$V_j=\frac{-\pi\sigma C_{S2}}{2(jl+d)^4}\ , \tag{24}$$

where σ is the atomic density within a layer. The C_{S1} term averages to zero.[27] The net substrate-mediated interaction with the film due to such terms is thus

$$\begin{aligned} V&\cong\sum_{j=1}^{N}V_j\simeq\int_0^{d/l}dj\,V_j\ ,\\ V&=-7\pi n C_{S2}(48d^3)^{-1}\ . \end{aligned} \tag{25}$$

TABLE I. Coefficient $\gamma(0)$ of the nonretarded d^{-3} chemical potential of a film calculated by various methods: γ_{FHH} is given in Eq. (5), γ_{series} in Eq. (19), and γ_{DLP} in Eq. (15); units are K Å ^{3}. Also shown is the series expansion parameter η_0, defined in Eq. (8).

		^{4}He	Ne	H_2	N_2	Ar	O_2	CH_4	Kr	Xe
η_0		0.019	0.062	0.072	0.13	0.14	0.14	0.17	0.18	0.23
glass	γ_{FHH}	1100	1640	2660	3590	3490	3380	4340	3860	3590
	γ_{DLP}	1100	1640	2650	4630	3690	3570	4730	4290	4630
quartz	γ_{FHH}	1130	1690	2600	4330	3500	3380	4210	3750	3280
	γ_{DLP}	1180	1790	2600	4480	3670	3580	4620	4200	4390
graphite	γ_{FHH}	1900	3280	4850	10 000	8780	8580	11 800	11 300	14 600
	γ_{series}	1900	3300	4910	10 200	9040	8820	12 400	11 700	15 600
	γ_{DLP}	1890	3290	4880	10 300	9100	8890	12 400	12 000	16 200
Si	γ_{FHH}	1950	3320	5430	10 900	9680	9390	13 500	12 800	17 400
	γ_{series}	1960	3380	5570	11 500	10 300	9940	14 600	13 900	19 600
	γ_{DLP}	1950	3370	5530	11 500	10 300	9930	14 600	14 000	20 000
Al	γ_{FHH}	2430	4300	6780	14 400	12 900	12 600	18 100	17 400	24 300
	γ_{series}	2450	4410	6980	15 400	13 900	13 500	19 900	19 300	27 900
	γ_{DLP}	2440	4390	6970	15 400	14 000	13 500	19 800	19 300	28 100
Au	γ_{FHH}	3100	5830	7850	18 200	16 400	16 100	22 100	21 700	29 800
	γ_{series}	3120	5950	8060	19 700	17 400	17 100	24 100	23 400	34 500
	γ_{DLP}	3100	5900	8000	19 000	17 300	17 000	23 800	23 400	33 300

The effect on γ of this energy coincides with the last term in Eq. (19). This leaves open the question of why a C_{S1} term appears in that expression. To understand, recall that the vanishing of the C_{S1} term mentioned above occurs in a calculation where the atom's z coordinate differs from that of the layer.[27] What if it does not? To assess this contribution, we write the λ function appearing above [Eq. (23)] in the case when the two adatoms lie in a common plane:[26]

$$\lambda(\rho)=(\rho^2+4z^2)^{-3/2}\rho^{-3}\left[\frac{4}{3}-\frac{4z^2}{\rho^2+4z^2}\right] . \tag{26}$$

Here, ρ is the separation between the atoms. The net in-plane energy per atom is then

$$\frac{U}{N}=\frac{C_{S1}}{2}\sum_i \lambda(\mathbf{r}_1,\mathbf{r}_i) , \tag{27}$$

where the factor $\frac{1}{2}$ cancels double counting and the $\mathbf{r}_i$ lie on sites of a triangular lattice. We use a continuum model to evaluate this:

$$\frac{U}{N}=\frac{C_{S1}}{2}\sigma\int_{\rho_m}^{\infty}d^2\rho\,\lambda(\rho) , \tag{28}$$

where the lower limit is defined in terms of the two-dimensional and three-dimensional densities:

$$\pi\rho_m^2=\sigma^{-1} , \tag{29}$$

$$4\pi\rho_m^3/3=n^{-1} . \tag{30}$$

The integral yields

$$U=NC_{S1}\pi(2z)^{-4}\sigma(s_m^{-1}-2s_m+s_m^3)/3 , \tag{31}$$

where in the limit of thick films ($\rho_m \ll z$)

$$s_m\equiv(1+4z^2/\rho_m^2)^{-1/2}\simeq\rho_m(2z)^{-1} . \tag{32}$$

Hence,

$$U=NC_{S1}\pi\sigma/(24z^3\rho_m)=NC_{S1}\pi n/(18z^3) . \tag{33}$$

This energy yields a contribution to the chemical potential identical to the C_{S1} term appearing in the DLP expansion, Eq. (19). This completes our derivation of the many-body correction terms appearing there. We may now understand these terms as arising from the substrate-mediated interaction.

A few remarks about this expansion are appropriate here; others will appear in the next section where numerical results are discussed. We note that terms proportional to the square of the adsorbate polarizability are included in (19), but none of higher order. In fact, we would expect terms of the form ΔC_{S1} and ΔC_{S2} arising for the same reason that ΔC_3 appears in the FHH relation, Eq. (5), i.e., the expression for γ arises from the difference in μ between the film and the bulk reference system. The omitted terms would, however, involve coefficients $C_{S1}^{a\text{-}a}$ proportional to α^3 or α^4, since g then is proportional to α in the reference system; see Eqs. (21) and (22). Finally, we note that there is substantial cancellation between the last two terms in Eq. (18) so that the series result is not very different from $\gamma_{\rm FHH}(0)$; see Table I.

C. Thick films (extreme retardation)

We consider here the case of small η, for which the general equation (3) becomes[14]

$$\mu=-\frac{3\hbar}{8\pi^2nc^3}\int_0^{\infty}d\omega\,\omega^3\int_1^{\infty}dp\,\exp(-2p\omega d/c)f(\omega,p) , \tag{34}$$

$$f(\omega,p)=\eta\left[\frac{s-p}{s+p}+\frac{(2p^2-1)(p\epsilon_s-S)}{p\epsilon_s+S}\right] , \tag{35}$$

$$S\equiv(p^2+\epsilon_s-1)^{1/2} . \tag{36}$$

For very large d the exponential becomes negligible, except for small ω. The function $f(\omega,p)$ may then be expanded in even powers of ω about $\omega=0$, since ϵ_s and η are quadratic in ω.[14] This leads to ω integrals which can be evaluated analytically. The result is

$$\gamma(d)\sim\frac{\Gamma}{d}[1+(c/\bar{\omega}d)^2] \text{ as } d\to\infty , \tag{37a}$$

$$\Gamma=[9\hbar c/(64\pi^2n)]\int_1^{\infty}dp\,f(0,p) , \tag{37b}$$

$$\Gamma=\frac{3\hbar c\alpha_0}{8\pi}\frac{\epsilon_{s0}-1}{\epsilon_{s0}+1}\phi(\epsilon_{s0}) , \tag{38}$$

$$\bar{\omega}^2=\frac{2}{5}\frac{\int_1^{\infty}dp\,f(0,p)}{\int_1^{\infty}dp\,f''(0,p)} , \tag{39}$$

in which a prime means differentiation with respect to ω and the subscript 0 means static value. Equation (38), which appears in the DLP paper, involves a dimensionless function ϕ, of order unity, which is evaluated therein. Note that only static response functions of the adsorbate and substrate enter this retarded limit, in which γ asymptotes as d^{-1}. According to Eq. (37), the frequency dependence of these functions determines the characteristic length for *deviation* from this fully retarded behavior. Qualitatively similar behavior was seen above to describe deviation from the nonretarded limit.

III. NUMERICAL CALCULATIONS

We have calculated $\gamma(d)$ from the DLP expression, Eq. (3), for the gases He, Ne, H_2, N_2, Ar, O_2, CH_4, Kr, and Xe on the surfaces glass, graphite, Si,[28] quartz, Al, and Au. The response functions required for input are monotonically decreasing functions of ω; here they are assumed to satisfy the simple dependencies:

$$\alpha(i\omega)=\frac{\alpha_0}{1+(\omega/\omega_a)^2} , \tag{40}$$

$$g(i\omega)=\frac{g_0}{1+(\omega/\omega_s)^2} , \tag{41}$$

except in the cases of glass and quartz. For quartz, dielectric data from Ref. 29 are used to compute $\epsilon(i\omega)$. For glass we use an empirical form provided by Kayser.[30] The coefficients in the approximate representations (40) and (41) are presented by Rauber *et al.* and yield analytic expressions for C_3, C_{S1}, and C_{S2}, the results of which lie typically within 10% of values calculated with more complicated data fits.[31,32]

Figure 1 shows the behavior of $\gamma(d)$ obtained from Eq. (3) in the case of He/graphite; we will soon see that this case is "typical" in a certain sense. We observe in the inset that the nonretarded value $\gamma(0)$ is appropriate only for very thin films. Deviation occurs even at $d \sim 10$ Å; $\gamma(d)$ is reduced by one-half for $d \simeq 180$ Å. This behavior is expected on the basis of the arguments in Sec. II A. We note, incidentally, that $d \gtrsim 100$ Å is the region of saturated films, where bulk fluid coexists a vertical distance h below the film. The relationship then is modified to incorporate in μ the gravitational energy difference:

$$\gamma(d)d^{-3}=mgh \ , \tag{42}$$

where m is the atomic mass and h is of order of a few cm.

At very large d, the calculated curve approaches the asymptotic dependence ($\gamma \rightarrow \Gamma/d$) predicted by Eq. (37) in the fully retarded regime. Note that the curves agree within 5% only for $d \gtrsim 1000$ Å. This value is consistent with expectation, described in Sec. II C.

The retarded behavior of $\gamma(d)$ for each of the other 53 systems of interest was found to be qualitatively similar. Indeed, the data are plotted in Fig. 2 in such a way as to exhibit a nearly universal functional dependence. We define a thickness $d_{1/2}$ by the relationship

$$\gamma(d_{1/2}) \equiv \gamma(0)/2 \ , \tag{43}$$

where values of $\gamma(0)$ and $d_{1/2}$ are presented in Tables I and II. One observes in Fig. 2 that a curve which fits the data quite well is given by the empirical relationship

$$\gamma^*(d^*)=[1+1.64(d^*)^{1.4}]^{-1/1.4} \ , \tag{44}$$

$$\gamma^* \equiv \gamma(d)/\gamma(0) \ , \tag{45}$$

$$d^* \equiv d/d_{1/2} \ . \tag{46}$$

Note that $\gamma^*(1) \equiv \frac{1}{2}$ and that, for $d^* \gg 1$, γ^* is proportional to d^{-1}, the theoretically fully retarded behavior. An alternative form, used elsewhere,[33] corresponds to

$$\gamma^*=(1+d^*)^{-1} \ . \tag{47}$$

This dependence is observed in Fig. 2 to be qualitatively, but not quantitatively, consistent with our results.

One might wonder whether the universal behavior found here is partly sensitive to the simplifying frequency dependencies assumed for α and ϵ. However, several systems have been shown to conform exactly or approximately to these dependencies;[34] moreover, the glass and quartz cases have not used any assumptions. Finally, we note that the prediction of Sabisky and Anderson[24] for He/SrF$_2$ falls on the curve in Fig. 2. Thus we presume that our inferred general behavior is a reliable conclusion.

We consider next the values of $\gamma(0)$ and $d_{1/2}$. In Sec. II B it was shown that $\gamma(0)$ has a small η_0 expansion, Eq. (19), of which the leading term, ΔC_3, represents the FHH approximation. We compare these values in Table I. Note that this expansion works well in predicting the values of $\gamma(0)$.

As to $d_{1/2}$, this can be estimated as in Sec. II to scale as c/ω_c, where ω_c is a characteristic frequency which depends on both substrate and adsorbate. A simple *ansatz* is

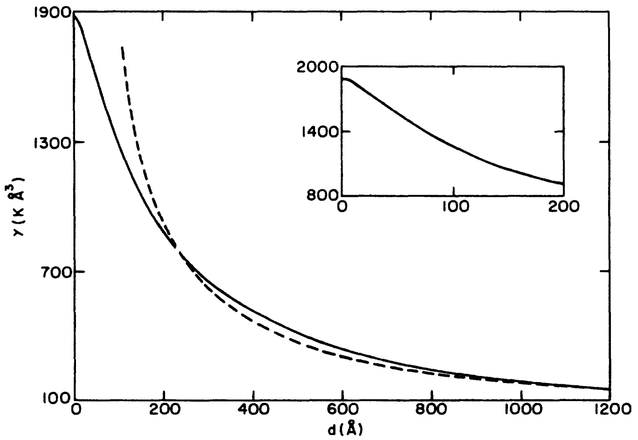

FIG. 1 Solid curve denotes the value of $\gamma(d)$ defined by Eq. (16) and calculated from the DLP expression (3) for He/graphite. In the absence of retardation, $\gamma(d)$ would not deviate from the value $\gamma(0)$. The dashed curve represents the asymptotic dependence $\gamma \propto d^{-1}$, corresponding to extreme retardation [the leading term of Eq. (37)]. Inset shows behavior at small d.

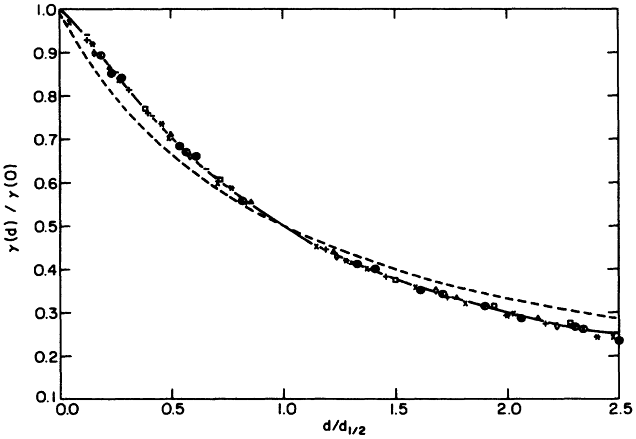

FIG. 2. Reduced curves illustrating the universal dependence of $\gamma(d)/\gamma(0)$ on the relative thickness $d^*=d/d_{1/2}$ (values tabulated in Tables I and II). The solid and dashed curves are Eqs. (44) and (47), respectively. Representative data shown are for He on glass (squares), graphite (crosses), and gold (circled crosses); Xe on glass (diamonds), graphite (asterisks), and gold (circled asterisks); H$_2$ on glass (triangles), graphite (pluses), and gold (circled pluses). Results for He/SrF$_2$ from Ref. 24 are shown as hyphens.

TABLE II. Values (in Å) of the characteristic length $d_{1/2}$ defined in Eq. (43) for various possible adsorption systems. The lengths in parentheses are values (in Å) of $c/[\omega_a \epsilon_a^{1/2}(0)]$ or c/ω_s for adparticle or substrate, respectively. Note approximate conformity to Eq. (48).

Substrate / Adsorbate	Glass	Quartz	Graphite (109)	Si (167)	Al (153)	Au (82)
^{4}He (69)	180	150	180	230	230	160
Ne (55)	190	160	170	230	220	150
H_2 (126)	220	210	230	280	280	210
N_2 (85)	210	180	200	260	250	170
Ar (85)	210	180	190	260	250	170
O_2 (80)	220	180	190	260	250	150
CH_4 (99)	200	180	200	270	260	180
Kr (89)	200	180	200	270	260	190
Xe (96)	180	150	200	270	270	180

$$d_{1/2}=\frac{c}{\omega_a[\epsilon_a(0)]^{1/2}}+\frac{c}{\omega_s}\,, \tag{48}$$

i.e., a sum of propagation lengths in the two media, including the refractive index in the film. As seen in Table II, this estimate agrees with the numerical results, the average error being 4%.

IV. RELATION TO EXPERIMENTS

Physisorbed film thicknesses have been measured for 50 years.[35] Many early experiments and some recent ones suffer from problems of poor surface quality or inadequate T and p resolution. The requirements become especially stringent in the thick-film regime. Thus, a film with $d=200$ Å involves a local pressure value within 1 part in 10^{-5} of saturation [according to Eq. (2)]. The equivalent of this fractional pressure difference is a comparably small fractional T change:

$$\frac{\Delta T}{T}=\frac{(\Delta \ln P)}{T}\left[\frac{d\ln P_0}{dT}\right]_{\mathrm{eq}}^{-1}. \tag{49}$$

In the case of He, for example, the derivative (evaluated along the equilibrium curve) is ~ 10/K. This yields a required experimental precision and uniformity of $\Delta T/T \lesssim 10^{-5}$ to assure sufficient accuracy in thickness.

Before proceeding to discuss specific experiments, we address a further technical point mentioned in connection with Eq. (2). If the gas in equilibrium with the film is *not* ideal, but instead has a non-negligible second virial coefficient $B(T)$, then the vapor's chemical potential relative to the value at saturation satisfies

$$\Delta\mu=\int_{P_0}^{P} dP'\frac{1}{n(P')}\simeq\left[1+\frac{BP_0}{k_BT}\right]k_BT\ln(P/P_0)$$

$$=(1+BP_0/k_BT)\Delta\mu_{\mathrm{ideal}} \tag{50}$$

to first order in B, omitting higher-order virial terms. In the case of ^{4}He near 2 K, for example, the correction factor relative to Eq. (2) in parentheses is about 0.95.[36] This leads to a small ($\sim 2\%$) increase in film thickness relative to the idealized prediction. We ignore it in the following discussion.

We review first of all a set of recent experiments involving adsorption on a vibrating graphite fiber. In doing so we must discuss the role of curvature. For a cylindrical wire, this modifies the equilibrium conditions via the Laplace pressure discontinuity across the interface, $\Delta p=\sigma_s/R$, where σ_s is the surface tension and R is the radius. In contrast, the actual experimental surface is locally flat because of faceting on an extended scale $l\sim 1$ μm; since $l \gg d$ the curvature correction should be omitted. In Table III we compare results of Taborek (at saturation) with the prediction of Eq. (42). Note that the DLP predictions are in qualitative agreement with experiment: the ratio d/d_{expt} varies between 0.8 and 1.4 for the five gases shown. The FHH predictions are 20–40% higher than these since $\gamma(d)/\gamma(0)$ is typically $\frac{1}{3}$ here. Thus, in most cases the FHH prediction overestimates the coverage for these gases.

Recent experiments of Zimmerli and Chan[7] have revealed some unforeseen problems with this technique, owing apparently to extended cracks in the fiber. These would seem to be responsible for an effective surface area about 3 times the wire's external area. Figure 3 displays their data, which they have normalized to coincide with the nonretarded theory in the thin-film regime.[37] Note

TABLE III. Predicted value from Eq. (42) of film thickness (in Å) at saturation on graphite, according to FHH theory, Eq. (5), and the present work, Eq. (3), using the DLP theory. Experimental results d_{expt} are from Taborek (Ref. 6), with estimated uncertainty of 20%; the He data are for He II.

Gas	d_{FHH}	d_{DLP}	d_{expt}
He	430	310	390
Ne	310	230	170
H_2	350	270	270
Ar	340	250	230
CH_4	500	360	250
Xe	270	220	290

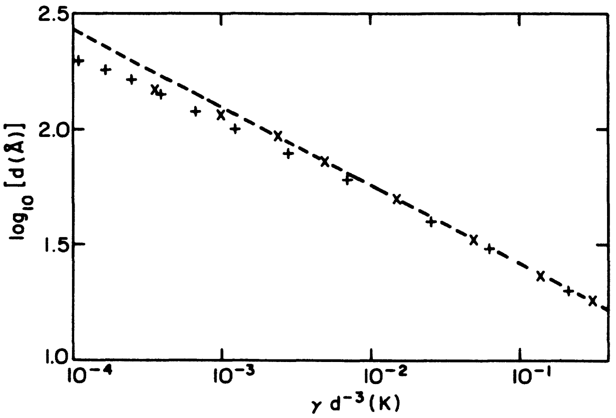

FIG. 3. Comparison between calculated results (solid curve) from Eqs. (1)–(3), and the experimental data (crosses) from Ref. 7, of the film thickness d for He on graphite.

some qualitative consistency with the predicted effect of retardation. It is evident that further study of graphite adsorption would be useful.

Recently, measurements have been made by Krim and Watts of film thickness of Ar, Kr, and Xe on Au.[12] The data are quantitatively consistent with our calculations over the region $d \lesssim 35$ Å. We hope that these data may be extended further into the retardation regime.

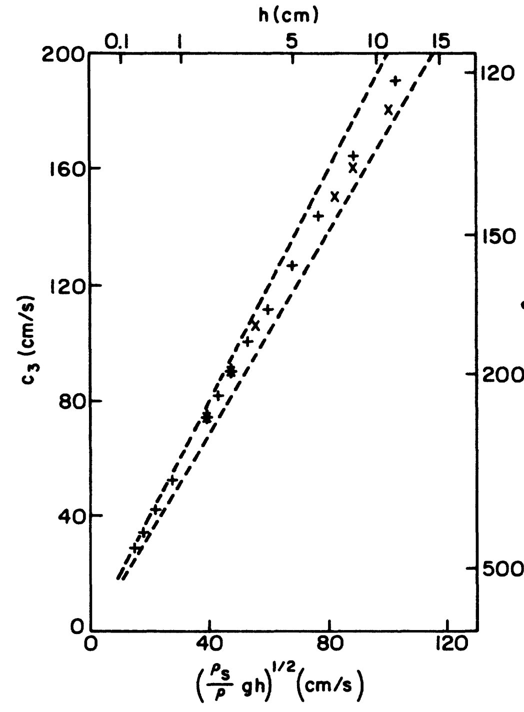

FIG. 4. Third-sound speed and film thickness (right-hand ordinate) for He on glass as a function of height and superfluid fraction. Calculations (pluses) from Eq. (52) and experimental data (crosses) from Ref. 40. While the data vary over the interval $1.2 < T < 1.5$ K, the calculations assume $\rho_s/\rho \simeq 0.94$, i.e., $T = 1.35$ K. The dashed lines are extrapolations of the extreme nonretarded and retarded limits of Eq. (52).

Some years ago, Hemming measured He film thickness in that regime using an ellipsometric method.[38] In Fig. 5 we compare the results with our calculations. A rather large discrepancy is observed. The theory systematically underestimates the thickness. We return below to this situation.

One of the potentially quite useful way of studying absorption potentials for ^{4}He is third sound, a wave in which only the superfluid fraction, ρ_s/ρ, of the film moves since it is unaffected by viscosity. Neglecting a usually unimportant entropy term, the velocity c_3 satisfies[39]

$$\frac{\rho}{\rho_s} m c_3^2 = d\left[\frac{\partial \mu}{\partial d}\right]$$

$$= |\mu|\left[3 - \frac{d\ln\gamma}{d\ln d}\right] . \tag{51}$$

For a saturated film, Eq. (42) is appropriate, yielding

$$c_3^2 = \frac{\rho_s}{\rho} gh \left[3 - \frac{d\ln\gamma}{d\ln d}\right] . \tag{52}$$

The term in parentheses is 3 in the absence of retardation, but it is 4 in the fully retarded region. As evident in this logarithmic variation and in Fig. 4, this difference is not a particularly easy way to deduce the role of retardation. Measurement of the thickness itself as a function of h would be more informative. Such measurements, done with capacitance or ellipsometric methods, are relatively few in the large-d limit relevant here.

V. SUMMARY AND DISCUSSION

This paper has evaluated the predictions of the DLP theory and established its relation to the FHH theory. We find similar features in the 54 cases studied, including

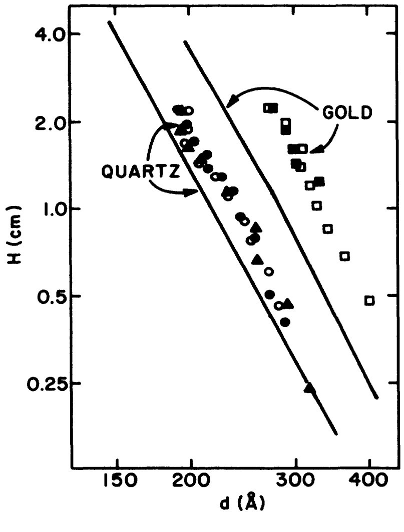

FIG. 5. Comparison between calculated results (solid curve) from Eqs. (1)–(13), and (42), and the experimental data (all points) from Ref. 38, of the film thickness d for He on quartz and gold substrates, respectively.

a common retardation behavior exhibited in Fig. 2. Thus, each adsorption system may be characterized by $\gamma(0)$, the nonretarded DLP coefficient, and $d_{1/2}$, the thickness (~ 200 Å), such that $\gamma(d)/\gamma(0)$ is one-half. We believe that the current data set is inadequate to draw definitive conclusions about the accuracy of the DLP theory. While the analysis of Sabisky and Anderson yielded remarkable agreement with experiment, the data in Fig. 5 show a systematic deviation. We see no reason to question one or the other of these experiments; the calculations suffer in both cases from the approximations discussed in the Introduction. Unfortunately, most measurements concerning multilayer films are performed in the regime of $\lesssim 20$ layers, where deviations from the continuum model are expected,[18,19,41] or in capillaries, where deviations from the plane surface potential are considerable[42] and effects of capillary condensation are pronounced.[43] We hope to address many-body effects and retardation for capillaries in future work.

We have shown that the FHH model provides the leading terms in a many-body expansion of $\gamma(d)$ in the nonretarded limit. The FHH result is not quite systematic in the sense of its only partially including terms proportional to the square of the adsorbate polarizability. Consequently, the FHH value is seen in Table I to approximate adequately the nonretarded limit only for small η_0. With the additional terms in the series equation (19) included, better agreement occurs.

We may summarize our results then by noting that Eqs. (44)–(46) provide the general behavior, with the quantities $\gamma(0)$ and $d_{1/2}$ given rather accurately by Eqs. (19) and (48), respectively. The parameters in those expressions are evaluated, or tabulated, for example, in Refs. 31, 32, and 34.

We close by urging experimentalists to address this unresolved problem, which presents intriguing questions about many-body properties in statistical thermodynamics.

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