

Retarded Van der Waals Force Theory of Stable Thick Films in Systems of Three Condensed Phases

We have employed the Lifshitz theory (1-4) of the retarded van der Waals attraction between macroscopic or colloidal bodies, to investigate the possibility that a relatively thick liquid film of one phase might form a stable layer between two other condensed phases. An essential component of this analysis was the important frequency dependence in the retardation, which has received little direct recognition up to the present. The system that we have studied was glycerol/n-alkanes/Teflon TFE.

The accepted, qualitative explanation of the retardation of the London (dispersion) force interaction (1, 5-7) takes note of the fact that the field due to an oscillating, molecular dipole is an electromagnetic disturbance, and hence, that it is propagated in space at the speed of light, c . In an exact treatment, two molecules at separation r are analyzed as coupled oscillators. In treating the coupling, they may be considered to be separate oscillators, interacting by the emission and reception of virtual photons. The oscillation of a temporary dipole in one molecule causes a virtual photon to be "emitted" by one molecule and "received" by the second, in which it excites the oscillation of an induced dipole. That oscillation leads to the "emission" of another virtual photon, which is "received" by the first molecule. The temporary dipole and the induced dipole oscillate synchronously and attract each other. If r is large, the "returned" electromagnetic oscillation, as "received" by the first molecule, will be retarded in phase; and so, although the two dipoles are still oscillating at the same frequency, the attraction is reduced.

For different frequencies of oscillation, the same lag in absolute time will cause different shifts in phase angle. (This fact appears to have been overlooked, in qualitative discussions of retardation.) If we consider, say, two oscillations at frequencies ω_1 and ω_2 , with $\omega_2 > \omega_1$, there will exist two distances, l_2 and l_1 , between two bodies, such that the retardation of phase angle will be the same. And l_2 will be smaller than l_1 .

Hence the change from an l^{-2} to an approximate l^{-3} distance dependence of the energy of interaction between two macroscopic, parallel plates (1) will occur at smaller values of l , the higher the frequency of the electromagnetic disturbance. Beyond the changeover region of values of l for the higher-frequency component, the energy of interaction will decay more rapidly than for the lower-frequency component. In effect, the former is a somewhat shorter-range force than the latter.

The nature of the Lifshitz theory is such that the frequency dependence of the retardation is handled automatically by the mathematical machinery, because of the presence of speed of light in Maxwell's equations.

We have carried out computations of the free energy of interaction between Teflon TFE and glycerol, in the presence of alkanes from n-pentane to hexadecane. The approximate equation (2) for the free energy of interaction $G_{132}(l)$, between phases 1 and 2 separated by a film of phase 3, whose thickness is l , is:

$$G_{132}(l) = \frac{kT}{\pi c^3} \int_{p=1}^{\infty} \sum_{n=0}^{\infty} \epsilon_3^{3/2} \xi_n^3 \times \int_l^{\infty} p^2 \left[\frac{\exp(2p\xi_n l \epsilon_3^{1/2}/c)}{\Delta_1 \Delta_2} - 1 \right]^{-1} dp dl, \quad [1]$$

where the prime indicates that the $n = 0$ term is given half weight in the sum.

$$\xi_n = n \left(\frac{2\pi kT}{\hbar} \right)$$

$$\Delta_1 = \frac{\epsilon_1 - \epsilon_3}{\epsilon_1 + \epsilon_3}$$

$$\Delta_2 = \frac{\epsilon_2 - \epsilon_3}{\epsilon_2 + \epsilon_3}$$

ϵ_i is the (frequency-dependent) dielectric permeability of phase i .

$$G_{132}(l) = - \frac{A_{132}(l)}{12\pi l^2}, \quad [2]$$

where $A_{132}(l)$ is the (distance-dependent) Hamaker coefficient. When the integration is carried out, it is found that

$$A_{132}(l) = \frac{3}{2} kT \sum_{n=0}^{\infty} \sum_{j=1}^{\infty} (\Delta_1 \Delta_2)^j \left(\frac{x_0}{j^2} + \frac{1}{j^3} \right) \exp(-jx_0), \quad [3]$$

where

$$x_0 = \frac{2\xi_n l \epsilon_3^{1/2}}{c}$$

$$j = 1, 2, 3, \dots$$

In evaluating $G_{132}(l)$, we have used the method of Parsegian and Ninham (3, 4), determining the frequency-dependent dielectric constant, $\epsilon(i\xi_n)$ in the microwave, infrared, and ultraviolet regions. The necessary

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TABLE I

Dielectric and Optical Properties of the Substances Employed

Material	ϵ_{∞}	ϵ_0	n_D^2	Characteristic frequencies (rad/sec)		
				$\omega_{MW} \times 10^{-8}$	$\omega_{IR} \times 10^{-14}$	$\omega_{UV} \times 10^{-16}$
Glycerol	42.5	4.16	2.136	8	3.28 (average)	1.895
PTFE	2.10		1.846	—	2.27	1.793
Pentane	1.844		1.819	—	5.54	1.877
Hexane	1.890		1.864	—	5.54	1.873

spectroscopic, refractive index, and dielectric constant data from the literature (8–13) were treated by well-known methods (4, 9, 13). Table I shows the relevant optical and dielectric data.

Figures 1 and 2 show the results of these calculations for n-pentane and n-hexane. It may be seen that there can be no stable film of n-pentane, of any thickness, between a layer of glycerol and surface of Teflon FEP. The only stable condition is one of molecular contact, in which pentane is excluded from the interfacial region. The Hamaker coefficient is positive for all values of l .

But for n-hexane, Fig. 2 shows there is a minimum of free energy, at $l = 250 \text{ \AA}$. The energy per square centimeter at the minimum, $G_{132}(l)$, is $-7.5 \times 10^7 kT$. The Hamaker coefficient was found to be negative for all values of l less than 140 \AA ; and it becomes positive only for l greater than 140 \AA . For higher n-alkanes, the minimum in G_{132} is less deep, and occurs at greater distances, e.g., 9500 \AA for hexadecane.

These results mean that a layer of n-alkane can exist, as a relatively thick, stable film, between bulk glycerol and Teflon TFE. Such a film has not been observed

heretofore. Preliminary experiments in this laboratory are in agreement with our prediction.

The problem that we are studying is appreciably different from the problem that was examined by Owens and Richmond (14) and by Del Cerro and Jameson (15). There is a conflict as to experimental results, between Refs. (15, 16), which we will not attempt to adjudicate here. It is clear, however, that the theoretical problem of two liquid phases and a gas is significantly different from that of three condensed phases. We will discuss this theoretical question more fully in a separate communication. The authors of Refs. (14, 15) used Lifshitz theory to attack the problem of the stability of a multilayer film (versus a submonolayer film (16)) of hydrocarbon on water. In Ref. (15), they reported that the chemical potential of a hydrocarbon film changed sign at a definite thickness, on account of the retardation effect. They found that the net A_{132} term remained positive for small values of separation, l , however. In this, Ref. (15) differs notably from our result, as would be expected from the intrinsic differences in the two theoretical problems.

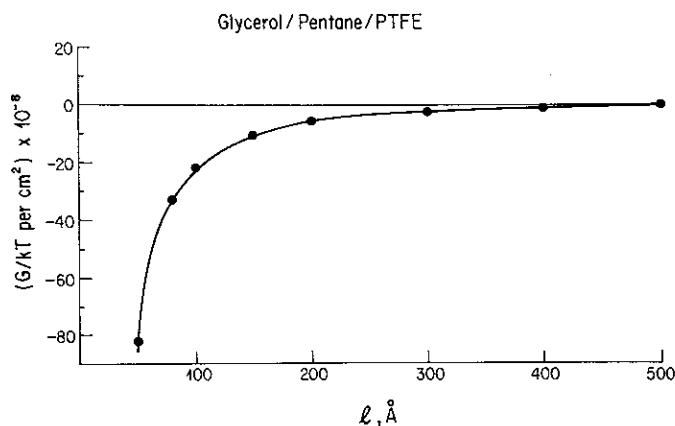


FIG. 1. Free energy of interaction as a function of distance for glycerol/n-pentane/Teflon TFE.

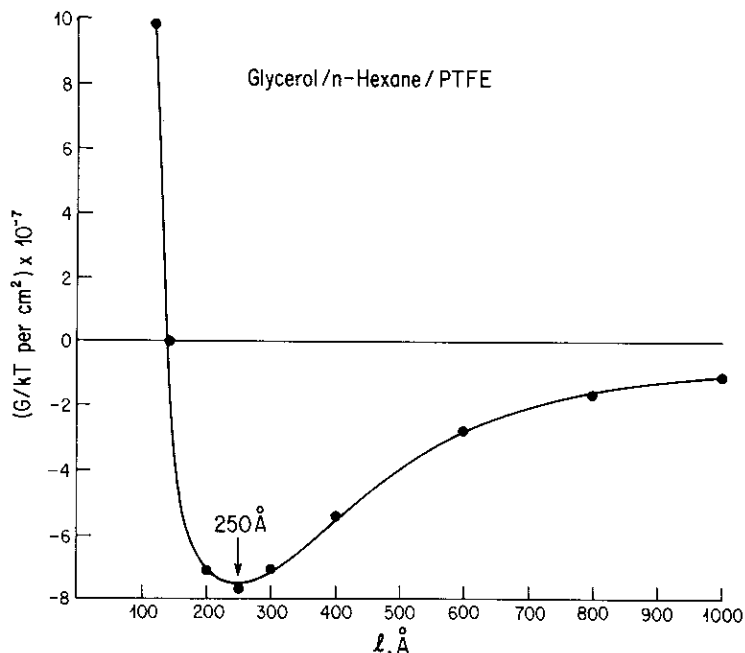


FIG. 2. Free energy of interaction as a function of distance for glycerol/n-hexane/Teflon TFE.

We will give further details of our theory, including a discussion of its implications with respect to disjoining pressure, and a description of experimental work, in a separate communication.

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MANOJ K. CHAUDHURY
ROBERT J. GOOD

Department of Chemical Engineering
State University of New York at Buffalo
Clifford C. Furnas Hall
Amherst Campus

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