Simple Semiempirical Method of Calculating van der Waals Interactions in Thin Films from Lifshitz Theory

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The influence of different representations of the dispersion dependence $\varepsilon(i\xi)$ on calculating van der Waals interactions from Lifshitz theory is studied. It is shown that with satisfactory accuracy $\varepsilon(i\xi)$ can be described by means of Krupp's empirical formula $[\varepsilon(i\xi)-1]/[\varepsilon(i\xi)+1]=a\cdot\exp(-b\,\xi)$. Making use of that formula a simple expression for the Hamaker function $A(h,T)$ is obtained. Numerical calculations are carried out, the results being compared with those of other authors and with experimental data.

Introduction

The macroscopic theory of Dzyaloshinskii, Lifshitz and Pitaevskii [1, 2] is the physically most satisfactory approach in calculating van der Waals interactions in thin films. The macroscopic expression for the force of interaction per unit area (the so called disjoining pressure) Π can be written in the form of the Hamaker law [3–5] $\Pi=-A(h,T)/6\pi h^3$, where $A(h,T)$ is a "Hamaker function" depending on the film thickness h and the temperature T. In order to calculate $A(h,T)$ one needs to know the dispersion dependence $\varepsilon(i\xi)$ (dielectric susceptibility to imaginary frequencies $i\xi$) of the interacting substances for ξ ranging from zero to infinity. Since such data are available only for a given number of substances, moreover in a limited frequency range, one has to make use of one or another approximate representation of $\varepsilon(\mathrm{i}\xi)$. In the present paper

a) we shall analyze the applicability of different representations of the dispersion dependence $\varepsilon(i\xi)$ and will show that with satisfactory accuracy it can be described by the empirical formula (1) Krupp [6] proposed;

b) making use of Krupp's formula we shall derive an approximate expression for $A(h,T)$, where the electromagnetic retardation at any film thickness and the influence of the medium are accounted for;

c) by means of the expression so obtained we shall calculate $A(h,T)$ for some systems and shall compare our results with those of other authors as well as with experimental data.

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Representation of the Dispersion Dependence $\varepsilon(i\xi)$

In a previous paper [7] we determined $\varepsilon(i\xi)$ using the approach of Ninham and Parsegian [8] and represented the results analytically through Krupp's empirical formula [6, 9]

$$\tilde{\Delta}=\frac{\varepsilon(i\xi)-1}{\varepsilon(i\xi)+1}=a\cdot\exp\{-b\,\xi\}\,, \qquad (1)$$

$0<a<1$ and $b>0$ being empirical constants. That allowed us to describe all frequency regions (those where relatively reliable experimental or theoretical data exist and the intermediate region, $10^{16}-10^{17}$ rad/s, where such information is missing and interpolation is necessary) with only one analytical expression. Here we shall carry out a more detailed analysis of the possibility to lower the arbitrariness of this interpolation by means of formula (1). That will be done for three substances (polystyrene [10], quartz [11] and diamond [12]) for which there are experimental dielectric data in a relatively wide frequency range (with upper limit ω^*). Figure 1 gives the plots of $-\ln\tilde{\Delta}$ vs. ξ for polystyrene (Fig. 1 a), quartz (Fig. 1 b) and diamond (Figure 1 c). At high frequencies (in the far uv and the soft x-ray regions) $\varepsilon(i\xi)$ was calculated from the plasma formula [8] and data in Table 1. At low frequencies (up to the mid uv) $\varepsilon(i\xi)$ was obtained using three different approaches:

I) from experimental dielectric data [13] neglecting the contribution from frequencies $\omega>\omega^*$;

II) from experimental dielectric data accounting for the contribution from frequencies $\omega>\omega^{*\,13}$;

III) by means of the resonance formula [8] and spectral data listed in Table 1; in that case the uv-region is described by one absorption peak at a resonance frequency corresponding to the first ionization potential.

When doing the interpolation from lower frequencies to frequencies where the plasma formula holds, one has to bear in mind that $-\ln\tilde{\Delta}(\xi)$ is a monotonically increasing function. Churaev[14] and Visser and Peterson[15] making use of approach I have carried out a curvilinear interpolation in the plot $\varepsilon(i\xi)$ vs. ξ from $\xi^* = \omega^*$ to plasma frequencies. Since in determining $\varepsilon(i\xi)$ the contribution from $\omega > \omega^*$ has been neglected, the values of $\varepsilon(i\xi)$ at $\xi \gtrsim 1.10^{16}$ rad/s are probably lowered. Ninham and Parsegian[8] have represented $\varepsilon(i\xi)$ by approach III and have done a straight-line interpolation in the plot $\varepsilon(i\xi)$ vs. ξ in the mid- and far uv, the accuracy of the interpolation significantly depending on the choice of the interpolation interval. In the straight-line interpolation in the plot of $\ln\tilde{\Delta}$ vs. ξ (shown in Fig. 2 with full lines) suggested previously[7] the assumption that Eq. (1) holds in the whole frequency range is incorporated. The relatively good coincidence between values calculated by approach II and the straight line interpolation (see Fig. 1) seems to corroborate this assumption. If the true values lie between those obtained from approaches I and II, this interpolation would give higher values of $\varepsilon(i\xi)$. In the case of substances, for which experimental $\varepsilon''(\omega)$ data are missing, that interpolation can be carried out using $\varepsilon(i\xi)$ values calculated by approach III, because all three approaches lead to similar results at low frequencies.

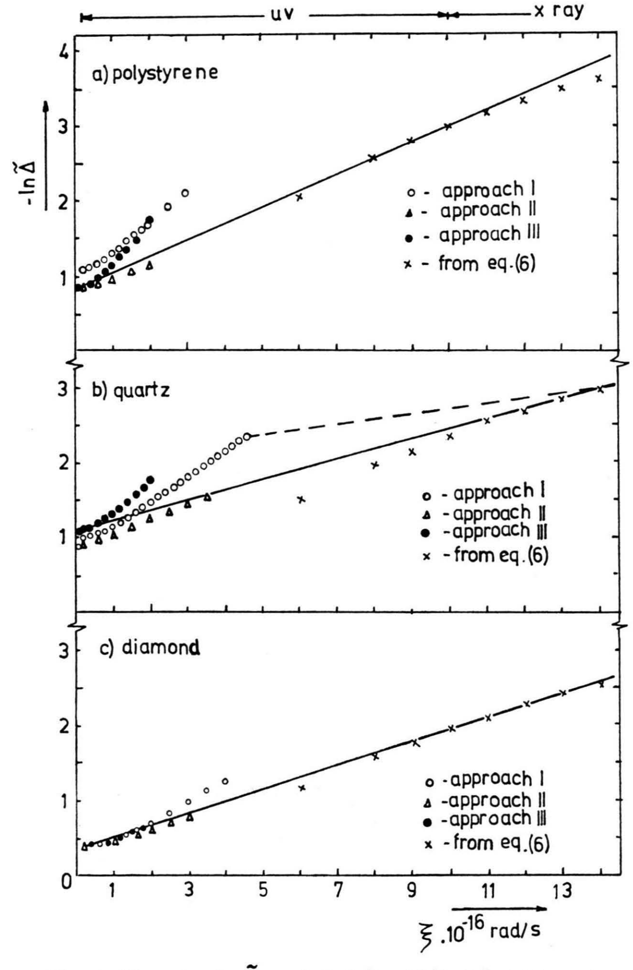

Fig. 1. Plot of $-\ln\tilde{\Delta} = -\ln[\varepsilon(i\xi)-1]/[\varepsilon(i\xi)+1]$ against imaginary frequencies ξ obtained by different approaches in determining $\varepsilon(i\xi)$ (see text) for a) polystyrene, b) quartz and c) diamond. The full lines represent the approximation of $\tilde{\Delta}$ by only one analytical function (1) in all frequency regions; the dotted line — an interpolation of the kind Churaev and Visser and Peterson proposed.

Approximate Analytical Expression of $A(h,T)$

Here we shall generalize the result for free films[7] for the interaction of three different phases: a thin plane-parallel film of substance 2 with thickness h, bounded by two semi-infinite media of substances 1 and 3. We shall simplify the general macroscopic equation for $A(h,T)$[2, 4] using the following approximations (see notations in[2, 4]): we shall put[1–3, 16] $s=p$; we shall neglect the unit with respect to the exponential term[1–3, 16]; at frequencies $\xi > \xi_m$ (in the cases considered below $m=1$), where the empirical formula (1) holds, we shall replace the summation on n by integration on ξ[1, 2, 16]; for a number of dielectrics it can be assumed that $a_1 a_2 \ll 1$. With these approximations and Eq. (1), using the procedure described previously[7], we obtain

$$A(h,T) = A_{n=0} + A^*_{22} + A^*_{13} - A^*_{12} - A^*_{23} + \delta A^*_{123}\,, \tag{2}$$

where

$$A_{n=0} = \frac{3}{4}\,k\,T \sum_{j=1}^{\infty} \frac{1}{j^3} \left(\frac{\varepsilon_{02}-\varepsilon_{01}}{\varepsilon_{02}+\varepsilon_{01}} \cdot \frac{\varepsilon_{02}-\varepsilon_{03}}{\varepsilon_{02}+\varepsilon_{03}} \right)^j; \tag{3}$$

$$A^*_{ij} = \frac{3\,\hbar}{4\,\pi}\,a_i\,a_j\,\frac{\exp\{-(b_i+b_j+D\,h)\,\xi_m\}}{b_i+b_j+D\,h} \left[1 + D\,h\,\xi_m + \frac{D^2\,h^2\,\xi_m^2}{2} + \frac{D\,h\,(1+D\,h\,\xi_m)}{b_i+b_j+D\,h} + \frac{D^2\,h^2}{(b_i+b_j+D\,h)^2} \right], \quad i,j = 1,2,3; \tag{4}$$

Table 1. Data * used in calculating the dispersion dependence $\varepsilon(i\,\xi)$.

Substance	ε_0	c_{ir}	ω_{ir}, rad/s	c_{uv}	ω_{uv}, rad/s	N, el/cm^3
Polystyrene [3]	2.53	—	—	1.53	$1.29\cdot10^{16}$	$3.37\cdot10^{23}$
Fused quartz [19]	3.78	1.82	$1.88\cdot10^{14}$	0.96	$1.77\cdot10^{16}$	$6.61\cdot10^{23}$
Diamond	$n^2=5.84$	—	—	4.5	$1.71\cdot10^{16}$	$10.56\cdot10^{23}$

* If not specially specified all numerical values of the quantities used in the calculations throughout the paper are taken from Handbook of Chemistry and Physics [20].

$$\delta A^*_{123}=\frac{3\hbar}{4\pi}\sum_{i=0}^{2}\sum_{j=0}^{2}\sum_{k=0}^{2} q\,(-1)^j a_1{}^i a_2{}^{j+1} a_3{}^k\,\frac{\exp\{-[i\,b_1+(j+1)\,b_2+k\,b_3+D\,h]\,\xi_m\}}{i\,b_1+(j+1)\,b_2+k\,b_3+D\,h}$$
$$\cdot\left\{1+D\,h\,\xi_m+\frac{D^2\,h^2\,\xi_m{}^2}{2}+\frac{D\,h(1+D\,h\,\xi_m)}{i\,b_1+(j+1)\,b_2+k\,b_3+D\,h}+\frac{D^2\,h^2}{[i\,b_1+(j+1)\,b_2+k\,b_3+D\,h]^2}\right\}, \tag{5}$$
$$q=0 \text{ when } i+j+k\neq 3 \qquad \left.\begin{matrix} q=1 \text{ when } i\neq j\neq k \\ q=2 \text{ when } i=j=k=1\end{matrix}\right\} i+j+k=3\,;$$
$$D=2\,\overline{\varepsilon_2{}^{1/2}}/c\,; \quad \overline{\varepsilon_2{}^{1/2}}=\tfrac{1}{2}[\varepsilon_2{}^{1/2}(i\,\xi_m)+\varepsilon_2{}^{1/2}(i\infty)]\,;$$

$\varepsilon_{0\text{i}}$ is static dielectric constant of substance i, $2\pi\hbar$, k and c are respectively Planck's and Boltzmann's constants and velocity of light in vacuo, a_{i} and b_{i} are the empirical constants [see Eq. (1)] of substance i. For non-polar substances $\xi_m=0$ and $A_{n=0}=0$.

With $D\,h=0$ Eqs. (2) – (5) give the non-retarded Hamaker constant. The other limiting case of retarded interaction ($A\sim h^{-1}$ resp. $\Pi\sim h^{-4}$) is obtained at $D\,h\gg b_i+b_j$.

The first temperature dependent term in (2) is significant only when at least one of the interacting substances is polar. If in (2) we put $A_{n=0}=\delta A^*_{123}=0$ we obtain an expression coinciding in form with the compound microscopic Hamaker constant[17]. Therefore this sum can be considered as being "additive term" in the dispersion interaction. However this is rather additivity of interactions in a macroscopic sense of the phases as a whole and not of the intermolecular interactions. In fact in the respective A^*_{ij} the electromagnetic retardation across a condensed medium is taken into account by means of the parameter D [see Eq. (4)] and the empirical constants a and b are related to the respective macroscopic phase as a whole. The non-additive term δA^*_{123} in Eq. (2) depends on the properties of all three interacting phases. It is identically zero for interaction across vacuum ($a_2=0$) or for free films ($a_1=a_3=0$).

Numerical Calculations

The approximate methods of calculating the dispersion dependence, considered in the first part, differ mainly in the manner $\varepsilon(i\,\xi)$ is described in the mid- and far uv. The interpolation in that region is especially important when $h\to0$, since owing to electromagnetic retardation the contribution from the high frequencies in the interaction decreases with increasing the film thickness[4]. Consequently it is most convenient to make the comparison between the different interpolation schemes on the basis of the values of $A(h=0)$ calculated in different ways. The systems for which calculations were carried out will be devided in three types: 1) non-retarded interaction across vacuum, 2) non-retarded interaction across a dense medium, 3) retarded interaction across a dense medium. The data necessary for our calculations (cases 1 a, 1 b, 2 a, 2 b and 3 a see below) are collected in Table 2.

Table 2. Data used in calculating Hamaker functions.

Substance *	a	$b\cdot10^{17}$, s/rad	$N\cdot10^{-23}$, el/cm^3
Decane [21]	0.336	2.1	2.53
Diamond	0.705	1.5	10.56
Hydrocarbon II [8]	0.342	1.9	3.34
Polyethylene [3]	0.420	2.1	3.21
Polypropylene [3]	0.390	2.1	3.10
Polystyrene [3]	0.433	2.1	3.37
Teflon [3]	0.317	1.2	7.38
Quartz [19]	0.300	1.3	6.61
Water [3]	0.287	1.7	3.34

* For all substances $\xi_m=\xi_1=2.41\cdot10^{14}$ rad/s.

The reference number denotes the source of the spectral data used in the resonance formula; for diamond see Table 1. The constants a and b are obtained from the plots $\ln\tilde{\Delta}$ vs. ξ (see Figure 1).

The values of $A(h=0)$ for systems of type 1 are presented in Table 3. They are calculated as follows:

1 a) from Eq. (2), where $A_{n=0}=\xi_m=Dh=\delta A^*_{123}=A^*_{13}=A^*_{12}=A^*_{23}=0$; $\varepsilon(i\xi)$ calculated using approach III with straight-line interpolation in the plot $\ln\tilde{\Delta}$ vs. ξ (see the first part),

1 b) same as 1 a but cutting off the contribution from frequencies higher than $\xi^*=\omega^*$,

1 c) $\varepsilon(i\xi)$ calculated using approach I without interpolation[11, 18],

1 d) $\varepsilon(i\xi)$ calculated using approach I with curvilinear interpolation in the plot $\varepsilon(i\xi)$ vs. ξ[14, 15],

1 e) $\varepsilon(i\xi)$ calculated using approach III with curvilinear interpolation in the plot $\varepsilon(i\xi)$ vs. ξ[19].

The values of A(0.293 °K) for systems of type 2 are presented in Table 4. They are calculated as follows:

2 a) from Eq. (2) with $Dh=0$ and neglecting δA^*_{123}; $\varepsilon(i\xi)$ calculated using approach III with straight line interpolation in the plot $\ln\tilde{\Delta}$ vs. ξ,

2 b) same as 2 b but cutting off the contribution from $\xi>\xi^*$,

2 c) $\varepsilon(i\xi)$ calculated using approach III without interpolation[3].

The functions $A(h, 293\ °\mathrm{K})$ of systems plastic-water-plastic are presented in Figure 2. They are calculated as follows:

3 a) from Eq. (2), neglecting δA^*_{123}; $\varepsilon(i\xi)$ calculated using approach III with straight-line interpolation in the plot $\ln\tilde{\Delta}$ vs. ξ (full curves in Figure 2),

3 b) $\varepsilon(i\xi)$ calculated using approach III without interpolation (dotted curves in Figure 3)[3].

The data presented in columns 1 a and 1 d in Table 3 illustrate the influence of the interpolation scheme on $A(h=0)$. The relative difference between the values obtained by the methods 1 a and 1 d is 10–20% [except the system PS-vacuum-PS, for which the frequency range where $\varepsilon''(\omega)$ data are established is the narrowest]. The true values of $A(h=0)$ lie probably between those of columns 1 a and 1 d. The uncertainty caused by neglecting the contribution to the interaction across a dense medium from frequencies in the mid- and far uv can be estimated from the data in Table 4. While in the interaction in the system water-hydrocarbon-water the contribution from this frequency range is indeed immaterial (as Ninham and Parsegian[4, 8] have shown), for the other four cases it is important (compare columns 2 a and 2 c in Table 4). It follows from the comparison of the data in columns

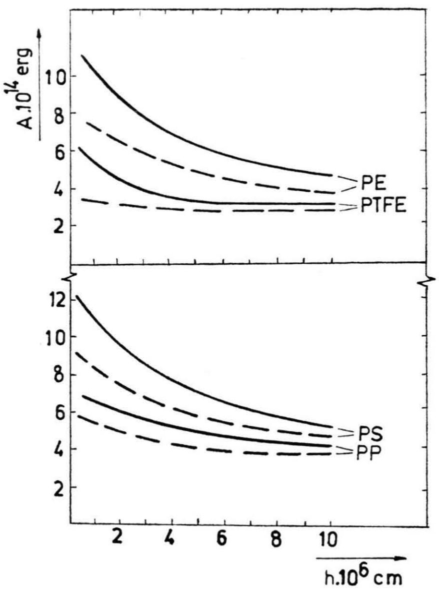

Fig. 2. Plots of Hamaker functions $A(h, 293\ °\mathrm{K})$ against thickness h of various plastics (polystyrene—PS, polyethylene—PE, polypropylene—PP and teflon—PTFE) interacting across water film. The full curves represent the results of calculations according to method 3 a, the dotted curves — the results of Gingell and Parsegian[3] obtained by method 3 b (see text).

Table 3. Values of $A(0)\cdot 10^{13}$ erg (Hamaker functions in the non-retarded limit) for interaction across vacuum obtained by various methods of calculation (see text).

System	$\omega^*\cdot 10^{-16}$	Method of calculation				
	rad/s	1 a	1 d	1 b	1 c	1 e
PS—vacuum—PS *	3.00	11.2	7.3[15]	8.1	6.6[18]	—
Quartz—vacuum—quartz	4.55	8.7	7.9[14]	6.0	6.5[11]	5.5[19]
Diamond—vacuum—diamond	4.55	42	33[15]	31	28[18]	—
Water—vacuum—water	4.55	6.1	5.4[15]	4.8	4.3[18]	—

* PS — polystyrene. — Superscript number denotes reference where the respective value is taken from.

Table 4. Values of $A(0, 293\ ^\circ\mathrm{K}) \cdot 10^{13}$ erg (Hamaker functions in the non-retarded limit) for interaction across dense medium obtained by various methods of calculation (see text).

System	Method of calculation			
	2 a	2 b ($\xi^* = 2 \cdot 10^{16}$)	2 b ($\xi^* = 1.5 \cdot 10^{16}$)	2 c
$H_2O - hc^* - H_2O$	0.12	0.12	–	–
$PE - H_2O - PE$ *	1.10	0.94	0.76	0.80[3]
$PP - H_2O - PP$ *	0.74	0.67	0.56	0.60[3]
$PS - H_2O - PS$ *	1.23	1.03	0.84	0.90[3]
$PTFE - H_2O - PTFE$ *	1.09	0.37	0.35	0.36[3]

* hc—hydrocarbon II[8], PE—polyethylene, PP—polypropylene, PS—polystyrene, PTFE—teflon. — Superscript number denotes reference where the respective value is taken from.

2b ($\xi^* = 2 \cdot 10^{16}$), 2b ($\xi^* = 1.5 \cdot 10^{16}$) and 2c in Table 4 that the method 2c virtually does neglect the contribution from $\xi > 1.7 \cdot 10^{16}$ rad/s. It is to be expected the error thus introduced to be lower at higher film thicknesses (the electromagnetic retardation cutting off the contribution from higher frequencies). In fact the values of $A(h=0)$, obtained by different methods but neglecting the contribution from frequencies $\xi > \xi^*$ (see columns 1b and 1c in Table 3), are differing less than the results obtained by the same methods but with integration up to $\xi = \infty$. This effect is illustrated in the case of retarded interaction in Figure 2.

Finally we shall corroborate our calculations with experimental data for the system water-decane-water. In Table 5 values of $A(h, 293\ ^\circ\mathrm{K})$ at the noted film thicknesses, calculated with method 3 a, are compared with the experimental results of Requena and Haydon[22] and Krugliakov et al.[23], the coincidence being satisfactory.

Table 5. Calculated and measured values of $A(h, 293\ ^\circ\mathrm{K})$ for the system water—decane—water.

	h, Å	$A \cdot 10^{13}$ erg	Ref.
Experiment	42–65	4.0 *	22
Experiment	48	2.7	23
Calculated	40–60	3.9	this work

* This value is the mean of 12 values obtained by measuring contact angle of films stabilized with different surfactants.

In conclusion we can say, that the simple formulae proposed in the present paper can ensure satisfactory accuracy when calculating van der Waals interactions in thin films.

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[1] E. M. Lifshitz, Sov. Phys. J. E. T. P. **2**, 73 [1956].

[2] I. E. Dzyaloshinskii, E. M. Lifshitz, and L. P. Pitaevskii, Advan. Phys. **10**, 165 [1959].

[3] D. Gingell and V. A. Parsegian, J. Coll. Interface Sci. **44**, 456 [1973].

[4] B. W. Ninham and V. A. Parsegian, Biophys. J. **10**, 646 [1970].

[5] V. A. Parsegian and B. W. Ninham, Biophys. J. **10**, 664 [1970].

[6] H. Krupp, Advan. Colloid Interface Sci. **1**, 111 [1967].

[7] C. S. Vassilieff and I. B. Ivanov, Colloid Polymer Sci. **254**, 431 [1976]; Proc. Int. Conf. Colloid Surface Sci., Budapest 1975, Vol. 2, p. 199, Akademiai Kiado, Budapest 1976.

[8] B. W. Ninham and V. A. Parsegian, J. Chem. Phys. **52**, 4578 [1970].

[9] W. Schnabel, cited in J. Visser, Advan. Colloid Interface Sci. **3**, 331 [1972].

[10] R. H. Partridge, J. Chem. Phys. **47**, 4223 [1967].

[11] F. Wittmann, H. Splittgerber, and K. Ebert, Z. Phys. **245**, 354 [1971].

[12] R. A. Roberts and W. C. Walker, Phys. Rev. **161**, 730 [1967].

[13] Our calculations are carried out with the Kramers-Kronig integral where $\varepsilon''(\omega)$ is approximated by a step-function[11, 14]

$$\varepsilon(i\xi) = 1 + \frac{1}{\pi} \sum \varepsilon''_{ik} \ln \frac{\omega_k^2 + \xi^2}{\omega_i^2 + \xi^2} + \int_{\omega^*}^{\infty} \frac{\omega\, \varepsilon''(\omega)}{\omega^2 + \xi^2}\, d\omega ,$$

the third term (contribution from $\omega > \omega^*$) being unknown. It could be estimated by means of the static dielectric const. ε_0:

$$\text{at} \quad \xi = 0 \int_{\omega^*}^{\infty} \frac{\varepsilon''(\omega)}{\omega}\, d\omega = \varepsilon_0 - 1 - \frac{2}{\pi} \sum \varepsilon''_{ik} \ln \frac{\omega_k}{\omega_i} ;$$

this expression can be substituted for the contribution from $\omega > \omega^*$ provided that $\omega^2 \gg \xi^2$ in the interval $\omega^* \leqq \omega < \infty$. This correction is influenced by the reliability of the experimental data in the microwave and ir-regions.

[14] N. V. Churaev, Kolloidn. Zhur. **36**, 323 [1974].

[15] J. Visser and G. C. Peterson, to be published.

[16] N. V. Churaev, Kolloidn. Zhur. **37**, 730 [1975].

[17] A. Scheludko, Advan. Colloid Interface Sci. **1**, 391 [1967].

[18] H. Krupp, W. Schnabel, and G. Walter, J. Coll. Interface Sci. **39**, 421 [1972].

[19] N. V. Churaev, Kolloidn. Zhur. **34**, 959 [1972].

[20] Handbook of Chemistry and Physics, 49-th ed., The Chemical Rubber Co., Ohio.

[21] D. E. Brooks, Y. K. Levine, J. Requena, and D. A. Haydon, Proc. Roy. Soc. Lond. A **347**, 179 [1975].

[22] J. Requena and D. A. Haydon, Proc. Roy. Soc. Lond. A **347**, 161 [1975].

[23] P. M. Krugliakov, J. G. Rovin, I. A. Bagaveev, and A. F. Korezky, in "Poverhnostnie sili v tonkih plenkah", p. 140, Izd. Nauka, Moskva 1974.